

ÉCOLE DOCTORALE
ENERGIE, MATERIAUX, SCIENCES DE LA TERRE ET DE L'UNIVERS

Laboratoire CEMHTI

THÈSE présentée par :
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Soutenue le : **[30 Septembre 2014]**

Pour obtenir le grade de : **Docteur de l'Université d'Orléans**

Discipline/ Spécialité : Sciences des matériaux

**Céramiques transparentes par cristallisation
complète du verre : application aux
aluminosilicates de strontium**

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This thesis is dedicated to

The memory of my endless love, my father...

the most compassionate mother in the world, my mother

my husband, my best friend, my second half and my soul mate

my beloved sisters Youssra, Hala and Maha

the tiny one growing inside me

My baby girl 😊

Acknowledgment

Coming to the end of these three unforgettable years, lots of memories flash back into my mind where lots of people have played a major role and without them, this thesis would not have been possible.

I would like first to express my deepest respect to my thesis director M. Guy MATZEN to whom I owe my profound gratitude for giving me the opportunity to work within his team. It was really my pleasure to complete my PhD studies within such a team. Thank you for your continuous asking, your understanding, your sympathy and your precious help since the first day I arrived to Orléans.

I would like also to take this opportunity to express my heartiest thanks and appreciation to Dr. Mathieu ALLIX, who has followed up my study in its finest details. Thank you for your good humor, motivation, disponibility, constructive ideas, for all the explanations and the fruitful discussions.

I would like also to express my gratitude to all the jury members for accepting the task of evaluating my work.

My kind respects goes to one of the most gentle person I have meet in CEMHTI Dr. Emmanuel VERON. Thanks for all your help and your disponibility in order to answer all my questions concerning diffraction, refinement... N.B My thesis is almost finished and still you have problems with preparing tabbouli and hommous ☺. I will be showing you the secrets soon☺.

I also owe my heartiest gratitude to Dr. Sébastien CHENU, a previous Post-doc at CEMHTI laboratory. It was really my pleasure to share the scientific research with someone like you. Thank you for all the motivation that you have showed me in order to learn French. I hope that we can always keep in touch and who knows maybe work together again.

I want also to express my sincere thanks to the NMR specialist Dr. Franck FAYON. Thank you for all the DFT calculations, the NMR experiments, and most importantly your explanations. Thank you for the motivation and curiosity that you have showed to my subject and all your constructive ideas.

I want also to express my gratitude to Dr. Cecile GENEVOIS, my office colleague ☺. Even though we have shared the office for just one year and few months, but it was really my pleasure. Thank you for all your kindness and the support that you have showed to me especially in the last few months, me and my baby appreciate it☺.

I would like also to thank Mrs. Sandra ORY for all the DSC measurements, and for her good humor. Sorry Sandra I was not the perfect candidate for making sports (but at least I have tried ☺).

I would like also to thank Dr. Domingos DE SOUSA MENESES for the IR measurements and Dr. Patrick SIMON for the Raman measurements.

I would like to thank all the Drs that we have collaborated with for different experiments in France, Spain and United States: Dr. Florence PORCHER, Dr. Manolo OCANA, Dr. Jean Christophe SANGLEBOEUF, Dr. Matthew SUCHOMEL and their corresponding teams.

My gratitude goes to the "Lebanese trio" Zalfa, Georges and Louis, it was really so nice to meet you, thanks for the three of you for all the help (btw it was not so bad when you left, it was a good opportunity to ameliorate my French language :p).

*Without forgetting also all the CEMHTI members because it is their presence and their kindness that create this lovely working ambiance. It was nice to meet Judith, Marina, Cedric, Romain (*2), Tayeb, Olga, Rudy, Julien (my previous office colleague ☺), Ophelie, Hao, Hua, Mounesha, Rob, Yann, Guillaume, Mohammad, Mathieu, Benjamin, Ana, Thomas and Fleur.*

Thanks to everyone who has participated either directly or indirectly in this accomplishment.

My love also goes to my friends and every single family member in Lebanon. You were far in distance but very close in your spirit.

My deepest love goes to my mother, and my sisters who have always been supportive in every step. Sorry for being always far from home during my masters studies in Beirut and even farther during my PhD study, but you do know your place in my heart. Thank you for turning the laptop's screen into sweet little home through skype each and every evening, which was my daily medication.

Last but never the least, my life partner, thanks for your continuous listening and motivation. Thank you for being there for me each time I needed your support. I will be there for you with our baby when it will be your turn. B7ebbak 7abibi ☺

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General Introduction

This manuscript represents the work carried out during three years on the elaboration and characterization of transparent polycrystalline ceramics using a full and congruent glass crystallization approach.

The interest in transparent polycrystalline ceramics is owed to their ability to replace single crystals in domains including optics, transparent armors, electronics, and scintillating devices.¹⁻³ Polycrystalline ceramics are attractive due to a wide range of accessible chemistries, shaping flexibility, doping level acceptance and mass production possibilities which are largely restrained in single crystals synthesis.⁴⁻⁷ Transparency in these advanced polycrystalline materials is ensured either by an optical isotropy (i.e. cubic symmetry) or a very small crystal size^{2, 4} (much smaller than the wavelength of the incident light as described by the Rayleigh-Ganz particle scattering theory⁸) and the absence of light scattering sites (pores, secondary phase...)⁴. Several materials have been developed, such as the cubic MgAl_2O_4 spinel used in transparent armor applications⁹, sesquioxides¹⁰ and Nd:YAG ceramics for laser application^{7, 11}, ZrO_2 and Lu_3NbO_7 ceramics for optical lenses and the nanometric rhombohedral Al_2O_3 .^{12, 13} Diverse synthetic approaches, either by hot pressure, vacuum, microwave or spark plasma sintering of specific nanometer-scale raw materials are employed. However, all these processes require complex sintering conditions, and it remains difficult to completely eliminate the presence of residual pores which strongly attenuates transparency.⁵

Full and congruent crystallization from a massive glass precursor, leading to dense polycrystalline materials, is a promising alternative which would overcome the drawbacks of single crystal and sintered ceramic materials.

Based on this direct bulk glass crystallization approach, a previous study realized by S. Alahrache at the CEMHTI laboratory had reported the synthesis of transparent polycrystalline BaAl_4O_7 ceramics.¹⁴⁻¹⁷ These new transparent polycrystalline ceramics can exist under two orthorhombic polymorphs ($\alpha\text{-BaAl}_4\text{O}_7$ and $\beta\text{-BaAl}_4\text{O}_7$).

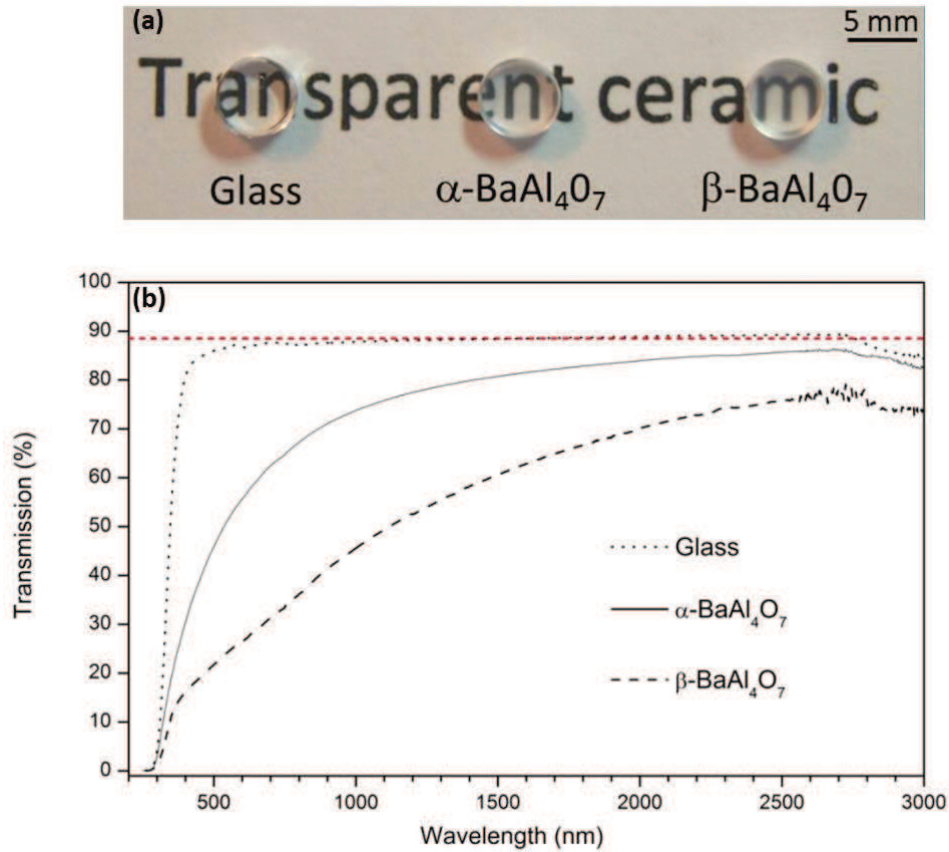


Figure 1 (a) BaAl₄O₇ parent glass, α -polymorph, and β -polymorph transparent polycrystalline ceramics. (b) Transmission spectrum of the three samples: BaAl₄O₇ parent glass (dot), α -polymorph (solid) and β -polymorph (dash)

Nevertheless, these transparent polycrystalline ceramics have limitations: i) high melting temperature of the glass precursor (≈ 2100 °C), ii) small synthesis scale (glass beads of roughly $\varnothing \approx 3 - 5$ mm) inherent to the employed glass synthesis method iii) non-perfect transparency (≈ 60 % and 40 % transmission at 633 nm for the α - and β -polymorph respectively) associated to a weak birefringence. Consequently, two main objectives have been identified for our current study:

- The elaboration of polycrystalline ceramic materials showing a maximum transparency, if possible equal to the theoretical maximum transmission. For this intent, we searched for materials with optical isotropy.
- The search for transparent polycrystalline ceramics which can be elaborated at a large scale.

This manuscript is divided in four Chapters.

Chapter I presents a bibliographic report of full crystallization from glass, its advantages over other common sintering techniques for the preparation of transparent polycrystalline ceramics. A brief report of transparent glass-ceramic/ceramic technology and the different advancements reported in this domain are also presented.

In chapter II, we detail the different synthesis procedures used for the elaboration of the glass precursors in this work (aerodynamic levitation and conventional classic melting/quenching), followed by the introduction of the different techniques, which served in the characterization of our materials in a complementary manner. These include microstructural characterization (scanning electron microscopy (SEM), transmission electron microscopy (TEM)), long-range order probing techniques (X-ray, synchrotron and neutron powder diffraction) which give information about the periodicity and the average structure of our materials, short-range order probing technique (nuclear magnetic resonance spectroscopy (NMR)), density functional theory (DFT) computations, as well as transmittance, luminescence, thermal and mechanical measurements.

In chapter III, the elaboration of the transparent polycrystalline $\text{Sr}_3\text{Al}_2\text{O}_6$ ceramic and its analogue material $\text{Sr}_3\text{Ga}_2\text{O}_6$ is realized. The aim of this chapter is to elaborate polycrystalline ceramics with cubic symmetry (optical isotropy) in order to achieve highest levels of transparency for ameliorated photonic applications. This result corresponds to the first objective of the thesis consecutive to that of BaAl_4O_7 transparent polycrystalline ceramics, for which birefringence resulting from optical anisotropy (orthorhombic symmetry) has resulted in transmittance loss by grain boundary scattering. The synthesis of these materials is demonstrated, followed by their different microstructural, mechanical, thermal and optical characterizations.

In chapter IV, a study on the system $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 2$) is performed. This system is divided into three solid solutions. Concerning the first ($0.8 \leq x \leq 2$) and the second ($0.5 \leq x \leq 0.68$) ones, transparent polycrystalline ceramics can be elaborated. Structural resolution of these new crystallized phases is determined based on synchrotron and neutron powder diffraction data. However, the third solid solution $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0.4$) appears to be the most interesting in terms of large size scalability and transparency remarkable level of the elaborated polycrystalline ceramics. The synthesis protocol of these transparent polycrystalline ceramics, with all the problems encountered and how they were overcome are discussed in details. The structural evolution of the solid solution is investigated based on Rietveld refinements against synchrotron and neutron powder

diffraction data. The microstructure (crystal size, porosity, grain boundaries) of these transparent polycrystalline ceramics is determined using SEM, high resolution TEM and STEM. The chemical Al/Si order in these materials is investigated and quantified at the local state throughout the solid solution using nuclear magnetic resonance spectroscopy. DFT calculations are monitored for two compositions of the solid solution. The complementary information provided by the contribution of different studies are used to explain the observed transparency of our polycrystalline oxide ceramic materials.

At the end of the manuscript, we present a general conclusion of this work in light of the results obtained, using the full and congruent glass crystallization approach. These results serve as a base for proposing a new concept for the elaboration of transparent polycrystalline ceramics, thus extending the development of the transparent polycrystalline ceramic domain.

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Chapter I

Crystallization from glass: state of the art

I.1 Crystallization from glass

Ceramics and glass-ceramics are materials elaborated by full or partial crystallization from glass respectively. The nature and the microstructure of the crystalline phase/s influence directly these materials specific properties (thermal, mechanical, electrical, biological, photonic...). Therefore, mastering the crystallization phenomenon, leads to the elaboration of ceramic and glass-ceramic materials with diverse properties and hence a wide range of technical applications. This is achieved through the control of the initial glass chemical composition and the control of the nature and microstructure of the crystalline phase (crystal size, morphology) during crystallization.

I.1.1 Theory of crystallization

Crystallization is defined as a thermal process consisting of two steps: nucleation, which generally takes place at a temperature slightly higher than the glass transition temperature (T_g), followed by crystal growth at a higher temperature depending on the composition. These two steps can take place separately (Figure 1a) or an overlap between them might occur (Figure 1b).

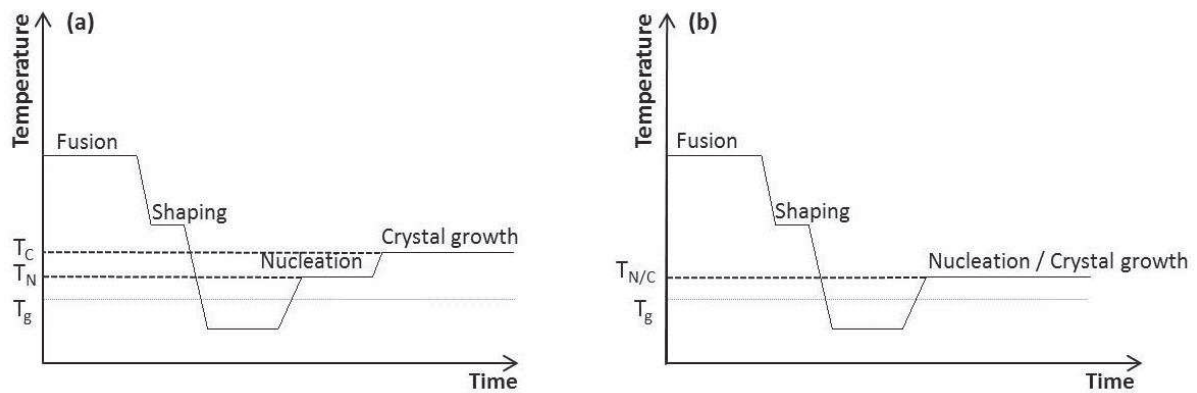


Figure 1 Glass crystallization process in (a) two steps and (b) one step

I.1.1.1 Nucleation

Nucleation is a very important stage because it controls the pathway of the overall crystallization. Different approaches have been proposed for describing the crystallization phenomenon. A simple theory which has been used to model the nucleation step is the classical nucleation theory (CNT). It was first proposed by Gibbs¹ and Arrhenius in 1875, further developed by Volmer, Weber and Farkas in 1927^{2, 3} and then modified in 1935 by Becker and Döring.⁴ The CNT theory is based on two hypotheses: i) the nuclei formed are of

spherical shape, with a radius r and an interface minimizing the surface energy, ii) the same composition, density, structure and properties are obtained for the nuclei and the crystals because the microscopic nucleus is considered as a macroscopic entity. The CNT theory exhibits limitations due to disagreements between its predictions and real experimental data for certain systems⁵, it accounts qualitatively but not quantitatively for the observed physical phenomena. Consequently, other theories have been proposed which have been discussed in details in other publications.^{5,6} However, up to date, there is still no comprehensive theory for describing the whole crystallization process.

In the case of crystallization from glass, two types of nucleation are considered: homogeneous and heterogeneous.

I.1.1.1.a Homogeneous and heterogeneous nucleation

In homogeneous nucleation, the crystallized phase develops spontaneously, with the same probability in any given point of the material, due to density fluctuations and kinetic energy depending on temperature. Homogeneous nucleation corresponds to the transformation of a nuclei from a metastable state (glass) to a more stable state (crystal), favored by the lower volume free energy of the crystal state compared to that of the liquid state (Figure 2a).

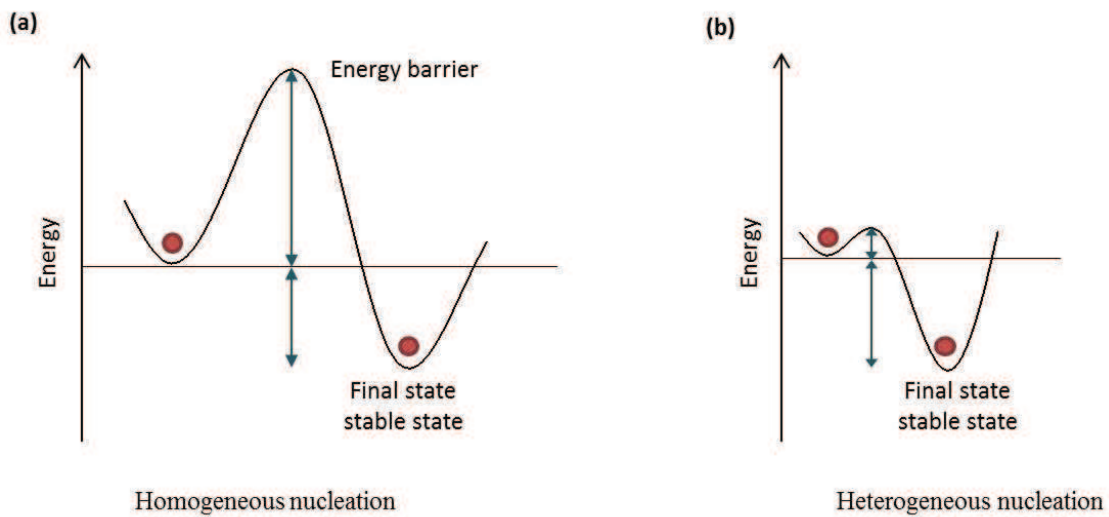


Figure 2 Scheme representing the energy barrier of homogeneous nucleation (a) and heterogeneous nucleation (b)

The glass to crystal transformation requires a certain energy barrier to be crossed which is represented by:

$$W = 4\pi r^2 \gamma + \frac{4\pi}{3} r^3 \Delta G_V + \Delta G_E \quad (1)$$

With W the energy barrier, r the radius of the nucleus, γ the surface tension nuclei/liquid, ΔG_V the variation in free volume energy between the crystal and the liquid ($\Delta G_V = G_c - G_l$) and ΔG_E the variation in elastic energy.

The first derivative of this equation gives the maximum work W^* required for a nucleus with critical radius r^* to cross the energy barrier.

$$W^* = \frac{16\pi}{3} \frac{\gamma^3}{\Delta G_V^2} \quad r^* = -\frac{2\gamma}{\Delta G_V} \quad (2)$$

When speaking about nucleation, one should also mention the steady-state nucleation rate which represents the number of supercritical nuclei formed per unit volume of the glass per unit time, represented by the following equation

$$I(T) \propto \frac{h}{3\pi d_\lambda^3 \eta} \exp\left(\frac{W^*}{k_B T}\right) \quad (3)$$

With k_B the Boltzmann constant, h the Plank's constant, d_λ the jump distance and η the viscosity.

The pre-exponential term represents the kinetic factor (including the viscosity). The exponential term represents the thermodynamic factor. It is the temperature of the system which determines whether the kinetic or the thermodynamic term dominates.

On the other hand, heterogeneous nucleation (Figure 2b) is initiated by specific nucleation sites such as impurities, bubbles, surface defects or interfaces. It is also called catalyzed nucleation. The matter that one has heterogeneous nucleation is due to the fact that the driving force for forming the nuclei starting from the previous mentioned nucleation sites is higher than that of the parent glass. This introduces the term of contact angle θ between the substrate (or catalyst) and the melt. In this case, all the surface tension forms should be considered (substrate-crystal, crystal-melt and melt-substrate). Therefore, the work required for the formation of a nucleus by heterogeneous nucleation is given by:

$$W_{het} = W_{hom} \times f \quad (4)$$

Where

$$f(\theta) = \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4} \quad (f \leq 1) \quad (5)$$

For heterogeneous nucleation:

- i) The heterogeneous nucleation rate is always smaller than the homogeneous nucleation rate.
- ii) The same critical radius r^* exists for both homogeneous and heterogeneous nucleation processes.
- iii) The contact angle (θ) plays a major role in the determination of heterogeneous nucleation rate, where for $\theta=\pi$, f is equal to one and thus one returns to homogeneous nucleation. The higher the value of the contact angle, the more the nucleation mechanism is close to homogeneous nucleation.

Due to the quantitative limitations of the classical nucleation theory, modifications for the classical nucleation theory^{7, 8} or even new more complex approaches have been developed.⁹⁻¹³ However, even recently developed theories remain incomplete, keeping the search of a general complete theory of nucleation a subject always under study.

I.1.1.1.b Nucleating agents

Heterogeneous nucleation is much more common than homogeneous nucleation. Nucleating agents, generally under the form of metallic elements (Au, Ag, Pt, Pd) or oxides (ZrO₂, TiO₂, P₂O₅, CeO₂, ZnO₂, etc.), can be added to make the heterogeneous nucleation occur in the volume.¹⁴⁻¹⁸ Their presence increases the rate of nucleation and hence leads to obtaining materials with more controlled and desired properties.¹⁹⁻²¹

I.1.1.2 Crystal growth

Crystal growth starts when the nuclei reach a critical size r^* . Crystal growth can start even when nucleation is not completed, or the two processes can be totally separated i.e. only nuclei already formed will grow into larger crystals. In case of crystal growth, the crystallization rate is defined by the diffusion of the glass matrix towards the crystal interface. Three models can be considered for describing the crystal growth rate: normal growth, surface crystallization and screw dislocation growth.⁶ For this study, and according to different systems studied, normal growth and surface crystallization which demonstrates an oriented growth will be discussed later.

I.1.2 Transparent glass-ceramics

Glass-ceramic materials are formed by controlled crystallization of the parent glass. The glass precursor is first melted, quenched and shape-processed. After that, it is thermally partially crystallized to obtain the glass-ceramic material. Nucleating agents such as ZrO_2 , TiO_2 can be added to the initial glass composition to force the nucleation step. Phase separation can also be induced by the addition of phase separation initiator.^{22, 23} This phenomenon influences directly the nucleation/crystallization mechanism, where the crystal size becomes directly dependent on the size of phase separation. The mechanism of phase separation, controlled by the glass composition and synthesis conditions, gives glass-ceramic materials with different microstructures and therefore different applications.²⁴⁻²⁶

Glass-ceramics are composed of crystals dispersed in a glass matrix, with a crystalline phase volume percentage commonly ranging from a few to more than 90 %. A glass ceramic can be composed of one or more glass and crystalline phases. The formed crystals can have the same composition as the initial parent glass (congruent crystallization), or a different composition. The first glass-ceramic material, based on a lithium alumino-silicate composition, was accidentally developed in the 1950's by Dr. S.D. Stookey.²⁷ The advantages of glass-ceramic over glass and ceramic lie in the coupling of the glass and ceramic properties. A certain number of desired properties is unattainable in glass or ceramic material independently, such as thermal resistance coupled to transparency (glass-ceramics for cooking ware) or high strength combined to translucency, biocompatibility, chemical durability (glass-ceramics for dental restoration) can be only obtained in glass-ceramic materials. Another important advantage is the wide variety of possible microstructures of glass-ceramics. Glass phases can have different microstructures, and crystalline phases can exhibit an even wider variety of microstructures which affect the properties of the obtained glass-ceramic. As a consequence, by varying the initial glass composition and controlling the microstructure of the crystalline phases, a wide variety of glass-ceramics can be developed with diverse properties and applications.

Beside the glass-ceramic preparation method from bulk glass through a controlled nucleation and crystallization process, sintering techniques are also widely reported in the literature.²⁸⁻³² Powder sintering techniques are used when surface crystallization dominates, causing considerable density changes between the crystalline and the amorphous phases.³³ Surface crystallization is observed for glasses with a reduced glass transition temperature ($T_{gr} = T_g/T_f$) higher than 0.58.^{34, 35} Parent glass are finely grinded and then fired. The

crystallization is believed to start at the glass-particle interface serving as nucleating sites; thus eliminating the need for nucleation agents. However, the obtained glass-ceramics contain residual pores which are difficult to avoid even at high sintering pressures and temperatures. The quality of the obtained glass-ceramic is highly determined by the densification of the glass-powder.³⁶⁻³⁹

In this work, the optical transparency is the major property desired. This renders controlled nucleation and crystal growth of major importance.

1.1.2.1 Conditions required for obtaining transparency in glass-ceramics

During the crystallization process, the transparency of the obtained glass-ceramics can be totally, partially conserved or even totally lost. There exist different factors which decrease light intensity. These include scattering, atomic absorption and reflection (Figure 3).⁴⁰

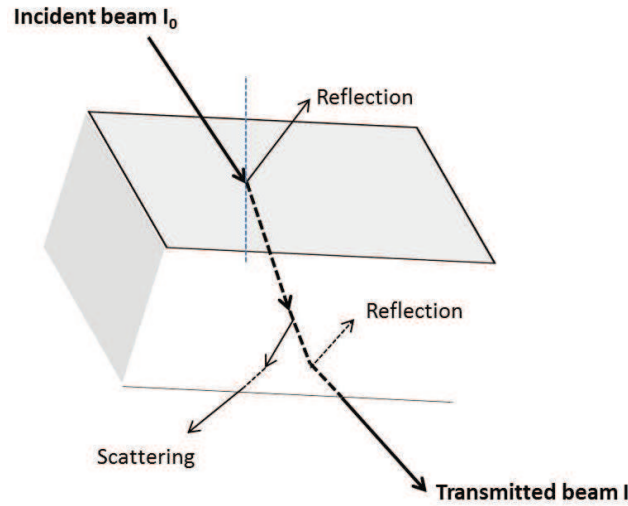


Figure 3 Schematic drawing showing the different light interactions through a transparent material

The transmitted intensity is described by the following equation:

$$I = I_0 (1 - R)^2 \exp[-(\beta + S)x] \text{ with } R = \left(\frac{n-1}{n+1}\right)^2 \quad (6)$$

Where I_0 represents the incident light intensity, I the transmitted light intensity, β the linear absorption coefficient, S the scattering coefficient, x the optical path length, R the reflection and n the index of refraction of the material.

For glass-ceramics, with their microstructure composed of micro or nanocrystallites dispersed in glass matrix, non-linear optical properties arise causing attenuation of light intensity. Two models exist in the literature for explaining the elastic scattering in glass-ceramics based on crystal size: i) the Rayleigh model⁴¹ applied for glass-ceramics with crystal size smaller than the wavelength of light, ii) the Mie model⁴² applied for glass ceramics with crystal size larger than the wavelength of light. However, in the case of transparent glass-ceramics, nano-sized crystallites are common and thus the Rayleigh model is usually considered.

The Rayleigh model⁴³ is given by the following equation

$$I = \frac{(1+\cos^2\theta)}{L^2} \frac{8\pi^4}{\lambda^4} r^6 \left[\frac{M^2-1}{M^2+1} \right]^2 I_0 \quad (7)$$

Where I represents the scattered light intensity, I_0 the incident light intensity, θ the scattering angle, r the particle radius, L the distance between two scattering centers and M the ratio of the refractive index of the crystallites to that of the surrounding glass matrix.

Based on this relation, it can be deduced that for obtaining a minimum scattering intensity, at least one of the following two conditions should be fulfilled: i) $M \approx 1$, which signifies a matching refractive index between the amorphous phase and the crystalline phase. It is also important to have isotropic materials (no birefringence). ii) $\frac{r^6}{\lambda^4} \ll 1$, which implies a crystal size much smaller than the wavelength of light.

Therefore, according to Rayleigh model, for glass ceramic materials to be transparent in the visible range, the crystal size should be in the range of 15 nm with an accepted difference of 0.1 in refractive indices of the glass matrix and isotropic crystalline phase.⁴⁴ According to Beall and Pinckney, based on Hoper's model, a crystal size of 30 nm and a difference in refractive indices of 0.3 can be accepted for obtaining transparent glass-ceramics.⁴⁵ Other recent modeling theories of turbidity are also reported in order to set the maximum crystal size allowed for conserving transparency in glass ceramics.⁴⁶⁻⁴⁸

1.1.2.2 Different transparent glass-ceramics families

Different types of transparent glass-ceramics have been reported. The most common and firstly synthesized are based on silicates and aluminosilicates.⁴⁹⁻⁵³ Glass-ceramics with compositions based on chalcogenides⁵⁴⁻⁵⁷, fluorides and oxyfluorides^{22, 58-63} have also been reported for photonic applications and transparency retained in the infrared region. But these

later compositions show limitations in terms of mechanical properties (chalcogenides), cost and chemical stability (fluorides).

1.1.2.3 Transparent glass ceramics applications

The wide variety of glass compositions, in addition to the different microstructures of glass-ceramics obtained by controlled crystallization; result in a wide application range of glass-ceramic materials. The main applications of glass-ceramics^{6, 64}, include the following:

- i) Consumer applications present in everyday life, these include mainly glass ceramics used for kitchen applications such as cooking dishes, that can withstand high temperature fluctuations and thermal shocks. An example is the Keraglass[®] (Eurokera: Corning/St. Gobain/France) which represents an excellent candidate for producing consumer goods thanks to its low linear coefficient of thermal expansion, resistance to high temperature and stability to food and stains.
- ii) Optical applications, such as Zerodur[®] glass-ceramic⁶⁵⁻⁶⁷ used in telescope mirrors given its high light transmission (80 – 90 %), good chemical durability, thermal conductivity and low coefficient of thermal expansion.
- iii) Technical applications, such as the Pyroceram[®] 9606⁶⁸ used as radome considering their homogeneity, low dielectric constant, low coefficient of thermal expansion, high strength and high abrasion resistance.
- iv) Medical applications, such as IPS e.max[®] (Ivoclar) glass ceramic used for dental restoration owed to its mechanical, biological and esthetic properties.
- v) Other applications including electronic (BPO₄ glass-ceramics), architectural (Neoparies[®] glass-ceramic) and energy applications where a wide list exists in the literature for all the interesting applications of different transparent glass-ceramics.^{5, 6,}

22, 24, 46, 48, 64, 69-74

Figure 4 represents some examples of transparent glass-ceramics with their corresponding microstructure images.

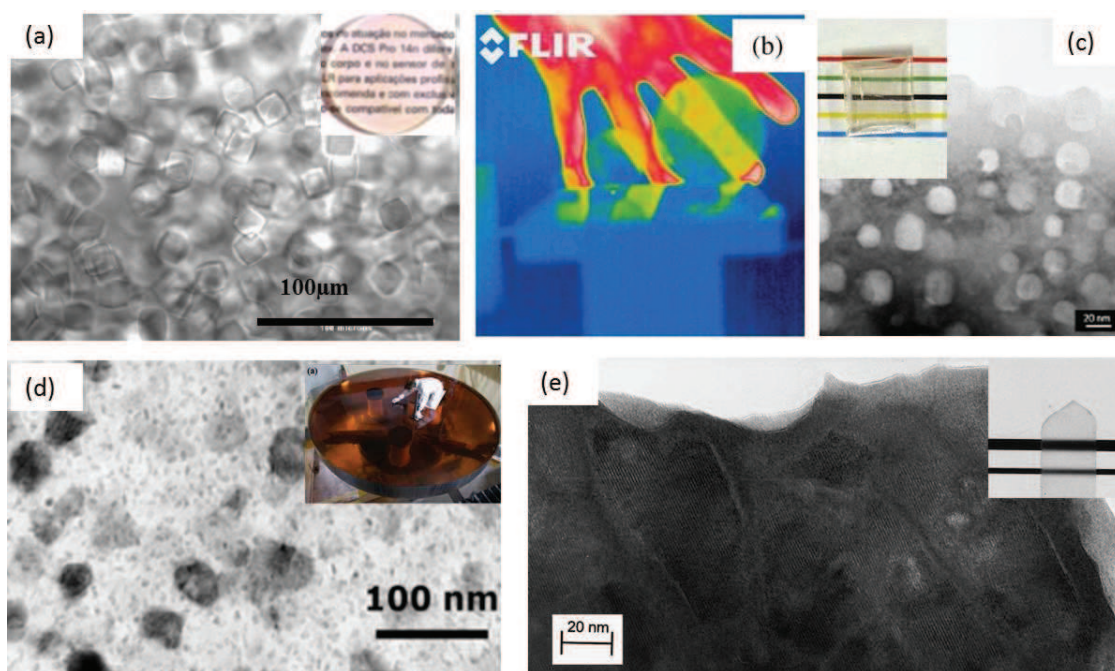


Figure 4 (a) $\text{Na}_2\text{O-CaO-SiO}_2$ glass-ceramic⁷⁵ (b) Infrared picture of the $80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3$ glass-ceramic⁷⁶ (c) $\text{Sr}_2\text{TiSi}_2\text{O}_8$ glass ceramic⁷⁷ (d) ZERODUR ($\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$) glass-ceramic⁶ (e) Fluorozirconate glass-ceramic⁷⁸

I.1.2.4 Limitations of transparent glass-ceramics

Despite the enormous advances in the transparent glass-ceramic field and the wide range of applications, the complete crystallization of these glass ceramics represents a major challenge. In glass-ceramics the transparency can be achieved only through a careful partial crystallization of nanometer-scale microstructure precipitates (crystallite sizes much smaller than the incident wavelength as described by the Rayleigh-Ganz⁷⁹ particle scattering theory and/or a minimized difference in the refractive index between the crystallites and the glass matrix.⁴⁰ To overcome these obstacles, complete crystallization appears to be an interesting approach.

I.2 Transparent ceramic technology

With the increasing demand of materials for photonic applications, such as high energy lasers, scintillating devices, optical lenses and transparent armour and the desire to replace single crystals, transparent polycrystalline ceramic technology has emerged.

I.2.1 Need and interest in replacing single crystals

Single crystals, with their continuous crystalline structure, absence of grain boundaries and defects, exhibit unique properties for applications in highly technological domains especially optics and electronics^{80, 81} (Figure 5).

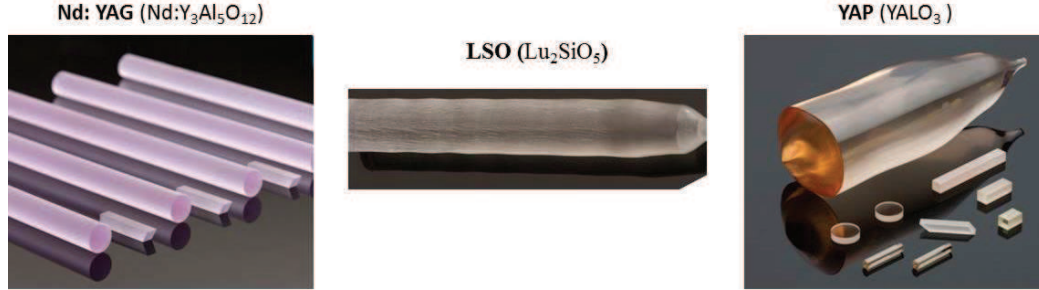


Figure 5 Examples of commercially used single crystals. From left to right: Nd:YAG; $\text{Nd:Y}_3\text{Al}_5\text{O}_{12}$ (YAG) used for solid state-lasers, Lu_2SiO_5 and YAP; YAlO_3 for scintillators

Single crystals required for highly technological applications can be elaborated in laboratories under extreme conditions; this presents an economical challenge, in addition to other limitations including restricted doping level, low shaping flexibility and most importantly the narrow range of compositions which can be elaborated as single crystals.⁸² On the other hand, transparent polycrystalline ceramics offer a wide range of compositions that can be used, high doping level, easy shaping and lower cost fabrication method in comparison with single crystals.

I.2.2 Transparency conditions in polycrystalline ceramics

A perfect transparent material is one in which light propagates without changing direction. Thus one defines the theoretical maximum transmission (T_{th}) (absence of scattering and absorption losses) which is given by the following formula:

$$T_{th} = \frac{1-R}{1+R} \quad (8)$$

$$\text{With } R = \frac{(n-1)^2}{(n+1)^2}$$

$$T_{th} = \frac{2n}{n^2+1} \quad (9)$$

Where R represents the light reflection at the entrance and at the exist of the material and n the index of refraction.^{83, 84}

However, most transparent materials exhibit scattering centers causing a deviation in the direction of light propagation through the material, which cause a significant loss in the theoretical maximum transmission. For transparent polycrystalline ceramics these scattering centers are presented by the grain boundaries, residual pores, secondary phase, double refraction, inclusions and surface roughness. These scattering centers are illustrated in Figure 6 given by Ikesue *et al.*⁸²

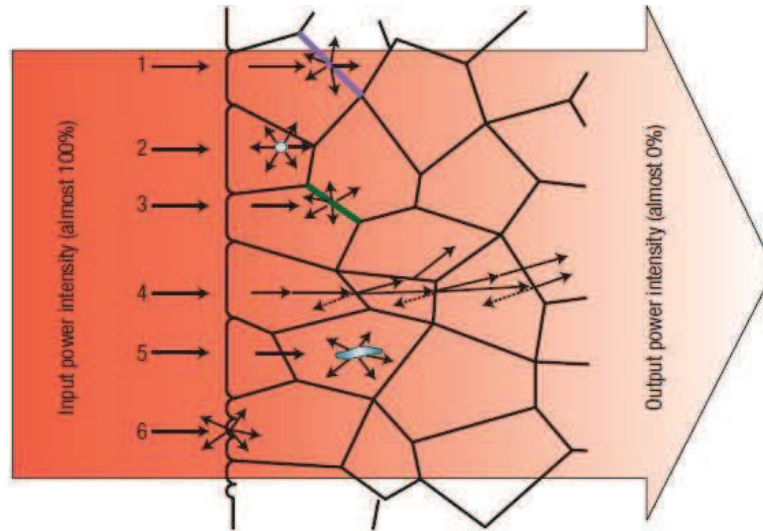


Figure 6 Schematic drawing of the different scattering centers in conventional microstructure of transparent ceramic. Strong scattering due to (1) a grain boundary, (2) residual pores, (3) secondary phase, (4) double refraction, (5) inclusions and (6) surface roughness in ceramics (Ikesue *et al.*⁸²)

- Grain boundaries between grains can be regarded as interfaces between two domains of different properties, causing light scattering. Largely thin clear grain boundaries minimize light scattering.
- Residual pores whether intergrain or intragrain represent optical properties largely different from the crystals, causing light to be intensely reflected or refracted resulting in opaque ceramics.
- Secondary phases presented at grain boundaries represent a common reason for opacity, which might result from starting materials impurities, contamination during synthesis process or excessive additives.
- Double refraction, defined also as birefringence, is present in optically anisotropic materials, where an additional light scattering is observed on passing from one grain to another.

- Surface roughness or surface finish, considered as external factor where a ceramic with smooth surface scatters light much less than a ceramic with a rough surface.

For cubic transparent polycrystalline ceramics (optically isotropic), the scattering sources are presented by grain boundaries, secondary phases and mainly residual pores. The elimination of residual pores (especially intragrain pores) represents a major challenge, and has been the subject of several studies⁸⁵⁻⁸⁷ where even very small residual porosity appeared to affect the obtained ceramics transparency. Residual porosity represents a significant drawback for the final optical properties and applications.⁸⁷

Concerning non-cubic transparent polycrystalline ceramics (optically anisotropic), scattering is caused by the birefringent splitting of the light at grain boundaries and diffuse scattering at residual pores and secondary phases. The refractive index of the material becomes highly dependent on the different crystals orientations, where a considerable change in the beam direction is obtained at each grain boundary between two crystals. For optically anisotropic (non-cubic) materials, the existing birefringence renders the transparency more dependent on the crystal size in order to minimize the birefringent scattering losses. A very small crystal size⁸⁴ (much smaller than the wavelength of the incident light as described by the Rayleigh-Ganz particle scattering theory⁸⁸) is an essential condition for ensuring transparency in most cases.

For developing transparent polycrystalline ceramics, the conventional strategy resides in eliminating all the light scattering sources including residual pores, and secondary phases at the grain boundaries, birefringence (for non-cubic materials) and large grain size. Meanwhile, for optically anisotropic materials with small birefringence values, less scattering is obtained for large crystal size (less interface area).

I.2.3 Transparent polycrystalline ceramics: properties and applications

Transparent polycrystalline ceramics offer various advantages due to their cost-effectiveness, shaping flexibility and mass production. These general features, when coupled with specific mechanical, optical, thermal, photonic or electric properties, offer different domains of application for transparent polycrystalline ceramics.

- i) Transparent polycrystalline ceramics with high property homogeneity, high doping concentration, multifunctional composite structure and large emission and

absorption cross section are essential for laser applications⁸⁹ such as the cubic Nd:YAG, Yb:Y₂O₃, Yb:Sc₂O₃ and Yb:Lu₂O₃ transparent polycrystalline ceramics.⁹⁰⁻⁹²

- ii) Transparent polycrystalline ceramics with high density, very high refractive indices up to 2 or special dispersion characteristics make them ideal hosts materials for optical lenses applications such as cubic Lu₃NbO₇ and ZrO₂ transparent ceramics.^{93, 94}
- iii) Transparent polycrystalline ceramics with superior mechanical and thermal properties offer great candidates for armor applications such as cubic transparent polycrystalline MgAl₂O₄ ceramic^{95, 96} or the non-cubic nanometric synthetic α -Al₂O₃ sapphire and ruby^{97, 98}. Alumina being a birefringent material (non-cubic symmetry), it is more sensible to materials imperfections and demands a precise control of the crystal size to the nano-scale (crystal size smaller than the wavelength of light) and high density in order to retain the transparency of the parent glass.⁹⁹⁻¹⁰¹
- iv) Transparent polycrystalline ceramics with high density and ability to detect highly ionizing radiations are highly used for scintillating applications such as Lu₂O₃ and Y₂O₃ transparent polycrystalline ceramics.¹⁰²⁻¹⁰⁴

In addition to these applications, it is reported in the literature a wide list of transparent polycrystalline ceramics with different properties and applications.^{82, 84, 105-111}

I.2.4 Transparent polycrystalline ceramics sintering techniques

Sintering is the process converting a powder into a highly dense solid under high pressure and temperature. This technique is frequently adopted due to the high melting point of the raw materials. It has been widely used by ceramist to develop transparent polycrystalline ceramics with the minimum possible residual porosity.^{112, 113} Diverse synthetic approaches, either by hot pressure, vacuum, spark plasma or microwave sintering of specific nanometer-scale raw materials can be employed.

I.2.4.1 Hot pressure sintering (HP)

Hot pressure sintering allows simultaneous application of heat and pressure for the fabrication of hard and brittle materials.^{114, 115} HP sintering has been employed for the

synthesis of transparent polycrystalline ceramics¹¹⁶, such as transparent MgAl_2O_4 spinel nanoceramics¹¹⁷, transparent aluminium garnet nanoceramics (YAG)¹¹⁸, transparent electro-optic ceramics such as $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ transparent ceramic (PLZT)¹¹⁹, transparent $\text{Yb}:\text{CaF}_2$ ceramics.¹²⁰ An upgrade of this technique, named hot iso-pressure sintering (HIP), consists of increasing the density of ceramics by using a pressure applied from all directions in addition to both high temperature and isostatic gas pressure.¹⁰⁵ HIP sintering has been widely used for the synthesis of transparent ceramics such as alumina (Al_2O_3).^{97, 98} Some transparent polycrystalline ceramics have also been synthesized by a hot pressure sintering followed by hot isostatic pressing such as spinel MgAl_2O_4 .^{121, 122}

1.2.4.2 Vacuum sintering

Vacuum sintering corresponds to the sintering of ceramics under vacuum.¹⁰⁵ This sintering process is used mainly for the elaboration of transparent garnet and rare earth sesquioxides ceramics such as Y_2O_3 ^{123, 124}, Sc_2O_3 ^{125, 126} and even YAG ceramics¹²⁷ can be elaborated by vacuum sintering followed by thermal annealing treatment.

1.2.4.3 Spark plasma sintering (SPS)

Spark plasma sintering (SPS) is a relatively new developed technique used for the preparation of fully dense transparent polycrystalline ceramics.¹²⁸⁻¹³¹ This technique combines simultaneously a pressure and an electric current directly applied on the sample. The significant advantage of the SPS technique when compared with other sintering techniques lies in the Joule heating within the sample, allowing one to obtain dense ceramics in short processing time with complete powder consolidation.¹³² This technique has been the subject of many important reviews¹³³, and transparent ceramics synthesized by this technique also have been widely reported in the literature including sesquioxides¹³⁴, YAG^{135, 136}, ZrO_2 ¹³⁷ and MgO .¹³⁸

1.2.4.4 Microwave sintering

The microwave sintering technique is different from the conventional sintering techniques. It converts the absorbed microwaves into heat within the sample, resulting in greater energy efficiency, smaller grain size and better mechanical properties.¹³⁹ Microwave

sintering has been used to prepare several transparent polycrystalline ceramics, such as transparent aluminium oxynitride ceramics (ALON)¹⁴⁰ and transparent mullite ceramics.¹⁴¹

1.2.4.5 Sintering techniques limitations

The above described sintering techniques, although possessing many advantages in comparison with single crystals synthetic route, exhibit some limitations. They require complex and expensive sintering conditions (high pressure and temperature) in addition to the required specific nanometer-scale raw materials where the particle size distribution can have significant effects on the sintering.¹⁴²⁻¹⁴⁴ Residual pores; a major light scattering source; are also very difficult to avoid.¹⁴⁵ A precise control of the sintering rates, sintering atmosphere which might have an enormous effect on the densification of the material is a quite challenging process.¹⁴⁵⁻¹⁴⁷ For the SPS technique a major drawback is given by the carbon contamination and segregation (caused by the use of graphite die) which restrains the materials optical properties.¹⁴⁸ These drawbacks of the sintering techniques have restrained the number of produced transparent polycrystalline ceramics.¹⁴⁵

1.2.5 Transparent polycrystalline ceramics by full crystallization from glass

Regarding the complicated and time consuming sintering processes discussed previously, complete crystallization from glass appears to be as an interesting alternative approach. Complete and congruent crystallization from glass is a promising method to overcome all the drawbacks of single crystal and different sintering techniques which should open the way to wide industrial applications. Using this synthetic route, wide range of compositions could be synthesized and complex large scale shapes could be fabricated in a fast and cost-effective way. The priori of this synthetic route that must be first satisfied, is to ensure that the chemical composition of the desired crystalline phase is located in the glass-forming region.

1.2.5.1 Full crystallization from glass

Full crystallization from glass is an innovative synthetic route opening the way to the elaboration of dense polycrystalline transparent ceramics. It consists of preparing the parent glass, followed by a thermal treatment in order to totally crystallize it. Using this method, two challenges must be overcome: (i) the synthesis of a glass with the aimed ceramic composition

(to ensure congruent crystallization) and (ii) the retention of transparency during the crystallization process.

In 2004 Rosenflanz *et al.*¹⁴⁹ reported the synthesis of nano-scale crystalline alumina with rare-earth oxide ceramics ($\text{Al}_2\text{O}_3\text{-RE}$, RE=La, Gd and Y). Glass microspheres ($\approx 140\ \mu\text{m}$) were prepared by flame-spraying technique, followed by densification in a graphite furnace by pressure-less sintering or hot pressing in order to obtain the transparent ceramics. This approach although lying under full crystallization from glass approach, a post-sintering step with a precise control of crystal size (nano-scale) is essential to develop and conserve the transparency of the obtained polycrystalline ceramics.

Another transparent non-cubic $\text{LaAlO}_3/\text{t-ZrO}_2$ nano-ceramic was elaborated by an amorphous sintering followed by controlled crystallization (ASCC) method.¹⁵⁰ For the preparation of these transparent ceramics, glass powders were synthesized, sintered by viscous flow and then converted to transparent nano-ceramics with a post-heat treatment.¹⁵¹ However, due to the reduced light scattering from birefringence, the transmittance of $\text{LaAlO}_3/\text{t-ZrO}_2$ nanoceramic (1.0 mm thick) was just up to 68% at 800 nm, and a great volume shrinkage was observed to occur during crystallization. This ASCC method possesses the same problems of the SPS sintering technique consisting of sample contamination which limits its optical application.

Later in 2012, Allix *et al.*¹⁵²⁻¹⁵⁴ reported the synthesis of new transparent BaAl_4O_7 polycrystalline ceramics synthesized by full crystallization from glass (Figure 7a). The originality of this approach resides in the simple thermal annealing treatment of massive bulk glass to obtain transparent polycrystalline ceramics with no necessity for high pressure, complex and expensive sintering techniques. These ceramics can exist under two orthorhombic polymorphs. Even though they exhibit micron scale crystal sizes and optical anisotropy (birefringence due to their orthorhombic symmetry), their high transparency was associated to the complete absence of porosity, very thin grain boundaries and small birefringence (~ 0.01 obtained from DFT calculation). The α -polymorph also appears to be more transparent than the β -polymorph due to smaller crystal size compared to the β -polymorph ($0.5 - 2\ \mu\text{m}$ grain size for the α -polymorph and $1 - 5\ \mu\text{m}$ for the β -polymorph) observed using transmission electron microscopy (Figure 7b-c).

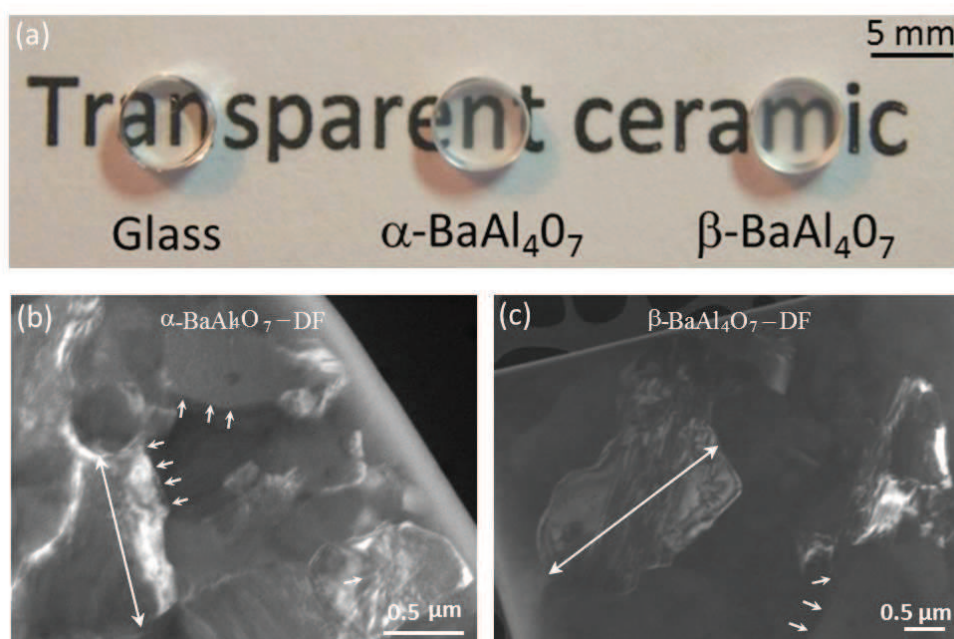


Figure 7 Transparent polycrystalline ceramics prepared by glass crystallization: (a) from left to right, BaAl_4O_7 parent glass, α -polymorph and β -polymorph transparent ceramics respectively. (b) and (c) Dark field transmission electron microscopy images of α -polymorph and β -polymorph respectively showing the larger crystal size for the β -polymorph, the thin grain boundaries and no porosity for both polymorphs.¹⁵²

1.2.5.2 Further advancements required

Despite all the achievements in the transparent polycrystalline ceramics field, further research is still required due to the currently increasing demand of transparent ceramics for different applications such as optical lenses, transparent armour, scintillators and lasers. The great advantages of massive synthesis, wide range of composition candidates, shape flexibility and cost effectiveness offered by full crystallization from glass over that of single crystals and sintering techniques makes this approach appear as a very promising route for the elaboration of transparent polycrystalline ceramics for photonic applications. The reported BaAl_4O_7 ceramics, exhibit a weak birefringence which hinders high transparency levels to be reached. Another limitation of this composition is its high melting temperature (2000 – 2200 °C), which necessities the use of a specific melting system (aerodynamic levitation) that limits the large scale application of the material. A greater level of transparency is highly desirable for efficient optical and even photonic applications. For this purpose, the synthesis of a material exhibiting perfectly isotropic optical properties (cubic structural symmetry), should demonstrate higher transparency and would probably achieve the maximum theoretical transmission. In addition, large scale transparent ceramics that can be prepared by this relatively simple, non-expensive full crystallization approach should be very interesting due

to the limited sample size synthesis by aerodynamic levitation (glass beads with $\varnothing \approx 3 - 5$ mm).

The aims of this study consist first in the synthesis of transparent polycrystalline ceramics with optical isotropy and thus ameliorated transparency and second going further for a larger scale massive application of transparent polycrystalline ceramics prepared by full crystallization from glass.

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Chapter II

Methods and experimental techniques

In this chapter, the different experimental techniques used throughout the manuscript are detailed. These mainly include glass and polycrystalline ceramic synthesis procedures, their structural characterization at different scales (average and local), using electron microscopy (SEM and TEM), powder diffraction and nuclear magnetic resonance spectroscopy (NMR) probing techniques, DFT calculations in addition to the techniques used for physical properties characterization (optical transmission, luminescence and mechanical properties).

II.1 Transparent polycrystalline ceramic synthesis

II.1.1 Glass synthesis

The elaboration of transparent polycrystalline ceramics starts with glass synthesis, which is a very crucial step and worth time spending. The quality of the ceramic to be obtained is dependent on the quality (i.e. homogeneity) of the parent glass. In this thesis, two different glass preparation techniques have been used: the classic melting/quenching process realized in a commercial electric furnace and the aerodynamic levitation coupled to laser heating system. The choice between these two techniques relies on two different criteria: first the melting temperature of the oxide mixture and second the cooling rate required to avoid uncontrolled devitrification.

II.1.1.1 Classic melting/quenching process (electrical furnace)

A commercial electrical furnace (Nabertherm, $T_{\max} = 1750\text{ }^{\circ}\text{C}$) has been used in the case of oxide compositions melting at a maximum temperature of $1700 - 1750\text{ }^{\circ}\text{C}$ and when no special quenching procedure was required to avoid devitrification during cooling.

For classic melting/quenching, the glass preparation takes place according to the following procedure which is represented in Figure 1:

- Weighing stoichiometric amounts of precursors.
- Homogenizing the oxide mixture dispersed in ethanol using a mortar and pestle.
- Introducing the dried oxide powder mixture into platinum crucible.
- Introducing the crucible into a pre-heated furnace (temperature and time adjusted according to the sample composition).

- Quenching of the crucible in air or water (dependent on the sample and further manipulation to be realized)

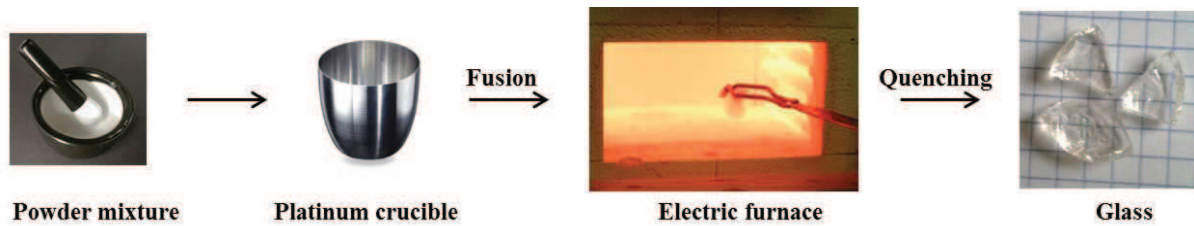


Figure 1 Glass synthesis procedure followed during classic melting quenching approach in a typical commercialized electric furnace

II.1.1.2 Aerodynamic levitation coupled to laser heating

Levitation techniques have been developed for studying materials at high temperatures while keeping them in a contactless environment. Levitation techniques prevent induced contaminations which may cause undesired heterogeneous nucleation and provides supercooling rates.¹⁻⁴ The contactless and high temperature aspects of levitation are essential criteria in the studies of refractory materials. In this study, aerodynamic levitation coupled to laser heating system (Figure 2) developed in the CEMHTI laboratory^{5, 6} has been employed for oxide mixtures with a melting temperature higher than 1750°C, and/or for compositions requiring a very fast quenching rate to avoid devitrification. The used aerodynamic levitator is coupled to two CO₂ lasers ($\lambda = 10.6 \mu\text{m}$) irradiating the top and the bottom of the sample, therefore allowing a homogeneous melting of the compacted powder at very high temperatures ($T_{\text{max}} \approx 3000^\circ\text{C}$). The cut off of the two lasers results in a fast quenching rate of roughly 300 °C/s, which is sufficient to avoid devitrification for our compositions. Moreover, the aerodynamic levitation presents the advantages of being a contactless process where no contamination appears to occur between the sample and the nozzle. It also provides, through the use of an enclosure, the ability to control the synthesis atmosphere via the gas used to levitate the sample.

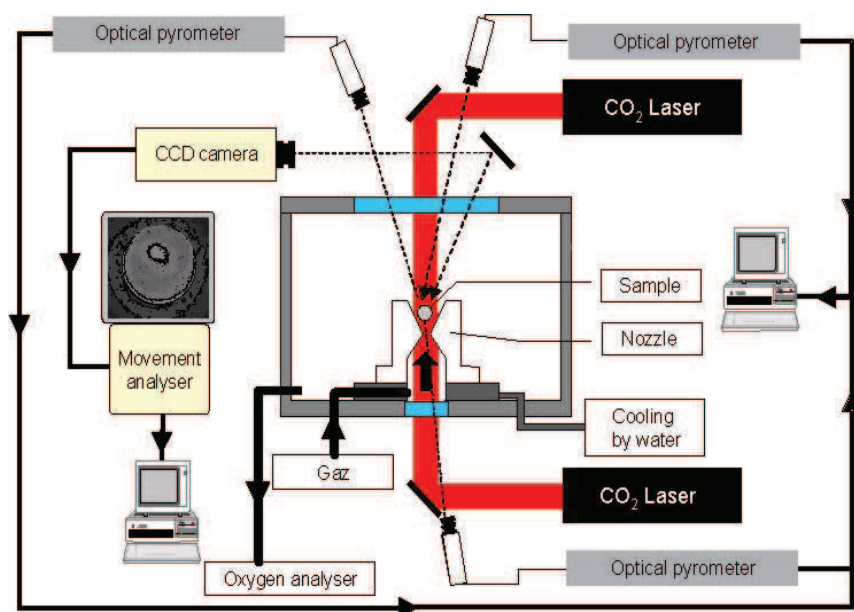


Figure 2 Drawing of the aerodynamic levitator coupled to laser heating system

The glass preparation using the aerodynamic levitator coupled to laser heating takes place according to the following procedure presented in Figure 3:

- Weighing stoichiometric amounts of precursors.
- Homogenizing the oxide mixture dispersed in ethanol using a mortar and pestle.
- Pressing the dried powder into a pellet using a pelletizer and a uniaxial press.
- Placing a small portion of the pellet onto the metallic nozzle where it is levitated by a controlled gas flux.
- Melting the sample by controlling the power of the two CO₂ laser beams. The gas levitating the sample allows it to spin and to obtain a circular homogeneous melted bead.
- Cutting-off the lasers to ensure fast quenching. Glass beads of 3-5 mm in diameter are typically obtained.

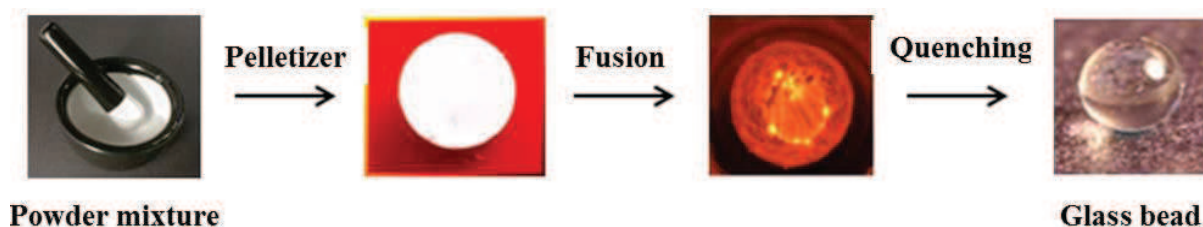


Figure 3 Glass synthesis procedure followed during aerodynamic levitation coupled to laser heating

II.1.2 Glass crystallization

Consequently to glass synthesis, a thermal annealing treatment is required to crystallize the glass. The choice of the thermal treatment parameters basically depends on the information obtained by differential scanning calorimetry (DSC).

II.1.2.1 Thermal Analysis (differential scanning calorimetry DSC)

Differential scanning calorimetry measures the heat flow into a material as a function of time and temperature under controlled atmosphere. This heat flow is associated with different physical and chemical thermal transitions. The apparatus used in this work is a DSC 96 SETARAM equipped with a MHTC 96 hf-DSC sensor for measuring the heat capacity of materials up to 1600 °C.

The configuration of this apparatus consists of two ceramic chambers. Inside one of these chambers is placed an empty crucible (reference) and in the second is placed a crucible containing the sample (in powder or bulk form). These two chambers being vertically arranged are connected to each other by two conducting plates with twenty thermocouples. The differential detector thus formed completely envelopes the experiment chamber, thereby providing global and precise measurements. Vacuum control and gas switching are all fully automated and computer controlled. The chambers can withstand high vacuums and in our study all the DSC measurements were realized under constant argon flow according to the program presented Figure 4 unless otherwise stated.

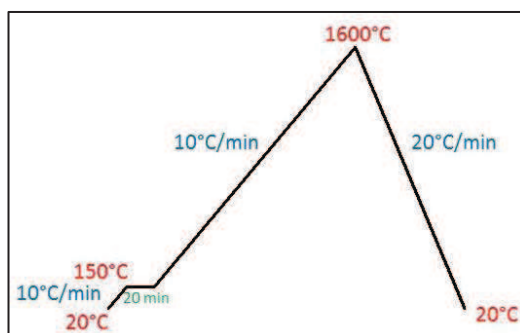


Figure 4 Heating program used during DSC measurements in this study

Using DSC, different quantitative and qualitative information could be obtained. In our study we are interested in the following properties: glass transition (appearing as a small endotherm resulting from a strong variation in the heat capacity of the sample), crystallization (exothermic phenomenon) and melting (endothermic phenomenon) (Figure 5).

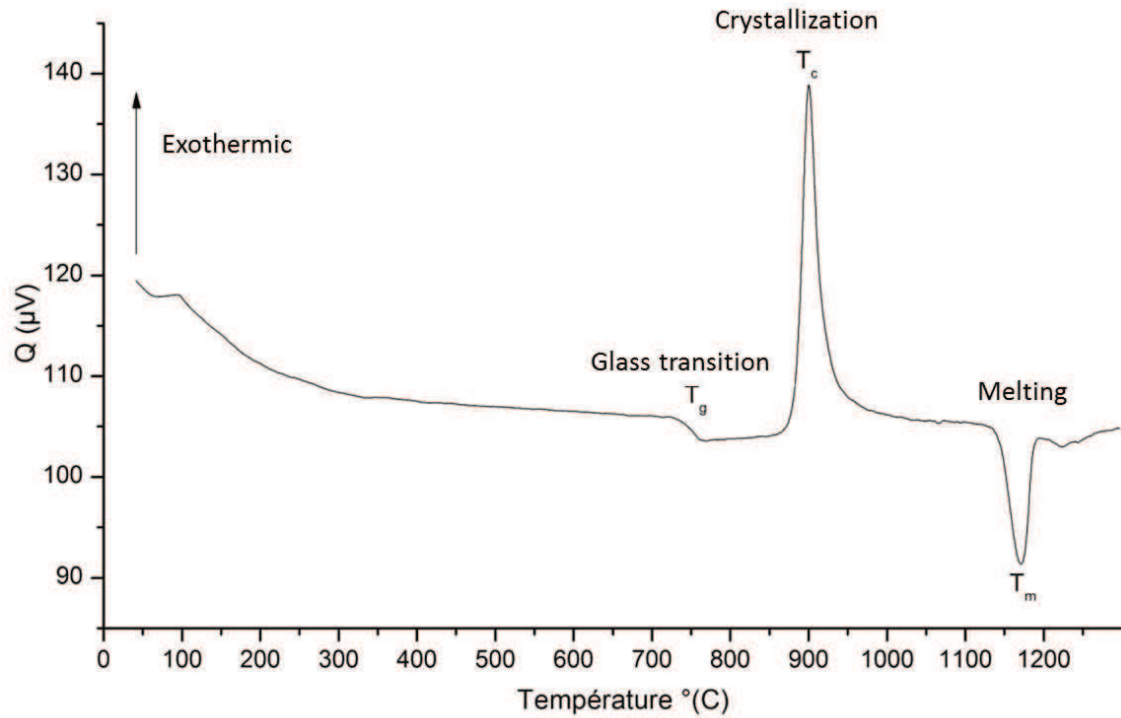


Figure 5 Typical DSC thermogram of a glass showing glass transition (T_g), crystallization (T_c) and melting phenomena (T_m) while heating

II.1.2.2 Heat treatment

After determining the thermal properties, a controlled thermal treatment of the glass at the corresponding crystallization temperature leads to the full ceramization of the glass, *i.e.* obtaining polycrystalline ceramics. The thermal crystallization treatment can also be performed under controlled atmosphere especially in the case of doped samples with doping agents having redox state sensitive to synthesis atmosphere. Different parameters play a major role in the crystallization process, the main ones being the crystallization temperature, annealing time, surrounding atmosphere. All those parameters need to be adjusted in order to find the best thermal treatment conditions for each sample.

II.2 Microstructure characterization

II.2.1 Scanning electron microscopy (SEM)

Scanning electron microscopy (Figure 6) coupled to Energy Dispersive X-Ray Spectrometer is used to obtain information about the samples surface morphology, chemical homogeneity, quantitative and qualitative chemical composition at the micrometer scale. In this manuscript, scanning electron microscopy was used mainly for visualizing the mosaic

crystalline microstructure of the transparent polycrystalline ceramics and the crystallite orientation.

In this work, an XL 40 ESEM (FEI) was used. The incident electrons emitted by an electron gun are thermoelectrically generated by passing an electrical current through a tungsten filament. These electrons are accelerated by applying a sufficient amount of potential (1 – 30 KV), then a set of different electromagnetic lenses is used to control their flow and generate a homogenous electron beam which can be focused and scanned on a definite spot on the sample's surface. The incident electrons with sufficient kinetic energy give different signals depending on the electron-sample interactions.

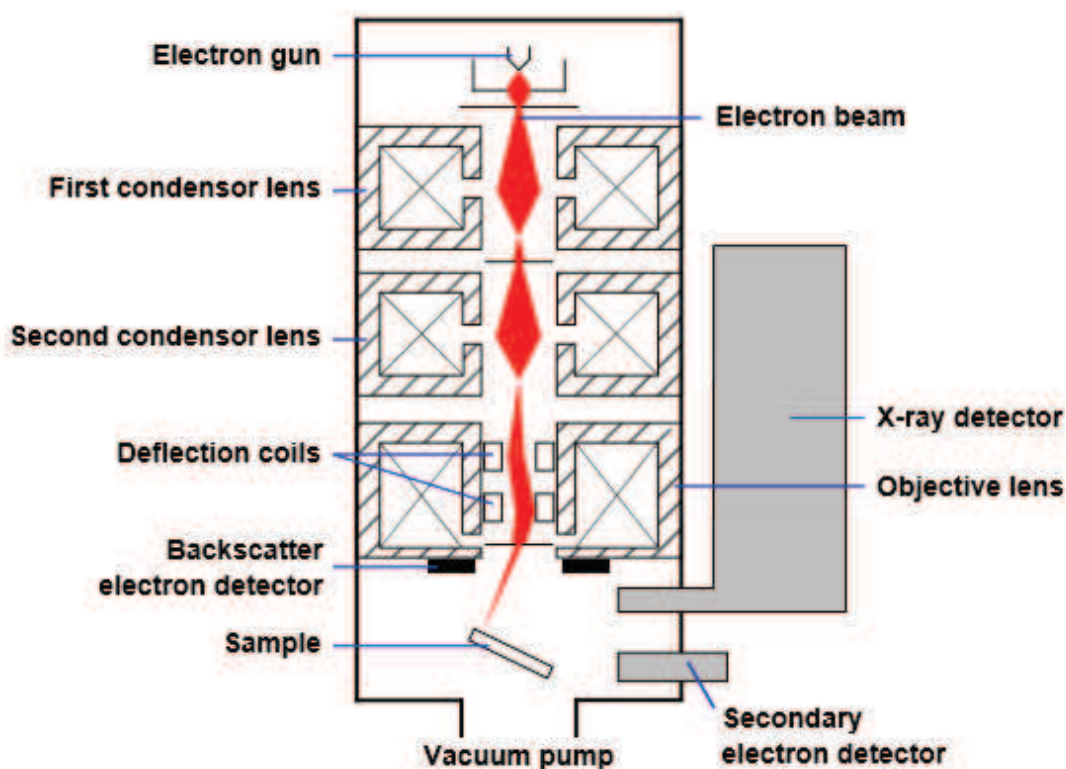


Figure 6 Drawing of a scanning electron microscope.

The signals notably include the secondary electrons (SE), backscattered electrons (BSE) and X-rays.

- *Secondary electrons (SE) imaging*

The incident electrons, with high kinetic energy, collide with the sample valence electrons, causing them to be ejected from their electronic level with lower energy (50 eV). The ejected electrons are called secondary electrons. Since the incident electron beam possesses high energy, each single electron from the beam leads to the emission of

thousands of SE. The low-energy ejected SE are collected by a detector having a positive potential on its face in order to attract them.

The contrast of the obtained image is highly dependent on the angle between the incident beam and the sample's surface where a local inclination in the sample leads to a variation in the incident beam angle, therefore providing information about the sample's surface morphology and topography.

- *Backscattered electrons (BSE) imaging*

When the incident electrons collide elastically with the samples nucleus and bounce back, they are called backscattered electrons. The quantity of these high-energy backscattered electrons is directly dependent on the atomic number Z of the atoms (high atomic number regions appear bright relative to regions with low atomic number). So the backscattered imaging mode gives information about the sample's chemical homogeneity and contrast between areas with different chemical compositions.

- *Elemental analysis by X-rays*

As the electron beam scans the surface, X-rays are produced by the inelastic collision of the incident electron with those of the sample's shell electrons. These excited electrons, while returning back to the lower energy stable ground state, in order to replace the ejected electrons, emit quantized X-rays. The energy of the emitted characteristic X-rays is measured and an X-ray energy spectrum is generated which serves as a signature of each element, therefore giving different information about the sample's chemical composition.

II.2.2 Transmission electron microscopy (TEM)

Transmission electron microscopy through three different operating modes (imaging, diffraction and energy dispersive spectroscopy analysis (EDS)), gives information concerning the crystalline structure and the chemical composition of the studied material. TEM was used in this study to examine the microstructure of the transparent polycrystalline ceramics (grain boundaries, porosity, and crystal size). It was also used in the structural determination of the new strontium aluminosilicate phases in Chapter IV (through electron diffraction mode) and chemical composition analysis (through EDS mode).

Transmission electron microscopy studies were realized using a Philips microscope CM20 operating at 200KV and using LaB₆ single crystal as an electron source in the Centre

de Recherche sur la Matière Divisée laboratory.⁷ High resolution STEM-HAADF imaging was realized in CRISMAT/CIMAP laboratories^{8, 9} on a JEOL ARM200F cold FEG TEM/STEM Cs double corrected machine.

Sample preparation:

For TEM observations, thin electron-transparent samples (<100 nm) are required. In this study three types of sample preparation were used:

- *Powder sample preparation*

A small quantity of powder is mixed with ethanol. A small drop of the suspension is placed on a Cu grid. This grid is then placed on the sample holder for insertion into the TEM. Images can be then collected on the edges of the sample which are sufficiently thin to be transparent to the electrons.

- *Focused ion beam (FIB) technique*

The sample is mounted on a cross section of a Cu plate. A Ga ion convergent beam is used to mill out areas of approximately 5 μm deep and 20 μm wide around the zone of interest. Once the sample dimension reaches the proper size (thickness < 100 nm), the application of a conventional lift-out technique is used to pluck the FIB milled sample and to fix it onto the Cu grid for later TEM observation.

The FIB lift-out technique was used for the $\text{Sr}_3\text{Al}_2\text{O}_6$ polycrystalline ceramics (Chapter III).

- *Tripod preparation*

An optically polished sample is cut into dimensions of 2.5 mm $\times$ 1.5 mm using a diamond saw wire. The sample is then mechanically polished with a tripod and inlaid diamond discs until 70 μm thickness. The last step consists of argon-iron milling using the precision ion polishing system (PIPS).

Tripod preparation was used for high-resolution observation of the grain boundaries in strontium aluminosilicate polycrystalline ceramics (Chapter IV).

In transmission electron microscopy, images or diffraction patterns can be obtained through different operating modes.

- *Imaging mode*

The images are formed from the transmitted or diffracted beam (Figure 7) or both for high resolution TEM. In the case of bright field image, the image is formed only from the transmitted beam (select direct beam with objective aperture). However, the dark field images are formed from a diffracted beam. The selection of the beam used to make the image is realized by placing a small aperture called "objective" in the back focal plane of the objective lens.

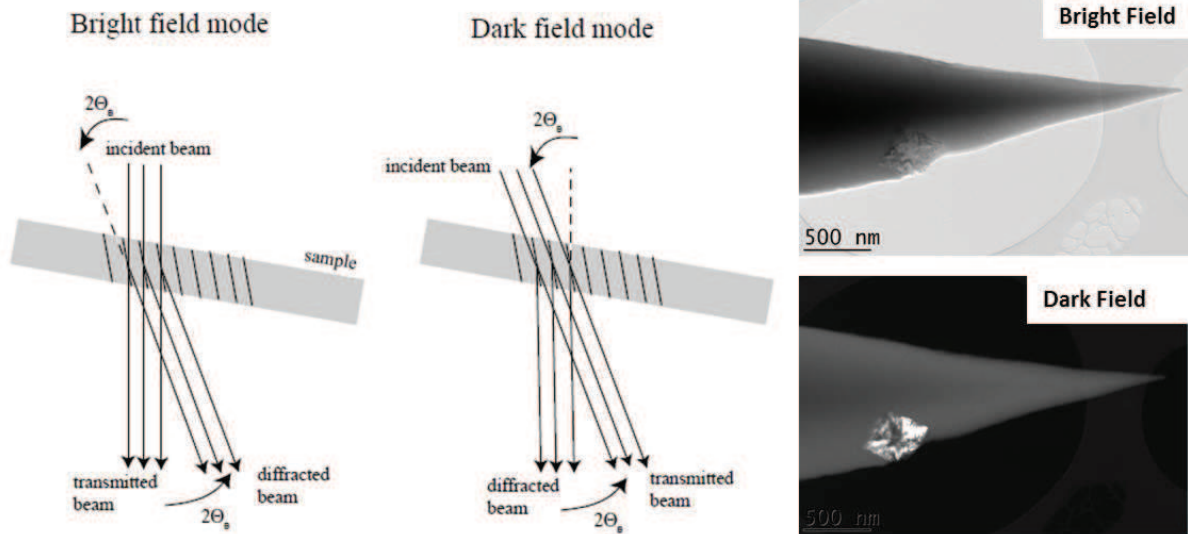


Figure 7 Bright and dark field imaging modes in transmission electron microscopy, with examples on the right (YAG-4Si glass-ceramic¹⁰)

In the bright field image, the crystalline parts in Bragg orientation will appear dark while amorphous parts appear bright. However, in the dark field image, only the crystals falling at the origin of the selected diffracted beam appear bright, while all the others appear dark.

- *Diffraction mode*

In the diffraction mode, using the selected area aperture situated in the image plane of the objective lens, a small part of the imaged sample is selected to be analyzed. The diffraction patterns allow the determination of the cell parameters and the possible reflection conditions which leads to the identification of the space groups.

- *Energy dispersive X-Ray spectroscopy analysis (EDS or EDX)*

This operating mode serves in the elemental analysis or chemical characterization of the sample. It is based on the principle that each element has a unique X-ray spectrum. The interaction of the high energy electrons with the sample results in the excitation of its electrons. X-rays will be emitted during the de-excitation process giving these characteristic peaks of each element allowing the chemical composition identification of the studied zone.

- *Scanning transmission electron microscopy-high angle annular dark field (STEM HAADF) imaging*

STEM is recognized as a type of TEM with electrons focused on a narrow beam but being scanned over the sample. The STEM-HAADF images are formed from electrons diffracted at high angle and allow collecting atomic resolution images with obtained contrast directly proportional to the atomic number $Z^{1.7}$ (heavier atoms contribute to brighter contrasts).

II.2.3 Density measurements

The density of the ceramic materials was determined based on Archimedes' principle. An object immersed in a liquid is subjected to three forces, its weight, tension and Archimedes up-thrust. The upwards force is equal to the weight of the liquid displaced by the object. Therefore, by double weighing the glass or the ceramic material in air and then when fully immersed in a liquid of known density (Figure 8), the density can be then calculated according to the following relation:

$$\mu = \frac{mass_{glass/ceramic\ in\ air} \times \mu_0}{mass_{glass/ceramic\ in\ air} - mass_{glass/ceramic\ in\ liquid}} \quad (1)$$

Where μ_0 represents the density of the corresponding liquid at a given temperature.

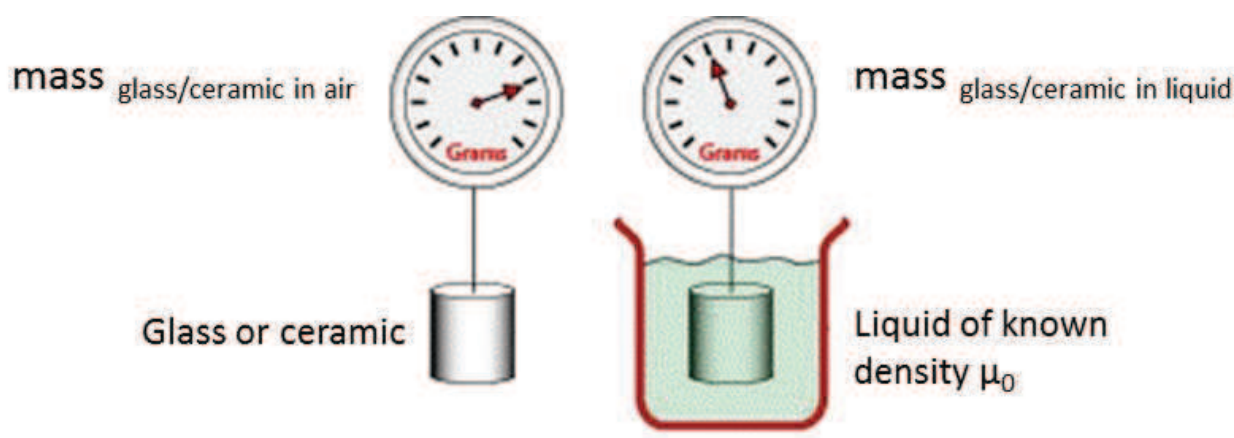


Figure 8 Schematic presentation of the density measurement using Archimedes' method

II.3 Structural Characterization

II.3.1 Powder Diffraction

Powder diffraction is a key technique used to obtain information concerning the average structure. Powder diffraction can be realized through different interactions, presented through laboratory X-ray, synchrotron and neutron diffraction.

II.3.1.1 Laboratory X-Ray diffraction (XRD)

X-ray powder diffraction is a technique used to study the material's crystalline structure. This technique was principally used in this work to check the nature of crystalline phases, crystallization evolution versus temperature and to determine the coefficient of thermal expansion. Powder diffraction data also served as input data for structural refinement and determination.

The used diffractometer was a D8 Advance (Bruker AXS) functioning in Bragg-Brentano geometry (Figure 9a). The radiations used were $K\alpha_{1,2}$ of copper ($\lambda=1.54060$ Å and 1.54439 Å respectively). The diffractometer is equipped with a linear detector Vantec-1 allowing rapid acquisition of diffraction over a wide angular range (12° in 2θ).

The diffractograms for structural refinement studies were registered over the $8-125^\circ$ 2θ range with an acquisition time of 3 seconds and a step size of 0.0164° .

Other diffractograms for regular verification of amorphous and crystallized samples were registered over the $8-70^\circ$ 2θ range with an acquisition time of 1 second and a step size of 0.0164° .

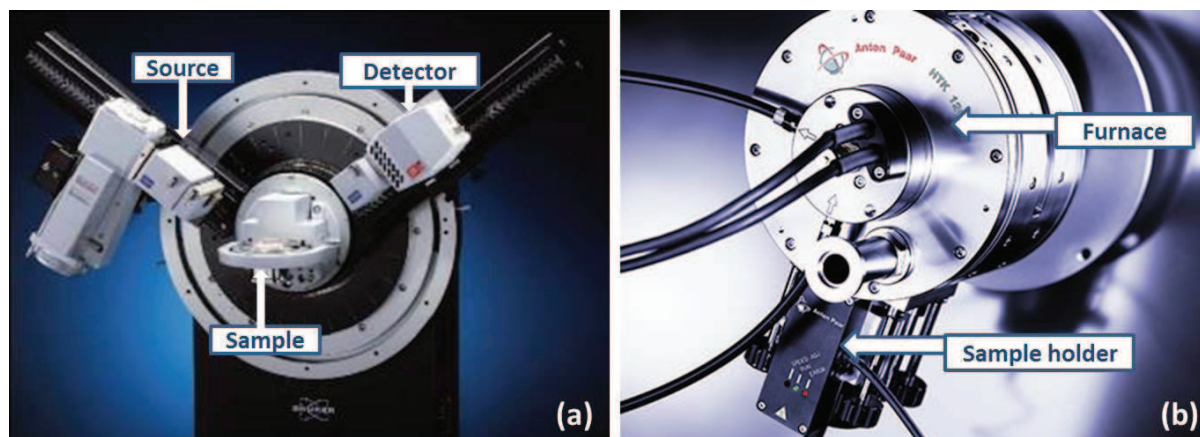


Figure 9 D8 Advance Bruker AXS diffractometer in Bragg-Brentano geometry at ambient temperature (a), equipped with furnace Anton Paar HTK 1200N (b)

For X-ray diffraction conducted at high temperatures, the same diffractometer was used, this time the sample holder equipped with a furnace Anton Paar HTK 1200N model (Figure 9b). This furnace, thanks to the resistive element Kanthal, allows the sample to be heated up to 1200 °C while running diffractogram acquisition at the same time. Powder samples were placed in an alumina crucible of 0.8 mm depth, sometimes a thin platinum disc was placed in the bottom of the crucible in order to avoid interaction between the sample and the alumina crucible.

II.3.1.2 Synchrotron powder diffraction

Synchrotron powder diffraction was used when higher resolution than that available using laboratory X ray diffraction was required.

The synchrotron diffraction data reported in this thesis were realized in collaboration with Dr. Matthew Suchomel on the 11-BM beam line¹¹ (Argonne National Laboratory, APS, USA¹²) which offers a resolution of $\Delta Q/Q < 2.10^{-4}$. The samples in form of powder were introduced into Kapton capillaries of 1 mm in diameter. As the studied compositions possess an acceptable absorption ($0.5-1.0 \mu\text{m}\times\text{r}$) of X-rays^{13, 14}, no special protocol was followed in the preparation of the capillaries. The diffraction data were collected on a spinning sample (60 Hz) over the $0.5 - 60^\circ 2\theta$ range with a 0.001° step size at room temperature using a $\lambda = 0.413978 \text{ \AA}$ wavelength.

II.3.1.3 Neutron powder diffraction

In neutron powder diffraction, neutron interaction occurs with atomic nuclei, thus providing complementary information to that accessible by X-ray powder diffraction. Contrary to X-ray powder diffraction, the intensity of the neutron powder diffractions is independent of the elements atomic number Z . This renders neutron powder diffraction as an ideally suited technique for distinguishing between elements with adjacent atomic numbers such as Al and Si in addition to the localization of light atoms in the crystalline structures such as oxygen.

Another advantage provided by neutron powder diffraction is the significant intensities obtained at high diffraction angles due to the independence of the scattering length on the angle of diffraction, where the only fall-off in the intensities as a function of the scattering angle is due to the thermal motion of the atoms.

These advantages render neutron powder diffraction an adapted complementary technique for this study, even though its resolution ($\Delta Q/Q \approx 2.10^{-3}$) is lower than that provided by X-ray powder diffraction.

Neutron powder diffraction experiments were realized in collaboration with Dr. Florence Porcher in the Laboratoire Léon Brillouin (LLB)¹⁵ associated with the reactor ORPHEE. The neutron diffraction data were collected for 22 h on a 5 g sample over the 4.5 - 121° 2θ range using a 0.05° step size and a 1.225 Å wavelength.

II.3.1.4 Structure determination and structural refinement from powder diffraction

The structural determinations and structural refinements were carried out from powder diffraction data based on Le Bail and Rietveld methods¹⁶⁻¹⁸ using Jana2006 software.¹⁹ The *ab initio* structural resolution of the new crystalline structures was realized using the charge flipping method^{20, 21} via the program SUPERFLIP²² implemented in the Jana2006 software.

Le Bail method

The Le Bail refinement is considered as a pre-step for the Rietveld refinement, used to refine the whole profile, determine the cell and profile parameters before the recall of the structural model for its refinement.

This method requires knowledge of the system symmetry and space group (determined from reflection conditions) and approximate cell parameter values (obtained using auto-indexation programs and/or electron diffraction) of the crystalline structure. Nevertheless, the knowledge of the structural entity (nature, positions and occupancy of atoms present in the cell) is not necessary.

For profile refinement based on diffraction data, a Pseudo-Voigt function (pV) is used which combines the effects of the instrument (Gaussian profile) and that of the sample (Lorentzian):

$$pV(2\theta) = \eta L(2\theta, H) + (1 - \eta)G(2\theta, H) \quad (2)$$

Where L represents the Lorentzian part, G the Gaussian part, η the ratio of the Lorentzian to that of the Gaussian function, 2θ the diffraction angle and H the full width at half maximum.

The full width at half maximum corresponding to the Gaussian function is given by the following equation:

$$H_G = 0.5 (U \tan^2 \theta + V \tan \theta + W + Z/\cos^2 \theta) \quad (3)$$

The full width at half maximum corresponding to the Lorentzian function is given by the following equation:

$$H_L = X \tan \theta + Y / \cos \theta \quad (4)$$

Where U , V , W , X , Y and Z are refinable parameters. U and V are related to defects, Y and Z to crystal size, V and W to the instrument.

By running out several iterating cycles while refining the different parameters (U , V , W , X , a , b and c), the calculated profile may converge to that of the measured profile. The Le Bail refinement leads to obtaining precise profile and cell parameter values.

Rietveld method

Rietveld refinement is a method originally developed by Hugo M. Rietveld^{16, 17} for refining powder diffraction data, in order to extract information of the crystalline structure.

For this study, the Rietveld method was used to refine the data obtained by X-ray, synchrotron and neutron powder diffraction. It was used to refine the crystal structures which served in obtaining information concerning cell parameters, atomic positions and their

occupancy notably. The basis of the Rietveld method consists of using a non-linear least square algorithm, in order to minimize the difference between the measured diffraction profile and the calculated one; i.e. the residual function M :

$$M = \sum_i w_i (y_{obs\ i} - y_{calc\ i})^2 \quad (5)$$

w_i : weight associated with each measured intensity ($w_i = 1/y_{obs}$)

y_{obs} : observed intensity at angle $2\theta_i$

y_{calc} : calculated intensity at angle $2\theta_i$

The calculated intensity (y_{calc}) is given by the sum of different contributions of all peaks that overlap at this point.

$$y_{calc} = Y_{bi} + \sum_{\varphi=1}^N S_{\varphi} \sum_{k=k1}^{k2} J_{\varphi k} \cdot LP_{\varphi k} \cdot O_{\varphi k} \cdot M \cdot |F_{\varphi k}|^2 \cdot \Omega_{i\varphi k} \quad (6)$$

Y_{bi} : intensity of the background noise at the position $2\theta_i$

S_{φ} : scale factor for the phase φ

$J_{\varphi k}$: multiplicity factor of the k^{th} reflection.

$LP_{\varphi k}$: Lorentz-polarization factor

$O_{\varphi k}$: correction factor of preferential orientation

M : correction function of absorption and/or micro absorption

$|F|_{\varphi k}$: structure factor (including atomic displacement, site occupancy, thermal agitation parameters, atomic diffusion factor).

$\Omega_{i\varphi k}$: peaks profile function

Starting with a structural model, all the above parameters should be refined until the calculated pattern converges well with the experimental data. Thus, the minimization of the function M (i.e. convergence of the calculated profile with the measured profile) permits to obtain different information concerning the crystalline structure.

The profile fit can be judged by regarding the plot of the experimental and the calculated profiles. The difference between the two can be related either to profile-parameter problem (difference in peak form), or to a deficiency in the structural model (dis-match of integrated intensities or position problems).²³

The convergence of data can be also controlled numerically by different parameters, which ensure the reliability and the quality of the calculated profile after each cycle of refinement^{24, 25}, these include:

- The agreement profile R
$$Rp = 100 * \frac{\sum_i |y_{obs\ i} - y_{calc\ i}|}{\sum_i y_{obs\ i}}$$
- The weighted-profile R
$$Rwp = 100 * \sqrt{\frac{\sum_i Wi(y_{obs\ i} - y_{calc\ i})^2}{\sum_i Wi(y_{obs\ i})^2}}$$
- The Bragg-intensity R
$$R_{Bragg} = 100 * \frac{\sum_i |I_{obs} - I_{calc}|}{\sum_i I_{obs}}$$

Where I_{obs} and I_{calc} represent respectively the observed and the calculated integrated intensity of the i^{th} reflection.

R_{Bragg} consists on the basic parameter for judging the agreement between the experimental data and the proposed structural model. However, the Rwp parameter is dominated by the precision of the profile function and it is relatively low sensitive to structural parameters.

There exist also two other parameters which give information about the quality of refinement:

The goodness of fit (G.O.F.):
$$\chi^2 = \left(\frac{R_{wp}}{R_{exp}} \right)^2 = \frac{M}{N-P+C}$$

$$R_{wp} = 100 * \sqrt{\frac{(N-P+C)}{\sum_i Wi.(y_{obs\ i})^2}}$$

Where

$N-P+C$: number of degrees of freedom

N : number of independent observations

P : number of adjusted parameters

C : number of constraints between the parameters

M : function to be minimized

Ideally, χ^2 should converge toward a value of 1.

ab-initio structural resolution

X-ray and neutron diffraction play a major role in the structure determination of crystalline materials which are not available in the form of single crystals. The structure determination from powder diffraction is known to be more complex than that of single crystals. The data obtained for crystalline materials are actually a projection of a three-dimensional diffraction pattern onto one dimension (radial distance from the reciprocal space origin), and consequently the diffraction peaks are overlapped. In addition, broadening caused by crystal lattice defects can also make the extraction of structure factor amplitudes a further complicated procedure. But thanks to continuous advancement in powder diffraction techniques and resolution models, structure determination appears an easier task even for highly complex crystalline structures.

The first step in powder crystal structure determination consists in indexing the diffractogram of the new crystalline structure; this corresponds to finding the unit cell parameters which permits the assigning of the Miller indices, namely hkl , to each peak position in the diffractogram. This step can either be realized by the re-construction of the reciprocal lattice by electron diffraction (TEM) or by auto-indexing programs using such as TREOR^{26, 27} and DICVOL²⁸ softwares. The reliability of these diffraction powder pattern indexing can be evaluated by the figure of merit.^{29, 30}

The second step is the extraction of intensities from the powder diffraction diagram with the greatest possible precision. The Le Bail method³¹ is used for this purpose. The refinement of the total profile and the unit cell constraints leads to minimizing the choices of the space group when certain reflection families are absent. This step can be realized with the help of different softwares like Checkgroup³² and the Space group test implemented in the Jana2006 software.¹⁹ Electron diffraction patterns also largely aids in choosing the space group for a specific crystalline structure.

The third step consists of proposing a crystallographic model starting from the indexed intensities. The structural determination of the new crystalline phases in this study were realized by the method charge flipping^{20, 21} with the help of the SUPERFLIP program^{22, 33} implemented in the Jana2006 software. The SUPEFLIP program is used for the application of the charge-flipping algorithm in the structure solution of crystalline structures from powder and neutron diffraction data. Charge flipping is an iterative structure solution method based

on the alternating modification of the electron density in direct space and structural factors in reciprocal space.

The synchrotron powder diffraction data first enables the localization of the cationic network (Sr^{2+} , Si^{4+} , Al^{3+} in this study) within the unit cell. The crystallographic model formed is then used for calculating the structural factors which served in the inspection of the Fourier maps using Jana2006 software. Neutron powder diffraction data are then after used for the precise localization of the light atoms (oxygen in our case).

Once a complete structural model is proposed, and good starting values of profile, unit-cell parameters and background contribution are obtained, the last step which is Rietveld refinement; described previously; can be started.

Ab-initio structure determinations of new crystalline phases presented in this work have been realized by Dr. Mathieu Allix and Dr. Emmanuel Veron at the CEMHTI laboratory.

II.3.2 Nuclear magnetic resonance spectroscopy

Solid state nuclear magnetic resonance spectroscopy (NMR) is a powerful short-range probing technique used in our study to provide information about the local structure of ceramic materials.

II.3.2.1 Principle

The magnetic properties of an atom are characterized by the existence of a quantum number of nuclear spin I . NMR studies require nuclei with $I \neq 0$. The nucleus of such an atom is considered as a charge particle spinning around its axis. This spinning movement generates an angular momentum I and thus a magnetic moment μ . It is the interaction between this magnetic moment μ and an external applied magnetic field B_0 which causes the nucleus to precess around the magnetic field and generates the NMR phenomena. This interaction is known as Zeeman Effect.³⁴

At the fundamental state (absence of magnetic field) all the nuclear spins are disoriented and possess the same energy; they are called degenerate. The application of a magnetic field B_0 provokes the split into $2I+1$ possible orientations (Zeeman Effect) with different energies separated by Larmor frequency (ν_0), equal to the frequency of precession

around the magnetic field ($\nu_0 = \gamma B_0 / 2\pi$). With γ is the gyromagnetic ratio of the studied nucleus.

II.3.2.2 NMR interactions in solids

Different types of interactions are experienced by a nucleus placed in a magnetic field. These vary between each other and can contain valuable information about the nucleus environment. This information once extracted can yield a deeper understanding of the molecular structure.

The magnetic field around each nucleus is affected by the electronic cloud of the neighboring nuclei. Different interactions arise either through spatial proximities or through bonding connectivities, which are known to be as anisotropic interactions interfering with the Zeeman interaction. These interactions include:

i) Chemical shift interactions

The electrons around the studied nucleus are caused to circulate due to the external applied magnetic field B_0 , resulting in the creation of another magnetic field which can add or subtract B_0 (shields or deshields). Since electronic clouds around nuclei cannot be always spherically symmetric, different possible orientations of the magnetic field with respect to that of B_0 thus yield different NMR frequencies. The nucleus is therefore subject to a local magnetic field equal to the sum of the applied and induced magnetic fields:

$$B_{local} = B_0 + B_{CS} = (1 + \sigma) B_0 \quad (7)$$

Where, σ is the chemical shielding tensor. It represents the chemical shielding interaction dependence on the orientation.

In solid state NMR, this chemical shift anisotropy interaction gives rise to broad powder patterns causing chemically different sites to overlap with each other.

ii) Direct dipole-dipole interaction

The direct dipole-dipole interaction represents the direct through-space interaction between the magnetic moments of two NMR active nuclei. These spatial interactions may occur between nuclear spins of a same nucleus (homonuclear dipolar

coupling) or different kinds of nuclei (heteronuclear dipolar coupling). The interaction, being internuclear-distance dependent, provides information about interatomic distances and the different chemical connectivities between species. The dipole-dipole interaction is directly proportional to the product of the gyromagnetic ratio of the two interacting nuclei and is independent of the applied magnetic field B_0 .

iii) Indirect dipole coupling or J-coupling interaction

This coupling represents the indirect through-bond interaction between the magnetic moments of two nuclei. The nuclear spins are coupled together through the help of the molecular electrons. This type of interaction is considered the weakest among the other types of interactions and thus it is not easily detectable by solid state NMR.

iv) Quadrupolar interaction

Quadrupolar interaction is present in the majority of magnetically active nuclides in the periodic table that have integer spins ($3/2$, $5/2$, $7/2$...). Such nuclei possess quadrupole moment interacting with the external and internal magnetic fields, and also with the electric field gradient (EFG) which results from the asymmetric distribution of charges around the nucleus. Quadrupolar interactions can interfere with the Zeeman interaction depending on the degree of distortion in the local charge distribution.

The consequence of the quadrupolar coupling is a first order broadening of all the possible transitions called satellite transitions (ST) but not the central transition ($-1/2 \leftrightarrow 1/2$). However, the central transition is affected by the presence of residual second order quadrupolar broadenings, making the analysis of NMR spectra a much more complicated process. Figure 10 shows the energy level diagram for a nucleus with $I=5/2$ (such as the ^{27}Al nucleus studied in this work) obtained after each type of anisotropic interactions.

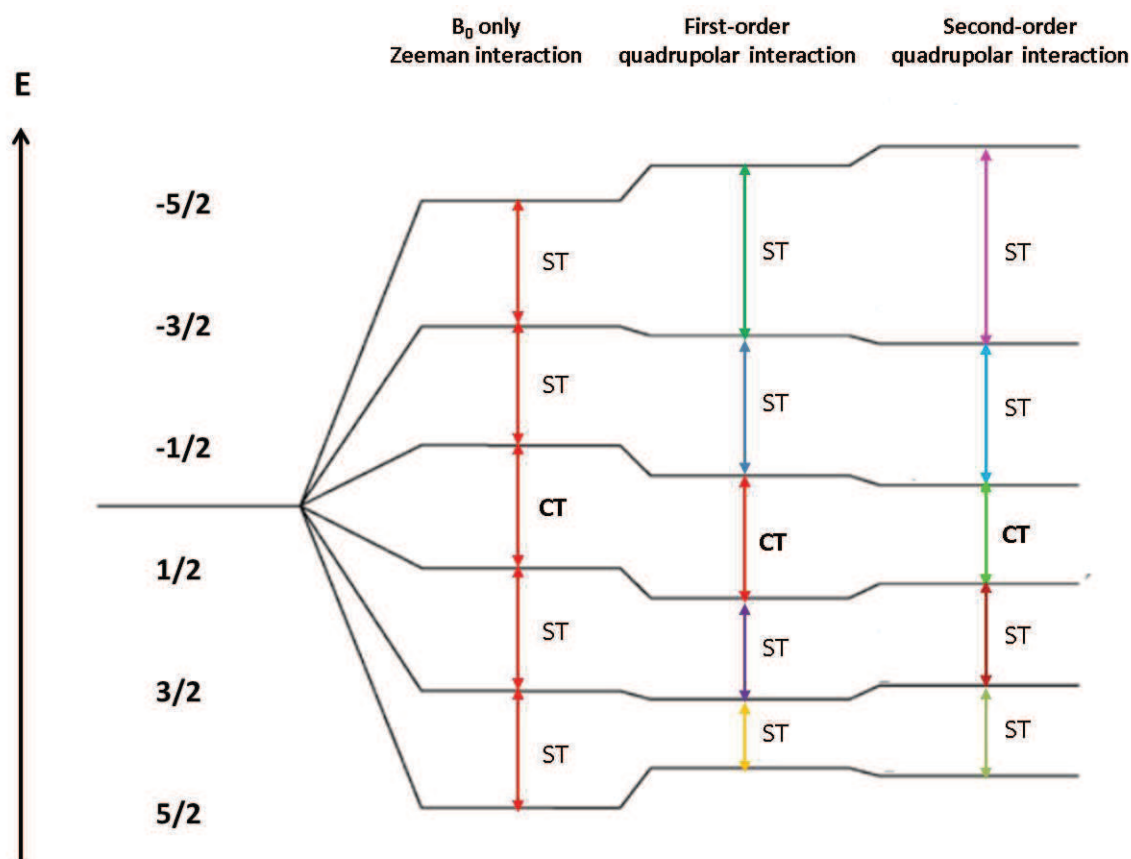


Figure 10 Energy level diagram of a spin-5/2 system showing the Zeeman interaction, first- and second- order quadrupole perturbation of the energy levels.

II.3.2.3 Nuclei studied in this thesis

In this thesis two types of nuclei were studied by NMR, ^{29}Si and ^{27}Al whose properties are represented in Table 1.

Table 1 Nuclear spin, natural abundance (%), gyromagnetic ratio (γ) and Larmor frequency (ν_0) for $B_0=7.05$ T for ^{29}Si and ^{27}Al

Isotope	Nuclear spin	Natural abundance (%)	γ (10^7 rad T $^{-1}$ s $^{-1}$)	ν_0 (Mhz)
^{29}Si	1/2	4.7	-5.314	59.701
^{27}Al	5/2	100	-1.803	78.27

The ^{29}Si nucleus has a nuclear spin of $I=1/2$, which signifies the absence of quadrupolar interactions. The resolution of the ^{29}Si spectra is considered to be high even though possessing a relatively low natural abundance, thanks to its narrow resonance lines.

The two main sources of broadening in ^{29}Si NMR spectra are the dipole–dipole and the chemical shift anisotropy interactions, the first is averaged to zero and the second to single isotropic value of chemical shifts by magic angle spinning (MAS)^{35–37} which will be discussed in the following part.

Silicon can be 4, 5 or 6-coordinated with a 50 ppm chemical shift variation between them.³⁴ For silicate structures, the network is built up of tetrahedral units (silicon in 4-coordination) with different polymerization degrees. The “Q” notation can be used to signal the bonding of a silicon atom to four oxygen atoms. The superscript value in Q^0 , Q^1 , Q^2 , Q^3 and Q^4 units indicates the number of other network-forming elements bonded to oxygen.³⁴ The increasing number of Si–O–Si linkages leads to more negatively ^{29}Si chemical shift values.

Concerning aluminosilicates, the ^{29}Si chemical shifts are further affected by the aluminium atoms falling in the second coordination sphere of the silicon atom. Changes in ^{29}Si chemical shifts result from the substitution of the four silicon atoms by Al atoms. These shifts thus range from -102 to -116 ppm for Q^4 (0Al) units with no bonded Al atoms, -97 to -107 ppm for Q^4 (1Al) species with one bonded Al, -92 to -100 ppm for Q^4 (2Al) species with two bonded Al, -85 to -94 ppm for Q^4 (3Al) species with three bonded Al and -82 to -92 ppm for Q^4 (4Al) species with four bonded Al as shown in Figure 11. These shifts can overlap, which can lead to information concerning the degree of Al for Si substitution, which then provides information about the degree of disorder of the aluminosilicate network.

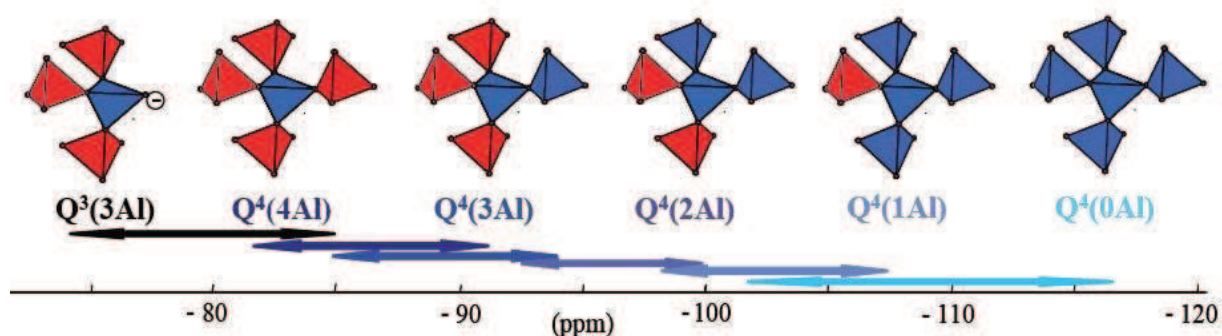


Figure 11 Typical ranges of ^{29}Si chemical shifts of $Q^n(m\text{Al})$ species in aluminosilicates³⁸

^{27}Al has a nuclear spin of 5/2, and hence the non-spherical distribution of the nuclear electric charge results in a nuclear quadrupolar moment which interacts with the electric field gradient causing broadening and distortion of the peaks and displacement of the isotropic chemical shifts.

In aluminosilicate materials, AlO_4 tetrahedra are exclusively connected to SiO_4 species because direct Al-O-Al links are theoretically forbidden by the Lowenstein's Rule.³⁹ The Al tetrahedral chemical environments are described using the q_m^n notation, where n is the number of bridging oxygen atoms and m is the number of bonded AlO_4 units ($0 \leq m \leq n \leq 4$).

II.3.2.4 One dimensional Magic Angle Spinning (MAS) NMR experiment

In NMR experiments, the resolution of the obtained spectra is highly minimized by the anisotropic interactions (chemical shifts, dipolar interactions, J-coupling and quadrupolar interactions). The chemical shift anisotropy (CSA) and the dipolar coupling Hamiltonians are orientation-dependent and can be averaged to zero if this orientation-dependency is vanished. This is achieved when the angle between the external magnetic field and the internuclear vector is equal to 54.74° (magic angle). The spinning axis forming an angle of 54.74° with the magnetic field, leads to the elimination of the chemical shift anisotropy and dipolar interactions and therefore the production of narrow lines form the logic of the magic angle spinning technique.

Experimentally, finely grounded powder is introduced into a zirconia rotor, placed into rotation in a stator through gas flow as presented in Figure 12.

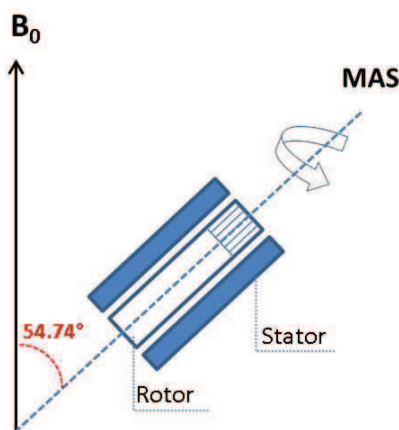


Figure 12 Schematic drawing of the magic angle spinning (MAS) principle

^{29}Si and ^{27}Al NMR experiments were performed on Bruker Advance spectrometers running at magnetic fields of 9.4 and 17.6 T, respectively. The ^{29}Si quantitative magic angle spinning (MAS) NMR spectra were recorded with a spinning frequency of 7 kHz, a pulse duration of $1.05 \mu\text{s}$ (25° flip angle) and a recycle delay of 60 s. The ^{27}Al quantitative MAS spectra were recorded with a spinning frequency of 30 kHz, a pulse duration of $0.36 \mu\text{s}$ (15° flip angle) and a recycle delay of 0.5 s.

For ^{27}Al MAS-NMR spectra, the first order of the quadrupolar broadening is not totally removed and the second order is not eliminated by magic angle spinning. However, other experiments can be applied for this purpose such as multiple quantum (MQ) NMR experiments.

II.3.2.5 Two dimensional MQ-MAS NMR experiment

Multiple quantum magic angle spinning is a solid state NMR method used for quadrupolar nuclei ($I > 1/2$) for obtaining a high resolution spectrum by averaging the anisotropic interactions. It was first proposed by Professor Lucio Frydman and coworkers in 1995.^{40, 41} It is a two dimensional NMR experiment which correlates the high resolution isotropic spectrum (vertical dimension) to the anisotropic central transition MAS spectrum (horizontal dimension).

The ^{27}Al 2D MQ-MAS spectra were acquired at a magnetic field of 17.6T and a spinning frequency of 30 kHz using a three pulse Z-filter sequence.⁴² The pulse durations for the triple quantum coherence excitation and reconversion were of 3.2 and 1.2 μs , respectively, with radio-frequency field strength of 116 kHz. The duration of the central transition selective pulse was of 4.3 μs . 20 t_1 increments of 133.3 μs (corresponding to four rotor periods) with 312 transients, each were collected using a recycle delay of 1s.

II.3.2.6 Fitting NMR spectra: Dmfit

Dmfit is a program developed in the CEMHTI laboratory by Dr. Dominique Massiot and coworkers.⁴³ This program, by providing different models accounting for different parameters (chemical shifts anisotropy, first and second order quadrupolar interactions, full width at half maximum FWHM, Gaussian/Lorentzian ratio...), permits the modeling and fitting of experimental 1D and 2D NMR spectra leading to the extraction of the different spectrum parameters.

Dmfit was used in this study to fit ^{29}Si and ^{27}Al NMR spectra which enable their interpretation as will be presented in Chapter IV.

II.3.3 Density functional theory (DFT)

The density functional theory is considered as a powerful tool used for the computational modeling of the quantum states of multi-electron systems in order to investigate their structural, magnetic and electronic properties. The DFT approach was first proposed by Hohenberg, Kohn and Sham⁴⁴ to replace the determination of wavefunction. The wavefunction is dependent on the number of electrons (N) constituting the system. The mathematical resolution of this wavefunction becomes very complicated with increasing the number of variables (N of electrons). Meanwhile, DFT approach considers the electronic charge density (ρ) as the key variable in the determination of the atoms quantum states which is only dependent on the electron's Cartesian coordinates (x, y and z). The term functional is used to associate a function to a number where the energy of the system is a functional of the electronic density, which is a function of the electrons spatial coordinates (x, y and z). Once the electronic density of the studied system is known, its wave function could be easily determined.

Anisotropic crystalline structures exhibit non-equivalent axes which interact with light in a manner dependent upon the crystalline lattice orientation with respect to the incident light. The phenomenon of light interaction with the non-equivalent axes is referred to as double refraction or birefringence.

DFT calculations in this study were performed to predict the birefringence via the refractive index components of the transparent polycrystalline ceramics.

For this purpose, modeled periodic structures were obtained by an optimization of the initial crystalline structures obtained from Rietveld refinements of powder diffraction data. The structural optimization was effected using ultra-soft pseudopotentials (USPP)⁴⁵ generated using the on-the-fly generator (OTF_USPP) included in CASTEP. The pseudopotential approximation is introduced to overcome the complicated all-electron potential; the core electrons are considered to be frozen without having an effect on the interaction between atoms. Therefore the wavefunction can be replaced by pseudo-wavefunction, where only the valence electrons play a major role in the atomic interactions. This simplifies the DFT calculations and makes them faster.

The reliability of these optimized models used for further calculation should be assured by a relative good agreement between the experimental and calculated cell parameters and atomic positions. These modeled periodic structures were then used to perform DFT

calculation of the imaginary and real parts of the dielectric function with the CASTEP^{46, 47} code. The refractive index can therefore be determined from the following relation:

$$n = \left(\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1}{2} \right)^{1/2} \quad (8)$$

NMR experiments and DFT calculations were realized through an internal collaboration with Dr. Franck Fayon at CEMHTI laboratory.

II.4 Properties characterization

II.4.1 Optical properties

II.4.1.1 Transmittance measurements

Transmittance is the term used to describe the process by which the incident light traverses a material from one surface side to the opposite side (Figure 13a). The transmittance is simply equal to the ratio of the transmitted beam intensity (I) to that of the incident beam intensity (I_0) as given by the following Beer-Lambert law

$$T = \frac{I}{I_0} \quad (9)$$

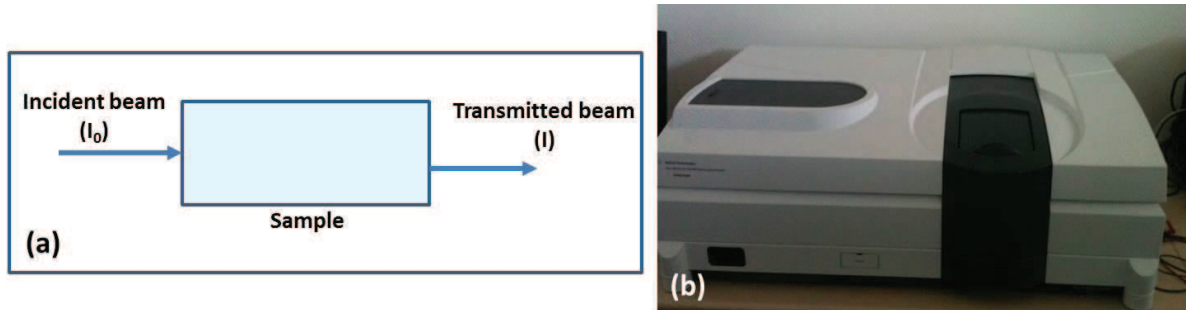


Figure 13 (a) Schematic drawing of beam transmittance through the sample (b) UV – Vis – NIR Cary 5000 spectrophotometer at CEMHTI laboratory

The transmittance measurements were performed using a Cary 5000 spectrophotometer (Figure 13b) running in the visible and near-infrared range (200-2500 nm) in order to quantify the transparency of the polycrystalline ceramics. The measurements were run out on optically polished samples with two parallel surfaces. The polishing was carried out using the machine Mécapol P320, using SiC abrasive papers with grain size ranging from 106 to 2.5 microns.

The measured transmittance value is compared to the maximum theoretical transmission value T_{th} . This later is calculated from the measured refractive index (n) according to the following equation.

$$T_{th} = \frac{2n}{n^2+1} \quad (10)$$

II.4.1.2 Luminescence measurements

Luminescence phenomena correspond to light emissions which are not thermal in origin. The use of an excitation source leads to the jump of an electron out of its ground state into an excited state. When this electron jumps back to its ground state it emits this energy in the form of light whose wavelength is directly related to the energy difference between the two levels.

The luminescence measurements were carried out in collaboration with Dr. Manuel Ocana Jurado and Dr. Ana Isabel Becerro in the Instituto de Ciencia de Materiales de Sevilla in Spain⁴⁸ on a Horiba/Jobin-Yvon Fluorlog-3 spectrofluorometer. This spectrofluorometer is equipped with a Xenon lamp of 450W, as a source of continuous excitation from 200 to 1000 nm. The wavelength selection of excitation is performed through a double monochromator and that of the emission through a single monochromator. The intensity of the monochromatic radiation is measured by a Hamamatsu photomultiplicateur R928.

In the case of luminescence study in the IR range, the measurements were carried out in collaboration with Dr. Fernando Cussó in the Departamento de Física de Materiales, Universidad Autónoma de Madrid.⁴⁹

II.4.1.3 Scintillation measurements

Scintillation is the property of a material to convert the energy of an ionizing radiation (X rays, gamma rays, alpha particles, beta particles) into visible or UV light.

In our case, scintillation tests were realized through collaboration with Dr. Christophe Dujardin in the Institut Lumière Matière, Université de Lyon.^{45, 50} X-ray excitation was performed using a Philips X-ray tube equipped with a W anode. The high voltage (HV) was set at 35 kV, and the current was set at 30 mA. Collection of the emitted light was ensured by an optical fiber coupled to a monochromator (Shamrock 500) and a EMCCD camera (Newton, Andor). For scintillation decay time measurements, the 100 ps X-ray pulse width

was produced with an X-ray tube triggered by a pulsed laser (Hamamatsu PLP10 and S20 cathode type). Scintillation photons detection was realized by a PMA165 photomultiplier tube and a PicoHarp 300 time correlated single-photon counting system, both from PicoQuant, ensuring a time resolution inferior to 150 ps.

II.4.2 Mechanical properties measurement

Measurements of the mechanical properties have been undertaken in order to compare the hardness and the reduced modulus between the glass and their corresponding ceramic materials.

These mechanical properties were measured with a nano mechanical testing system, Ti950 Triboindenter, Hysitron Inc in the LARMAUR laboratory through a collaboration with Dr. Jean-Christophe Sangleboeuf, Université de Rennes 1.⁵¹ A number of 100 Berkovich indents were performed on optically polished surfaces at a 10 mN load. Loading and unloading rates were kept constant and equal to 1 mN/s, with a dwell time of 10 s at maximum load. The loading vs. displacement curves were recorded and the Oliver-Pharr method was used to compute the reduced modulus. The hardness value was computed from the area function of the indenter tip and the maximum penetration depth at maximum load.

The Ti950 Triboindenter, Hysitron (Figure 14a) offers in-situ scanning probe microscopy (SPM) imaging which allows the verification that the tests have been done in the right place (Figure 14b). It also allows the observation and quantification of materials deformation incurred during testing.

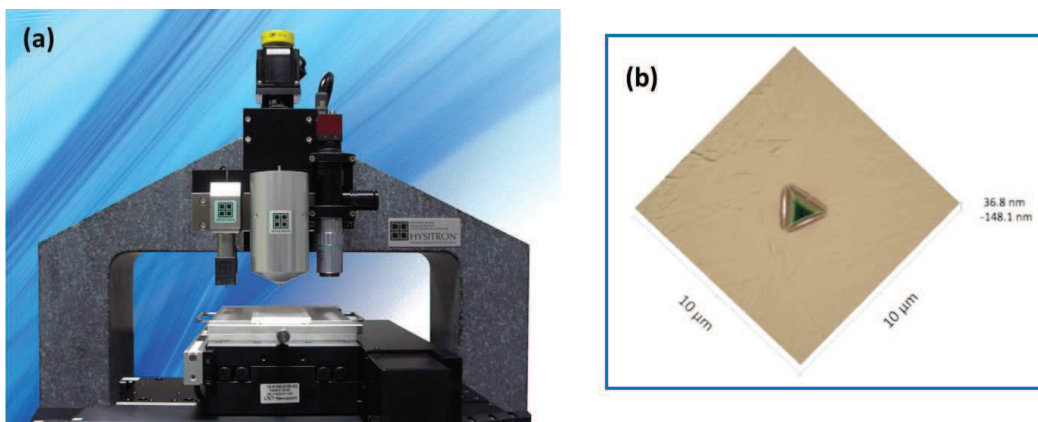


Figure 14 (a) Ti950 Triboindenter - Hysitron. (b) An SPM image of the indent left by Berkovich tip on $\text{Sr}_3\text{Al}_2\text{O}_6$ glass sample.

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Chapter III

$Sr_3Al_2O_6$ and $Sr_3Ga_2O_6$:

Novel transparent polycrystalline ceramics

In this chapter we study the elaboration and characterization of highly transparent optically isotropic polycrystalline ceramics (cubic symmetry). Optical isotropy overcomes one of the considerable light scattering sources in transparent ceramics which is birefringence. This makes crystal size control in isotropic transparent polycrystalline ceramics of lower impact on the obtained transparency.

The glass synthesis and the direct congruent glass crystallization processes are described. The transparency of the obtained polycrystalline ceramics is discussed in terms of their microstructure (crystal size, grain boundaries, porosity and isotropy). We also monitor the hardness, reduced elasticity modulus and the coefficient of thermal expansion of the transparent polycrystalline ceramic. From an application point of view, the wide doping hosting structure of the transparent polycrystalline ceramic offered by the employed synthetic route allows the utilization of different doping agents according to the required application. Thus, ceramics with different dopings are studied, which show their range of application as phosphorescent materials in the visible and IR ranges.

III.1 Glass and transparent polycrystalline ceramic synthesis

III.1.1 Why $\text{Sr}_3\text{Al}_2\text{O}_6$ and $\text{Sr}_3\text{Ga}_2\text{O}_6$ compositions?

Glass preparation represents the first step of the transparent polycrystalline ceramics synthetic route. Compositions which can be vitrified are required for ceramic preparation by full glass crystallization. $\text{Sr}_3\text{Al}_2\text{O}_6$ and $\text{Sr}_3\text{Ga}_2\text{O}_6$ have been chosen as compositions for the synthesis of transparent polycrystalline ceramics for three main reasons:

- i. The first one corresponds to the vitrification domains of the $\text{SrO}-\text{Al}_2\text{O}_3$ system. These domains were determined by the preparation of different strontium aluminate compositions $(x)\text{SrO}-(100-x)\text{Al}_2\text{O}_3$. Two vitrification domains have been obtained using the aerodynamic levitation coupled to laser heating for the system $\text{SrO}-\text{Al}_2\text{O}_3$ which are comprised between 37 - 40 molar % and 55 - 75 molar % of SrO (Figure 1). The chosen compositions lie at the limit of the second vitrification domain (75% SrO - 25% $\text{Al}_2\text{O}_3/\text{Ga}_2\text{O}_3$).

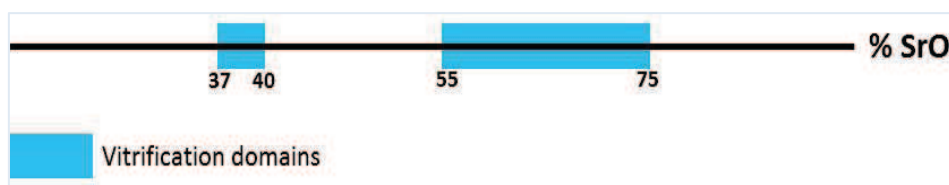


Figure 1 $\text{SrO-Al}_2\text{O}_3$ vitrification domains (aerodynamic levitation coupled to laser heating system)

- ii. $\text{Sr}_3\text{Al}_2\text{O}_6$ and $\text{Sr}_3\text{Ga}_2\text{O}_6$ crystalline phases are known to exhibit a cubic symmetry (Figure 2).^{1, 2} This optical isotropy should play an important role in obtaining polycrystalline ceramics with high transparency level.

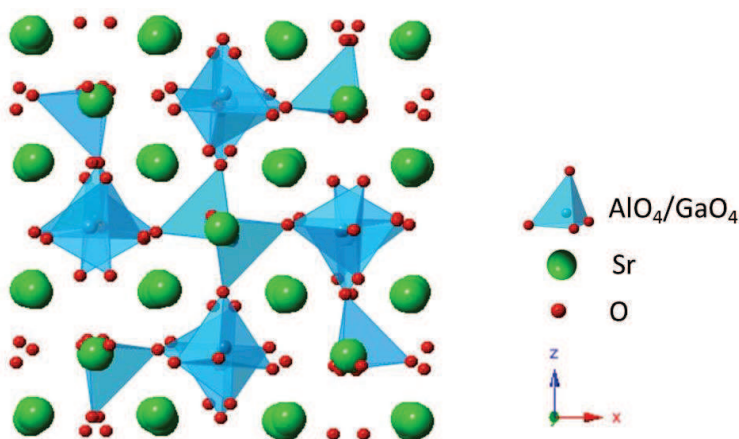


Figure 2 (a) Cubic crystal structure of $\text{Sr}_3\text{Al}_2\text{O}_6$ ($\text{Pa}\bar{3}$, $a=15.85 \text{ \AA}$)¹ and $\text{Sr}_3\text{Ga}_2\text{O}_6$ ($\text{Pa}\bar{3}$, $a=16.10 \text{ \AA}$)²

- iii. Strontium aluminate materials are known for their photoluminescence and persistent afterglow properties.³⁻⁶ Remarkably, Matsuzawa *et al*⁷ showed that SrAl_2O_4 co-doped with $\text{Dy}^{3+}/\text{Eu}^{2+}$ prepared via solid state reaction exhibits very long green afterglow (several hours in the darkness). The $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Eu}^{3+}$ powder phosphor synthesized by sol-gel and microwave-assisted routes exhibits strong red luminescence.⁸ These remarkable properties beside the advantage of large doping level provided by full glass crystallization synthetic route permits the study of luminescence properties of strontium aluminates using different doping agents.

III.1.2. Elaboration of transparent ceramics by full crystallization from glass

$\text{Sr}_3\text{Al}_2\text{O}_6$ and $\text{Sr}_3\text{Ga}_2\text{O}_6$ glasses have been synthesized using the aerodynamic levitator coupled to two CO_2 lasers. The compositions were melted at around 1800°C . Glass beads of 3-5 mm in diameter have been obtained by quenching (up to $300^\circ\text{C}\cdot\text{s}^{-1}$) resulting from the sudden cut-off of the laser beams. Contactless synthesis and fast quenching are essential to ensure vitrification of the two compositions.⁹ The complete amorphousness of the obtained glass beads has been verified using powder X-ray diffraction and transmission electron microscopy (TEM).

The thermal behavior of the as-elaborated $\text{Sr}_3\text{Al}_2\text{O}_6$ and $\text{Sr}_3\text{Ga}_2\text{O}_6$ glass materials has been recorded using differential scanning calorimetry (DSC) (Figure 3).

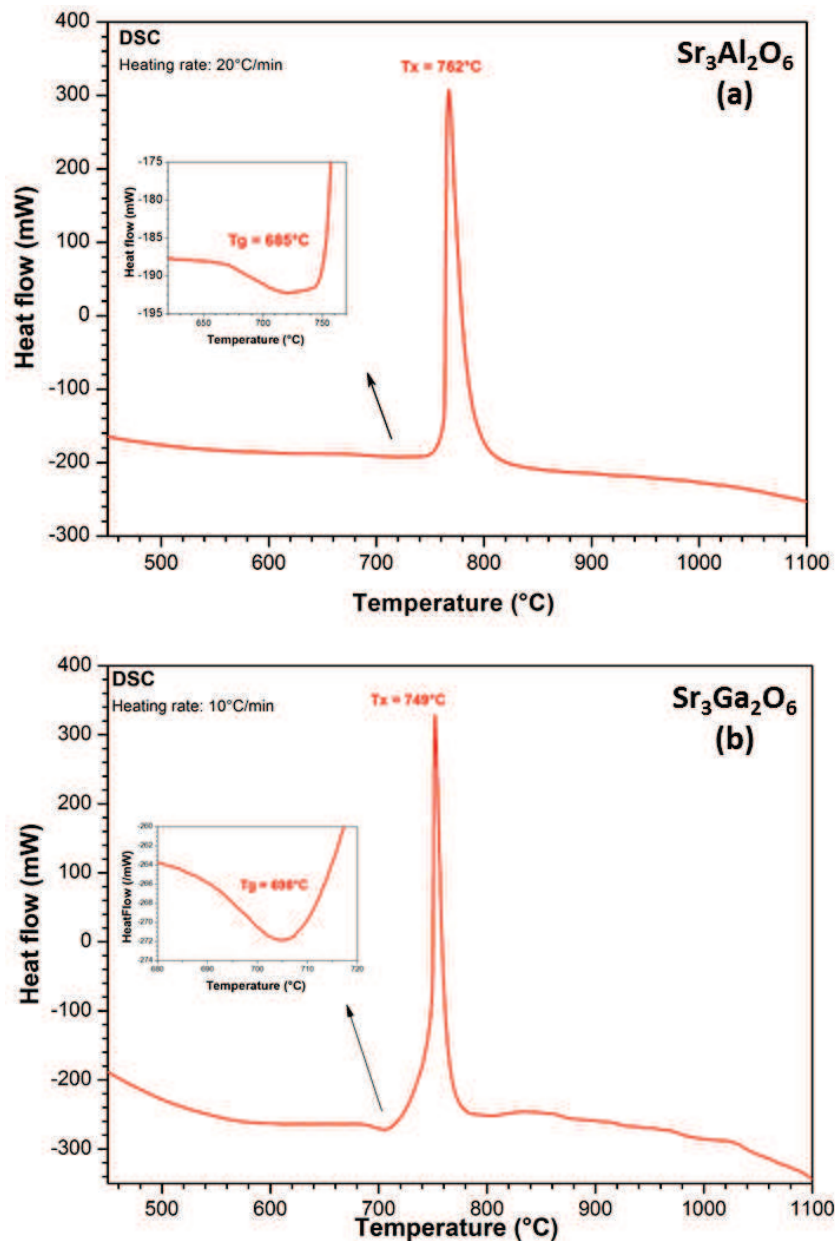


Figure 3 DSC thermogram of the (a) $\text{Sr}_3\text{Al}_2\text{O}_6$ and (b) $\text{Sr}_3\text{Ga}_2\text{O}_6$ glasses

As shown in Figure 3a, the thermogram of the $\text{Sr}_3\text{Al}_2\text{O}_6$ composition shows a weak glass transition at 685(1) °C and an intense exothermic peak at 762(1) °C corresponding to the crystallization of the cubic $\text{Sr}_3\text{Al}_2\text{O}_6$ phase (ICSD 71860 - PDF 01-081-0506)¹ as proved by powder X-Ray diffraction (Figure 4a).

Similarly for $\text{Sr}_3\text{Ga}_2\text{O}_6$ thermogram (Figure 3b) a glass transition at 698(1) °C and a single exothermic peak at 749(1) °C corresponding to the crystallization of the cubic $\text{Sr}_3\text{Ga}_2\text{O}_6$ phase (ICSD 93803 - PDF 01-070-7937) in Figure 4b were recorded.

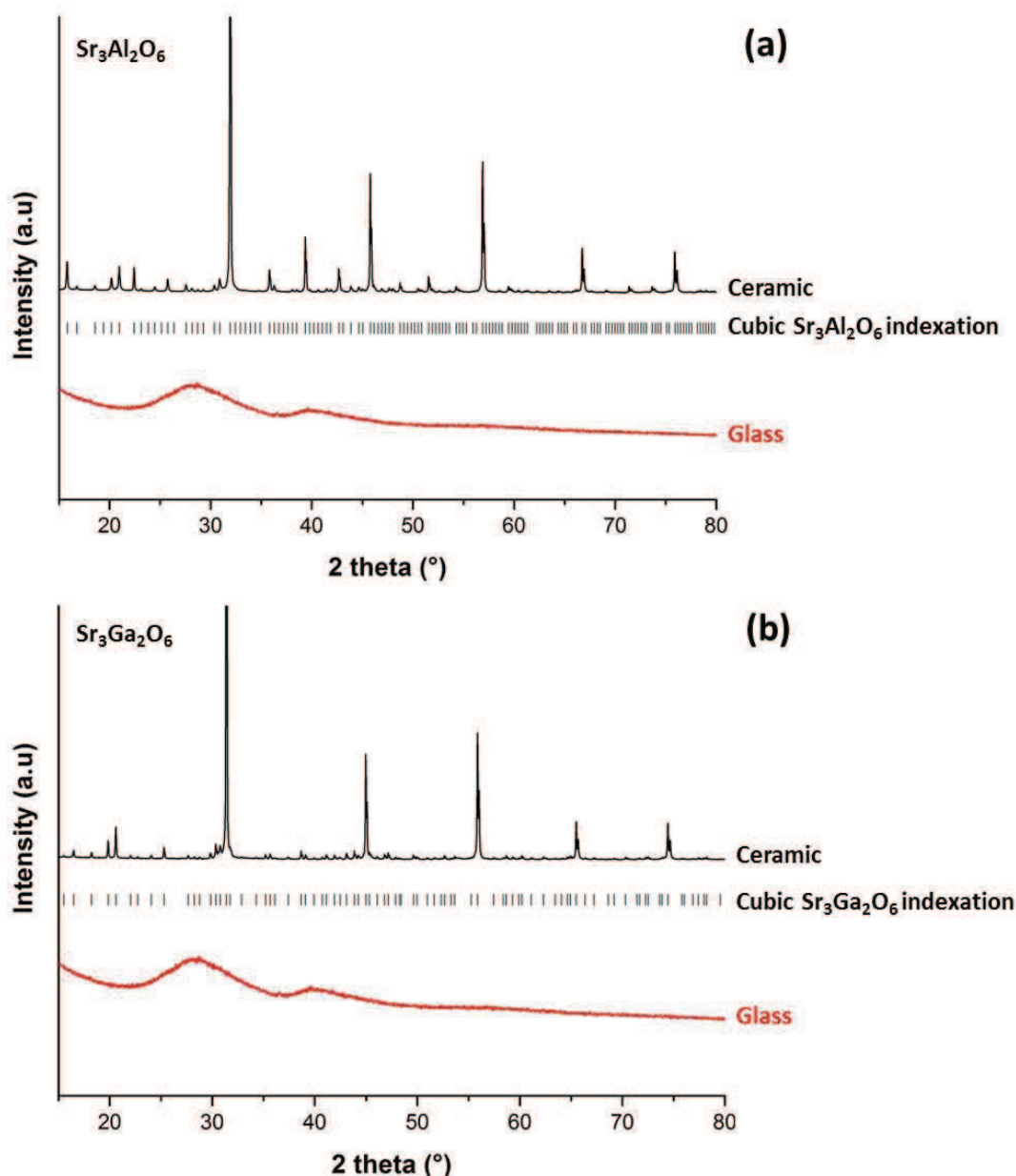


Figure 4 (a) X-ray powder diffraction patterns of the $\text{Sr}_3\text{Al}_2\text{O}_6$ glass and ceramic obtained. The indexation corresponds to the cubic $\text{Sr}_3\text{Al}_2\text{O}_6$ phase (ICSD 71860, PDF 01-081-0506). (b) X-ray powder diffraction patterns of the $\text{Sr}_3\text{Ga}_2\text{O}_6$ glass and ceramic. The indexation corresponds to the cubic $\text{Sr}_3\text{Ga}_2\text{O}_6$ phase (ICSD 93803 - PDF 01-070-7937)

From these thermal parameters obtained from DSC measurements, a simple thermal crystallization treatment at 840 °C for 5 hours has been used in order to fully crystallize the $\text{Sr}_3\text{Al}_2\text{O}_6$ glass. The powder X-ray diffraction pattern is indexed with the cubic $\text{Sr}_3\text{Al}_2\text{O}_6$ phase (ICSD 71860, PDF 01-860-0506), (Figure 4a).¹ No additional peaks indicating the presence of a secondary crystalline phase are detected, indicating the single crystallization of cubic $\text{Sr}_3\text{Al}_2\text{O}_6$ phase.

The resulting highly transparent polycrystalline ceramic is hardly distinguishable from its corresponding parent glass (Figure 5). No amorphous area could be detected under TEM examination and even longer thermal annealing treatments at this temperature did not change transparency behavior or improved the crystallinity, proving once more the full crystallization of the parent glass. Full crystallization could be also performed at lower temperatures but in this case longer time is required to completely crystallize the corresponding glass. However, ceramization at higher temperatures led to ceramics with lower transparency. This slight loss of transparency could be explained by the strong thermal expansion constraints affecting the sample and thus inducing porosity which thus presents a light scattering source.



Figure 5 $\text{Sr}_3\text{Al}_2\text{O}_6$ glass and its corresponding transparent polycrystalline ceramic obtained by thermal annealing of the glass at 840°C for 5 hours

Using a similar preparation method, the analogous gallate transparent polycrystalline ceramic $\text{Sr}_3\text{Ga}_2\text{O}_6$ has been elaborated by annealing the corresponding parent glass at 750 °C for 2 hours 30 minutes (Figure 6).



Figure 6 $\text{Sr}_3\text{Ga}_2\text{O}_6$ glass and the corresponding polycrystalline transparent ceramic obtained by thermal annealing of the glass at 750 °C for 2 hours 30 minutes

However both the glass and the ceramic gallate materials are slightly hygroscopic. An alteration of the sample surface is observed after a few hours in ambient atmosphere. This deterioration prevents high transparency to be maintained and so may be a strong drawback for commercial applications. This moisture sensitivity has been reported for several alkaline earth aluminate phosphors such as $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$.¹⁰ However, different methods have been proposed to protect these phosphors from moisture such as coatings using organic or inorganic materials (strontium fluoride, nitrides, SiO_2).¹¹⁻¹⁴ Therefore utilization of $\text{Sr}_3\text{Ga}_2\text{O}_6$ material would require encapsulation or passivation.^{10, 15}

III.2 Characterization of the transparent ceramics

Due to the fact that $\text{Sr}_3\text{Ga}_2\text{O}_6$ ceramic is slightly hygroscopic, we focused on $\text{Sr}_3\text{Al}_2\text{O}_6$ transparent polycrystalline ceramic in terms of characterization and application.

III.2.1 Transparency in terms of microstructure

The $\text{Sr}_3\text{Al}_2\text{O}_6$ polycrystalline ceramics show an outstanding transparency as shown in Figure 7. This transparency covers a wide optical range from the visible to the infra-red range (from 300 nm up to 6 μm). The absorption observed in the transmission spectrum below 300 nm corresponds to the optical band gap absorption of the strontium aluminate sample. Another absorption band is observed around 3 μm which corresponds to a small quantity of moisture in the sample (O-H bonds). This O-H bond should be eliminated by carrying out the synthesis under controlled atmosphere, which demands specialized equipment (glove box, fusion and annealing systems under controlled atmosphere). The average refractive index of the $\text{Sr}_3\text{Al}_2\text{O}_6$ transparent polycrystalline ceramics has been measured to be 1.70 ± 0.02 . On this basis, the maximum theoretical transmission was calculated as $87.4 \pm 0.5 \%$.

By regarding the transmission curve we can notice that the difference between the measured transmittance and the calculated theoretical value is very small, which indicates that only a very small amount of scattering centers are present within the transparent polycrystalline $\text{Sr}_3\text{Al}_2\text{O}_6$ ceramic. The high transmission value remains constant up to 6 μm in the IR range due to the relatively low phonon energy, especially when compared to that of silicate based compositions commonly used in the ceramic technology.¹⁶ Alkaline earth aluminates being famous for their luminescence properties,^{6, 7, 17-19} the elaboration of such a transparent ceramic is of high technological interest as the excitation radiation and the light emission response would be enhanced by orders of magnitude compared to common opaque bulk ceramics prepared from solid state synthesis (only their surface being active). Such a transparent polycrystalline material can thus compete with single crystal technology with much lower cost, more compositional flexibility (less or even no segregation of the doping agents during crystallization).

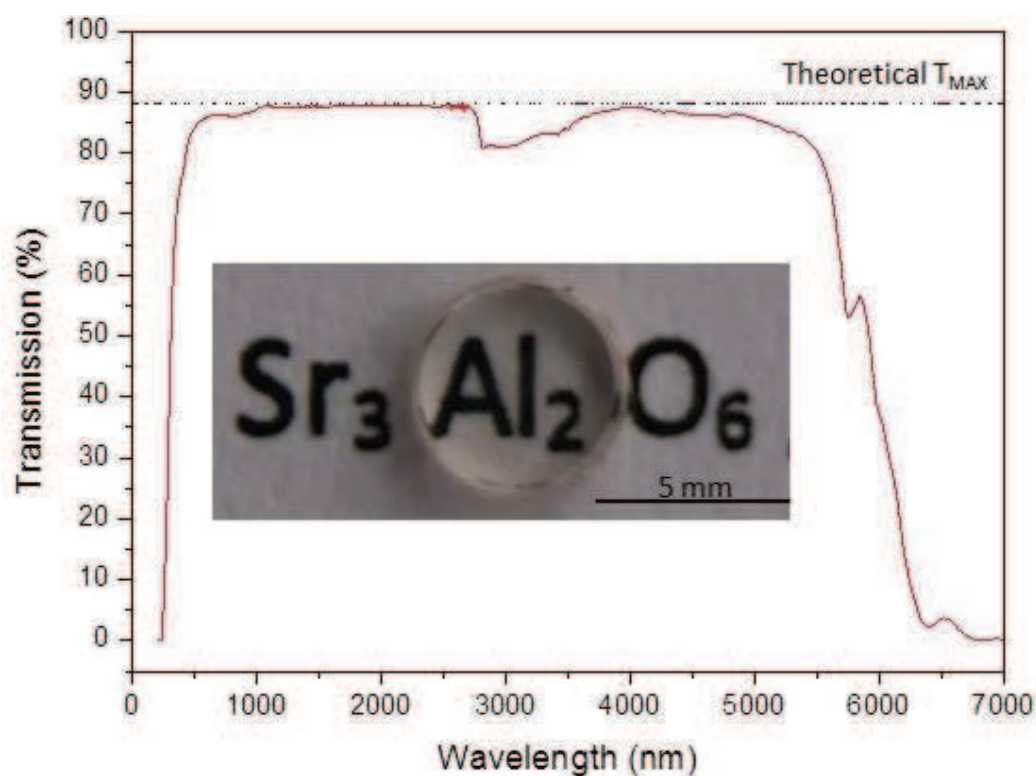


Figure 7 Transmission spectrum of the $\text{Sr}_3\text{Al}_2\text{O}_6$ transparent polycrystalline ceramic (1.5 mm thick sample). The dotted line represents the theoretical maximum transmission calculated to be $87.4 \pm 0.5\%$ for an average refractive index of 1.70 ± 0.02 . A photograph of the $\text{Sr}_3\text{Al}_2\text{O}_6$ polycrystalline ceramic is embedded

In order to explain the outstanding transparency of the polycrystalline $\text{Sr}_3\text{Al}_2\text{O}_6$ ceramics, the microstructure of the material has been investigated. For this purpose, TEM images were recorded on a sample prepared by focused-ion-beam (Figure 8).

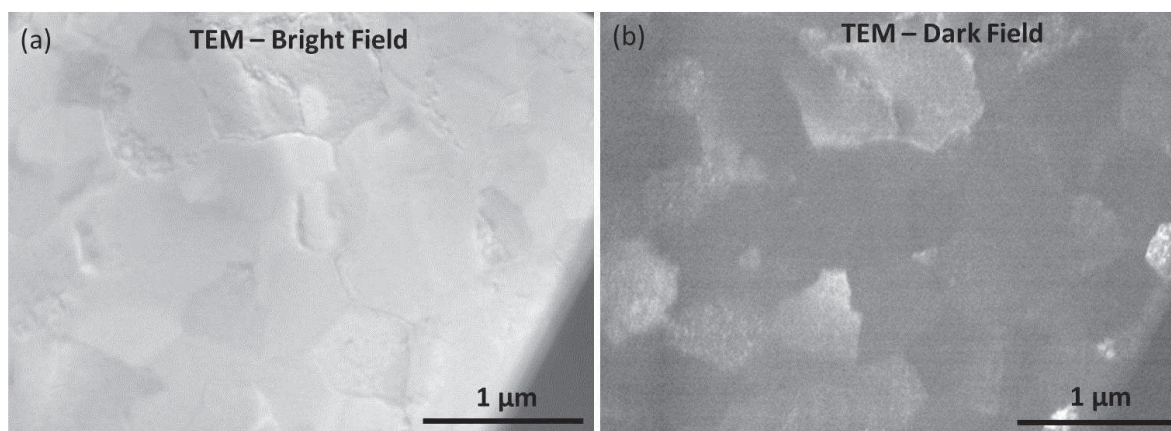


Figure 8 (a) Bright field transmission electron microscopy image of the $\text{Sr}_3\text{Al}_2\text{O}_6$ transparent polycrystalline ceramic showing high density (high compactness/no porosity), narrow grain boundaries and fine microstructures ($\sim 0.5\text{-}2\text{ }\mu\text{m}$ grain size). (b) The dark field pattern recorded on the same area clearly reveals the grain morphology

A typical bright field transmission electron microscopy image is shown in Figure 8a and the corresponding dark field pattern presented in Figure 8b reveals a selection of crystals, allowing the grain morphology to be distinguished more clearly. The patterns show a very dense mosaic microstructure with micrometric grain size, similar to the images observed in previous transparent polycrystalline ceramics obtained from solid state reaction under high pressure.²⁰⁻²³ No porosity could be detected and the grain boundaries appear very narrow, proving the strong advantage and easiness of crystallization from glass process rather than solid state reaction/sintering to obtain fully dense polycrystalline ceramics. An average crystal size comprised between 0.5 and $2\text{ }\mu\text{m}$ can be estimated. From these microstructure observations, it appears that the achievement of such a highly transparent ceramic is made possible through the combination of high density (absence of pores) and very thin grain boundaries. Both achieved by the crystallization from glass elaboration method, besides the structural and optical isotropy (no birefringence) inherent to the cubic $\text{Sr}_3\text{Al}_2\text{O}_6$ structure.

III.2.2 Density measurement

For further confirmation of the absence of porosity, the theoretical density of the cubic $\text{Sr}_3\text{Al}_2\text{O}_6$ ($\rho_{\text{th}} = 4.13 \text{ g.cm}^{-3}$; obtained from Rietveld refinement of the $\text{Sr}_3\text{Al}_2\text{O}_6$ cubic structure)¹ is compared to that measured using the Archimedes' principle (Table 1). The almost matching values of calculated theoretical density and measured theoretical density of $\text{Sr}_3\text{Al}_2\text{O}_6$ ceramic, confirm the TEM observations of the absence of porosity.

Table 1 Density calculation of the $\text{Sr}_3\text{Al}_2\text{O}_6$ ceramic materials ($\rho_{\text{ethanol at } 23.5^\circ\text{C}} = 0.78635 \text{ g.cm}^{-3}$) using Archimedes' method

	$m_{\text{air}} \text{ (g)}$	$m_{\text{ethanol}} \text{ (g)}$	$\rho = \frac{m_{\text{air}} * \rho_{\text{ethanol}}}{m_{\text{air}} - m_{\text{ethanol}}} \text{ (g.cm}^{-3}\text{)}$
$\text{Sr}_3\text{Al}_2\text{O}_6$ polycrystalline ceramic	0.0764	0.0619	4.13(2)

III.2.3 Vitrification attempts of $\text{Sr}_3\text{Al}_2\text{O}_6$ composition by classic melting/quenching method

Different tries have been undertaken to prepare the $\text{Sr}_3\text{Al}_2\text{O}_6$ glass composition in a commercial electric furnace using different types of crucibles (Pt, Pt+Rh, Al_2O_3 and Mo). However, they were all unsuccessful for obtaining a clear transparent material. The $\text{Sr}_3\text{Al}_2\text{O}_6$ powder precursors placed in Pt+Rh or Mo crucible at 1600°C for 20 minutes has resulted in brown sintered ceramic. Whereas when placed in Al_2O_3 crucible at 1600°C for 20 minutes has resulted in obtaining a brown melt.

Interestingly, when a pure Pt crucible was used, a brown transparent material has been obtained at 1650°C . XRD analysis of this sample showed crystallization in the cubic $\text{Sr}_3\text{Al}_2\text{O}_6$ phase (Figure 9).

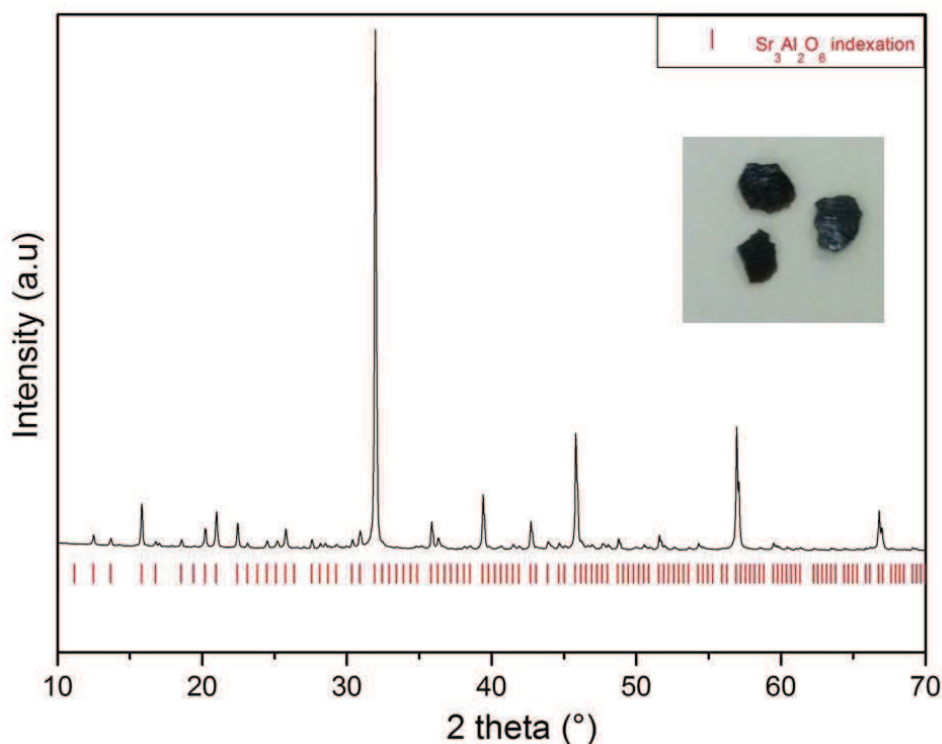


Figure 9 X-ray powder diffraction patterns of the $\text{Sr}_3\text{Al}_2\text{O}_6$ composition prepared in the furnace (the inset shows the corresponding photo)

This attempt showed that vitrification of the $\text{Sr}_3\text{Al}_2\text{O}_6$ composition could not be achieved by classic melting/quenching method. Meanwhile a dense ceramic crystallized with the proper $\text{Sr}_3\text{Al}_2\text{O}_6$ cubic phase has been obtained. However the transmittance of the obtained material is very low given the strong brown coloration. This coloration can be linked to Pt solubility in the material which results from the corrosion of the platinum crucible.²⁴ A contactless technique and super cooling rate appear essential for the vitrification of the $\text{Sr}_3\text{Al}_2\text{O}_6$ composition. It is expected that production of larger quantities of glass sample can be realized using a conventional induction or electric arc high temperature melting industrial process.

III.2.4 Mechanical properties

Hardness and reduced elasticity modulus measurements have been both carried out on $\text{Sr}_3\text{Al}_2\text{O}_6$ glass and polycrystalline ceramics by nano-mechanical testing system (Ti950 Triboindenter, Hysitron Inc). A number of 100 Berkovich indents were performed on optically polished surfaces at a 10 mN load. Loading and unloading rates were kept constant

and equal to 1 mN/s, with a dwell time of 10 s at maximum load. The hardness value is computed from the area function of the indenter tip and the maximum penetration depth at maximum load.

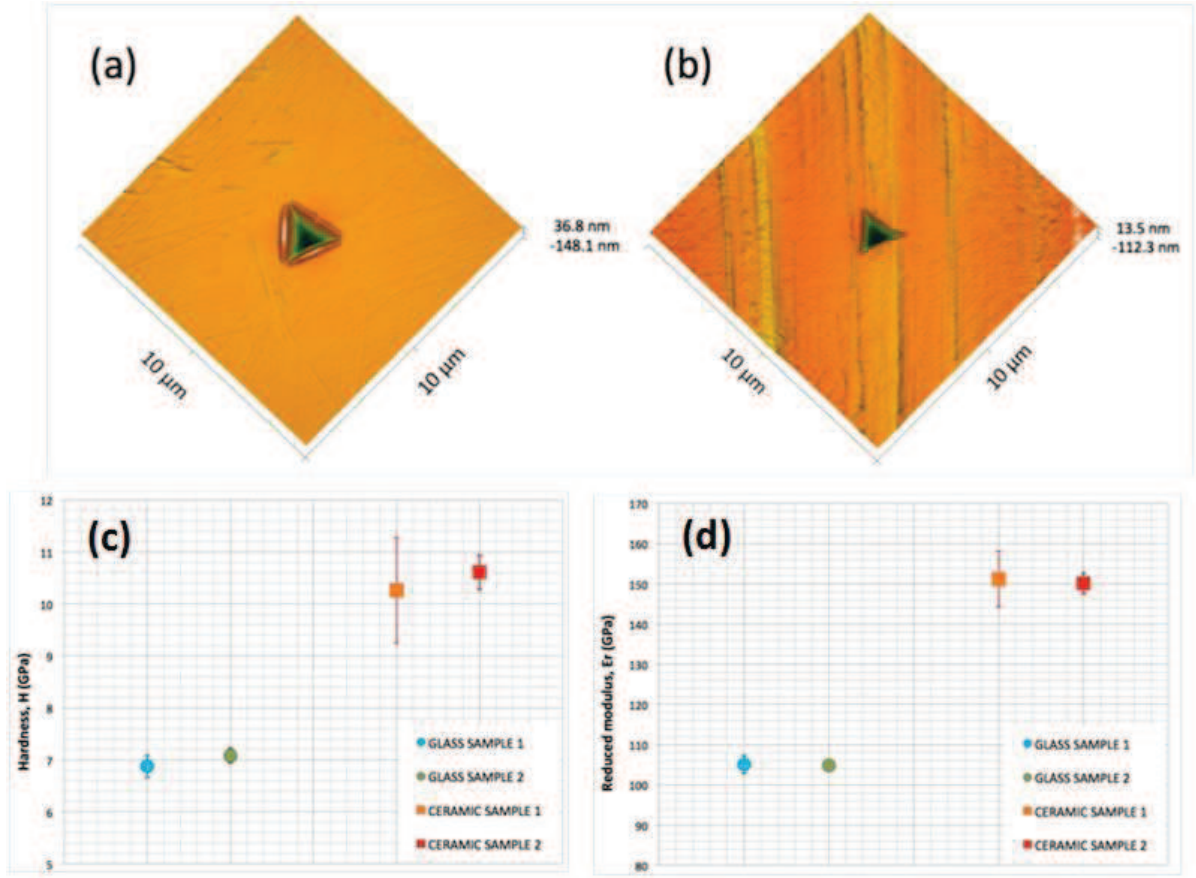


Figure 10 Scanning probe microscopy images (Hysitron TI-950) of 10 mN Berkovich indentation imprints on: a) the $\text{Sr}_3\text{Al}_2\text{O}_6$ glass and b) the $\text{Sr}_3\text{Al}_2\text{O}_6$ ceramic. c) Hardness and d) reduced modulus values of the $\text{Sr}_3\text{Al}_2\text{O}_6$ glass and ceramic. Two samples from two different batches (1 and 2) were tested. Each reported value is a mean value over at least 100 measurements, error bars are the respective standard deviation of the data set

In-situ scanning probe microscopy (SPM) images of the nanoindentations (Figure 10a and b) show no cracks or fractures around the indent zone for the 10mN load. The scratches observed in Figure 10b correspond to non-perfect polishing.

As shown in Figure 10c and d, the results are quite reproducible for the glass measurements. However, a small dispersion is observed in the hardness and reduced elasticity modulus measurements of the polycrystalline ceramic sample. This could be linked to the ceramic material microstructure. We observe a significant increase of both the hardness, $H_{\text{glass}} = 7$ to $H_{\text{ceramic}} = 10.5$ GPa and the reduced modulus (105 GPa to 150 GPa). However the

smaller hardness value obtained for the $\text{Sr}_3\text{Al}_2\text{O}_6$ transparent polycrystalline ceramics compared with other ceramics used for armor applications²⁵ could be directly related to the micron scale crystal size in our $\text{Sr}_3\text{Al}_2\text{O}_6$ polycrystalline ceramics. Several studies in the literature show the positive effect of nano-sized crystallites on improving the mechanical properties of transparent polycrystalline ceramics.²⁶⁻³² The increased hardness in these studies has been explained by the increased area fraction of grain boundaries which prohibit the dislocation motions.

III.2.5 Thermal properties

The coefficient of thermal expansion (CTE) represents a key technical property to be investigated in ceramics. Ceramic materials for high temperature applications such as cookware and telescope mirrors should have very low coefficient of thermal expansion.³³ Otherwise fracture may occur as a result of thermal shocks (thermal stress induced by rapid temperature changes). The thermal shock resistance of a material is inversely proportional to the elasticity modulus and the thermal expansion coefficient.

CTE measurements have been carried out by *in situ* high temperature XRD experiments. We have studied the variation of the unit cell parameters as a function of temperature. According to Sun *et al.*³⁴ volumetric CTE equation, a plot of $\ln(V-V_0)$ versus $(T-T_0)$ leads to the volumetric coefficient of thermal expansion (β_0). Hence, the linear coefficient of thermal expansion can be calculated knowing that we have a cubic symmetry ($\beta_0/3$).

$$\text{Volumetric CTE} \quad \beta_0 = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)$$

$$\text{Then} \quad \ln(V-V_0) = \beta_0(T - T_0)$$

Where V_0 is the measured volume at ambient temperature (T_0).

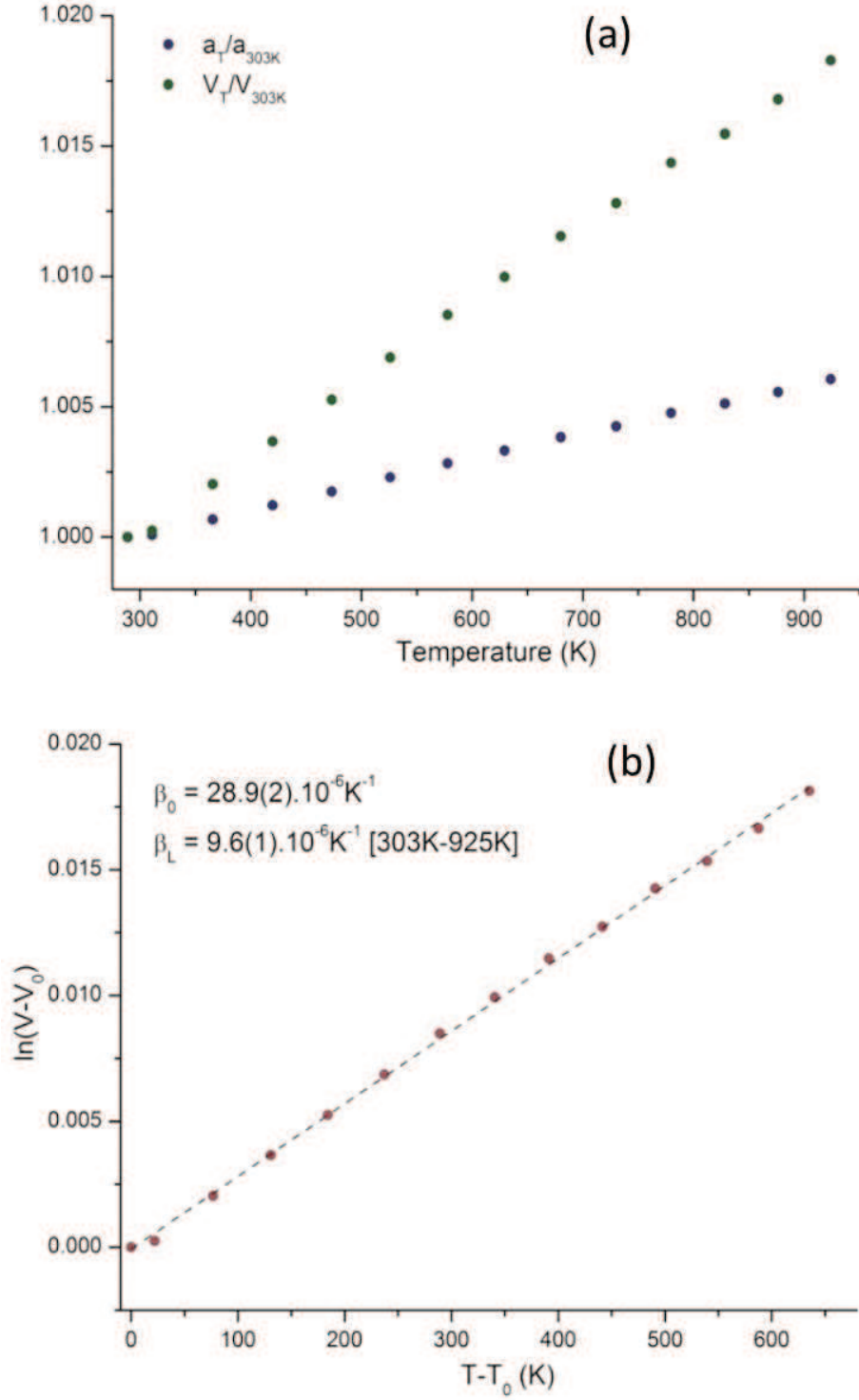


Figure 11 (a) Normalized unit cell parameters for $\text{Sr}_3\text{Al}_2\text{O}_6$ as a function of temperature. (b) Plot of $\ln(V-V_0)$ versus $(T-T_0)$ from RT to 925 K for $\text{Sr}_3\text{Al}_2\text{O}_6$

Figure 11a shows the linear increase of the cell parameter as a function of temperature and thus an increase of the cell volume. From Figure 11b, the volumetric coefficient of

thermal expansion obtained is equal to $28.9(2) \cdot 10^{-6} \text{ K}^{-1}$. The linear coefficient of thermal expansion was then calculated as equal to $9.6(1) \cdot 10^{-6} \text{ K}^{-1}$.

Given the fully dense (pore free) polycrystalline microstructure of our $\text{Sr}_3\text{Al}_2\text{O}_6$ material, the linear CTE obtained by HT-XRD can be directly compared to values measured by dilatometry. The $\text{Sr}_3\text{Al}_2\text{O}_6$ CTE is then close to the value reported in the literature for the SrAl_2O_4 ceramic ($7.8 \cdot 10^{-6} \text{ K}^{-1}$).³⁵

The obtained CTE value lies within the range of comparatively low coefficients of thermal expansion for ceramics. However, the obtained value could be assigned to its highly dense and non-porous structure. Pores; normally containing air with low thermal conductivity; are considered to impede the propagation of thermally induced cracks and thus improve materials thermal shock characteristics.

III.2.6 Optical properties

Alkaline earth aluminates have been widely studied for their optical properties, more especially for their promising phosphorescent properties.^{6, 7, 17, 36} Here, we show that the $\text{Sr}_3\text{Al}_2\text{O}_6$ material may be used as a matrix for different doping with various related applications both in the visible and infrared ranges. Eu^{3+} , Er^{3+} and Ho^{3+} single-doping agents have been chosen to show visible (for Eu^{3+}) and infrared (for Er^{3+} , Ho^{3+}) luminescence. Remarkably, radioluminescence properties can equally be demonstrated using Ce^{3+} doping.

III.2.6.1 Luminescence measurement

Regarding europium doping, we have tried different levels of doping (2.5 and 5 atomic %). In order to confirm the incorporation of europium within the $\text{Sr}_3\text{Al}_2\text{O}_6$ structure, we performed Eu: $\text{Sr}_3\text{Al}_2\text{O}_6$ cell parameters refinement from XRD data on different doping levels (0, 2.5 and 5%). The table presented inset in Figure 12 shows a decrease of the cell parameter, as expected when substituting the Sr^{2+} ions ($1.180 \text{ \AA}$ in VI coordination) by the smaller radius Eu^{3+} ($0.89 \text{ \AA}$ in VI coordination).³⁷ As a consequence, Eu^{3+} induces some structural rearrangements due to the additional positive charge which could be compensated by Sr^{2+} vacancies as shown by previous computational study on $\text{Sr}_3\text{Al}_2\text{O}_6$ doped by trivalent rare-earth dopants.³⁸

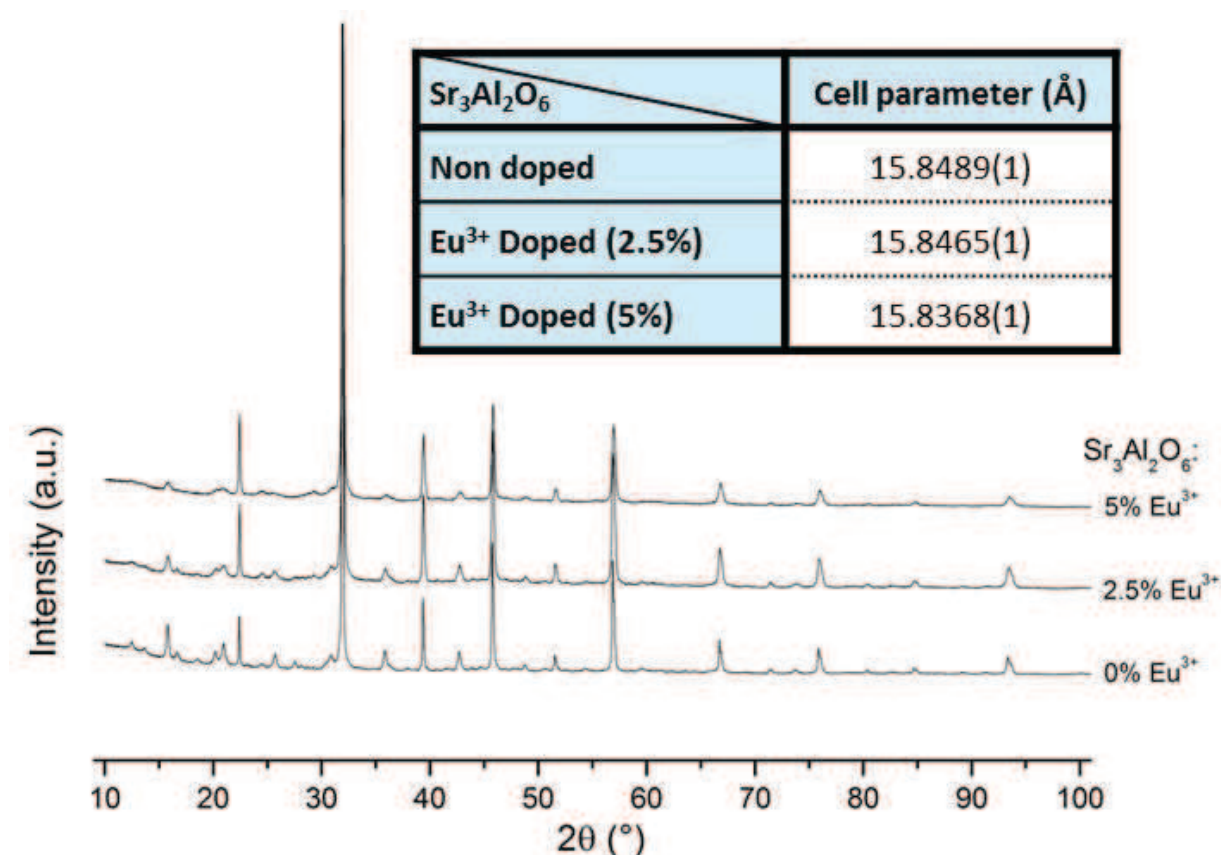


Figure 12 X-ray powder diffraction patterns of the europium doped transparent polycrystalline ceramics samples ($\text{Sr}_3\text{Al}_2\text{O}_6$ (0%), $\text{Sr}_{2.925}\text{Eu}_{0.075}\text{Al}_2\text{O}_6$ (2.5%) and $\text{Sr}_{2.85}\text{Eu}_{0.15}\text{Al}_2\text{O}_6$ (5%)). Inset: evolution of the Eu^{3+} : $\text{Sr}_3\text{Al}_2\text{O}_6$ cell parameters as a function of the europium substitution content. The non-doped, 2.5% doped and 5% doped samples correspond respectively to the $\text{Sr}_3\text{Al}_2\text{O}_6$, $\text{Sr}_{2.925}\text{Eu}_{0.075}\text{Al}_2\text{O}_6$ and $\text{Sr}_{2.85}\text{Eu}_{0.15}\text{Al}_2\text{O}_6$ formula

After proving the incorporation of Eu^{3+} within the $\text{Sr}_3\text{Al}_2\text{O}_6$ structure, the luminescence measurements have been carried out on the 5% Eu doped sample. Figure 13a shows the excitation spectrum for the 5% Eu-doped $\text{Sr}_3\text{Al}_2\text{O}_6$ ($\text{Sr}_{2.85}\text{Eu}_{0.15}\text{Al}_2\text{O}_6$) ceramic monitored at 611 nm. This spectrum consists of several typical bands in the 200–450 nm range similar to those previously reported for $\text{Sr}_3\text{Ga}_2\text{O}_6:\text{Eu}^{3+}$ powder ceramics,³⁹ which were attributed to an $\text{Eu}^{3+}/\text{O}^{2-}$ charge transfer band (CTB; broad feature centred at 272 nm) and to the direct excitation of the Eu^{3+} cations from the ground state to higher levels of the 4f manifold (weaker bands at >300 nm).

The emission spectrum of this Eu^{3+} doped sample (Figure 13b), obtained either using an excitation wavelength of 272 (CTB) or 393 nm (the most intense Eu^{3+} excitation band corresponding to the $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition) displayed similar emissions, most of them at $\lambda > 570$ nm due to the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 1, 2, 3$, and 4) electronic transitions characteristic of the Eu^{3+}

cations. However, the intensity of these emissions was noticeably higher when exciting at 272 nm, indicating the most efficient excitation of Eu^{3+} through the charge transfer band. It can be also observed that the most intense emissions appeared in the 580–620 nm range. These are responsible for the strong red luminescence observed for this sample (Figure 13b inset). Finally, it is important to mention that the relative intensity of the $^5\text{D}_0\text{--}^7\text{F}_2$ emission band was higher than that associated to the $^5\text{D}_0\text{--}^7\text{F}_1$ transition, which is expected for Eu^{3+} cations located in crystallographic sites without an inversion center, as it is the case for the Sr polyhedra in the $\text{Sr}_3\text{Al}_2\text{O}_6$ structure.

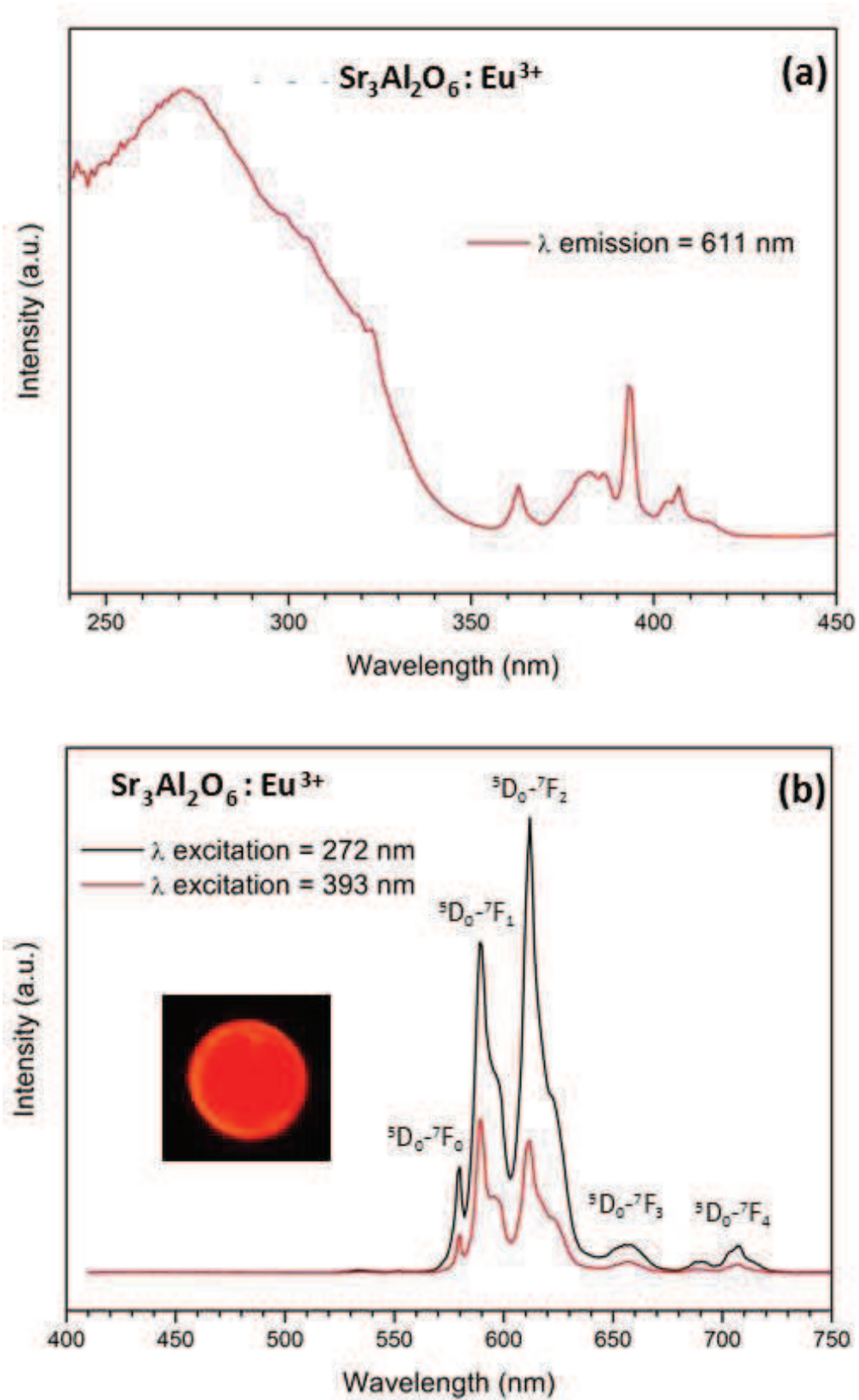


Figure 13 (a) Excitation ($\lambda_{\text{em}} = 611 \text{ nm}$) and (b) emission ($\lambda_{\text{ex}} = 272$ and 393 nm) spectra of the 5% Eu^{3+} -doped $\text{Sr}_3\text{Al}_2\text{O}_6$ sample. (Inset) Picture of the $\text{Eu}:\text{Sr}_3\text{Al}_2\text{O}_6$ sample recorded under UV excitation

Figure 14a and Figure 15c show the absorption spectra of Er-doped and Ho-doped $\text{Sr}_3\text{Al}_2\text{O}_6$ polycrystalline ceramics which were measured using a Perkin Elmer Lambda 1050 spectrophotometer. The spectra consist of several absorption bands, which appear clearly identified over a background increasing towards the shortest wavelength region of the spectra. This background may be associated to light scattering in the ceramic.^{40, 41} The different absorption bands of the rare earth ions are clearly visible and correspond to transitions from the ground state, $^4\text{I}_{15/2}$ for Er^{3+} and $^5\text{I}_8$ for Ho^{3+} , to the different excited state multiplets that are labeled in the figure.

Figure 14b and Figure 15d show the luminescence spectra of the transparent Er-doped and Ho-doped $\text{Sr}_3\text{Al}_2\text{O}_6$ polycrystalline ceramics obtained under constant wavelength excitation using the 488 nm emission of an Ar^+ laser (National Laser Company NLC800, 250 mW). The insets include the energy level structure together with the relevant transitions for each cation. In the case of Er^{3+} (Figure 14), the excitation reaches the $^4\text{F}_{7/2}$ multiplet, which relaxes to the $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ levels, from where an intense green emission (550 nm , $^2\text{H}_{11/2}, ^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) takes place. The excitation relaxes also partially non radiatively to lower lying excited state multiplets, giving rise to a cascade of different emissions, in the visible and near infrared range: $\sim 670 \text{ nm}$, ($^2\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$), $\sim 980 \text{ nm}$ ($^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$) and the characteristic IR emission at $1.5 \mu\text{m}$ from the lowest excited state multiplet ($^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$).

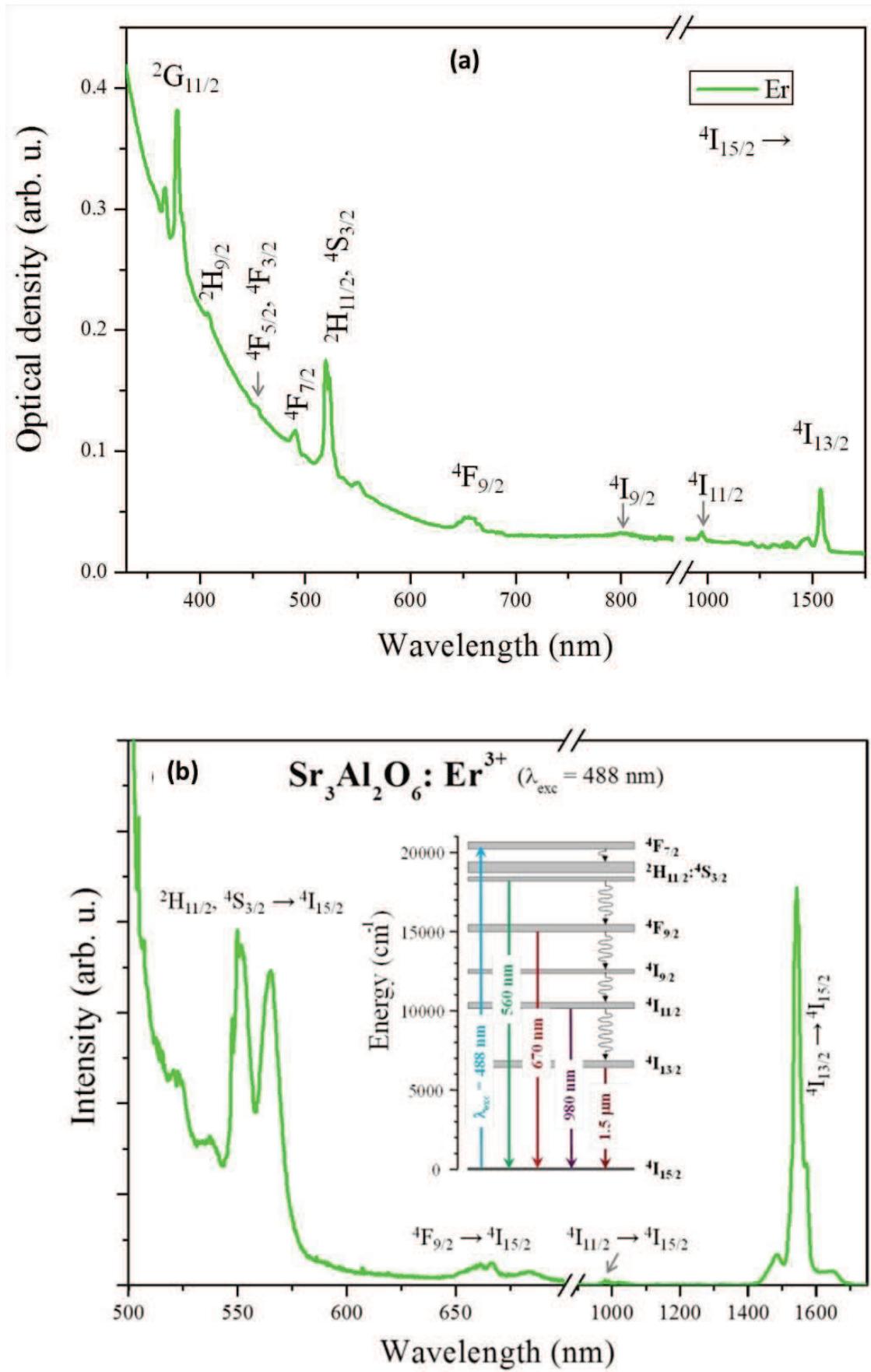


Figure 14 (a) Absorption and (b) emission ($\lambda_{\text{ex}} = 488 \text{ nm}$) spectra of the 1% Er^{3+} -doped $\text{Sr}_3\text{Al}_2\text{O}_6$ ceramic

In the case of Ho^{3+} (Figure 15), the excitation reaches the $^5\text{F}_3$ multiplet, which relaxes to the $^5\text{F}_4$: $^5\text{S}_2$ levels first and then to other lower lying multiplets, giving rise to several characteristic emissions in the visible and near IR range; ~ 660 nm, ($^5\text{F}_5 \rightarrow ^5\text{I}_8$), ~ 750 nm ($^5\text{F}_4$: $^5\text{S}_2 \rightarrow ^5\text{I}_7$) and $1.2\mu\text{m}$ ($^5\text{I}_6 \rightarrow ^5\text{I}_8$); that are also labeled in the Figure 14b. The observed emissions are in accordance with those observed in other Er and Ho doped hosts^{42, 43} notably the characteristic IR emission at $1.2\mu\text{m}$ from the lowest excited state multiplet ($^5\text{I}_6 \rightarrow ^5\text{I}_8$).

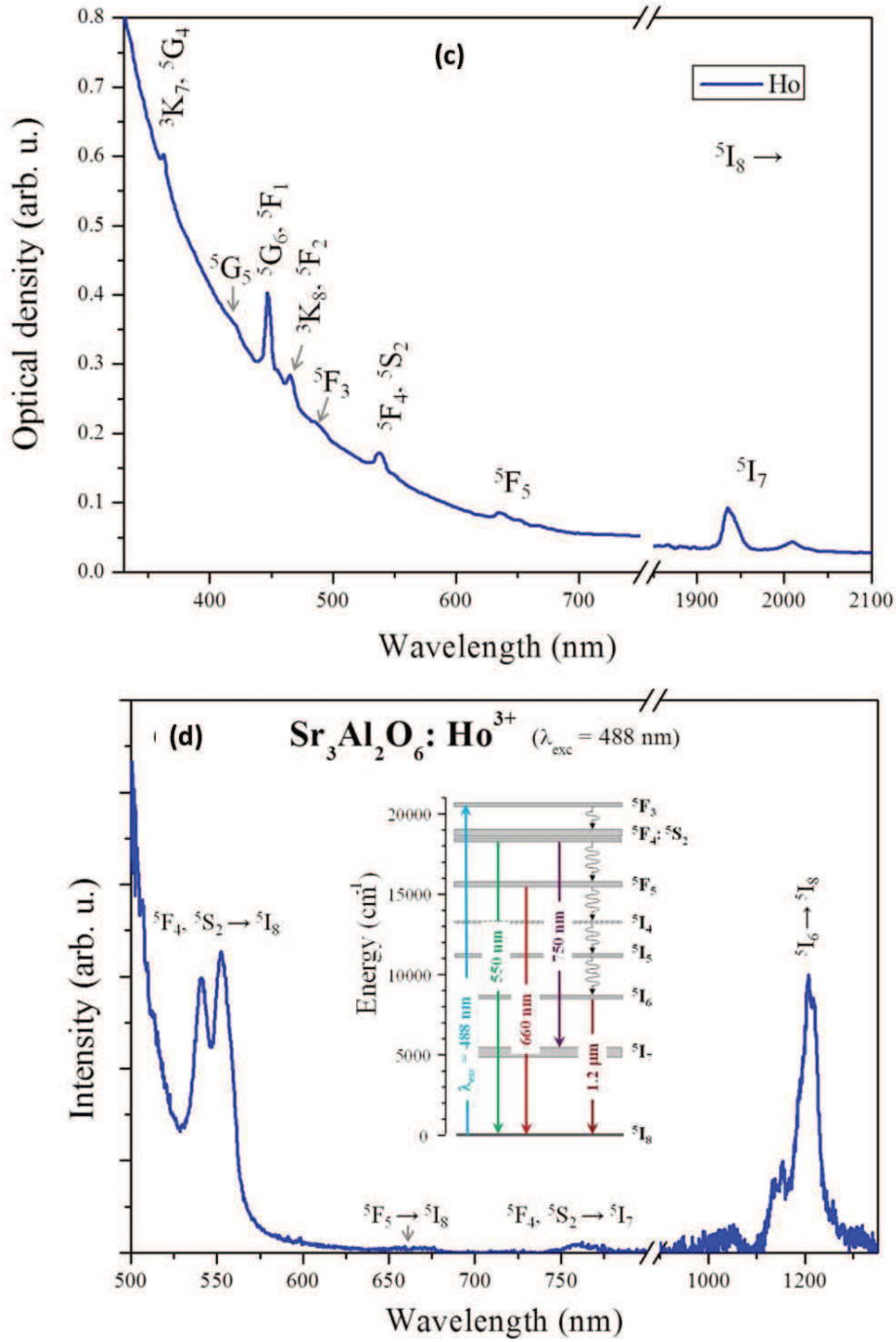
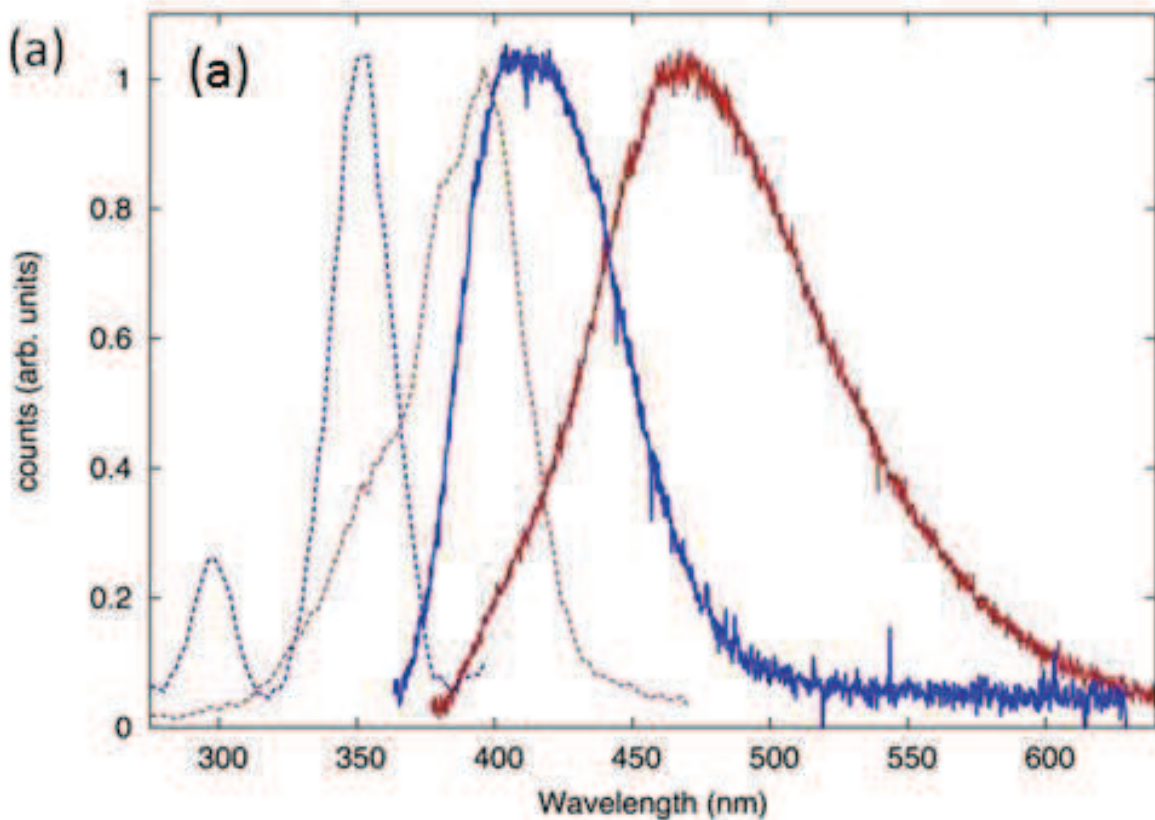


Figure 15 (c) Absorption and (d) emission ($\lambda_{\text{ex}} = 488$ nm) spectra of the 1% Ho^{3+} -doped $\text{Sr}_3\text{Al}_2\text{O}_6$ sample

III.2.6.2 Test of scintillation properties

Scintillating materials (e.g. single crystals, powders, thin films and ceramics) have the capacity to emit visible or UV photons under ionizing radiations. A synthesis route permitting the low cost scalable production of transparent bulk material (compared to single crystal) with scintillating properties is of high interest. Depending on the application, a compromise between the two of the most important parameters for scintillation (i.e. yield and the time response) is to be made. For counting technique applications, rather fast time response is mandatory to avoid pill-up (sub-microsecond). In this view, most common activators are Ce^{3+} and Eu^{2+} , which exhibit fast and efficient radiative electric dipole transition from $5d^14f^{n-1}$ to $4f^n$ configurations. Nevertheless, due to complex relaxation processes prior to the emission of light, having fast and efficient luminescence under photon excitation does not guaranty the efficiency and fast timing response under ionizing radiation. In this frame, photoluminescence spectroscopy and radioluminescence spectra of the cerium doped samples as well as luminescence decay under pulsed X-ray excitation have been performed and are presented in Figure 16.



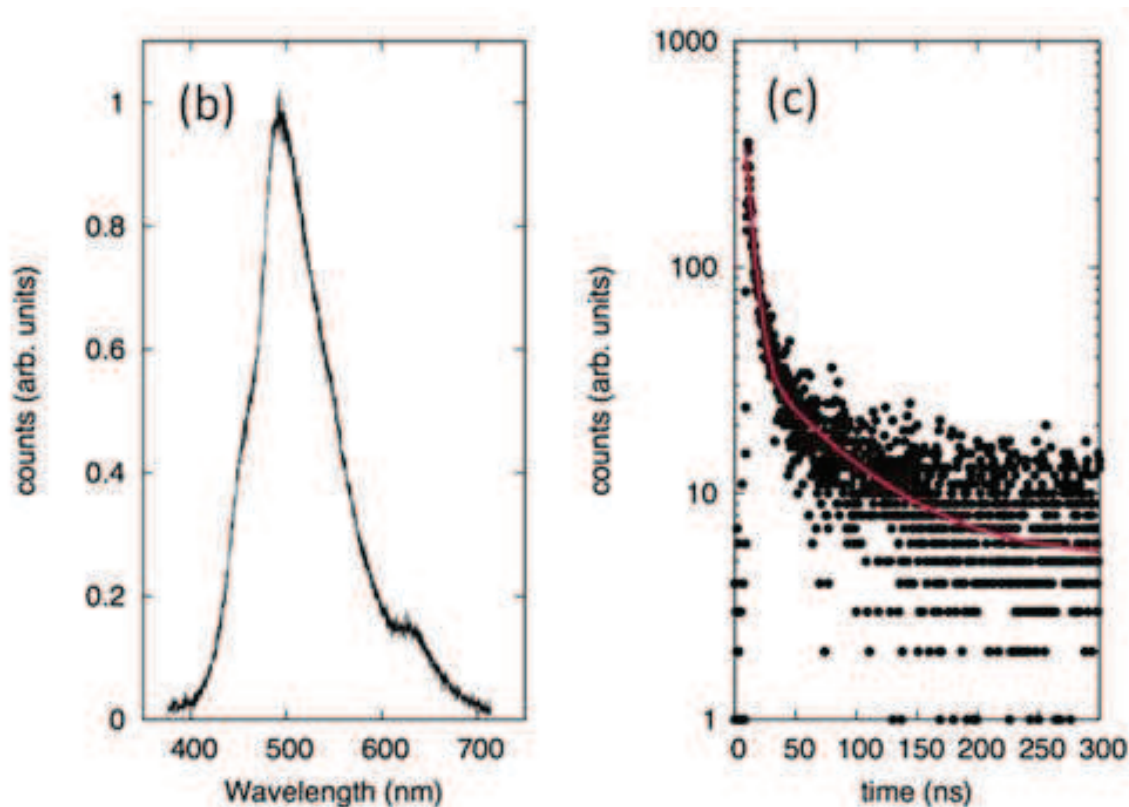


Figure 16 (a) Room temperature luminescence (solid line) and excitation spectra (dashed line) of the $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Ce}^{3+}$ glass (blue spectra, excitation recorded at 350nm and emission at 420nm) and the $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Ce}^{3+}$ transparent ceramic (red spectra, excitation recorded at 365nm and emission at 500nm). (b) Room temperature radioluminescence spectrum of the $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Ce}^{3+}$ transparent ceramic (excitation conditions: W anode, HT35kV, I=25mA). (c) Scintillation decay time under pulsed X-ray excitation (W anode, HT 30kV)

In the glass sample, the cerium emission spectrum peaks at 415 nm and the two related excitation bands observed are typical for cerium in a low symmetry site (Figure 16a). In the crystallized form, the emission spectra recorded under UV excitation (365 nm) is red shifted (centered at 470 nm), indicating a stronger crystal field. The excitation spectrum of the emission at 500 nm consists of several unresolved bands. These spectral behaviors are quite similar to the ones previously observed in the same material prepared by solid state reaction.⁴ However, a small red shift in the emission spectrum is observed and the ratio intensity in the excitation bands is not identical. Since the full crystallization from glass process does not follow the same thermodynamic pathway as compared to solid state reaction, a different distribution of cerium on the crystallographic sites of the $\text{Sr}_3\text{Al}_2\text{O}_6$ may be considered for the transparent ceramics. Some differences in the charge compensation ($\text{Sr}^{2+}-\text{Ce}^{3+}$), which has a significant effect on the excitation bands as pointed out by the authors using additional co-dopants, may as well be considered. Under X-ray excitation, the emission spectrum of the

crystallized compound is similar to that observed under UV excitation while under the same excitation and light collection condition, no scintillation is detected in the glass material. This corresponds to a general tendency of scintillating materials exhibiting better efficiency when crystallized as compared to amorphous phases. Under pulsed X-ray excitation (100 ps timing resolution), the scintillation decay time can be fitted with a two exponential decay with decay constants of 5.8 ns and 66 ns (fit presented Figure 16c). The short decay clearly indicates a quenching process which is in good agreement with the rather weak scintillation yield observed as compared to the standard cerium doped crystals such as $Lu_2SiO_5:Ce^{3+}$ (a rough comparison gives around 50 to 100 times lower). Nevertheless, it indicates that this synthesis route enables to produce scintillating material, which can be applied to other composition exhibiting higher scintillation yield.

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Chapter IV

Large scale transparent

$Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ polycrystalline ceramics

$Sr_3Al_2O_6$ transparent polycrystalline ceramics, although having a transparency level almost matching the maximum theoretical transmission of 87.4 %, can only be elaborated at a small scale. The parent glass should be elaborated in a contactless environment in order to avoid contamination and with a super cooling rate in order to ensure vitrification. Production of larger quantities of glass sample could be performed using a conventional induction or electric-arc high-temperature melting industrial process. In this chapter we focus on the elaboration of transparent polycrystalline ceramics where the starting glass precursor can be elaborated easily on a large scale.

For the preparation of large scale samples, a vitrification agent must be added in the nominal compositions in order to lower the melting temperature and improve the vitrification tendency of oxide mixtures containing Al_2O_3 . Our research has then been directed toward the synthesis of aluminosilicate ceramics. These later are widely used in engineering applications as refractory materials^{1, 2}, where ceramics with high Al_2O_3 content present remarkable mechanical resistance. Although the presence of SiO_2 in aluminosilicates is considered to weaken this resistance, it imports numerous advantages such as lowering sintering temperature and production costs.³ Moreover, the properties of these two oxides when combined with other oxides (strontium, barium, lithium, calcium, magnesium) lead to ceramic or glass-ceramic materials with specific thermal, mechanical and optical properties.⁴⁻¹⁰ In this chapter we are interested in the elaboration of transparent strontium aluminosilicate polycrystalline ceramics. This study starts from the well-known $SrAl_2O_4$ composition, which is widely reported as one of the most remarkable long-lasting green luminescent material when co-doped with Eu^{2+} and Dy^{3+} .¹¹ However this composition exhibits high melting temperature. The combined properties of aluminosilicates and strontium aluminate pose an interesting subject and provide an insight for a triple system $SrO-Al_2O_3-SiO_2$ to be studied. For this purpose a successive addition of SiO_2 to the initial $SrAl_2O_4$ composition is realized for glass vitrification investigation in a first step and then the possibilities of transparent polycrystalline ceramic elaboration are studied.

The system is presented by the following formula $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 2$) lying within $SrAl_2O_4$ and $SrAl_2Si_2O_8$ compositions. Throughout this tie line the increased silica content is expected to lower the melting temperature of the oxide mixture precursor and enhance vitrification process. The vitrification of a series of compositions is investigated followed by the elaboration of transparent polycrystalline ceramics by full glass

crystallization. A combination of different approaches is used to characterize the obtained transparent polycrystalline ceramics at multi-scale.

IV.1 $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 2$) system

IV.1.1 Solid solution localization in the $SrO-Al_2O_3-SiO_2$ ternary diagram

This chapter is devoted to the study of compositions located between $SrAl_2O_4$ and $SrAl_2Si_2O_8$. These are presented by the dashed line in the following ternary diagram (Figure 1).

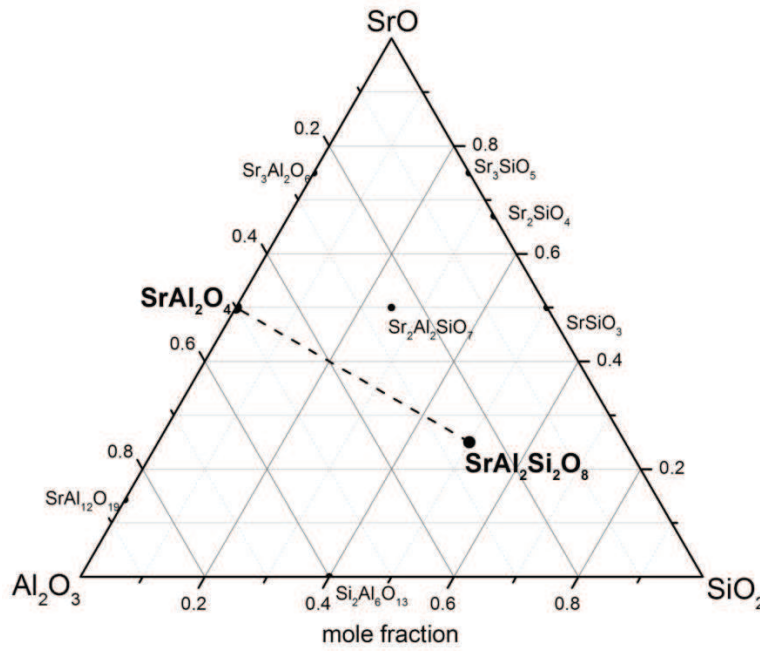


Figure 1 $SrO-Al_2O_3-SiO_2$ ternary diagram showing the localization of the studied system $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 2$)

$SrAl_2O_4$ exhibits three polymorphs: two high-temperature hexagonal polymorphs and a low-temperature monoclinic polymorph shown by a study realized by Avdeev M. *et al.*¹² The phase transitions between the different space groups have shown that $SrAl_2O_4$ undergoes two reversible phase transitions:

- Monoclinic ($P2_1$, $a=8.4$ Å, $b=8.8$ Å, $c=5.1$ Å) $\leftrightarrow$ hexagonal ($P6_3$, $a=8.9$ Å, $c=8.5$ Å) phase transition at approximately 680 °C.
- Hexagonal ($P6_3$, $a=8.9$ Å, $c=8.5$ Å) $\leftrightarrow$ hexagonal ($P6_322$, $a=5.1$ Å, $c=8.5$ Å) phase transition at a higher temperature (860 °C).

The monoclinic $SrAl_2O_4$ polymorph, when co-doped with Eu^{2+} and Dy^{3+} , consists one of the most important long lasting green luminescent materials studied in the literature.¹³⁻¹⁸

However, due to its high synthesis temperature, different conventional synthesis methods have been employed such as solid state reaction¹⁹, co-precipitation²⁰, sol-gel-microwave processes²¹, hydrothermal and combustion processes^{22, 23}. It can also be synthesized as nanomaterials for applications for which the optical properties are size dependent.^{24, 25} Meanwhile, the only reported process for their synthesis in the form of single crystals is the LHPG (laser heated pedestal-growth) method.²⁶ The drawbacks of this crystal growth method are related to the limited fiber diameter (0.8 mm) obtained and to the low synthesis rate (4 mm/min).

On the other hand, different $SrAl_2Si_2O_8$ polymorphs have been reported. The monoclinic form is characterized by its low dielectric constant, low coefficient of thermal expansion, resistance toward oxidation and reduction. It is used as a ceramic composite material for applications at high temperature. It has been widely studied by NASA for the preparation of suitable matrix for aerospace applications.^{27, 28} The hexagonal polymorph (P63/mcm), due to its metastability, is considered as an undesired polymorph. This hexagonal polymorph exhibits high coefficient of thermal expansion and its reversible transformation to the orthorhombic polymorph is accompanied by volume changes inducing micro-cracks in the corresponding ceramic. The kinetics of these transformations has also been investigated.^{27, 29, 30}

IV.1.2 Glass synthesis throughout the solid solution

Glass vitrification attempts have been carried out on different compositions (Table 1) starting from $SrAl_2O_4$ followed by successive SiO_2 addition, till reaching the $SrAl_2Si_2O_8$ composition. Twelve compositions have been considered, all of which correspond to the general formula $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ where $x = 2, 1.6, 1.2, 0.8, 0.68, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1$ and 0.

Strontium carbonate ($SrCO_3$, 99.9%, Strem Chemicals), aluminium oxide (Al_2O_3 , 99.98%, Alfa Aesar) and silicon oxide (SiO_2 , 99.8%, Alfa Aesar) were used as starting raw materials for the preparation of the oxide mixtures. Stoichiometric weighed proportions of oxide mixtures for each composition have been well homogenized. A first vitrification attempt has been carried out in a commercial electric furnace ($T_{max} = 1750$ °C). For compositions which have not melted or melted but not totally vitrified, aerodynamic levitator coupled to laser heating system has been employed. The complete amorphousness of each composition has been checked by subsequent powder X-ray diffraction. The glass elaboration

technique for each composition and the minimum melting temperature are summarized in (Table 1).

Table 1 Compositions of the studied $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 2$) system, with the oxide composition (mass %) and the glass elaboration method and temperature for each

x	Formula	Starting Oxide Composition (mass %)			Glass elaboration technique (elaboration temperature)
		SrO	Al ₂ O ₃	SiO ₂	
2	SrAl ₂ O ₄	50.40	49.60	0	
1.6	Sr _{1.8} Al _{3.6} Si _{0.4} O ₈	47.33	46.57	6.10	Aerodynamic levitator (~2000°C)
1.2	Sr _{1.6} Al _{3.2} Si _{0.8} O ₈	43.98	43.27	12.75	Aerodynamic levitator (≥1750°C)
0.8	Sr _{1.4} Al _{2.8} Si _{1.2} O ₈	40.31	39.66	20.03	Aerodynamic levitator (≥1750°C)
0.68	Sr _{1.34} Al _{2.68} Si _{1.32} O ₈	39.14	38.51	22.35	Electric furnace (~1720°C)
0.6	Sr _{1.3} Al _{2.6} Si _{1.4} O ₈	38.34	37.72	23.94	Electric furnace (~1720°C)
0.5	Sr _{1.25} Al _{2.5} Si _{1.5} O ₈	37.32	36.72	25.96	Electric furnace (~1720°C)
0.4	Sr _{1.2} Al _{2.4} Si _{1.6} O ₈	36.27	35.69	28.04	Electric furnace (~1700°C)
0.3	Sr _{1.15} Al _{2.3} Si _{1.7} O ₈	35.20	34.63	30.17	Electric furnace (~1700°C)
0.2	Sr _{1.1} Al _{2.2} Si _{1.8} O ₈	34.10	33.55	32.35	Electric furnace (~1700°C)
0.1	Sr _{1.05} Al _{2.1} Si _{1.9} O ₈	32.97	32.44	34.59	Electric furnace (~1680°C)
0	SrAl ₂ Si ₂ O ₈	31.81	31.30	36.89	Electric furnace (~1680°C)

For the $x=2$ composition, S. Alahrache showed in his thesis study³¹ (realized at the CEMHTI laboratory) that the $SrAl_2O_4$ composition can be prepared using the aerodynamic levitation coupled to laser heating system. This composition directly crystallizes in the monoclinic form ($P2_1$) during the cooling step while conserving its transparency (Figure 2).



Figure 2 $SrAl_2O_4$ transparent single crystals elaborated by aerodynamic levitation coupled to laser heating system³¹

He demonstrated that some of the elaborated beads did not show any diffraction peaks by XRD, whereas some others led to one or a few intense diffraction peaks (Figure 3). Moreover, these beads if crushed they show a diffraction pattern which is indexed by the $P2_1$ monoclinic $SrAl_2O_4$ phase (ICSD 160296 - PDF 01-076-7488). This condition of obtaining just one family of diffraction peaks or none at all is observed only in the case of single crystals. However, from these results it appeared impossible to elaborate the $SrAl_2O_4$ glass composition by the aerodynamic levitation coupled to laser heating system.

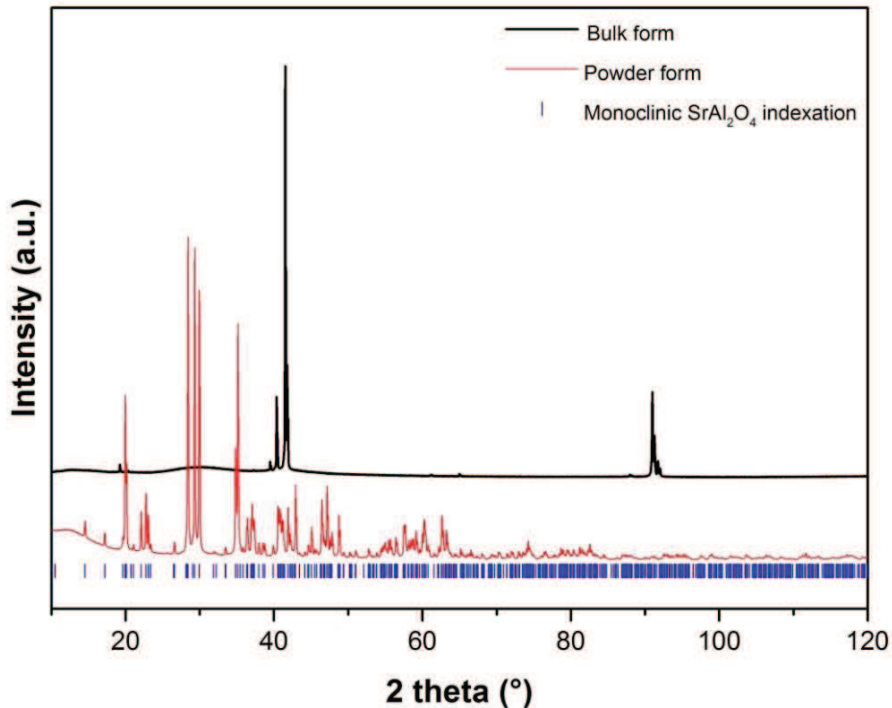


Figure 3 X-ray diffraction pattern of $SrAl_2O_4$ sample ($x=2$) elaborated by aerodynamic levitation coupled to laser heating, polished bead (black) and powder (red)

For the $x=1.6$ composition, totally amorphous glass beads have been obtained using the aerodynamic levitation technique coupled to laser heating. The relatively high melting point of this composition ($> 1750^\circ\text{C}$) prohibits its vitrification in a commercial electric furnace running up to 1750°C .

For the $x=1.2$ and 0.8 compositions, the oxide mixtures can be melted in our laboratory electric furnace. However both compositions have a crystallization tendency which has been confirmed by X-ray diffraction (Figure 4) while conserving their transparency. Complete vitrification in commercial electric furnace can be reached in case of a small quantity of oxide mixture ($< 1\text{-}2\text{ g}$ maximum) and a fast quenching of the crucibles in water. The additional amount of SiO_2 present in these two compositions has lowered the melting temperature of the oxide mixture; nevertheless complete vitrification requires a small quantity of glass precursor and a very fast quenching rate, or the use of the aerodynamic levitation coupled to laser heating system.

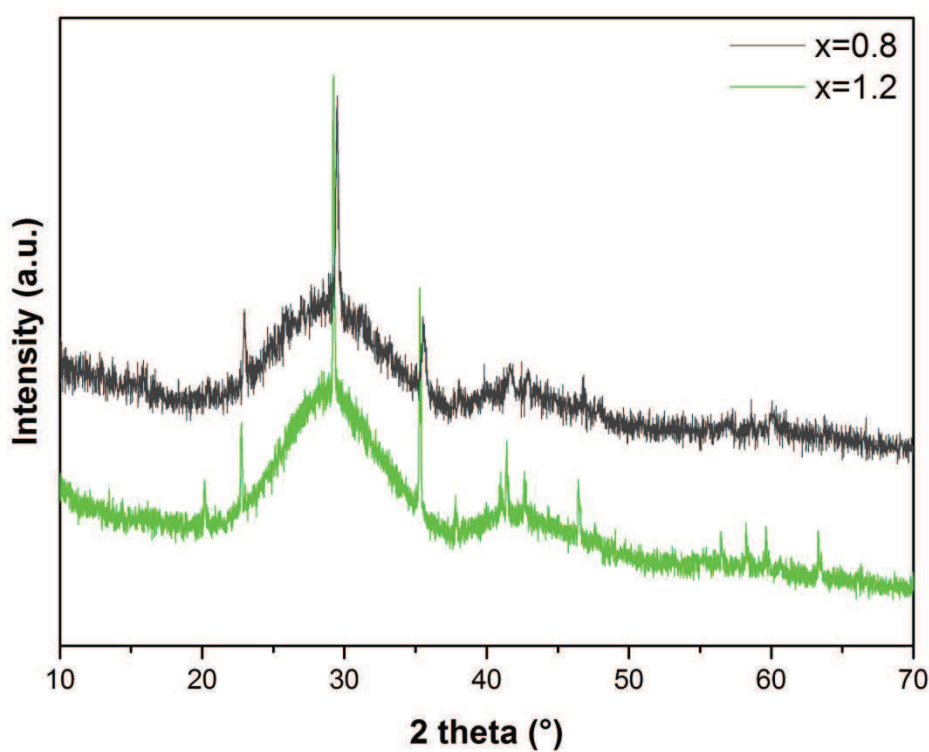


Figure 4 X-ray diffraction patterns of the $x=1.2$ and $x=0.8$ compositions when elaborated in commercial electric furnace at 1750°C

For the rest of the solid solution members $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 0.68$), all the glass compositions can be elaborated in our laboratory electric furnace. The increased vitrification ability can be attributed to the increased silica content in these compositions compared to the

first four members of the system ($x=2, 1.6, 1.2$ and 0.8). The vitrification tendency has been improved and the complete amorphousness of the obtained glass has been verified by X-ray powder diffraction. For the compositions prepared in the commercial electric furnace, large samples could be easily realized. Notably, starting from $x=0.4$ down to $x=0$ compositions with increased silica content 100 g samples can be easily vitrified.

IV.1.3 Full crystallization form glass

Following the glass synthesis, full crystallization of the eleven different compositions has been realized by single thermal treatments of the glass precursors, each at a corresponding temperature and for a certain period of time. The crystallization conditions for each sample (temperature (T) and time (t)) have been determined for each composition after numerous crystallization tries at different T and t. The X-ray diffraction patterns of the obtained polycrystalline ceramics are presented in Figure 5.

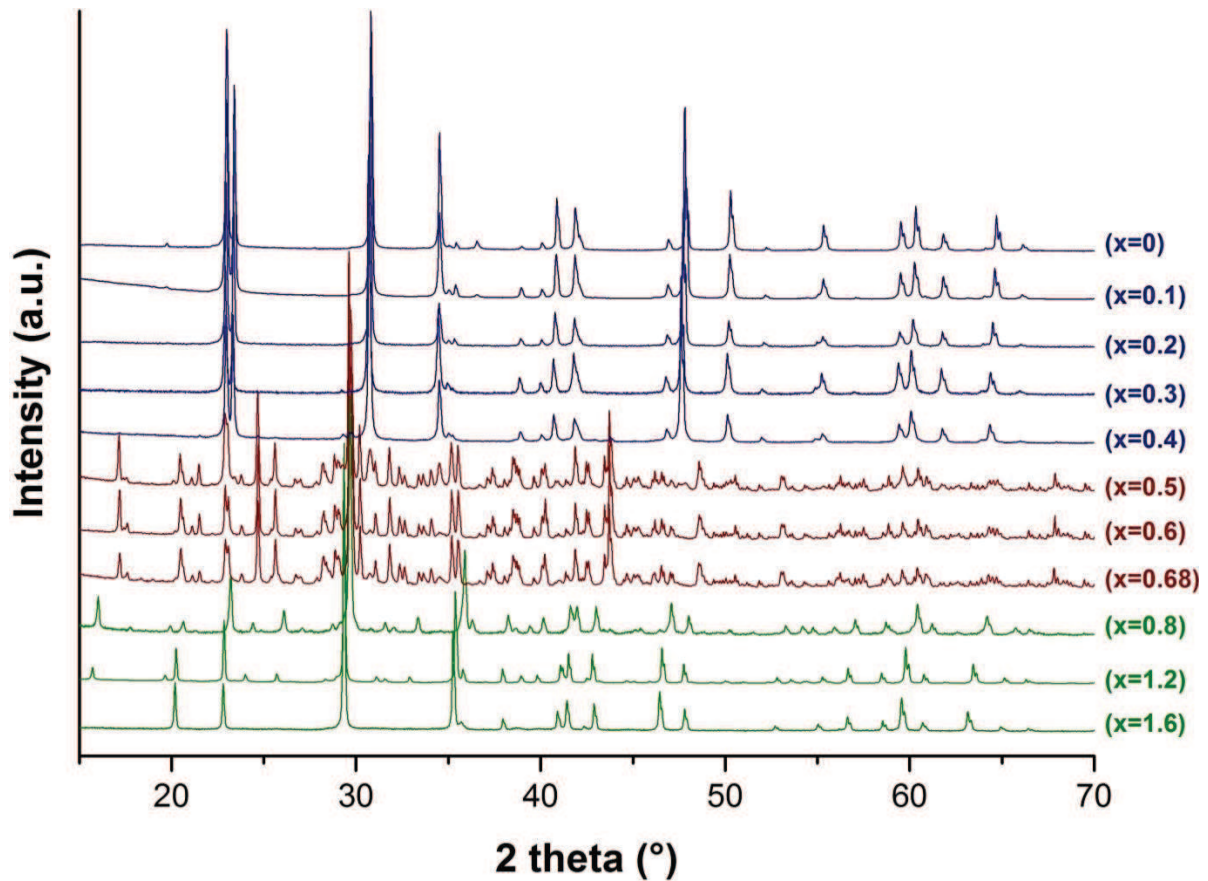


Figure 5 Normalized X-ray powder diffraction patterns of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 2$) solid solution ceramic compositions

From the analysis of the X-ray powder diffraction patterns (Figure 5) we have observed that, some of the composition lying between the two well-known compositions SrAl_2O_4 and $\text{SrAl}_2\text{Si}_2\text{O}_8$ crystallize in new phases, which could not be indexed. Notably, three different diffraction patterns appeared to exist which are represented by three different colors in Figure 5. Therefore the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 2$) system can be divided into three solid solutions:

1. The first solid solution $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0.8 \leq x \leq 2$) represented by green line in Figure 6.
2. The second solid solution $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0.5 \leq x \leq 0.68$) represented by red line in Figure 6.
3. The third solid solution $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0.4$) represented by blue line in Figure 6.

Each solid solution has been then separately studied.

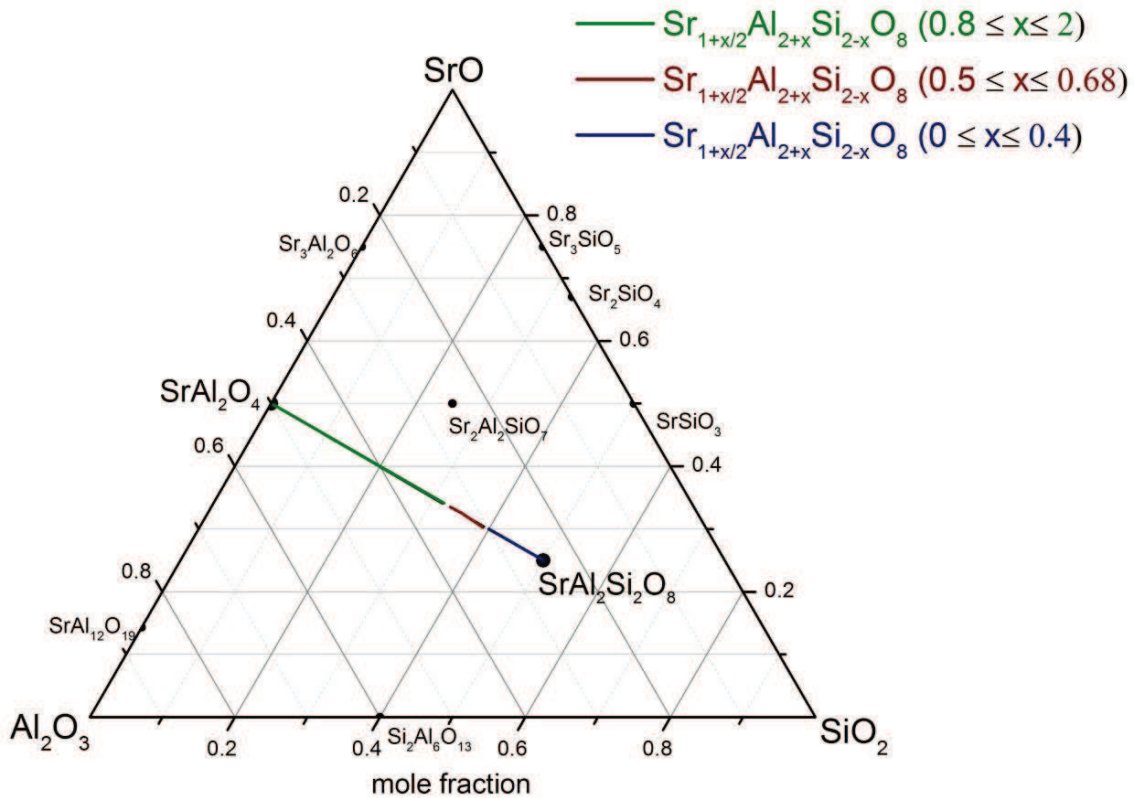


Figure 6 $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ternary diagram showing the localization of the 3 new solid solutions

IV.1.4 $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0.8 \leq x \leq 2$) solid solution

IV.1.4.1 Thermal analysis

Thermal parameters for each of the three glass compositions (≈ 472 mg each) of this solid solution ($x=1.6, 1.2$ and 0.8) have been determined using DSC measurements (Figure 7).

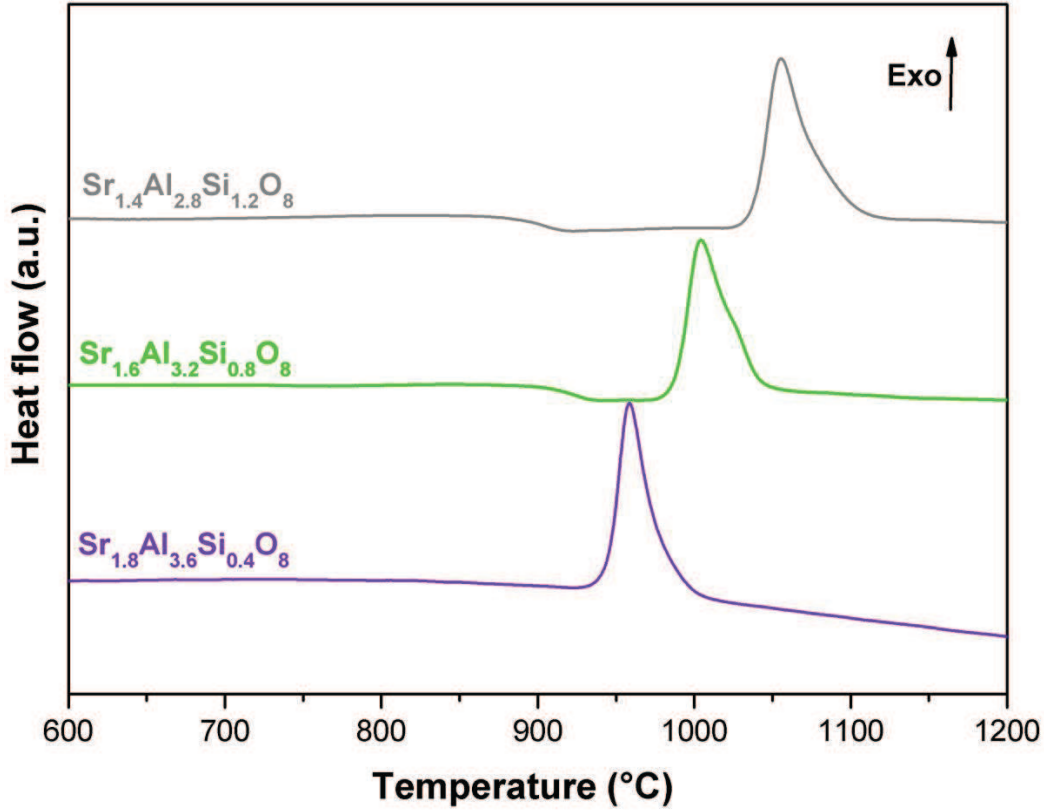


Figure 7 Normalized DSC thermograms of the different $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x=1.6, 1.2$ and 0.8) glass compositions

The thermograms show an endothermic transition corresponding to the glass transition (T_g) and a single exothermic peak corresponding to the crystallization of single phase (Figure 7) confirmed by X-ray powder diffraction (Figure 5). For the $x=1.6$ composition, the glass transition is masked by the crystallization peak. This signifies that crystallization could have taken place at the level of T_g , which can be explained by a strong viscosity causing a low glass stability. The crystallization tendency is expected for such a composition with very low silica content which has justified the requirement of the aerodynamic levitation coupled to laser heating, in order to ensure the complete vitrification of the composition (high melting T and fast cooling rate ≈ 300 °C/sec). For the other two compositions ($x=1.2$ and 0.8), a considerable decrease in the glass transition temperature T_g values is observed with the

increased level of Al substitution by Si (decrease of x). T_g decrease can be attributed to the larger average bond strength for Si-O compared to Al-O bonds.³² The Al substitution mechanism by Si is accompanied with a decrease in glass viscosity and improved glass stability.

Table 2 Glass transition and crystallization temperatures of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x=1.6, 1.2$ and 0.8) glass compositions obtained from DSC

Glass composition	T_g (°C) ± 2	T_c (°C) ± 2
$Sr_{1.8}Al_{3.6}Si_{0.4}O_8$ ($x=1.6$)		944
$Sr_{1.6}Al_{3.2}Si_{0.8}O_8$ ($x=1.2$)	926	988
$Sr_{1.4}Al_{2.8}Si_{1.2}O_8$ ($x=0.8$)	903	1038

On the other hand, a considerable increase of the crystallization temperature is observed with decreasing x (Table 2). This also highlights a better stability of the glass toward crystallization due to the increased level of Al substitution by Si.

IV.1.4.2 Elaboration of transparent polycrystalline ceramic by full crystallization from glass

Subsequently to glass preparation and thermal analysis study of the first solid solution compositions, the objective was to fully crystallize the glass compositions while conserving their transparency if possible.

For the $x=1.6$ composition, a thermal crystallization at 820°C with a 10 °C/min rate in an open air tubular furnace for 6 hours has resulted in highly transparent polycrystalline materials (Figure 8). The total crystallization has been verified by powder X-ray diffraction (Figure 10) and TEM observations. Thermal annealing at lower temperatures has necessitated much longer time in order to achieve the total crystallization, while annealing at higher temperatures have resulted in the creation of bubbles inside the materials which largely affected their transparency. Hence, the above indicated thermal treatment program (820 °C for

6 hours) appears to be optimized for conserving the transparency of the $x=1.6$ polycrystalline ceramics.

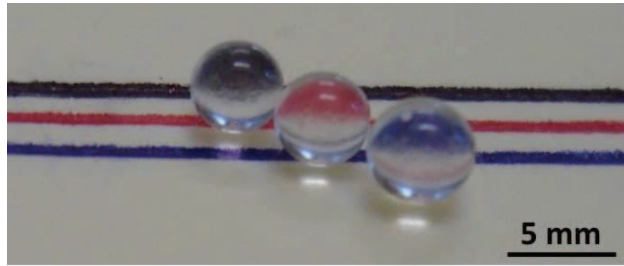


Figure 8 Photograph of the $Sr_{1.8}Al_{3.6}Si_{0.4}O_8$ ($x=1.6$) polycrystalline ceramic composition (thermal crystallization at 820 °C during 6 hours)

For the other two compositions ($x=1.2$ and 0.8), the crystallization process appeared to be very complicated where thermal crystallization at high temperature ($> 820^{\circ}C$) has resulted in the total crystallization of the samples with the apparition of bubbles and deformation of the sample shape (Figure 9b), whereas thermal treatment at lower temperature ($\leq 820^{\circ}C$) for long times has led to non-fully crystallized transparent ceramics (Figure 9a).

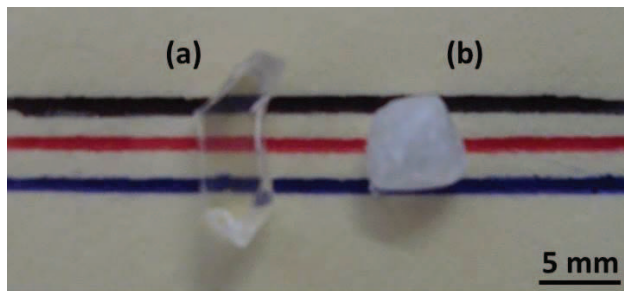


Figure 9 Photograph of the $Sr_{1.4}Al_{2.8}Si_{1.2}O_8$ ($x=0.8$) composition (a) glass-ceramic (b) polycrystalline ceramic

IV.1.4.3 Structure determination

The X-ray powder diffraction patterns of the three compositions have showed that some of the diffraction peaks of the single crystallized phase can be indexed with the hexagonal $SrAl_2O_4$ (P6₃, $a=8.9260 \text{ \AA}$, $c=8.4985 \text{ \AA}$) indexation (ICSD 160298 – PDF 01-074-8724) with a slight shift expected in our solid solution case. However, several peaks of very weak intensities have not been indexed by this hexagonal $SrAl_2O_4$ (P6₃) phase.

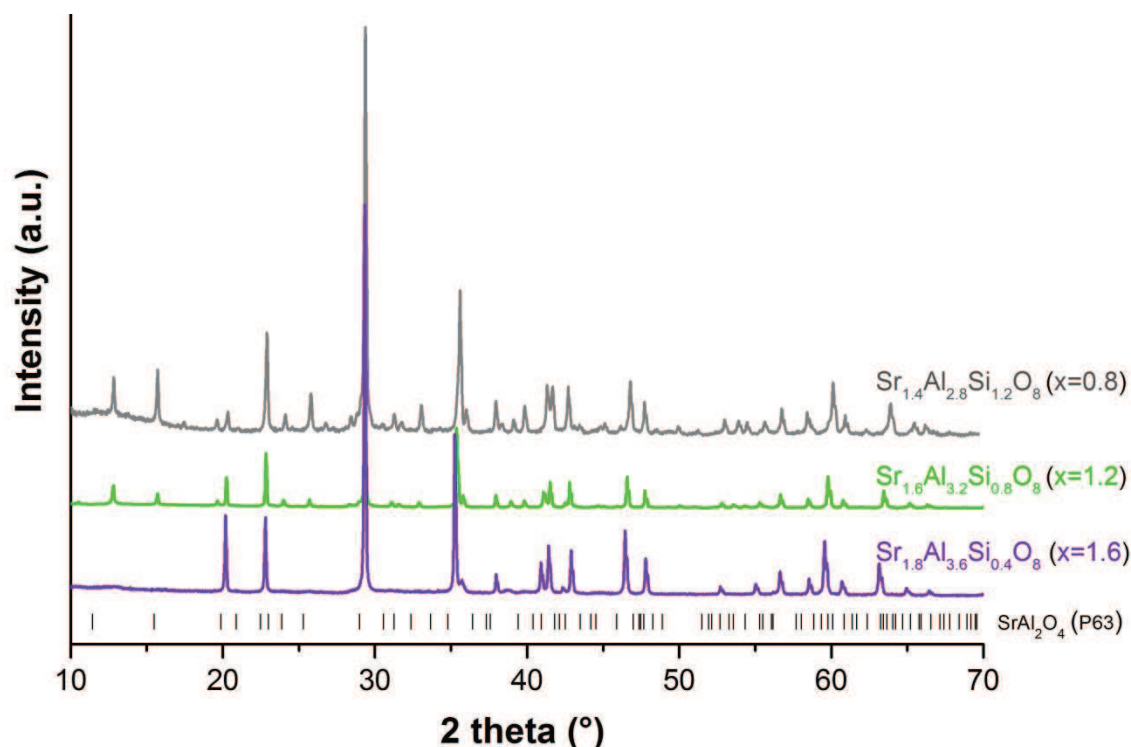


Figure 10 Laboratory X-ray powder diffraction patterns of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x = 1.6, 1.2$ and 0.8) polycrystalline ceramic compositions

The low intensity of the additional non-indexed peaks observed with decreasing x required a high resolution powder diffraction pattern for the structural refinement. Synchrotron X-ray powder diffraction has been performed in order to determine the unit cell and the symmetry of the corresponding crystallized phase.

Indexation of the Bragg peaks in synchrotron X-ray powder diffraction patterns has been realized using the TREOR software.³³ A hexagonal unit cell with doubled c cell parameter ($a=8.8$ Å and $c=16.9$ Å) compared to hexagonal $SrAl_2O_4$ (P6₃, $a=8.9$ Å, $b=8.5$ Å) has been first identified (Figure 11). No symmetric extinctions have been found for hkl , implying a primitive unit cell (P). The following reflection conditions have been obtained $hh\bar{2}hl : l=2n$ and $000l : l=2n$, suggesting P6₃mc, P-62c or P6₃/mcm as space group for this new crystalline structure. For each of the three possible space groups, and using the charge flipping^{34, 35} method (through the SUPERFLIP program^{36, 37} implemented in the Jana software), *ab initio* structure determinations have been performed from synchrotron powder diffraction data. This approach helped in the determination of the heavy cations (Sr^{2+} , Al^{3+} and Si^{4+}) and some of the light anions (O^{2-}) positions. A final Rietveld refinement step of the proposed structures against neutron diffraction data has assisted in the positioning of the final

oxygen atoms by the inspection of Fourier maps. The best agreement between experimental and calculated diffraction pattern has been obtained for the structural model with the P-62c space group.

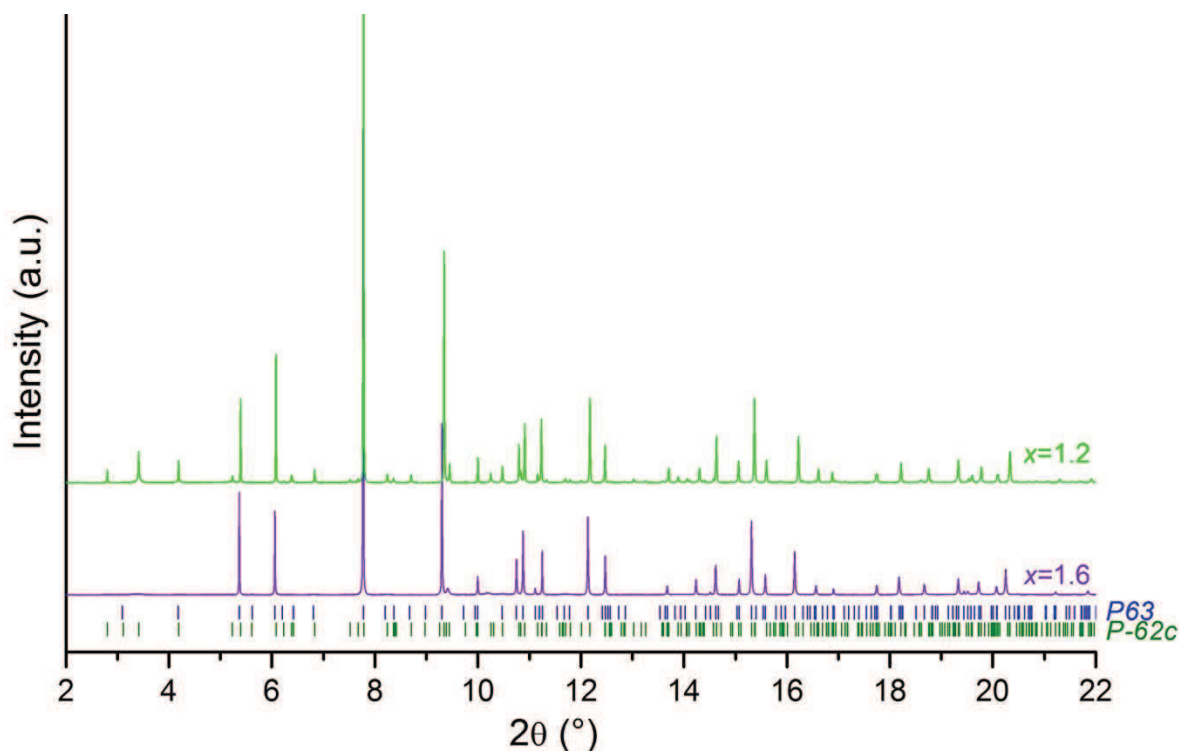


Figure 11 Synchrotron powder diffraction patterns of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x = 1.6$ and 1.2) polycrystalline ceramic compositions ($\lambda = 0.413978 \text{ \AA}$). Blue indexation: hexagonal $SrAl_2O_4$ crystalline phase ($P6_3$, $a=8.9 \text{ \AA}$, $b=8.5 \text{ \AA}$). Green indexation: for the first solid solution compositions ($x=1.6$, 1.2 and 0.8); $P-62c$, $a=8.8 \text{ \AA}$ and $c=16.9 \text{ \AA}$)

The Rietveld refinement plots of the synchrotron and neutron powder diffraction data for the $x=1.2$ composition are shown respectively in Figure 12 and Figure 13.

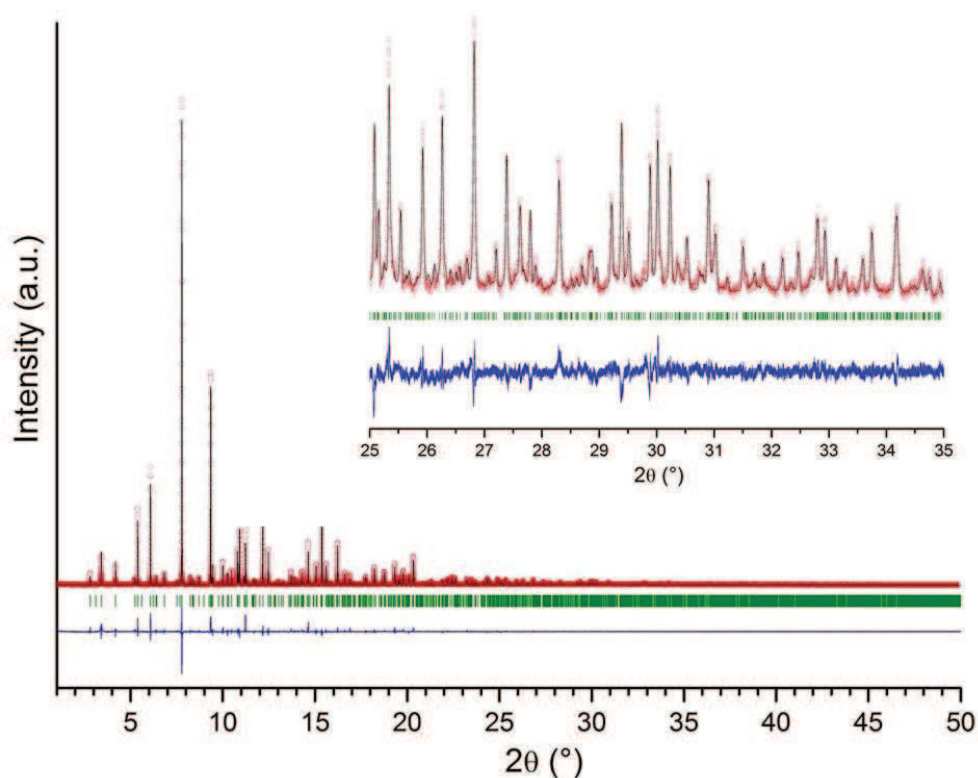


Figure 12 Rietveld refinement plot of ambient temperature powder synchrotron radiation diffraction data of the $x=1.2$ ceramic composition ($R_{wp}=11.86\%$, $R_p=9.80\%$, $G.O.F=2.22$). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines correspond to the reflection positions. Enlargement of the $25\text{--}35^\circ$ angular range (2θ) is embedded

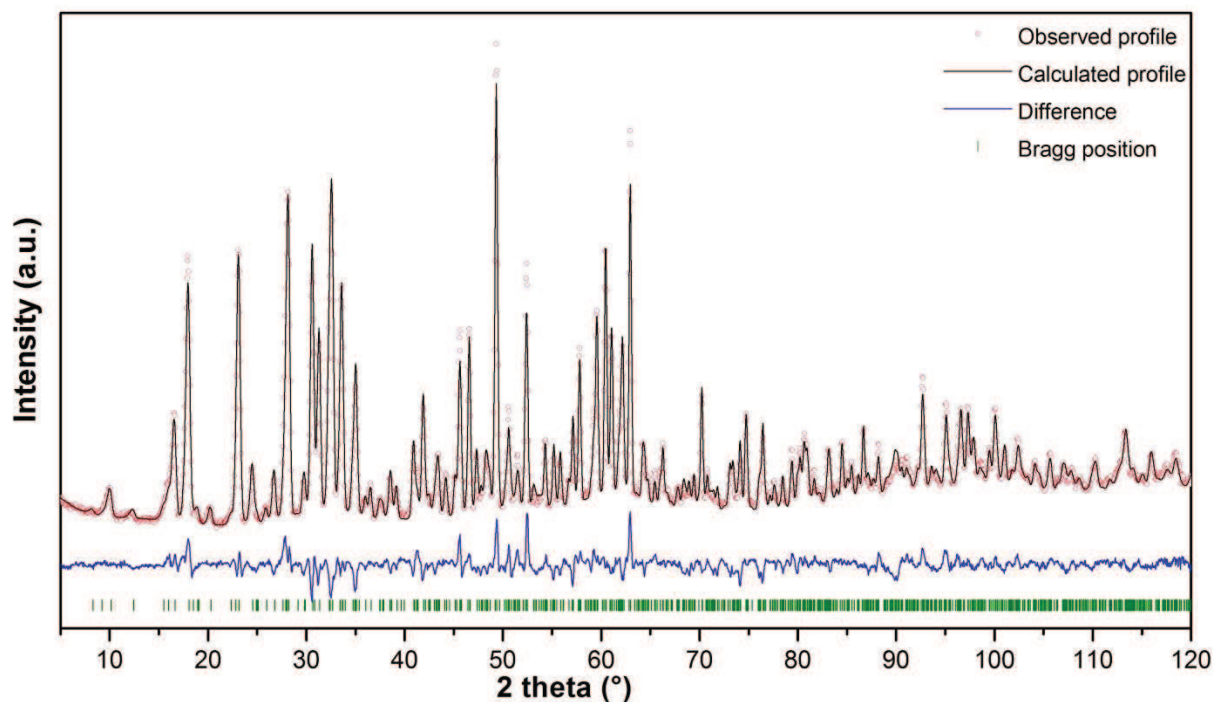


Figure 13 Rietveld refinement plot of ambient temperature powder neutron diffraction data of the $x=1.2$ ceramic composition ($R_{wp}=4.45\%$, $R_p=3.46\%$, $G.O.F=2.99$)

The structural parameters issued by Rietveld refinement (atomic positions, occupancy, cation-oxygen distances) are grouped in Table 3 and Table 4.

Table 3 Atomic coordinates and values of occupancy factor determined for $Sr_{1.6}Al_{3.2}Si_{0.8}O_8$ ($x=1.2$) from Rietveld refinement of the synchrotron powder diffraction pattern collected at ambient temperature

Atom	Site	x	y	z	Uiso	Occ.
Sr1	2c	0.33333	0.66667	0.25	0.0149(5)	0.873(3)
Sr2	2b	0	0	0.25	0.0131(6)	0.991(3)
Sr3	4f	0.66667	0.33333	0.99561(6)	0.0160(4)	0.943(3)
Sr4	2d	0.66667	0.33333	0.25	0.065(2)	0.353(3)
Sr5	2a	0	0	0	0.028(1)	0.732(3)
Al1	12i	0.6776(3)	0.0003(3)	0.09490(10)	0.0068(10)	0.8
Si1	12i	0.6776(3)	0.0003(3)	0.09490(10)	0.0068(10)	0.2
Al2	12i	0.9969(3)	0.3486(3)	0.14994(16)	0.0229(13)	0.8
Si2	12i	0.9969(3)	0.3486(3)	0.14994(16)	0.0229(13)	0.2
O1	12i	0.9192(6)	0.4466(8)	0.0997(2)	0.062(2)	1
O2	6g	0.7177(9)	0	0	0.080(6)	1
O3	6h	0.0090(7)	0.4038(7)	0.25	0.016(2)	1
O4	12i	0.8772(7)	0.1339(8)	0.1457(2)	0.032(2)	1
O5	12i	0.2123(9)	0.4172(5)	0.1302(2)	0.066(4)	1

Table 4 Interatomic distances for $Sr_{1.6}Al_{3.2}Si_{0.8}O_8$ ($x=1.2$) obtained from the synchrotron powder diffraction (11BM-APS) pattern collected at ambient temperature

Al/Si tetrahedron (Å)			Sr polyhedron (Å)		
(Al/Si)1 – O1	1.787(10)	Sr1 – O3 (x3)	2.626(6)	Sr4 – O1 (x6)	3.192(7)
(Al/Si)1 – O2	1.645(3)	Sr1 – O5 (x6)	2.780(7)	Sr4 – O3 (x3)	2.755(9)
(Al/Si)1 – O4	1.773(5)	Sr2 – O3 (x3)	3.515(9)	Sr5 – O2 (x3)	2.484(8)
(Al/Si)1 – O5	1.675(8)	Sr2 – O4 (x6)	2.635(6)	Sr5 – O4 (x6)	3.148(6)
(Al/Si)2 – O1	1.589(8)	Sr3 – O1 (x3)	2.611(8)		
(Al/Si)2 – O3	1.750(3)	Sr3 – O1 (x3)	3.546(9)		
(Al/Si)2 – O4	1.641(6)	Sr3 – O2 (x3)	3.183(8)		
(Al/Si)2 – O5	1.711(8)	Sr3 – O5 (x3)	2.854(7)		

The unit cell of this new hexagonal phase (P-62, $a \approx 8.8$ Å, $c \approx 16.9$ Å) contains five sites of Sr^{2+} (2 Strontium sites in addition to those present in hexagonal $SrAl_2O_4$ with space group $P6_322$), 2 mixed sites of Al^{3+} and Si^{4+} and five sites of O^{2-} (Figure 14).

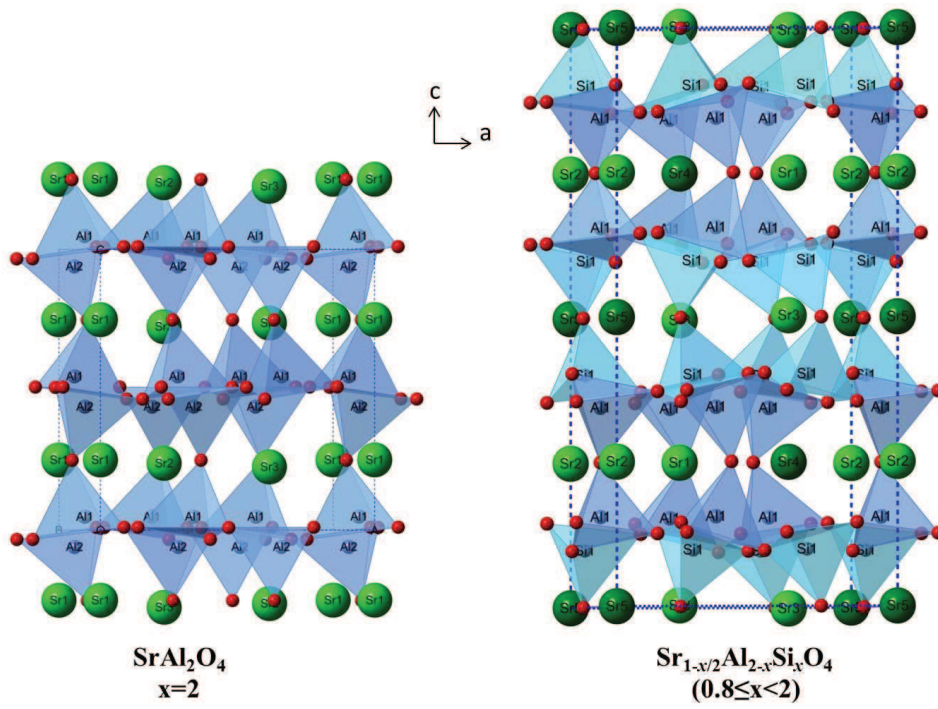


Figure 14 [010] view of the crystal structures of $SrAl_2O_4$ ($x = 2$) and $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x = 1.6, 1.2$ and 0.8)

The Rietveld refinements have shown that with the increased level of Al substitution by Si (i.e. when x decreases), strontium vacancies appear in two crystallographic sites Sr4 (2d) and Sr5 (2a) (Figure 14). These vacancies could be related to a charge compensation process: Si^{4+} is equivalent to $Al^{3+} + \frac{1}{2} Sr^{2+}$ for charge compensation (of $2 O^{2-}$), so the substitution of 2 Al by 2 Si implies 1 Sr vacancy to maintain electroneutrality compensation.

Transparent polycrystalline ceramics (Figure 8) with optical anisotropy can be elaborated in this solid solution ($x=1.6$). DFT calculations of the index of refraction are in current study to determine the birefringence in order to explain the observed transparency. However, only small-scale transparent polycrystalline ceramics can be elaborated. Therefore the other solid solutions have been considered where the precursor glass can be elaborated at larger scale with the increased silica content.

IV.1.5 $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0.5 \leq x \leq 0.68$) solid solution

IV.1.5.1 Thermal analysis

DSC measurements have been carried out on the three glass compositions ($x=0.68, 0.6$ and 0.5). The obtained thermograms are presented in Figure 15.

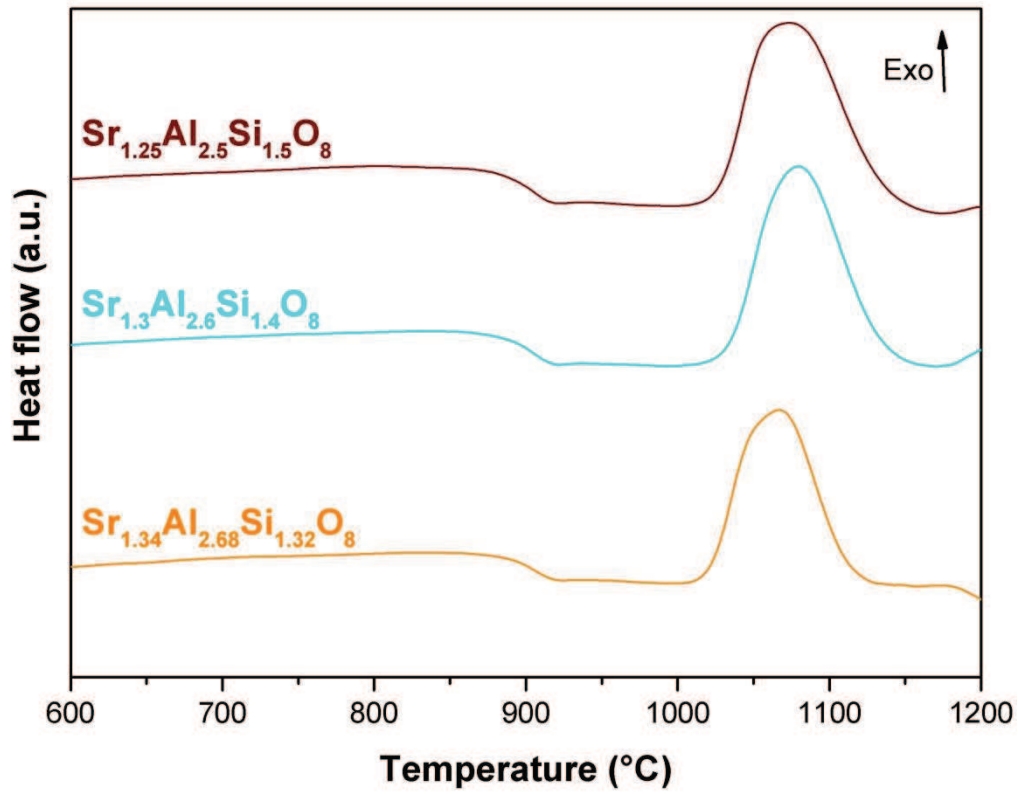


Figure 15 Normalized DSC thermograms of the different $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x=0.68$, 0.6 and 0.5) glass compositions

The thermograms show a single glass transition (T_g) at $\approx 906 \pm 2^\circ\text{C}$ and a single exothermic peak (T_c) corresponding to crystallization (Table 5).

Table 5 Glass transition and crystallization temperatures of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x=0.68$, 0.6 and 0.5) glasses obtained from DSC

Glass composition	T_g ($^\circ\text{C}$) ± 2	T_c ($^\circ\text{C}$) ± 2
$Sr_{1.34}Al_{2.68}Si_{1.32}O_8$ ($x=0.68$)	905	1022
$Sr_{1.3}Al_{2.6}Si_{1.4}O_8$ ($x=0.6$)	906	1027
$Sr_{1.25}Al_{2.5}Si_{1.5}O_8$ ($x=0.5$)	906	1034

A slight increase in the crystallization temperature is observed with increasing x . This accentuates the concept of obtaining a more stable glass with less crystallization tendency as silica content increases.

IV.1.5.2 Full crystallization from glass

A single thermal treatment has been carried out for each of the three compositions, which resulted in their total crystallization, as shown by X-ray diffraction (Figure 16) and transmission electron microscopy. Transparent polycrystalline ceramics can be elaborated within this solid solution. However, the nature of the crystallization mechanism (weak surface crystallization) necessitates very thin glass samples (<0.3 mm) to assure a full crystallization while conserving transparency.

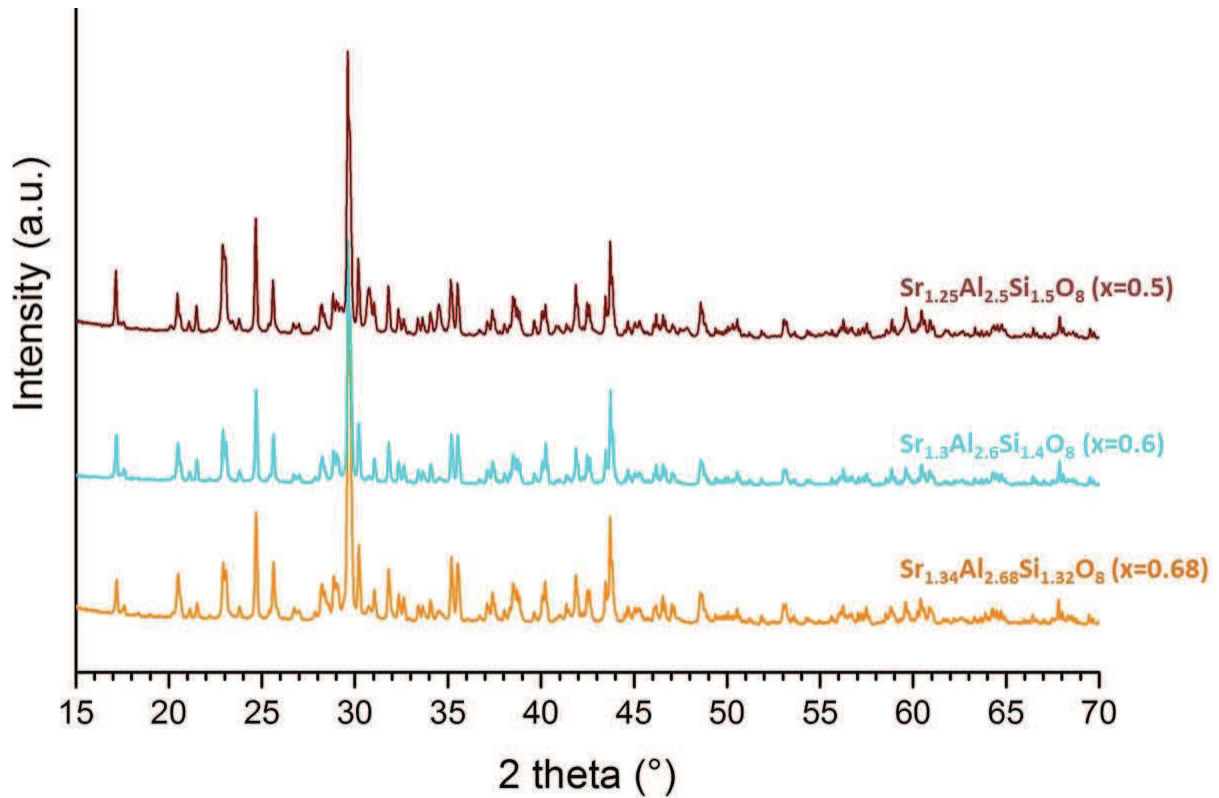


Figure 16 Laboratory X-ray powder diffraction patterns of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x = 0.68, 0.6$ and 0.5) polycrystalline ceramic compositions

For the X-ray powder diffraction patterns, no phase match could be realized using comparison with the PDF database (Powder Diffraction File). The transparent polycrystalline ceramics appear to crystallize in a new phase structure, non-reported before.

IV.1.5.3 Structure determination

The new phase structure elucidation has been determined *ab initio* using synchrotron and neutron powder diffraction. The same methodology presented before in the structure determination of the first solid solution has been adopted. TREOR and DICVOL softwares have been complementary employed for indexing the synchrotron powder diffraction pattern. An orthorhombic unit cell with the following cell parameters $a=8.3$ Å, $b=10.2$ Å, $c=17.5$ Å has been identified. No symmetric extinctions have been found for hkl , implying primitive unit cell (P). The following reflection conditions have been obtained $h0l$: $l=2n$ and $00l$: $l=2n$, suggesting Pmc2₁, P2cm or Pmcm as space group for this new crystalline structure. Crystallographic model structures for each of the three possible space groups have been determined *ab initio* using the charge flipping algorithm against synchrotron powder diffraction data. All the cations and most of the oxygen positions have been determined. Rietveld refinements of the proposed model structures against neutron powder diffraction data have helped in the determination of the final oxygen positions by the inspection of Fourier maps. The proposed model structure with Pmc2₁ space group gave the best agreement between experimental and calculated diffraction data. The Rietveld refinement plots of the synchrotron and neutron powder diffraction data for the $x=0.68$ composition are shown respectively in Figure 17 and Figure 18.

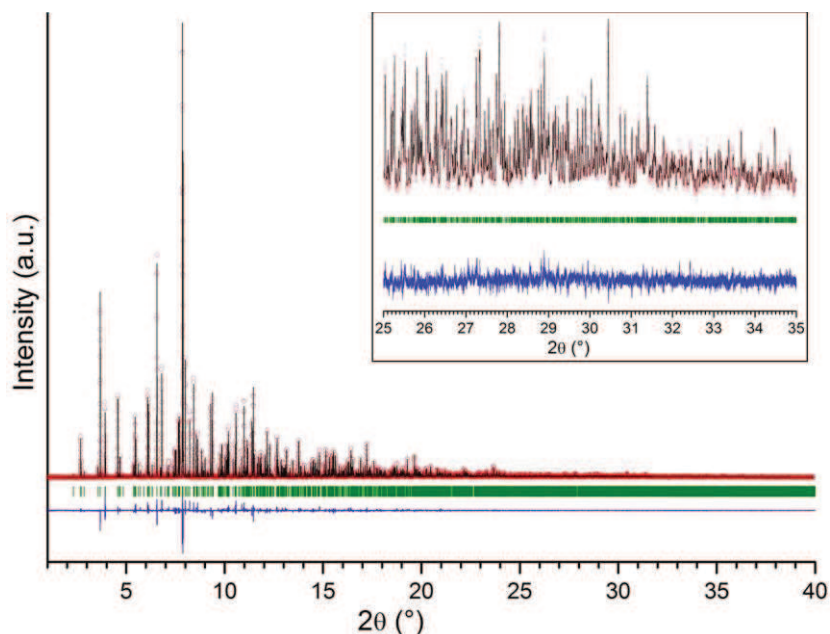


Figure 17 Rietveld refinement plot of ambient temperature powder synchrotron radiation diffraction data of the $x=0.68$ ceramic composition ($R_{wp}=7.67\%$, $R_p=6.70\%$, $G.O.F=1.45$). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines correspond to the reflection positions. Enlargement of the 25-35° angular range (2θ) is embedded

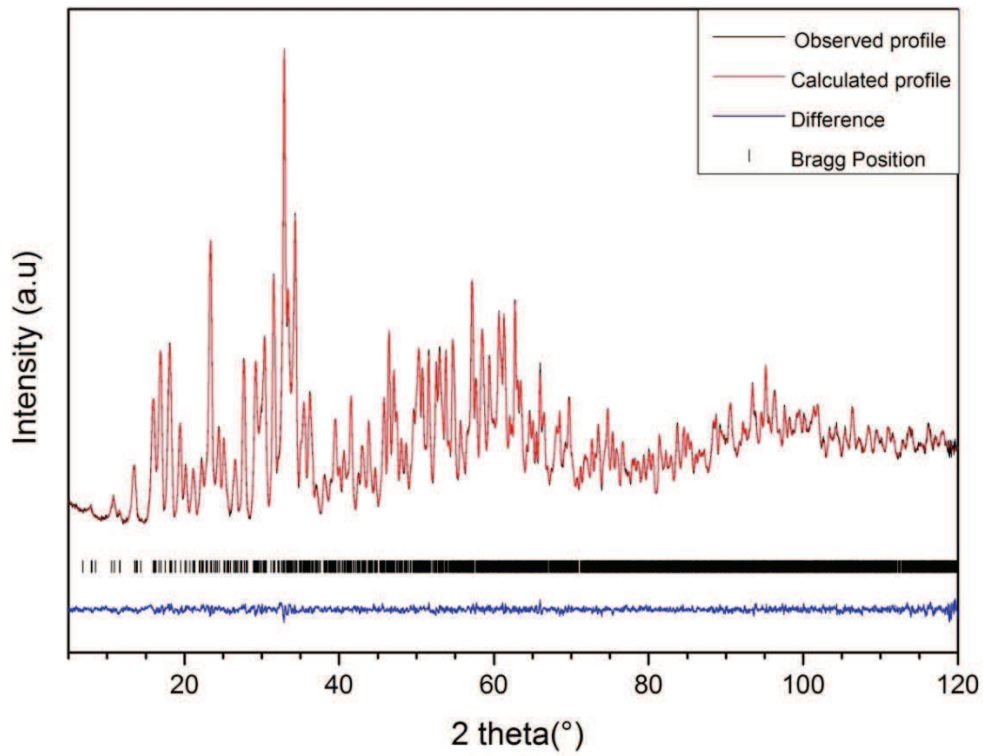


Figure 18 Rietveld refinement plot of ambient temperature powder neutron diffraction data of the $x=0.68$ ceramic composition ($R_{wp}=1.35\%$, $R_p=1.10\%$, $G.O.F=1.31$)

The detailed unit cell characteristics for each of the three compositions $x=0.68$, 0.6 and 0.5 are given in Table 6.

Table 6 Unit cell characteristics for the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0.5 \leq x \leq 0.68$) crystalline phase

Formula	$Sr_{1.25}Al_{2.5}Si_{1.5}O_8$	$Sr_{1.3}Al_{2.6}Si_{1.4}O_8$	$Sr_{1.34}Al_{2.68}Si_{1.32}O_8$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Pmc2_1$	$Pmc2_1$	$Pmc2_1$
Unit cell dimensions ($\text{\AA}$)	$a = 8.222837 (11)$ $b = 10.21431 (1)$ $c = 17.46516 (2)$	$a = 8.289157 (9)$ $b = 10.22115 (1)$ $c = 17.48112 (2)$	$a = 8.296202 (7)$ $b = 10.22540 (1)$ $c = 17.49654 (1)$
Cell volume ($\text{\AA}^3$)	1466.9(1)	1481.1(1)	1484.3(1)
Calculated density (g.cm^{-3})	3.1002	3.1362(1)	3.1550(1)

The structural parameters issued by Rietveld refinement (atomic positions, occupancy, cation-oxygen distances) for $x=0.68$ composition are grouped in Table 7 and Table 8.

Table 7 Atomic coordinates and values of occupancy factor determined for $Sr_{1.34}Al_{2.68}Si_{1.32}O_8$ ($x=0.68$) from Rietveld refinement of the synchrotron powder diffraction pattern collected at ambient temperature

Atom	x	y	Z	Occupancy factor	Sites
Sr1	0.5	0.8175 (1)	0.2385(1)	0.956(2)	2b
Sr2	0	0.5537(1)	-0.0133(1)	1	2a
Sr3	0	0.2677(1)	0.2619(1)	1	2a
Sr4	0.5	0.0419(1)	0.0113(1)	1	2b
Sr5	0	0.6795(1)	0.2769(1)	1	2a
Sr6	0	0.0502(10)	-0.0004(8)	0.085(2)	2a
Sr7	0.5	0.4948(3)	0.0104(2)	0.288(2)	2b
Sr8	0.5	0.7641	-0.1219	Not found	2b
(Al,Si)1	0.3136(2)	0.0845(2)	0.1735(1)	1	4c
(Al,Si)2	0.2991(3)	0.5344(2)	0.1697(2)	1	4c
(Al,Si)3	0.1863(2)	0.2968(2)	0.0695(2)	1	4c
(Al,Si)4	-0.3048(3)	0.2765(2)	-0.0915(2)	1	4c
(Al,Si)5	0.3034(3)	0.7846(3)	-0.0556(2)	1	4c
(Al,Si)6	-0.2998(2)	0.5509(2)	-0.1624(2)	1	4c
(Al,Si)7	0.1847(3)	0.8109(2)	0.1121(2)	1	4c
(Al,Si)8	0.1892(3)	0.9913(2)	0.3422(2)	1	4c

Table 8 Interatomic distances for $Sr_{1.34}Al_{2.68}Si_{1.32}O_8$ obtained from the synchrotron powder diffraction (11BM-APS) pattern collected at ambient temperature

Al/Si tetrahedron (average) (Å)		Sr polyhedron (average) (Å)	
(Al/Si)1 – O	1.7155	Sr1 – O (7)	2.752
(Al/Si)2 – O	1.726	Sr2 – O (7)	2.685
(Al/Si)3 – O	1.686	Sr3 – O (7)	2.630
(Al/Si)4 – O	1.734	Sr4 – O (7)	2.588
(Al/Si)5 – O	1.712	Sr5 – O (7)	2.720
(Al/Si)6 – O	1.699	Sr6 – O (7)	2.995
(Al/Si)7 – O	1.700	Sr7 – O (9)	2.973
(Al/Si)8 – O	1.677	Sr8 – O	

This new orthorhombic crystalline structure presents successive layers of strontium and AlO_4/SiO_4 tetrahedra (Figure 19). It has 8 Al/Si sites, 20 oxygen sites and 7 or 8 strontium sites (4 sites fully occupied and the remaining partially occupied).

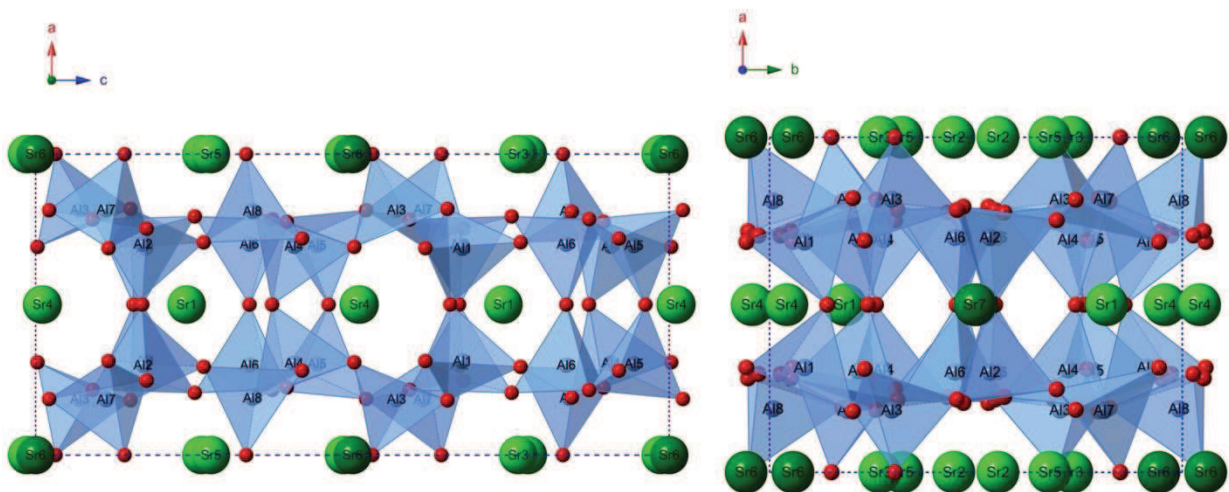


Figure 19 Crystal structures of $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0.5 \leq x \leq 0.68$)

Full details of all synchrotron powder diffraction refinements of the $x=0.6$ and 0.5 compositions are given in Supplementary information: Figures S1, S2 and Tables S1, S2.

Considering the relation between the first solid solution and the second solid solution it is worth noting that, for the first solid solution structure a complete evacuation of the Sr atoms on the sites Sr4 and Sr5 (Figure 14), leads to obtaining the structure of the $x=0.68$ sample. There exists a relation between the hexagonal phase and the orthorhombic phase. There appears to be a symmetry operation which links the two crystalline structures.

As mentioned previously, the weak surface crystallization mechanism constrains transparent polycrystalline ceramics elaboration to a sample thickness less than 0.3 mm in order to assure full crystallization. This solid solution $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0.5 \leq x \leq 0.68$) is also in current study. However, the third solid solution has been investigated for ameliorated polycrystalline ceramics properties (transparency and scalability).

IV.1.6 $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0.4$) solid solution

Remarkably, large scale samples (disks with $\varnothing \approx 4 - 5$ cm) can be easily elaborated starting from $x=0.4$ down to $x=0$ compositions with high silica content (28.04, 30.17, 32.35, 34.59, 36.89 mass % for $x=0.4, 0.3, 0.2, 0.1$ and 0 respectively). Interestingly, highly transparent polycrystalline ceramics can be elaborated by full glass crystallization. This $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 4$) solution has been studied and characterized using a multi-scale approach; combined X-ray and neutron powder diffractions for average structure study and nuclear magnetic resonance spectroscopy for local order investigation. Microstructure observations and DFT calculations are also undertaken for the characterization of the obtained transparent polycrystalline materials.

IV.2 Transparent $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0.4$) polycrystalline ceramics

IV.2.1 Elaboration of transparent polycrystalline ceramics

IV.2.1.1 Optimized glass synthesis conditions

Five compositions have been prepared ($x=0, 0.1, 0.2, 0.3$ and 0.4 which correspond respectively to $\text{SrAl}_2\text{Si}_2\text{O}_8$, $\text{Sr}_{1.05}\text{Al}_{2.1}\text{Si}_{1.9}\text{O}_8$, $\text{Sr}_{1.1}\text{Al}_{2.2}\text{Si}_{1.8}\text{O}_8$, $\text{Sr}_{1.15}\text{Al}_{2.3}\text{Si}_{1.7}\text{O}_8$ and $\text{Sr}_{1.2}\text{Al}_{2.4}\text{Si}_{1.6}\text{O}_8$ formula. The oxide powder mixtures have been placed in rhodium/platinum crucibles, introduced in a 1700°C pre-heated commercial electric furnace, left for 10 min,

heated up to 1750 °C for 10 min and back to 1700 °C for 30 min. Clear transparent bulk sample glasses have been obtained by simply quenching the crucibles in air, without noticing any glass crystallization. The complete amorphousness has been proved by X-ray diffraction as shown in Figure 20 for the $x=0.2$ composition. Same diffractogram patterns have been obtained for the five compositions of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 0.4$) solid solution.

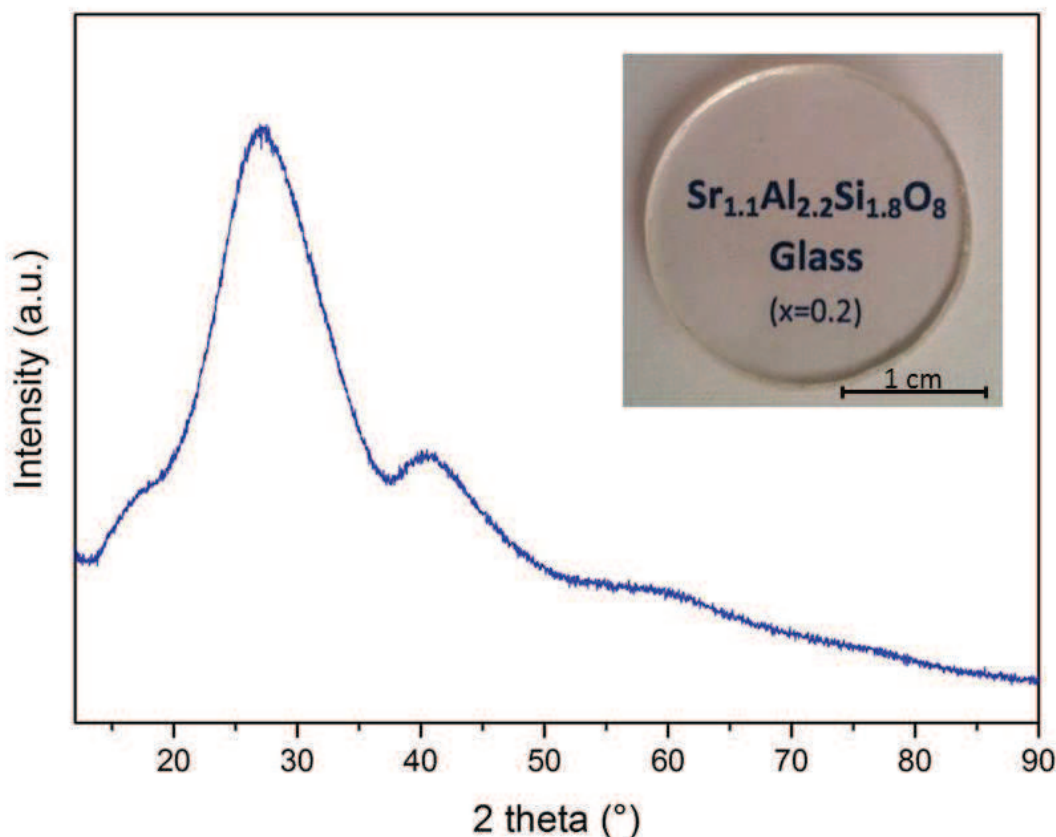


Figure 20 Laboratory X-ray diffraction data of the $x=0.2$ glass member of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ solid solution. Inset: photograph of the $x=0.2$ glass sample

IV.2.1.1 Evolution of glass thermal parameters

Each composition of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ solid solution (≈ 475 mg each) has been measured on DSC using a heating rate of 10 K/min, in order to extract the thermal parameters (glass transition and crystallization temperature).

Figure 21 shows the thermograms of the five compositions ($x=0, 0.1, 0.2, 0.3$ and 0.4). The endotherms observed correspond to the glass transition and the large exothermic peaks correspond to the glass crystallization.

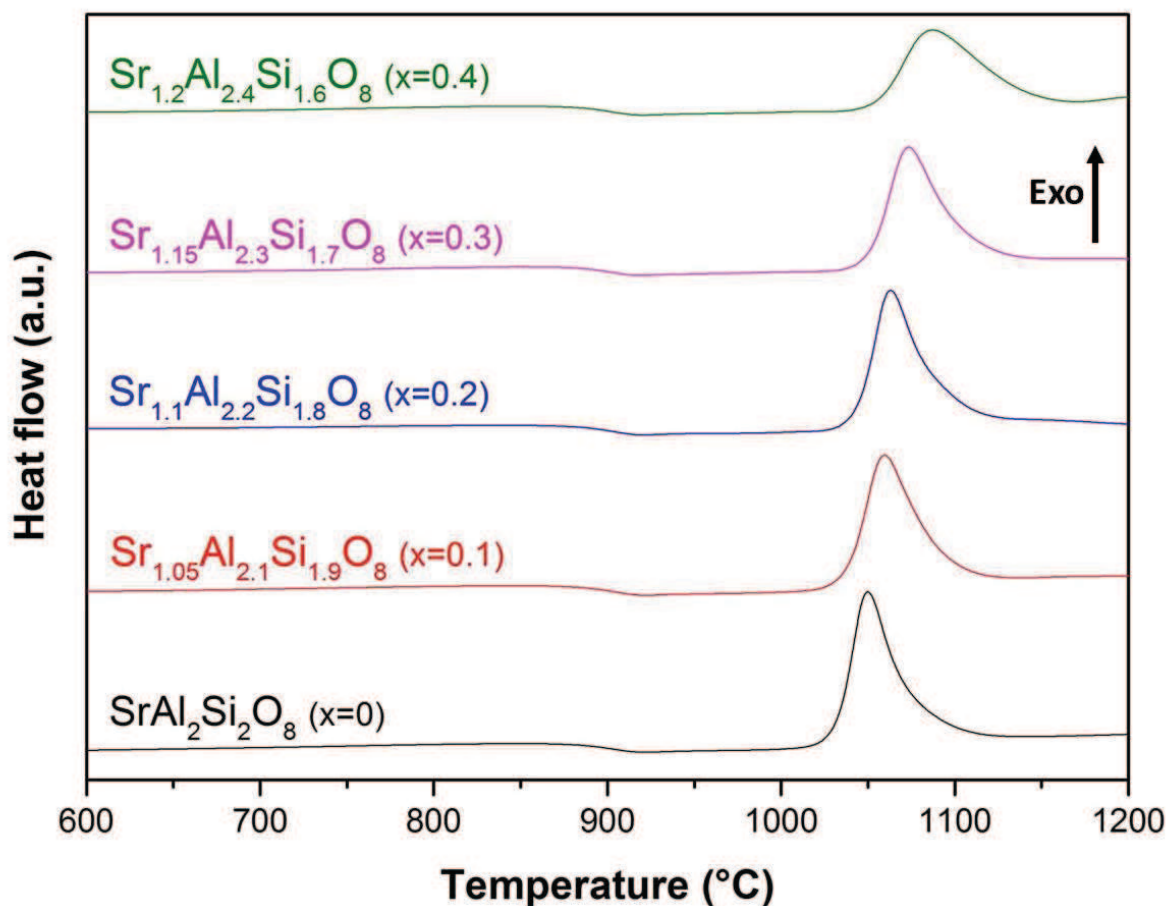


Figure 21 Normalized DSC thermograms of the different $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x=0, 0.1, 0.2, 0.3$ and 0.4) glass compositions

Detailed values of the glass transition temperatures and crystallization temperatures of the five glass compositions of the solid solution $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 0.4$) are listed in Table 9. An almost constant value for the glass transition has been obtained for all the five glass compositions ($\approx 905 \pm 2^\circ\text{C}$), and a single exothermic peak ranging from $1050 \pm 2^\circ\text{C}$ to $1090 \pm 2^\circ\text{C}$ have been observed.

Table 9 Glass transition and crystallization temperatures of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x=0, 0.1, 0.2, 0.3$ and 0.4) glasses obtained from DSC

Glass composition	T _g (°C) ± 2	T _c (°C) ± 2
$SrAl_2Si_2O_8$ ($x=0$)	907	1050
$Sr_{1.05}Al_{2.1}Si_{1.9}O_8$ ($x=0.1$)	905	1060
$Sr_{1.1}Al_{2.2}Si_{1.8}O_8$ ($x=0.2$)	904	1063
$Sr_{1.15}Al_{2.3}Si_{1.7}O_8$ ($x=0.3$)	903	1073
$Sr_{1.2}Al_{2.4}Si_{1.6}O_8$ ($x=0.4$)	904	1088

IV.2.1.3 Full crystallization from glass

For the glass samples a thermal treatment at $T_g-50^\circ\text{C}$ has been conducted on the five compositions in order to relieve the mechanical constraints inside the glass. The glass samples have been thinned to a thickness of approximately 1.5 mm before the crystallization step.

Finally a single heat treatment performed at 1020°C for 3 hours in an open air-atmosphere furnace has been sufficient to ensure the complete crystallization of the glass samples as confirmed by synchrotron powder diffraction data (Figure 22) and TEM observations.

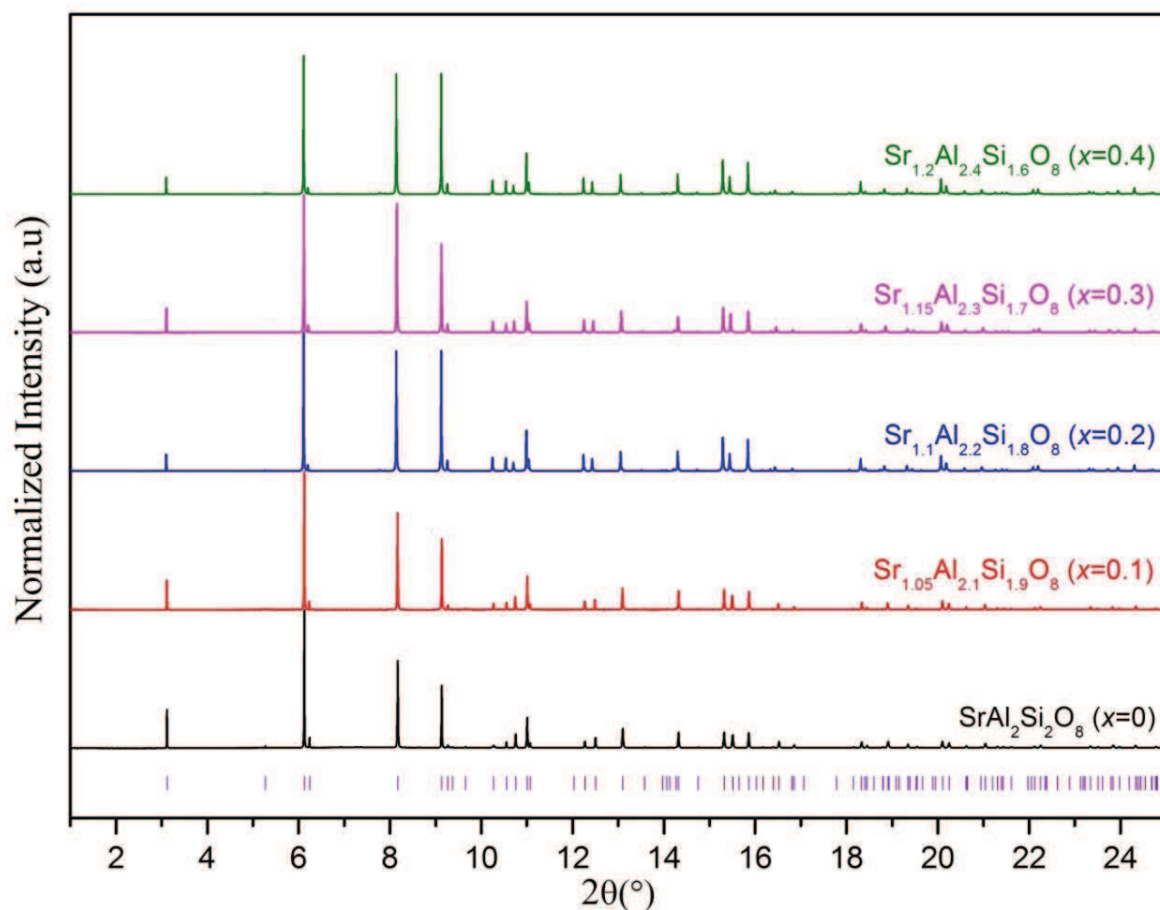


Figure 22 Normalized synchrotron powder diffraction patterns of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x = 0, 0.1, 0.2, 0.3$ and 0.4) ceramic compositions ($\lambda = 0.413978 \text{ \AA}$). The indexing at the bottom of the figure corresponds to the hexagonal $SrAl_2Si_2O_8$ structure (ICSD 416598, PDF 01-077-5105)

Following this thermal crystallization step, highly transparent homogeneous polycrystalline ceramic has been obtained, notably for the $x=0.2$ composition as shown in Figure 23.



Figure 23 Photograph of the $Sr_{1.1}Al_{2.2}Si_{1.8}O_8$ ($x=0.2$) transparent polycrystalline ceramic (1.5 mm thickness)

Figure 24 shows the five polycrystalline ceramics photos elaborated by full crystallization. The five polycrystalline ceramic compositions, even with very close stoichiometric compositions, exhibit an obvious evolving transparency from total opacity ($x=0$) to almost perfect transparency ($x=0.2$).

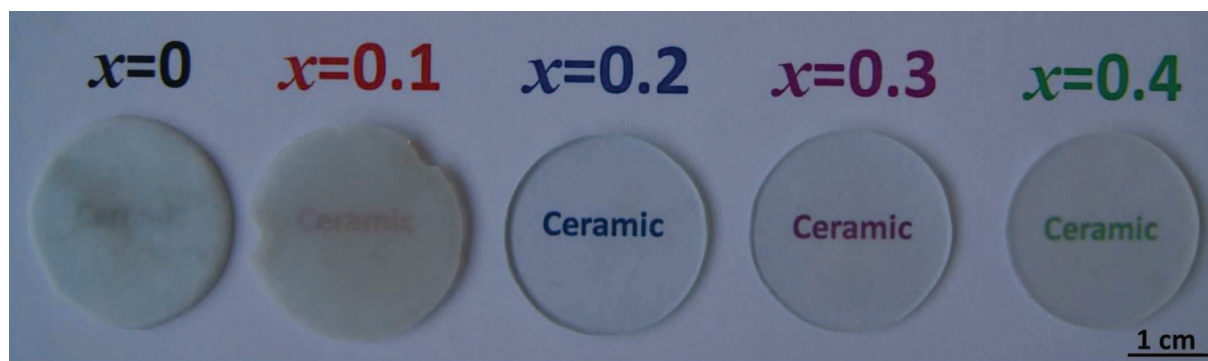


Figure 24 Photograph of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x=0, 0.1, 0.2, 0.3$ and 0.4) polycrystalline ceramics

The synchrotron powder diffraction patterns of these ceramics show a single polycrystalline phase (Figure 22) for each of the five compositions ($x=0, 0.1, 0.2, 0.3$ and 0.4). These patterns matches the hexagonal $SrAl_2Si_2O_8$ (ICSD 416598, PDF 01-077-5105)

indexation³⁸ even though $x=0.1, 0.2, 0.3$ and 0.4 have different compositions compared to $SrAl_2Si_2O_8$. A study of the structural evolution throughout these new materials has been carried out through a combination of synchrotron and neutron powder diffraction.

IV.2.1.4 Synthesis problems encountered by Pt incorporation

The optimized synthesis conditions, discussed in the previous part, have been determined after a detailed comprehension of the glass synthesis protocol. The quality of the synthesized glass had greatly affected the transparency of the obtained ceramics. A sufficient time has been essential for the oxide mixture to homogenize inside the electric furnace. Meanwhile, a slight “over-heating” of the glass compositions has resulted in a light yellowish color of the obtained glass, which has been later attributed to platinum incorporation inside the glass structure. This Pt incorporation has affected the crystallization process and hence the obtained transparency of our polycrystalline ceramics. Numerous tries have been carried out on the glass preparation step in order to optimize the synthesis conditions, for an improved quality of the obtained glass and thus that of the polycrystalline ceramic. As we can notice in Figure 25, the impact of the thermal glass preparation is very obvious on the obtained ceramics’ transparency.

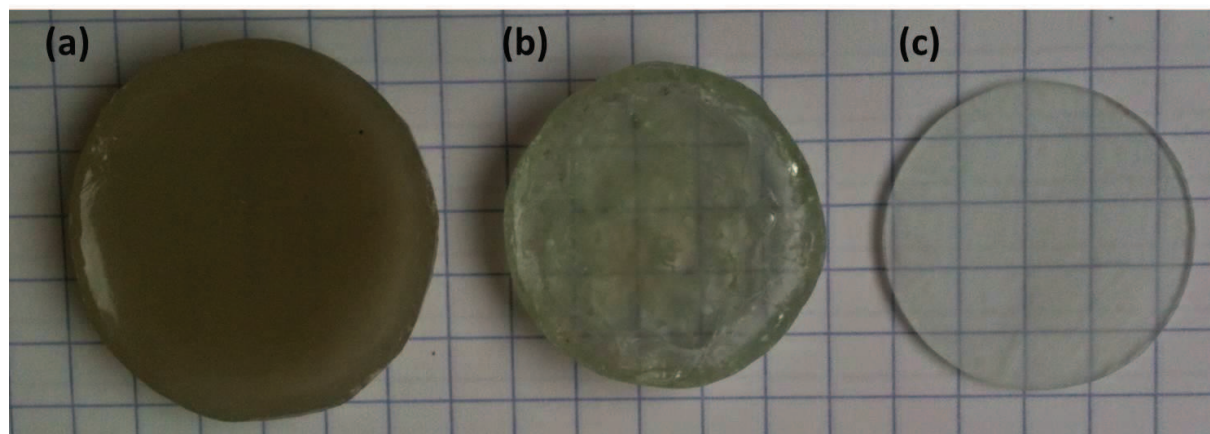


Figure 25 Photographs of $x=0.2$ polycrystalline ceramic samples elaborated similarly except for the time used for the vitrification of the glass precursor (a) long thermal preparation of glass, (b) non-sufficient thermal preparation of glass and (c) glass preparation according to the following program: $1700^{\circ}\text{C}(10\text{ min})+1750^{\circ}\text{C}(10\text{ min})+1700^{\circ}\text{C}(30\text{ min})$

Figure 25a shows the case of polycrystalline ceramic where the glass precursor has been elaborated through a very long thermal treatment. This kind of sample shows a lot of star shapes crystals, clearly observed by SEM images as shown in Figure 26 believed to be

induced by the presence of Pt. These crystals are at the origin of creation of micro cracks within the material.

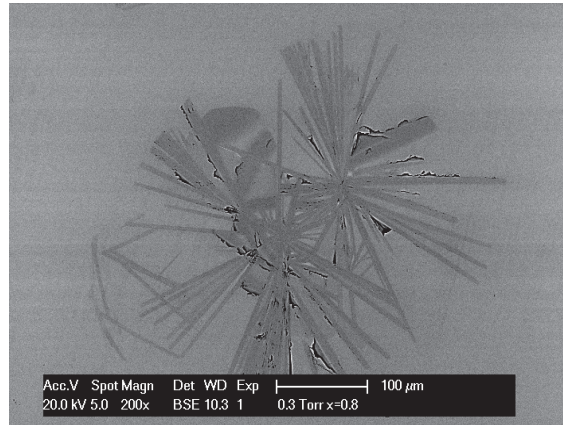


Figure 26 Micro cracks and star shape Pt-induced crystallization observed by scanning electron microscopy (SEM) in $x=0.2$ ceramic composition

Figure 25b presents the polycrystalline ceramics where the corresponding glass precursor has been prepared through a short thermal treatment program. The ceramic appears to be non-homogeneous with residual bubbles. These bubbles believed to result from the decarbonation of the strontium carbonate precursor, which have not been totally released from the glass with such a short thermal treatment program and high melt viscosity. Decarbonation step of the oxide powder mixture before the vitrification has been skipped in order to avoid sample-Pt interaction in the most possible manner. These bubbles alter the homogeneity of the obtained glass and are believed to act as nucleation sites during crystallization step³⁹, affecting the microstructure of the polycrystalline ceramics and hence their transparency.

Figure 25c presents the ceramic composition where the precursor-glass has been prepared according to an optimized thermal treatment program (1700 °C (10 min) + 1750 °C (10min) + 1700 °C (30 min)). The elaborated polycrystalline ceramic appears very homogeneous and transparent. This program has been adopted throughout all synthesis experiments presented further in this thesis for the five compositions of the solid solution ($x=0, 0.1, 0.2, 0.3$ and 0.4). This thermal program route appeared to be very reproducible for all the realized syntheses.

The Pt incorporation inside the structure has been confirmed with high resolution STEM-HAADF and energy dispersive X-rays spectroscopy (EDS). Figure 27a shows three zones where platinum identified by EDS analysis has been spotted lying on the grain

boundary between two crystals. Figure 27b shows a high resolution image of one of these zones. Pt appears to be crystallized. This platinum incorporation in the glass structures may have resulted from the corrosion of the Pt-crucibles during glass preparation inside the electric furnace. The Pt solubility in glass-melts has been the subject of different studies including silicate glasses⁴⁰⁻⁴³ which correlate well with our results.

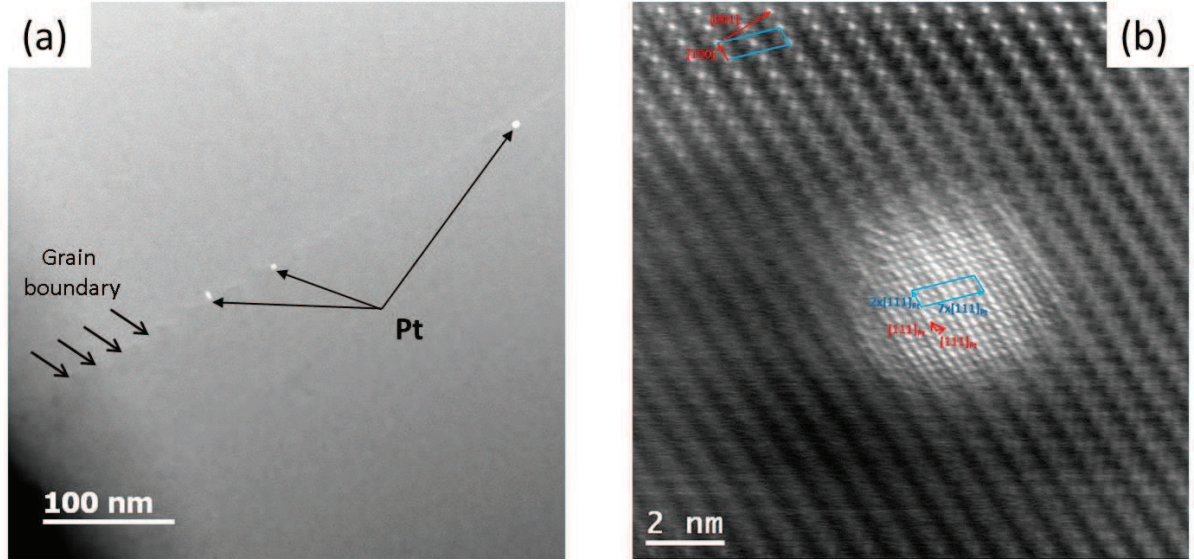


Figure 27(a) and (b) High resolution STEM-HAADF images on the $x=0.2$ polycrystalline ceramic composition

Moreover, careful analysis of Figure 27b evidences the correlation between the hexagonal crystallized phase ($a \approx 5.2 \text{ \AA}$, $b \approx 15.2 \text{ \AA}$) crystallized lattice presented in blue and the cubic structure of Pt ($a \approx 3.9 \text{ \AA}$) presented in red. The $[011]$ direction of the platinum grain is aligned with the $[100]$ direction of the $Sr_{1.1}Al_{2.2}Si_{1.8}O_8$ crystal, with a very slight distortion between them which satisfy the following two relations:

$$d_{100_{SrAl_2Si_2O_8}} = 2d_{111_{Pt}}$$

$$\|\vec{a} + \vec{c}\|_{SrAl_2Si_2O_8} = 7d_{111_{Pt}}$$

IV.2.2 Outstanding transparency in the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 < x \leq 0.4$) polycrystalline ceramics

In order to quantify the observed remarkable transparency, transmittance measurements were realized. The optical transmittance value measured for the $x=0.2$

composition (1.5 mm thickness) was found to be close to 90% all along the visible and near infra-red ranges (Figure 28). This outstanding result almost matches the maximum theoretical transmittance of 90.1% calculated from the measured refractive index of $n=1.59$ (Equation 1), indicating that almost no scattering centers exist within the polycrystalline ceramic.

$$T_{th} = \frac{2n}{n^2+1} \quad (1)$$

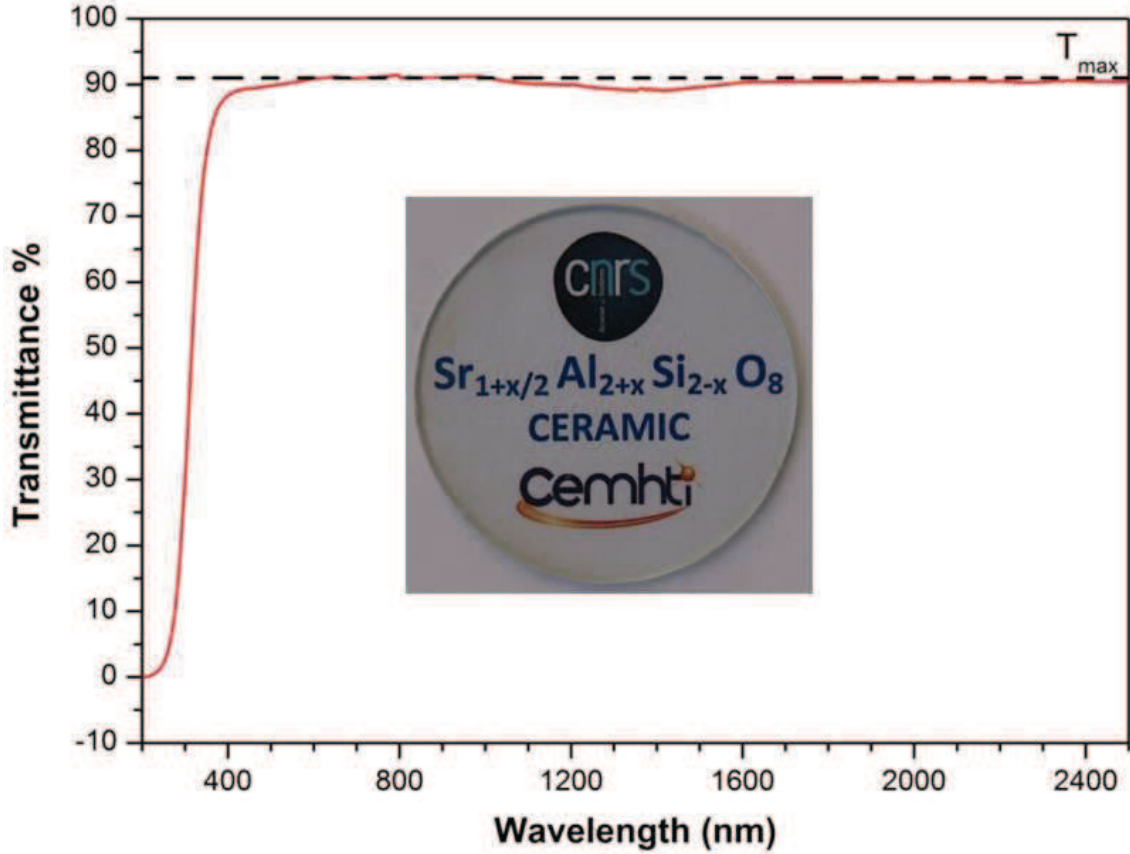


Figure 28 Transmission spectrum measured on a $Sr_{1.1}Al_{2.2}Si_{1.8}O_8$ ($x = 0.2$) transparent polycrystalline ceramic sample (1.5 mm thickness). Inset: photograph of the corresponding polycrystalline ceramic ($x=0.2$)

The transmittance reaches its theoretical limit of 90 % within the visible and near infrared ranges, which represents the highest reported value for polycrystalline oxide ceramics as shown in Table 10.

Table 10 Refractive index (n_∞) and maximum theoretical transmission values of transparent oxide polycrystalline ceramics reported in the literature

Composition	Refractive index (n_∞)	Maximum theoretical transmission (%)
$\text{Sr}_{1.1}\text{Al}_{2.2}\text{Si}_{1.8}\text{O}_8$	1.59	90.1
MgAl_2O_4 ⁴⁴	1.701	87.4
Al_2O_3 ⁴⁴	1.755	86.0
$\text{Y}_3\text{Al}_5\text{O}_{12}$ ⁴⁴	1.812	84.6
Y_2O_3 ⁴⁴	1.892	82.6
Lu_2O_3 ⁴⁵	1.900	82.4
Sc_2O_3 ⁴⁵	1.954	81.1
$\text{LaGdZr}_2\text{O}_7$ ⁴⁶	2.08	78.1
ZrO_2 ⁴⁴	2.113	77.3

IV.2.3 Structural study of the transparent polycrystalline ceramics

IV.2.3.1 Structural determination

The structure elucidation of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 < x \leq 0.4$) solid solution has been performed using a combination of transmission electron microscopy (electron diffraction mode) and powder diffraction data from high resolution synchrotron and neutron instruments.

Both electron diffraction (Figure 29) and powder indexing agree with a hexagonal unit cell ($\text{P6}_3/\text{mcm}$ space group, $a \approx 5.2 \text{ \AA}$ and $c \approx 15.2 \text{ \AA}$) matching the $\text{SrAl}_2\text{Si}_2\text{O}_8$ structure indexation.

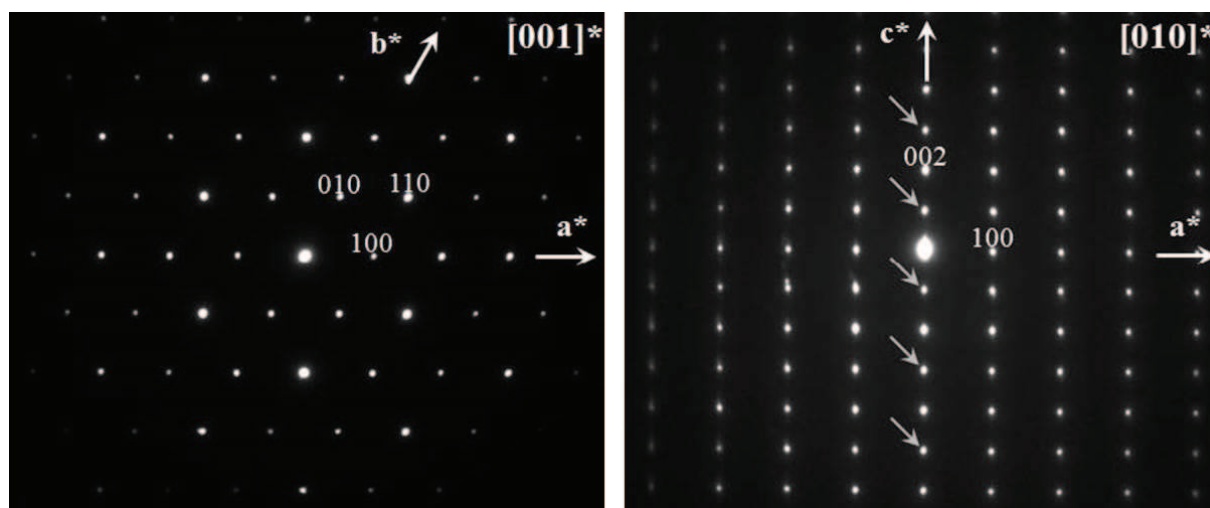


Figure 29 Experimental $[001]^*$ and $[010]^*$ electron diffraction patterns characteristic of the new $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 < x \leq 0.4$) solid solution

Figure 29 shows the experimental $[001]^*$ and $[010]^*$ electron diffraction patterns characteristic of the new $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 < x \leq 0.4$) solid solution. The reconstruction of the reciprocal lattice has led to the identification of $P6_3/mcm$ hexagonal unit cell with the following cell parameters $a \approx 5.2$ Å and $c \approx 15.2$ Å. Small grey arrows point to double diffraction reflections. No extra reflections or streaks have been observed during the electron diffraction study indicating no secondary crystallized phases.

The Le Bail method has been first used to refine the cell parameters (a , b and c), all the instrument parameters and those related to the profile (U , V , W , Z , X and Y) against synchrotron powder diffraction data.

The Le Bail refinements have revealed a linear evolution of the cell parameters (a and c) from $x=0$ and throughout the solid solution Figure 30.

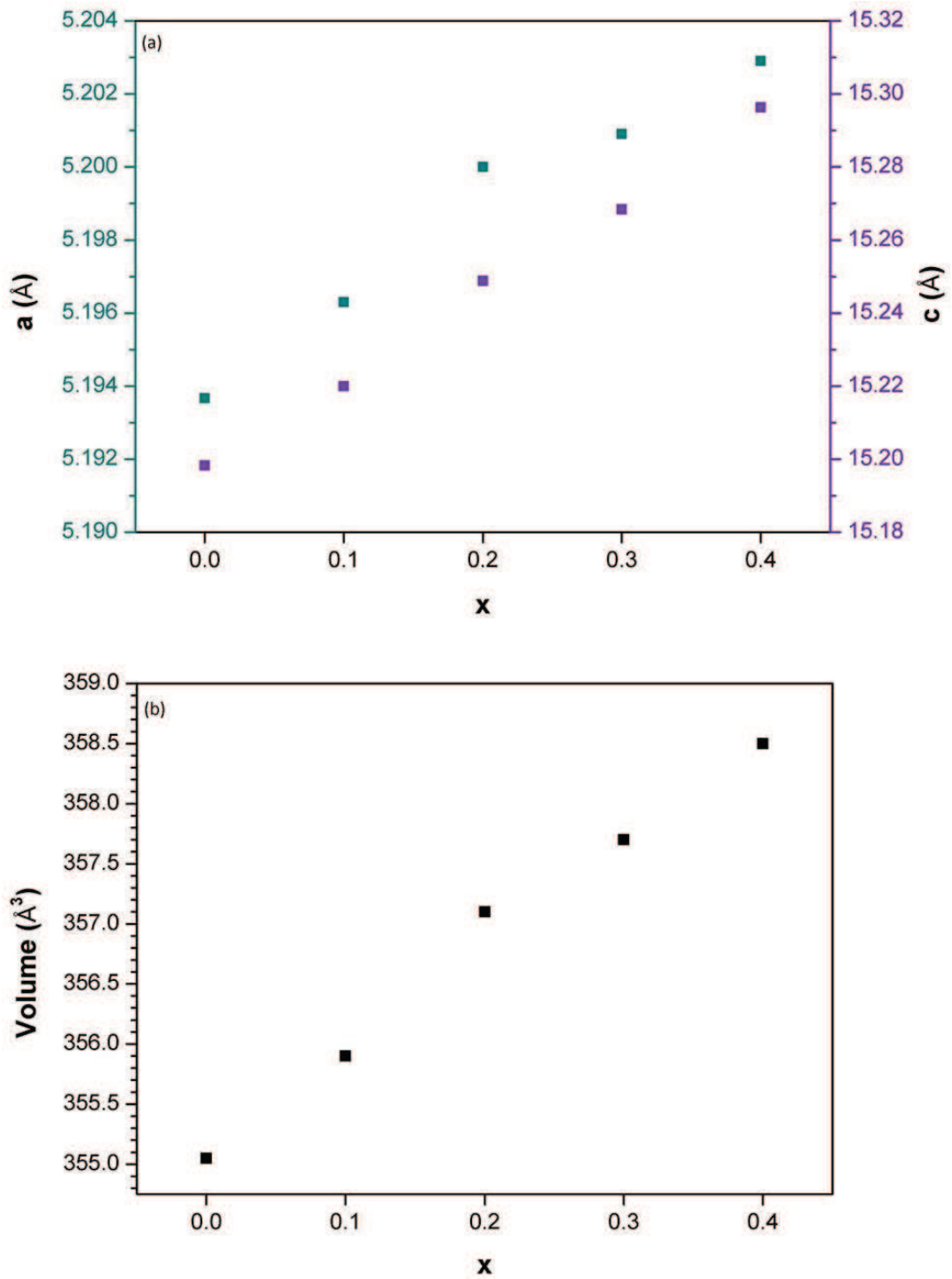


Figure 30 Variation of the unit cell (a) parameters and (b) volume of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ solid solution ($x = 0, 0.1, 0.2, 0.3$ and 0.4)

The cell parameters augmentation should be associated with a kind of atomic distribution. Such a change induces structural modification in order to accommodate this new distribution and thus cause this evolution in cell parameters and therefore the unit cell volume.

Rietveld refinements of synchrotron diffraction powder data were then performed for the atomic positions, their occupancy and the isotropic thermal agitation factors using the $P6_3/mcm$ $SrAl_2Si_2O_8$ average structure as a starting model (one Sr site, one mixed Al/Si site and two O sites all fully occupied) using a statistical Al/Si occupation of the tetrahedral sites and the cell parameters previously determined. A reasonable fit could then be obtained. However a deficiency of the average $SrAl_2Si_2O_8$ model appeared to exist with respect to the refinements of the diffraction patterns ($x=0.1, 0.2, 0.3$ and 0.4). The inspection of Fourier maps revealed an increasing scattering density on a new 2a $(0, 0, \frac{1}{4})$ crystallographic site. This scattering density has been assigned to an extra strontium site Sr2 (Figure 31c). This scattering density increased with increasing x value ($x=0 \rightarrow x=0.4$).

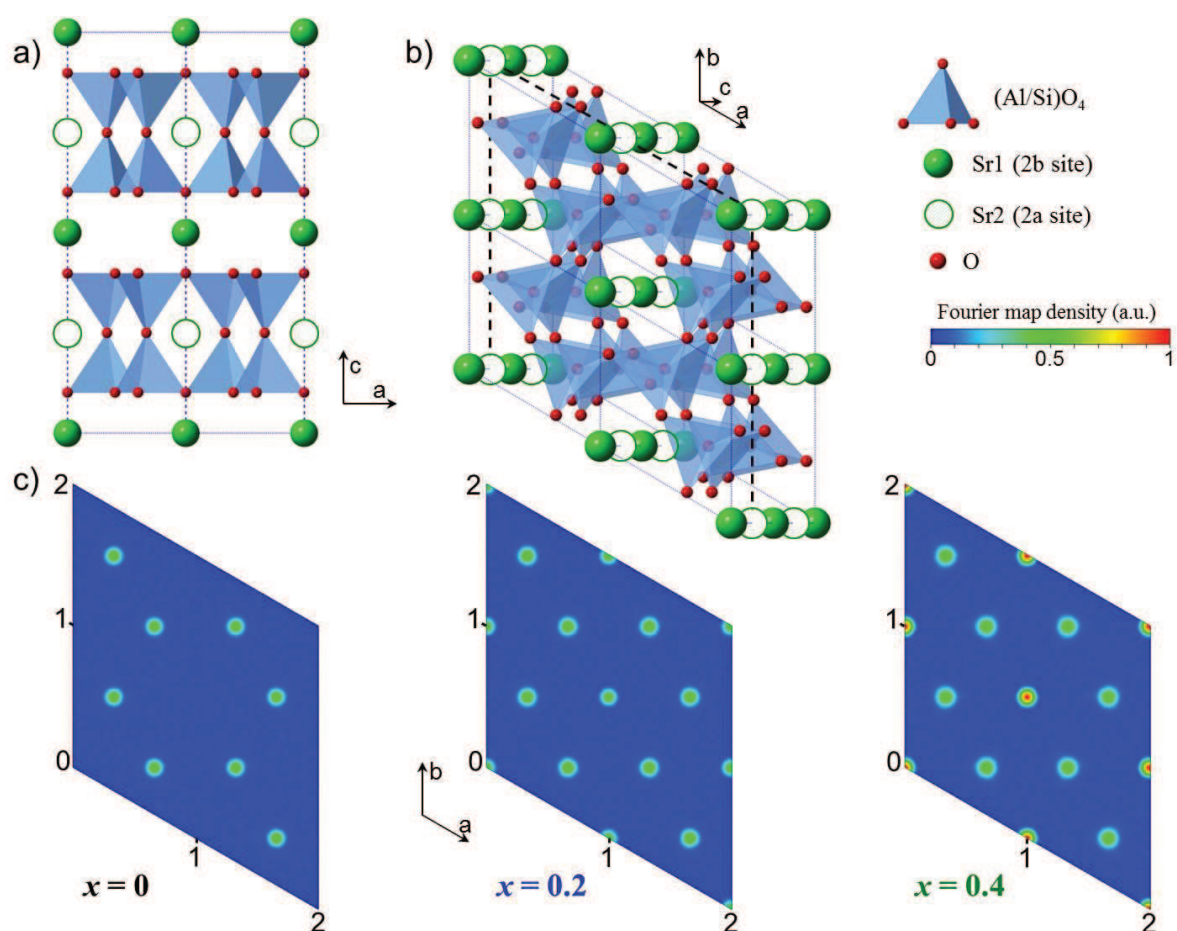


Figure 31 (a) $[010]$ view of the crystal structure of $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ $x = 0.1, 0.2, 0.3$ and 0.4 , (b) $[001]$ perspective view and (c) corresponding observed Fourier maps of the $x = 0, 0.2$ and 0.4 ceramic compositions (section at $z=0.25$)

The occupancy of this additional Sr2 site was then refined and a continuous increase of its content was observed along the substitution process (Figure 32). Theoretically, 5% Sr

are added successively with each single increase of x by 0.1. This corresponds to 0, 5, 10, 15 and 20% additional Sr for $x=0, 0.1, 0.2, 0.3$, and 0.4 compositions respectively, which matches the refined additional Sr2 occupancy data. Consequently, this linear increase of Sr2 site occupancy correlates in a logic manner with the substitution process and approves further that the increasing scattering density revealed by Fourier maps correspond to an additional strontium site in the structure.

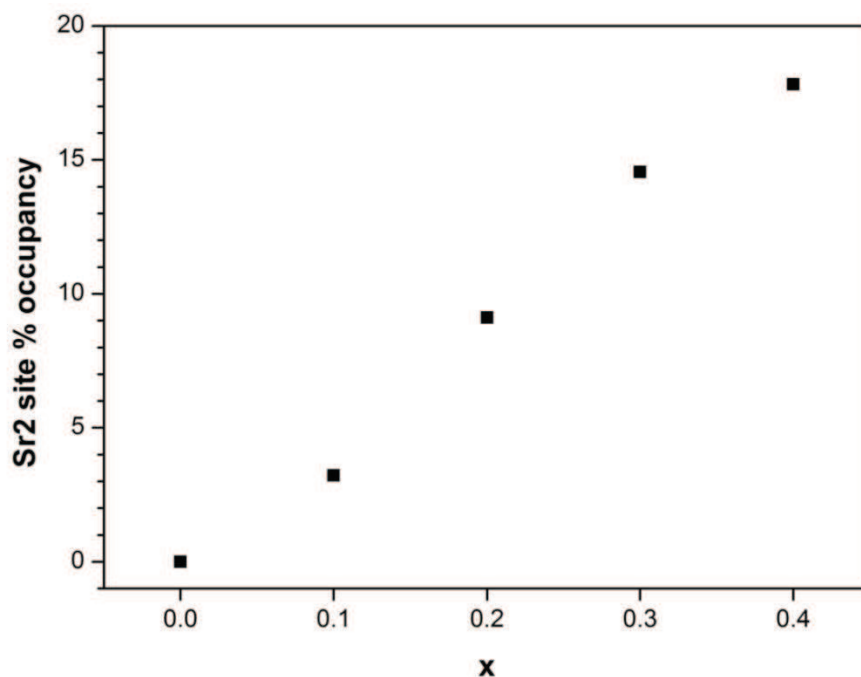


Figure 32 Refined occupancy of the Sr2 crystallographic site as a function of x along the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x=0, 0.1, 0.2, 0.3$ and 0.4) solid solution

Using the new structural model with this additional strontium site, Rietveld refinement has been performed. The Rietveld refinement of the synchrotron data for the five compositions converged very well with the experimental data giving relatively low value of Rwp for each composition, which signifies a good agreement between the calculated diffraction pattern and the experimental one.

Figure 33 shows the Rietveld refinement of the end member $x=0.4$ composition synchrotron powder diffraction data with the highest Sr2 site % occupancy. The refinement of the experimental red pattern leads to the calculated black pattern with the difference between the two presented in blue (Rwp = 8.06%, Rp = 6.33%, and G.O.F = 1.67). The set of green vertical lines corresponds to the reflection positions.

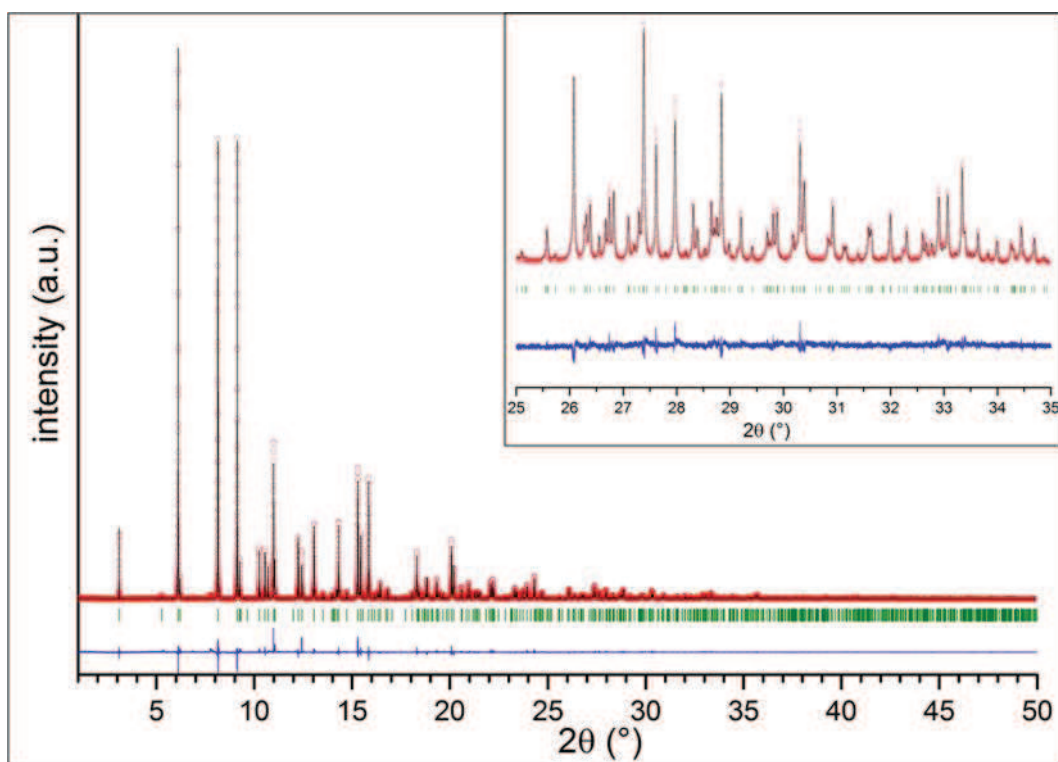


Figure 33 Rietveld refinement of the $Sr_{1.2}Al_{2.4}Si_{1.6}O_8$ ($x=0.4$) synchrotron powder diffraction data collected at room temperature (R_{wp} 8.06%, R_p = 6.33%, and $G.O.F$ = 1.67). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines corresponds to the reflection positions. Enlargement of the 25 - 35° angular range (2θ) is embedded.

The structural parameters including atomic positions, isotropic thermal agitation factors, site occupancy and selected inter-atomic distances of $Sr_{1.2}Al_{2.4}Si_{1.6}O_8$ ($x = 0.4$) are presented in Table 11, obtained from room temperature Rietveld refinement of synchrotron powder diffraction data. The Rietveld refinements of the other four compositions ($x=0$, 0.1, 0.2 and 0.3) are presented in Supplementary information (Figures S3-S6 and Tables S3-S6).

Table 11 Atomic positions and selected inter-atomic distances of $Sr_{1.2}Al_{2.4}Si_{1.6}O_8$ ($x = 0.4$) obtained from Rietveld refinement of synchrotron powder diffraction data

Atom	Site	x	y	z	Uiso	Occ.
Sr1	2b	0	0	0	0.01278(6)	1
Sr2	2a	0	0	0.25	0.0135(8)	0.174(1)
Al1	8h	0.33333	0.66667	0.1416(1)	0.00662(12)	0.587(1)*
Si1	8h	0.33333	0.66667	0.1416(1)	0.00662(12)	0.413(1)*
O1	4c	0.33333	0.66667	0.25	0.0213(4)	1
O2	12k	0.3973(1)	0	0.1022(1)	0.0135(3)	1

*: the Al/Si ratio was constrained using: (i) $occ(Al)=0.5+occ(Sr2)/2$ for compensating the positive charge induced by Sr2 and (ii) $occ(Al) + occ(Si) = 1$ (full site occupancy)

	Sr1-O (Å)		Sr2-O (Å)		Al/Si-O (Å)	
Sr1-O2 (x6)	3.4730(8)	Sr2-O1 (x6)	3.0022	Al/Si-O1	1.6517(4)	
Sr1-O2 (x6)	2.6000(8)	Sr2-O2 (x6)	3.0827(8)	Al/Si-O2 (x3)	1.7001(4)	

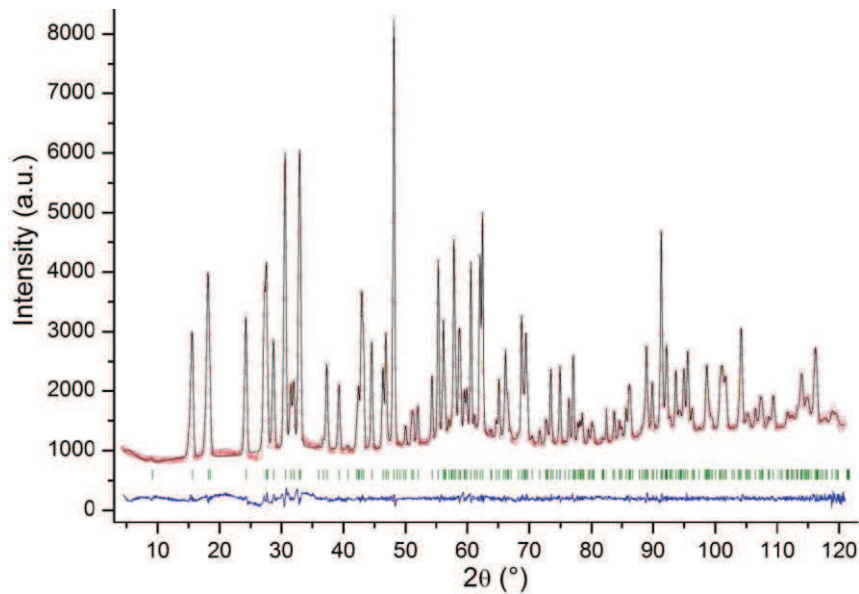
For a further confirmation of the proposed model specially the anionic network, neutron diffraction refinements have been performed. The choice of this technique is based on the limitation of the synchrotron X-ray diffraction, where the incident rays interacting with the electronic cloud of a nucleus, are highly affected by the atomic diffusion factor. This factor is dependent on the atomic number Z of the nucleus i.e. atoms with higher atomic number are better observed with X-ray diffraction. Si^{4+} and Al^{3+} possess nearly the same pattern of variation of this diffusion factor with θ thus complicating the distinguish process between them. However in neutron diffraction with the nucleus being the target, it is the coherent scattering length parameter which plays the major role in defining the sensitivity of the technique towards a specific nucleus.

Table 12 Coherent scattering length and absorption cross section of the atoms strontium, aluminum, silicon and oxygen

Atom	Coherent scattering length ($10^{-15} m$)	Absorption cross section
Sr	7.02	1.26
Al	3.45	0.23
Si	4.15	0.17
O	5.8	0.00019

As shown in Table 12 there exists a considerable difference between the coherent scattering length between Al and Si, thus permitting the easier distinguishing between these two atoms using neutron diffraction. In addition, the oxygen atom with its relatively large coherent scattering factor will permit much more precise determination of its structural parameters than that obtained by X-ray diffraction.

Figure 34 shows the Rietveld refinement of the proposed model with the additional Sr2 site against neutron powder diffraction data for the $x=0.4$ ceramic composition. The calculated diffraction pattern fits almost perfectly with the experimental neutron diffraction data (Rwp = 2.40 %, Rp = 1.65 %, and G.O.F = 2.00).

**Figure 34** Rietveld refinement of the $Sr_{1.2}Al_{2.4}Si_{1.6}O_8$ ($x = 0.4$) neutron powder diffraction data collected at room temperature (Rwp = 2.40 %, Rp = 1.65 %, and G.O.F = 2.00).

Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines corresponds to the reflection positions

Neutron powder diffraction refinements did not show any extra oxygen position related to Sr2, confirming that the extra positive charge imported by the extra strontium was compensated by a consequent Al/Si ratio.

Rietveld refinement have been also performed using a fully ordered P-3c1 model with one Al and one Si distinct crystallographic sites which can also be considered for $SrAl_2Si_2O_8$ (ICSD 416597). However, our synchrotron and neutron powder diffraction refinements using this model did not show any improvement or any Al/Si differentiation that would have implied this structural description. This reinforces the idea of existence of Al/Si disorder which needs to be confirmed by another technique.

IV.2.3.2 Unique glass crystallization synthetic access to the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 < x \leq 0.4$) system

The aim of this part has been to test the synthesis of the hexagonal $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 < x \leq 0.4$) phases through solid-state reaction. For this purpose several powder oxide ($SrCO_3$, SiO_2 , Al_2O_3) mixtures of the $x=0.4$ composition have been heat treated at different temperatures ranging from 800 °C to 1600 °C with 100 °C step size. The powder mixture has been run on X-ray diffraction after each heat treatment in order to check the existence of the hexagonal crystallized phase/s (Figure 35).

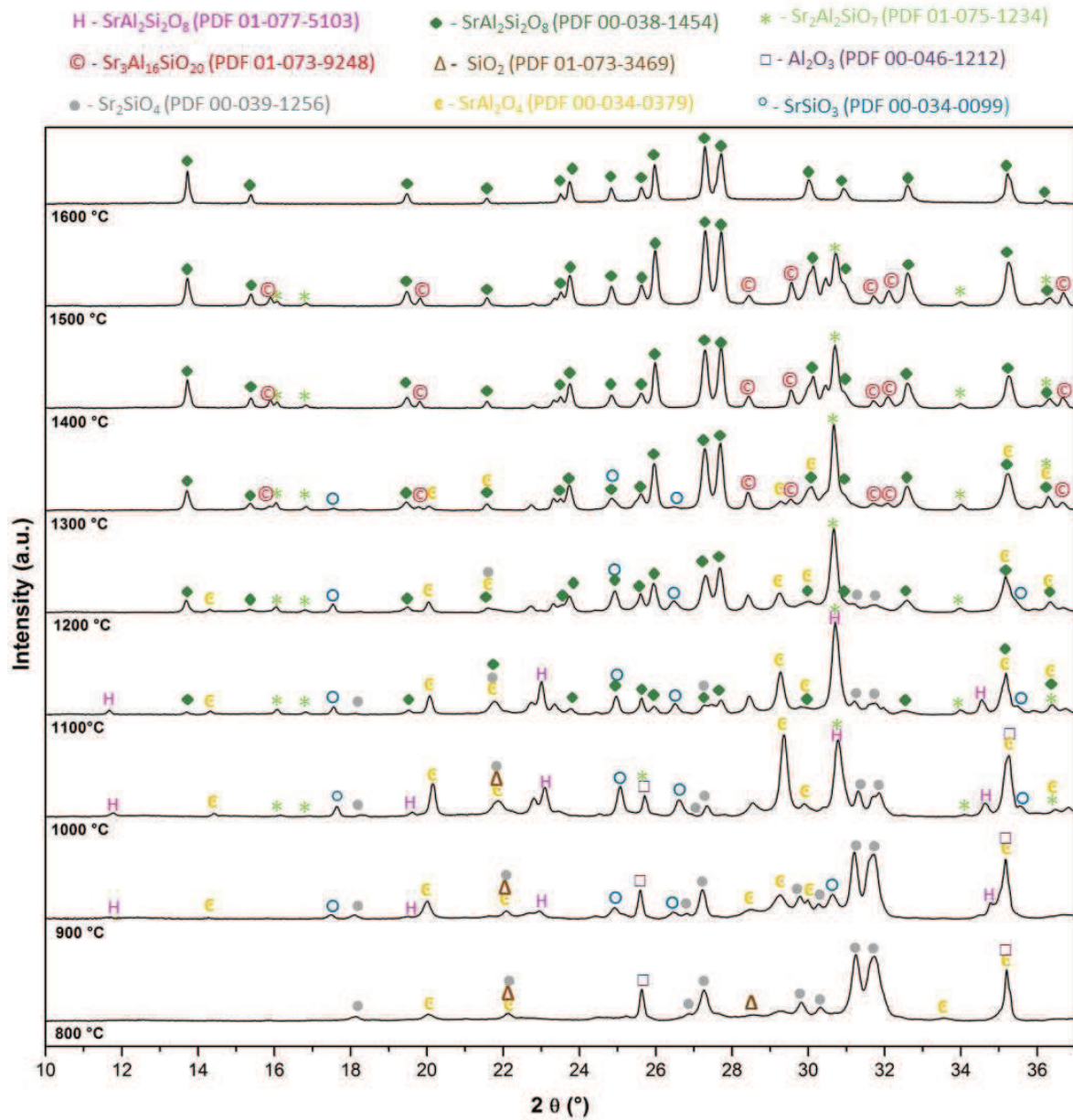


Figure 35 X-ray diffraction patterns of unsuccessful solid state synthesis attempts to elaborate the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x = 0.4$) solid solution

As we can observe in (Figure 35) no hexagonal $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x \neq 0$) phase could be detected at any of the temperatures between 800°C and 1600°C. The hexagonal $SrAl_2Si_2O_8$ ($x=0$) phase was found to co-exist with other phases only for samples treated at 900, 1000 and 1100°C. Above 1100°C the main phase appeared to be the monoclinic $SrAl_2Si_2O_8$ ($x = 0$) polymorph. These results showed that the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 < x \leq 0.4$) solid solution could not be synthesized by classic solid state reaction, contrary to the $Sr_{1-y/2}Al_{2-y}Si_{2+y}O_8$ ($0 < y \leq 0.3$)³⁸ solid solution which could be synthesized by the solid state reaction method.

Crystallization from glass for the date of this study affords unique synthetic access to the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 < x \leq 0.4$) system.

IV.2.4 Local structure study using NMR

After synchrotron and neutron diffraction refinements, no Al/Si differentiation was observed (one mixed Al/Si site); this necessitates the use of nuclear resonance spectroscopy (NMR) for a detailed study of this Al/Si local distribution. Thus ^{29}Si and ^{27}Al MAS and MQ MAS NMR experiments were registered.

In this part we study ^{29}Si and ^{27}Al NMR. We use the Q_m^n and q_m^n notations which correspond respectively to Si and Al tetrahedral with n bridging oxygens and m bonded AlO_4 units ($0 \leq m \leq n \leq 4$).

IV.2.4.1 ^{29}Si environment determination by solid state NMR

As described previously in Chapter II, the addition of aluminum to the second coordination sphere of silicon leads to change in the chemical shifts of the Q^4 units. This shift is dependent on the number of Al attached, so there exist four species $Q^4(1Al)$, $Q^4(2Al)$, $Q^4(3Al)$ and $Q^4(4Al)$ for aluminosilicates represented by Q_1^4 , Q_2^4 , Q_3^4 and Q_4^4 .

The NMR experiments have been carried out on 3 representing compositions of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ solid solution ($x=0$, 0.2 and 0.4).

Figure 36 shows the ^{29}Si MAS NMR spectra of the three compositions, $x=0$, $x=0.2$ and $x=0.4$, with their dmfit representing the individual contribution of each Q_m^4 Si unit.

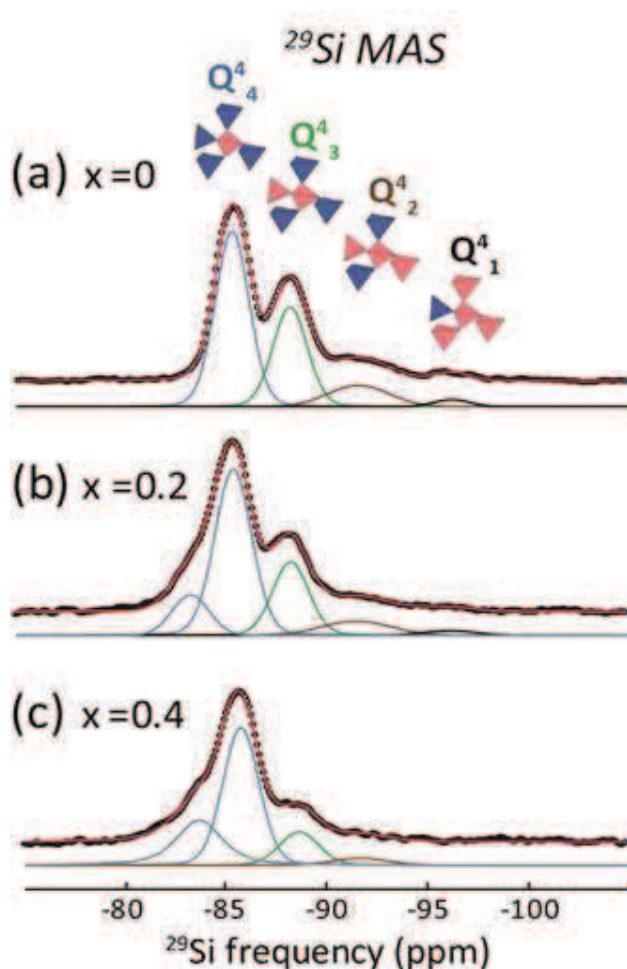


Figure 36 Experimental ^{29}Si quantitative MAS NMR spectra (black circles) of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ samples and their dmfit (red lines) (a) $x=0$, (b) $x=0.2$ and (c) $x=0.4$ ceramic compositions. The individual contributions (with Gaussian line shape) corresponding to the distinct Q_m^4 Si units are shown below the experimental spectra

For $x=0$, the four Q_m^4 units (Q_1^4 , Q_2^4 , Q_3^4 and Q_4^4) are present with their specific characteristics presented in Table 13.

For $x=0.2$, the ^{29}Si spectra shows a small shoulder appearing on the left side of the NMR spectrum (Figure 36), which corresponds to an additional contribution associated to a distinct type of Q_4^4 units. This could be associated to Q_4^4 units located in the vicinity of the extra strontium site. In comparison with the $x=0$ composition, a considerable increase is observed in the relative intensity of Q_4^4 species (54% for $x=0$ to 67% for $x=0.2$), whereas we observe a slight decrease in the intensities of the Q_3^4 , Q_2^4 and Q_1^4 species which is normally expected due to the decrease of Si content as x increases (Table 13).

For $x=0.4$, the shoulder appearing on the left side of the NMR spectrum (Figure 36) appears to be bigger than that observed in $x=0.2$ composition, and thus the percentage of the Q^4_4 units located in the vicinity of the extra strontium atoms has increased, which is logically expected due to the augmentation of the additional strontium site (Sr2) occupancy when increasing x . Furthermore, the relative intensity of the Q^4_4 units appears to be the biggest for the $x=0.4$ composition, in addition to the considerable decrease in the relative intensities of the Q^4_3 , Q^4_2 and even a null relative intensity for the Q^4_1 species (Table 13), due to the reduced amount of silicon in the $x=0.4$ composition.

Table 13 Isotropic chemical shifts δ_{ISO} (± 0.2), full width at half maximum Fwhm (± 0.2) and relative intensity I (± 2) of the ^{29}Si resonances corresponding to the different Si local environments in the structure of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ compounds determined from the fits of the ^{29}Si quantitative MAS spectra. ^{29}Si chemical shift were referenced relative to neat TMS ($Si(CH_3)_4$)

Sample	Unit	Label	δ_{ISO} (ppm)	Fwhm (ppm)	I (%)
x = 0	$Si(OAl)_4$	Q^4_4	-85.6	2.0	54
	$Si(OAl)_3(OSi)$	Q^4_3	-88.4	2.0	31
	$Si(OAl)_2(OSi)_2$	Q^4_2	-91.7	3.5	12
	$Si(OAl)(OSi)_3$	Q^4_1	-96.3	2.1	3
x = 0.2	$Si(OAl)_4$	Q^4_4	-83.5/-85.6	2.1/2.1	67
	$Si(OAl)_3(OSi)$	Q^4_3	-88.4	2.1	23
	$Si(OAl)_2(OSi)_2$	Q^4_2	-91.6	4.0	8
	$Si(OAl)(OSi)_3$	Q^4_1	-96.2	3.0	2
x = 0.4	$Si(OAl)_4$	Q^4_4	-83.6/-85.7	2.7/2.1	82
	$Si(OAl)_3(OSi)$	Q^4_3	-88.3	2.3	14
	$Si(OAl)_2(OSi)_2$	Q^4_2	-91.6	3.2	4
	$Si(OAl)(OSi)_3$	Q^4_1	-	-	0

IV.2.4.2 ^{27}Al environment determination by solid state NMR

The ^{27}Al MAS NMR spectra have been recorded on the three samples of the solid solution ($x=0$, $x=0.2$ and $x=0.4$). ^{27}Al being a quadrupolar nucleus, the spectra appeared very broad and thus it was difficult to assign each specie to its corresponding peak in order to extract the information concerning Al environment.

^{27}Al 2D MQ-MAS NMR spectra were then acquired (Figure 37) using the three pulse Z-filter sequence⁴⁷ in order to extract the NMR parameters, which will be later used to simulate the ^{27}Al MAS spectra in order to determine the percentages of the different Al species.

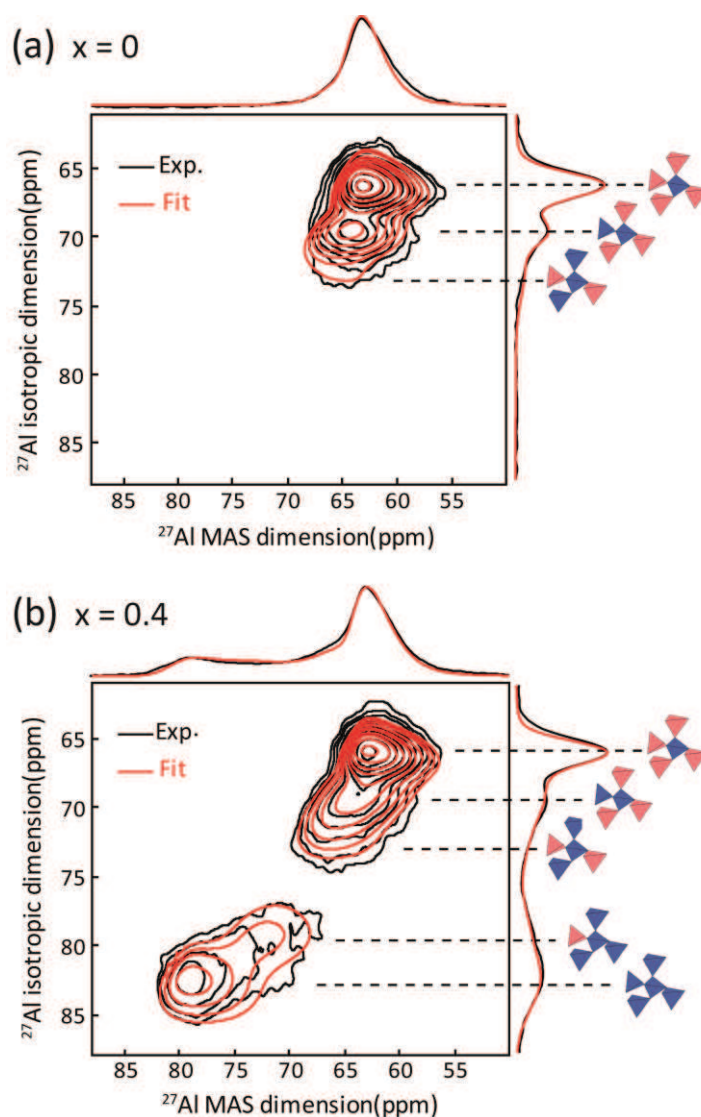


Figure 37 ^{27}Al experimental 2D MQMAS NMR (black lines) of (a) $SrAl_2Si_2O_8$ ($x = 0$) and (b) $Sr_{1.2}Al_{2.4}Si_{1.6}O_8$ ($x = 0.4$) ceramics with their best fits (red lines)

Figure 37 shows the experimental ^{27}Al 2D MQ-MAS NMR spectra (black lines) of the two solid solution ceramic compositions $\text{SrAl}_2\text{Si}_2\text{O}_8$ ($x=0$) and $\text{Sr}_{1.2}\text{Al}_{2.4}\text{Si}_{1.6}\text{O}_8$ ($x=0.4$) registered at 17.6 T with their best fit using DMFit software⁴⁸ represented by the red line. The projection along the MAS dimension is shown on top of the 2D spectra. The projection along the isotropic dimension is shown on the right side of the 2D spectra. The q_m^4 units can then be associated to the distinct ^{27}Al isotropic resonances (blue and red tetrahedra correspond to AlO_4 and SiO_4 units, respectively).

For the $x=0$ composition, three q_m^4 species are detected (q_0^4 , q_1^4 and q_2^4), which correspond respectively to Al atoms linked respectively to 0, 1 and 2 AlO_4 tetrahedra.

For $x=0.4$, two other q_m^4 species are observed in addition to those obtained for $x=0$ composition, these are the q_3^4 and q_4^4 units which correspond respectively to Al atoms linked to three and four AlO_4 tetrahedra respectively. This reflects the deviation from Lowenstein⁴⁹ rule which states that linkages between AlO_4 units are energetically unfavorable in aluminosilicate materials.

The quadrupolar and chemical shift parameters (isotropic chemical shift (δ_{ISO}), average quadrupolar constant ($\overline{C_Q}$), full width at half maximum of the Gaussian distribution of the quadrupolar constant (FWHM (C_Q)) and the asymmetry parameter of the quadrupolar tensor (η_Q) were determined from the fits of both 2D MQMAS and 1D MAS spectra (Figure 38).

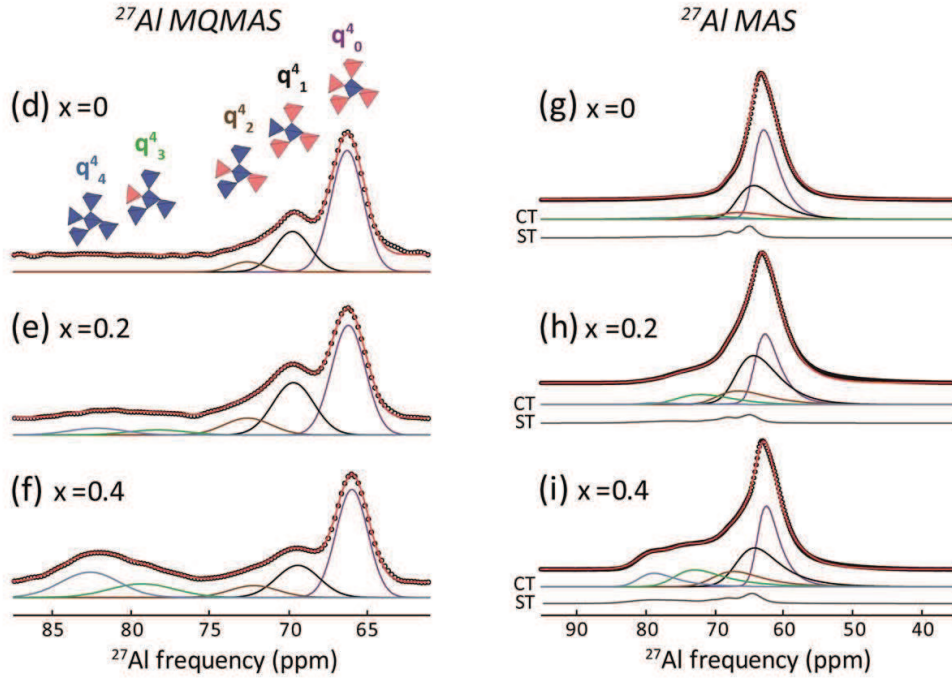


Figure 38 (d- f) ^{27}Al isotropic MQMAS spectra (black circles) and their best fit (red lines). (g- i) Experimental ^{27}Al quantitative MAS NMR spectra (black circles) of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ samples and their fit (red lines) (d, g) $x=0$, (e, h) $x=0.2$ and (f, i) $x=0.4$ ceramic compositions

In Figure 38, we observe the ^{27}Al MQ-MAS and ^{27}Al MAS spectra with their corresponding fit and the distribution of q^4_m species.

For $x=0$, four q^4_m units were detected (q^4_0 , q^4_1 , q^4_2 and q^4_3), with a very low intensity percentage for the q^4_3 unit (Table 14).

For $x=0.2$, the Al environment distribution becomes broader to include q^4_4 unit and the proportions of q^4_2 , q^4_3 and q^4_4 units increase with respect to those of $x=0$ ($33 \rightarrow 40$, $9 \rightarrow 14$, $3 \rightarrow 11$ % respectively) reflecting the formation of additional Al-O-Al linkages when x increase, providing local charge compensation of the extra strontium site in the structure, as no additional oxygen sites was proved to be formed based on neutron diffraction data in order to compensate for this additional positive charge imported by the additional strontium site.

For $x=0.4$, the Al environment distribution appears even to be broader than that observed for the $x=0.2$ composition, and with an increase in the relative intensity of the q^4_4 , q^4_3 and q^4_2 units ($1 \rightarrow 9$, $11 \rightarrow 18$, $14 \rightarrow 19$ %). This increase in the Al-O-Al linkages for the $x=0.4$ composition is directly related with the increased Sr2 site occupancy as we go throughout the solid solution toward higher x values, where more Al-O-Al bonds are formed.

Table 14 Isotropic chemical shifts ($\delta_{ISO} \pm 0.2$), average quadrupolar coupling constant ($\bar{C}_Q \pm 0.10$), full width at half maximum of the Gaussian distribution of the quadrupolar coupling constant ($Fwhm(C_Q) \pm 0.20$), asymmetry parameter of the quadrupolar tensor ($\eta_Q \pm 0.1$) and relative intensity ($I \pm 5$) of the ^{27}Al resonances corresponding to the different Al local environments in the structure of the $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ compounds ($x=0, 0.2$ and 0.4). The NMR parameters (δ_{ISO} , $\bar{C}$, $Fwhm(C_Q)$ and η_Q) were determined from the fits of both 2D MQMAS and 1D MAS spectra. ^{27}Al chemical shift were referenced relative to 1.0 M $Al(NO_3)_3$ aqueous solution.

Sample	Unit	Label	δ_{ISO} (ppm)	$\bar{C}_Q$ (MHz)	$Fwhm(C_Q)$ (MHz)*	η_Q	I (%)
x = 0	$Al(OSi)_4$	q^4_0	64.2	3.60	2.60	0.5	55
	$Al(OSi)_3(OAl)$	q^4_1	67.2	4.77	2.47	0.6	33
	$Al(OSi)_2(OAl)_2$	q^4_2	70.3	5.60	2.67	0.6	9
	$Al(OSi)(OAl)_3$	q^4_3	75.9	5.87	2.33	0.3	3
	$Al(OAl)_4$	q^4_4	-	-	-		0
x = 0.2	$Al(OSi)_4$	q^4_0	64.0	3.58	2.60	0.5	34
	$Al(OSi)_3(OAl)$	q^4_1	67.2	4.91	2.67	0.6	40
	$Al(OSi)_2(OAl)_2$	q^4_2	70.3	5.60	2.67	0.6	14
	$Al(OSi)(OAl)_3$	q^4_3	76.0	5.87	2.33	0.3	11
	$Al(OAl)_4$	q^4_4	80.5	4.60	3.33	0.6	1
x = 0.4	$Al(OSi)_4$	q^4_0	64.0	3.58	2.47	0.5	32
	$Al(OSi)_3(OAl)$	q^4_1	67.1	4.97	2.67	0.6	22
	$Al(OSi)_2(OAl)_2$	q^4_2	69.8	5.60	2.67	0.6	19
	$Al(OSi)(OAl)_3$	q^4_3	76.3	5.87	2.33	0.3	18
	$Al(OAl)_4$	q^4_4	81.0	4.60	3.33	0.6	9

IV.2.4.3 Confirmed Al/Si disorder by NMR

The presence of Al/Si chemical disorder in the structures of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0.4$) compounds was clearly confirmed by ^{29}Si and ^{27}Al MAS and MQ-MAS NMR experiments as just discussed. These allow a range of Si and Al tetrahedral chemical environments to be evidenced. They can be described using Q_m^n and q_m^n notations. For $\text{SrAl}_2\text{Si}_2\text{O}_8$, the distribution of Si and Al atoms in the tetrahedral sites results in four types of both Si (Q_m^4 , $m=4, 3, 2, 1$) and Al (q_m^4 , $m=3, 2, 1, 0$) environments which cannot be disentangled in the average long-range structure. The proportion of these various Si or Al environments directly reflects the deviation from the Loewenstein⁴⁹ rule stating that linkages between AlO_4 units are energetically unfavorable in aluminosilicate materials. When increasing x , the Al environment distribution becomes broader to include q_4^4 unit and the proportions of q_2^4 , q_3^4 and q_4^4 units increase reflecting the formation of additional Al-O-Al linkages required by the local charge compensation of the extra strontium site in the structure.

IV.2.5 Microstructural study

The existence of an anisotropic crystalline phase (hexagonal) and this outstanding transparency contradict with the general known conditions described by Rayleigh model for obtaining transparent ceramics. This necessitates a further microstructural study in order to understand and explain the observed transparency.

The microstructure of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 < x \leq 0.4$) transparent ceramics was examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high resolution STEM-HAADF.

IV.2.5.1 Transparent polycrystalline ceramic's morphology

Optically polished transparent ceramics were thermally etched in an open air electric furnace at 975°C during two hours in order to reveal the grain boundaries. The obtained samples were then used to collect SEM images (Figure 39).

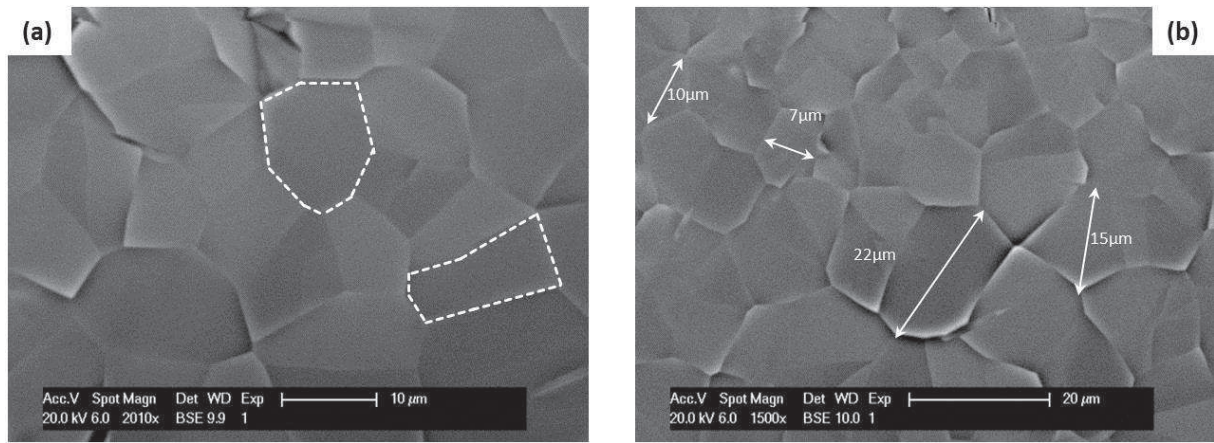


Figure 39(a) and (b) Scanning electron microscopy images of the transparent bulk $x=0.2$ polycrystalline ceramic sample thermally etched at 975°C for 2 hours

The image of the sample surface presented in Figure 39 displays a typical mosaic microstructure, usually observed for transparent polycrystalline ceramics obtained by high pressure/high temperature sintering processes.⁵⁰ The ceramic sample shows no porosity, thin grain boundaries, full dense structure and a crystal size of about 5-20 μm .

The structure of the thin grain boundaries was also further investigated by high resolution STEM-HAADF (Figure 40). The preparation method of the sample is explained in the experimental part (Chapter II).

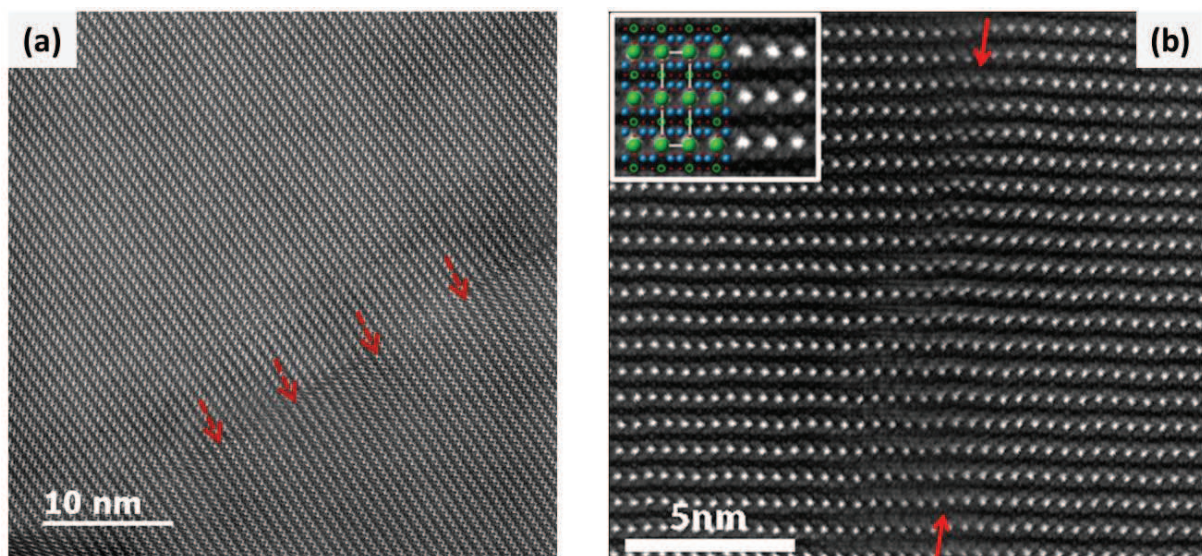


Figure 40(a) and (b) High resolution STEM-HAADF images of the interface between two slightly disoriented grains in $x=0.2$ transparent polycrystalline ceramic. Embedded in (b) the crystal structure obtained from powder diffraction

Figure 40 shows the very thin interface between two grain boundaries pointed by the red arrows. No residual glass phase or secondary phases are detected even at this scale, which confirms the total single crystallization of the transparent polycrystalline ceramics. The embedded square shows the crystalline structure obtained from powder diffraction which matches perfectly the atomic resolution image. The green Sr1 site appears bright, blue Si/Al is gray and the partially occupied open green Sr2 sites are dark gray. The red oxygen atoms are not visible due to their low atomic number Z.

Even though our polycrystalline ceramics exhibits a hexagonal anisotropic crystalline structure in addition to relatively large crystalline size, they are highly transparent. Their transparency was thus related to their non-porous structure and to the thin grain boundaries (no light scattering source due to microstructure).

IV.2.5.2 Surface crystallization and preferential orientation

Interestingly, a strong orientation of the crystallites perpendicular to the surface can be observed, as evidenced on the SEM image recorded along the sample section Figure 41. This observation results from heterogeneous surface nucleation crystallization process.

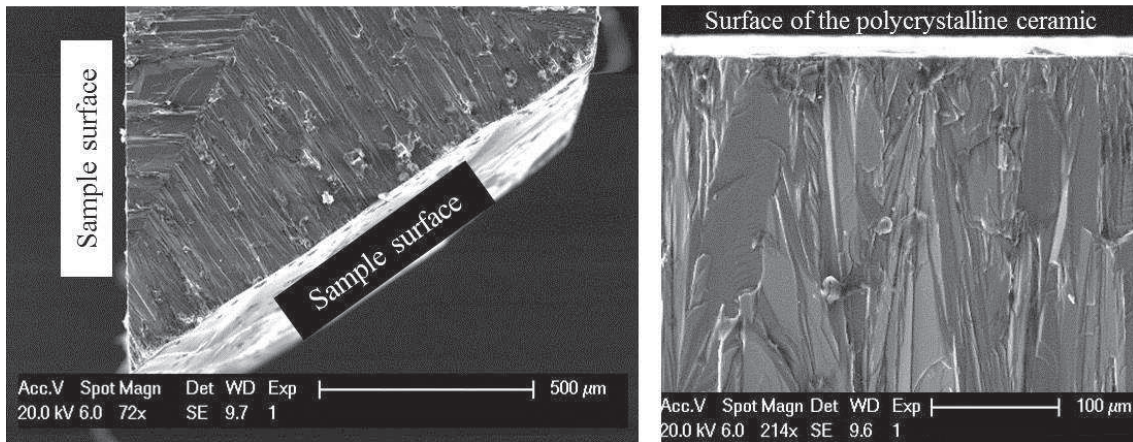


Figure 41 SEM images recorded on a section of $Sr_{1.1}Al_{2.2}Si_{1.8}O_8$ ($x=0.2$) polycrystalline ceramic sample

The preferential orientation is also confirmed by XRD data recorded on bulk and powder samples of the same solid solution composition $x=0.2$ polycrystalline ceramic (Figure 42). The diffractogram of the bulk sample shows enhanced $hh0$ reflection intensities compared to theoretical ones (those corresponding to powder sample). However, the

crystallization mechanism is not fully oriented as we can still observe all the other hkl reflections but with much weaker intensities compared to those of $hh0$ reflections (Figure 42).

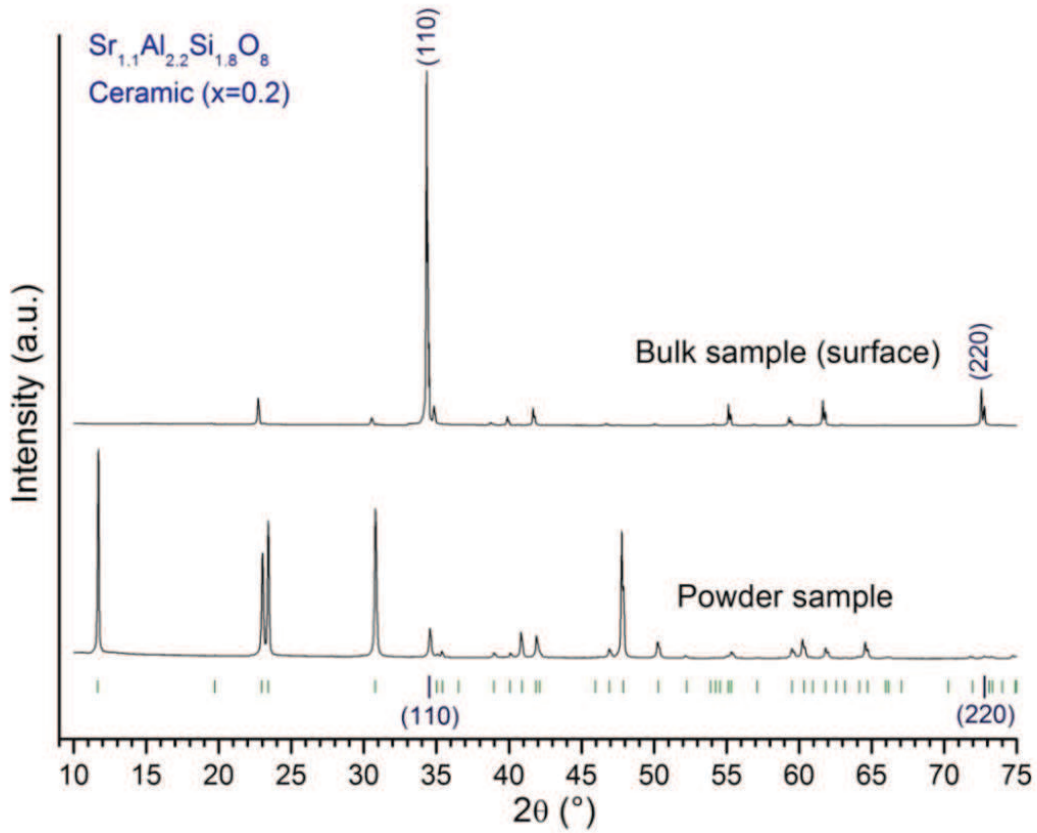


Figure 42 X-ray diffraction pattern recorded on bulk (top) and powder (bottom) samples of the $Sr_{1.1}Al_{2.2}Si_{1.8}O_8$ ($x=0.2$) ceramic

Using DSC, we have also studied the difference between thermograms obtained of bulk samples and powder samples for all the five compositions of the solid solution $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x=0, 0.1, 0.2, 0.3$ and 0.4).

Figure 43 displays the two thermograms of the $x=0.2$ glass composition registered on a bulk sample and powder sample. The glass transition temperature is slightly shifted toward a higher temperature ($\approx 904 \rightarrow \approx 922 \pm 2^\circ\text{C}$) for the bulk sample. The crystallization peak on the other hand appears to be broader and appears at higher temperature ($\approx 1222 \pm 2^\circ\text{C}$) when compared to that of the powder sample. The significance of this difference in the thermograms of glass samples in powder form or bulk form is related to the surface nucleation mechanism.

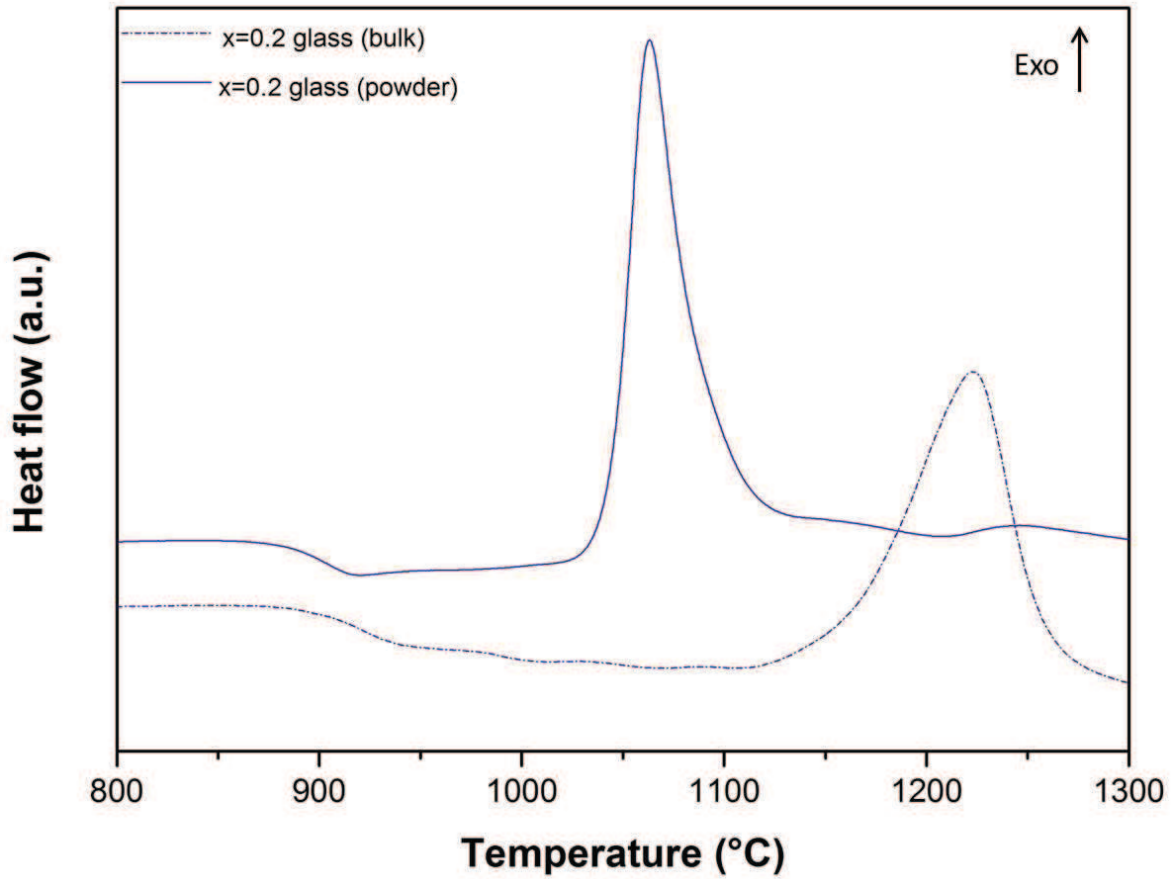


Figure 43 Normalized DSC thermograms recorded for $x=0.2$ glass composition using a heating rate of 10K/min (a) bulk sample form, (b) powder sample form

For the powder sample, the crystallization is faster and starts at a lower temperature due to the large surface area provided in comparison with the massif sample. In order to further confirm this surface nucleation mechanism and thus the absence of volume nucleation, the reduced glass transition parameter (T_{gr})⁵¹ has been determined. T_{gr} is defined by the ratio of the glass transition temperature to that of the melting temperature determined using DSC (Table 15).

Table 15 Reduced glass transition temperature (T_{gr}) calculated for $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ solid solution glass compositions ($x=0, 0.1, 0.2, 0.3$ and 0.4) using T_g and T_f

Glass composition	T_g	T_f	T_{gr}
$SrAl_2Si_2O_8(x=0)$	907	1374	0.66
$Sr_{1.05}Al_{2.1}Si_{1.9}O_8(x=0.1)$	905	1355	0.67
$Sr_{1.1}Al_{2.2}Si_{1.8}O_8(x=0.2)$	904	1359	0.67
$Sr_{1.15}Al_{2.3}Si_{1.7}O_8(x=0.3)$	903	1358	0.66
$Sr_{1.2}Al_{2.4}Si_{1.6}O_8(x=0.4)$	904	1380	0.66

Based on previous work by Zanotto,⁵² showing that for T_{gr} values higher than 0.58 the surface nucleation appears to be the dominant nucleation mechanism. This applies to the five compositions of the solid solution $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x=0, 0.1, 0.2, 0.3$ and 0.4) where a T_{gr} value of 0.66 is approximately obtained.

IV.2.6 Birefringence and transparency

The combination of structural anisotropy of the hexagonal $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 0.4$) structure, non-perfect alignment of the crystallite orientations and micrometer scale microstructure, would not typically result in the high optical transparency observed in these polycrystalline ceramics. The determined refractive index ($n=1.59$) represents an average value for all the crystal orientations within our material. So it would be interesting to determine the refractive index components along the two unit cell dimensions a and c in order to explain the observed transparency. To understand this seeming contradiction, the birefringence of the solid solution materials has been calculated through density functional theory (DFT) computations.

IV.2.6.1 DFT calculations

The refractive index components have been obtained from calculation of real and imaginary parts of the dielectric function $\epsilon(\omega)$ carried out from modeled periodic structures.

To account for the partial occupancy of the extra Sr site, the modeled structures consist of supercell of 2x2x1 unit cells of the average structure and computations were performed for $x=0$ and 0.25 compositions for which the supercell contain 0 and 1 extra Sr atom, respectively. The $x=0.2$ sample with less than one extra Sr atom was not taken because the calculation in this case necessitates to consider a much larger supercell which could not be realized.

IV.2.6.1.a Structural optimization

For each of the two compositions $x=0$ and $x=0.25$, thousands of models could be proposed in order to make the DFT computations. However, based on the NMR experiment results, structural optimization was realized by considering a selection of five models with different Al/Si ordering degrees for each of the two compositions $x=0$ and $x=0.25$. This DFT optimization of all the atomic positions was performed by minimizing the residual force on all the atoms up to $|F|_{\max}$ below $0.006 \text{ eV} \cdot \text{\AA}^{-1}$, fixing the cell parameters to those experimentally determined by synchrotron refinement. The parameters used for the geometry optimization and the DFT computations of the dielectric function $\epsilon(\omega)$ are represented in supplementary information (Table S9).

$x=0$ composition models

Figure 44 represents the modeled structures of the $SrAl_2Si_2O_8$ compound ($x = 0$) which consist of a supercell of 2x2x1 unit cells of the average structure with different Al/Si ordering configurations. The supercell contains 32 tetrahedral sites (occupied by Si or Al atoms) and a total of 104 atoms. The red and blue tetrahedra correspond to SiO_4 and AlO_4 units, respectively, and green spheres to Sr atoms.

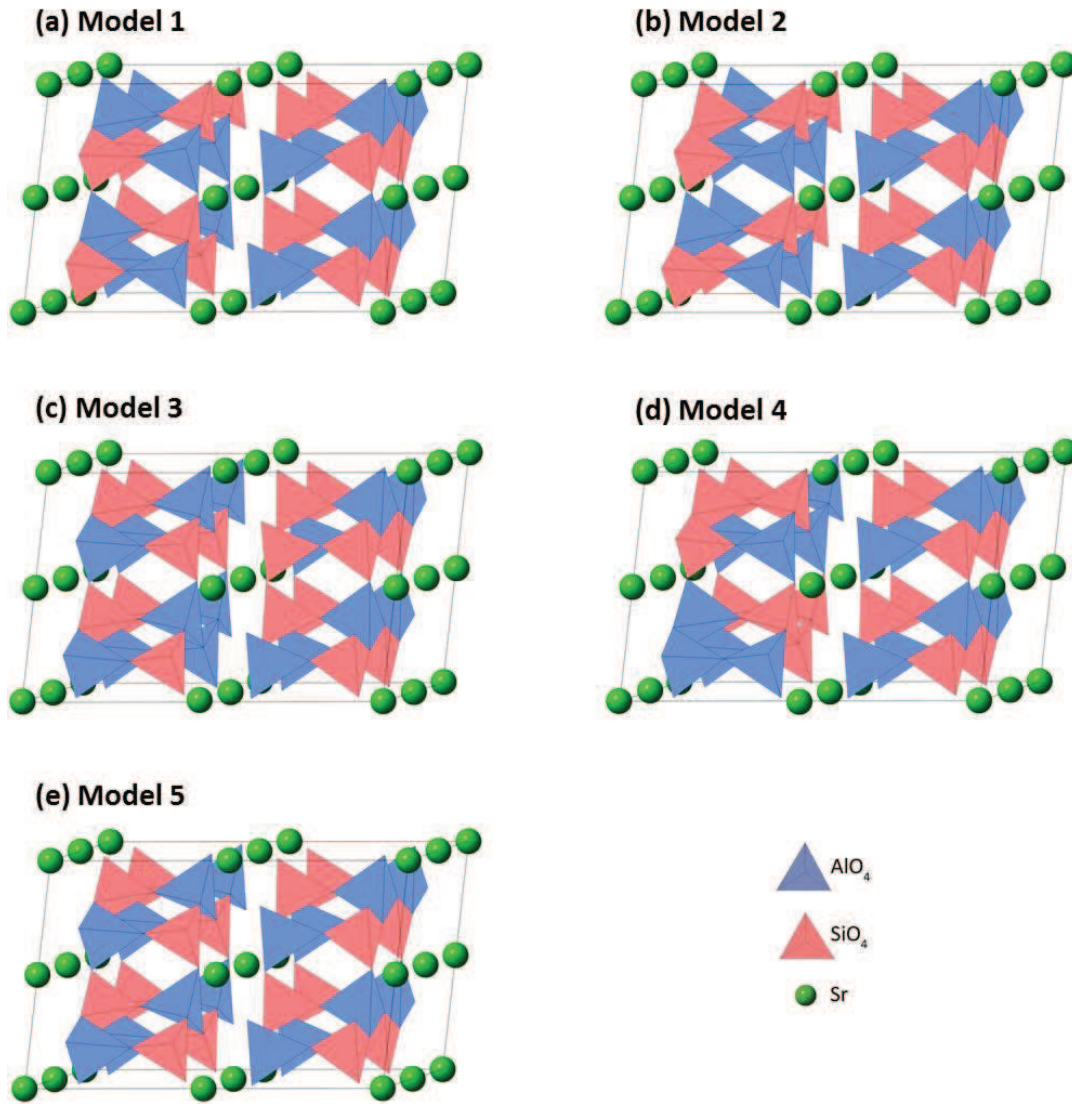


Figure 44 Modeled structures of the $SrAl_2Si_2O_8$ compound ($x = 0$)

Model 1 (Figure 44a) represents Al/Si ordering which closely accounts to the Al and Si distribution observed by NMR.

Models 2 to 4 (Figure 44b-d) when averaged represent an Al/Si ordering also close to that of the experimental observed Al/Si ordering.

Model 5 (Figure 44e) represents the lowest energy structure for the $SrAl_2Si_2O_8$ ($x=0$) composition. It is the most ordered structure.

The structural parameters of the different geometry-optimized model structures with $x = 0$ ($SrAl_2Si_2O_8$). The space group, the total energy relative to that of the lowest energy structure, the types and relative amounts of Si and Al environment and the

corresponding Si-O and Al-O average bond length are reported in supplementary information (Table S7).

$x=0.25$ composition models

Figure 45 represents the modeled structures of the compound ($x = 0.25$) which consist of a supercell of $2 \times 2 \times 1$ unit cells of the average structure with different Al/Si ordering configurations. The supercell contains 32 tetrahedral sites (occupied by Si or Al atoms) and a total of 104 atoms. The red and blue tetrahedra correspond to SiO_4 and AlO_4 units, respectively, and green spheres to Sr atoms.

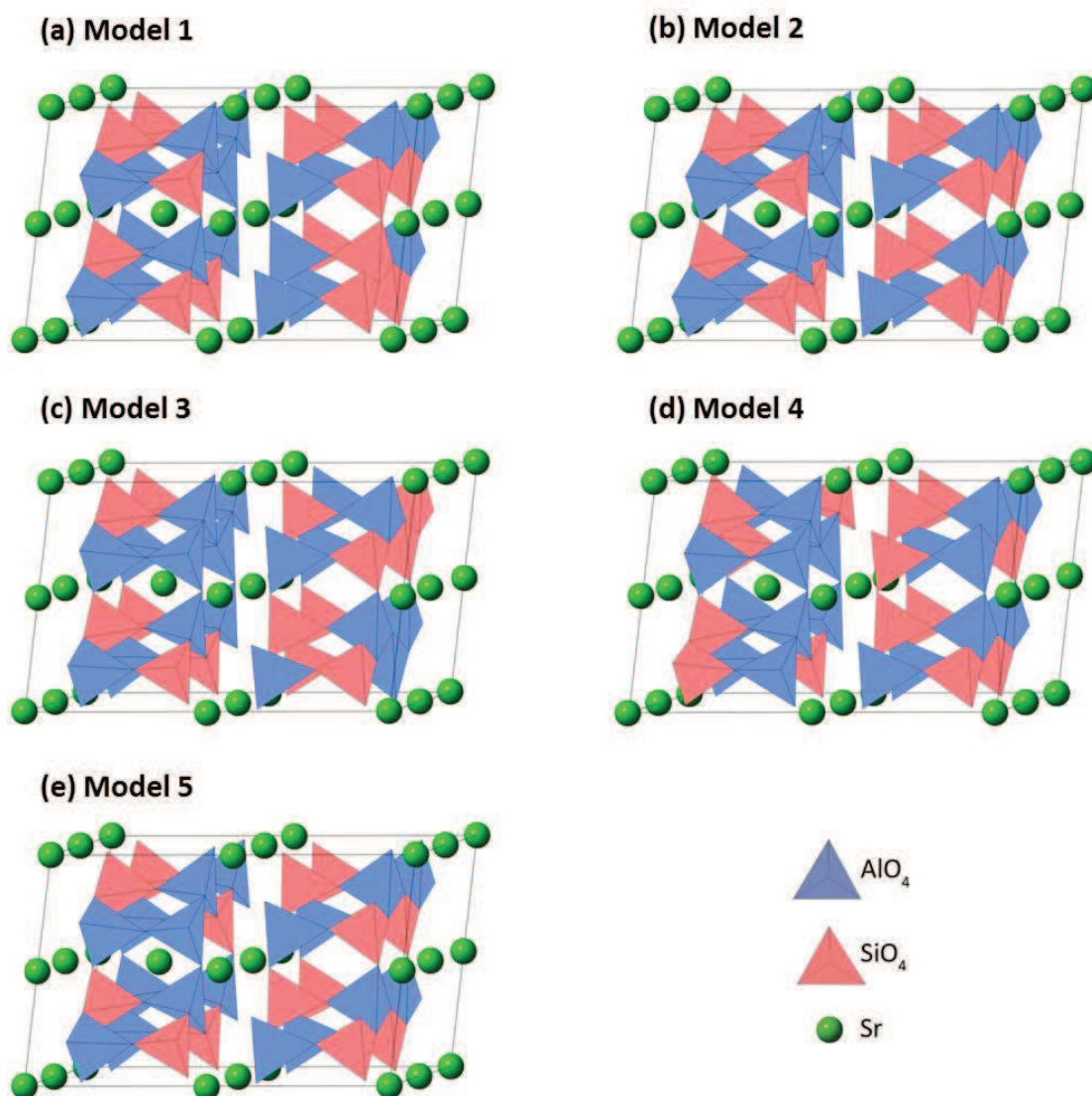


Figure 45 Modeled structures of the $Sr_{1.125}Al_{2.25}Si_{1.75}O_8$ compound ($x = 0.25$)

Similarly to $x=0$ composition, model 1 (Figure 45a) has Al/Si ordering which closely accounts for the observed distributions of Al and Si environments. Models 2, 3

and 4 (Figure 45b-d) when averaged accounts also for the observed Al/Si ordering and model five (Figure 45e) represents the lowest energy structure (most ordered).

The structural parameters of the different geometry-optimized model structures with $x = 0.25$ ($Sr_{1.125}Al_{2.25}Si_{1.75}O_8$). The space group, the total energy relative to that of the lowest energy structure, the types and relative amounts of Si and Al environment and the corresponding Si-O and Al-O average bond length are reported in supplementary information (Table S8).

IV.2.6.1.b Birefringence calculation

Following the structural optimization which accounted the most of the observed Al/Si ordering, and before the birefringence calculation, the reliability of the simplified model structures (with a limited number of atoms) used for the computations was investigated. This reliability was checked by comparing the DFT calculated ^{29}Si and ^{27}Al NMR spectra with the experimental ones using the CASTEP code (Figure 46).

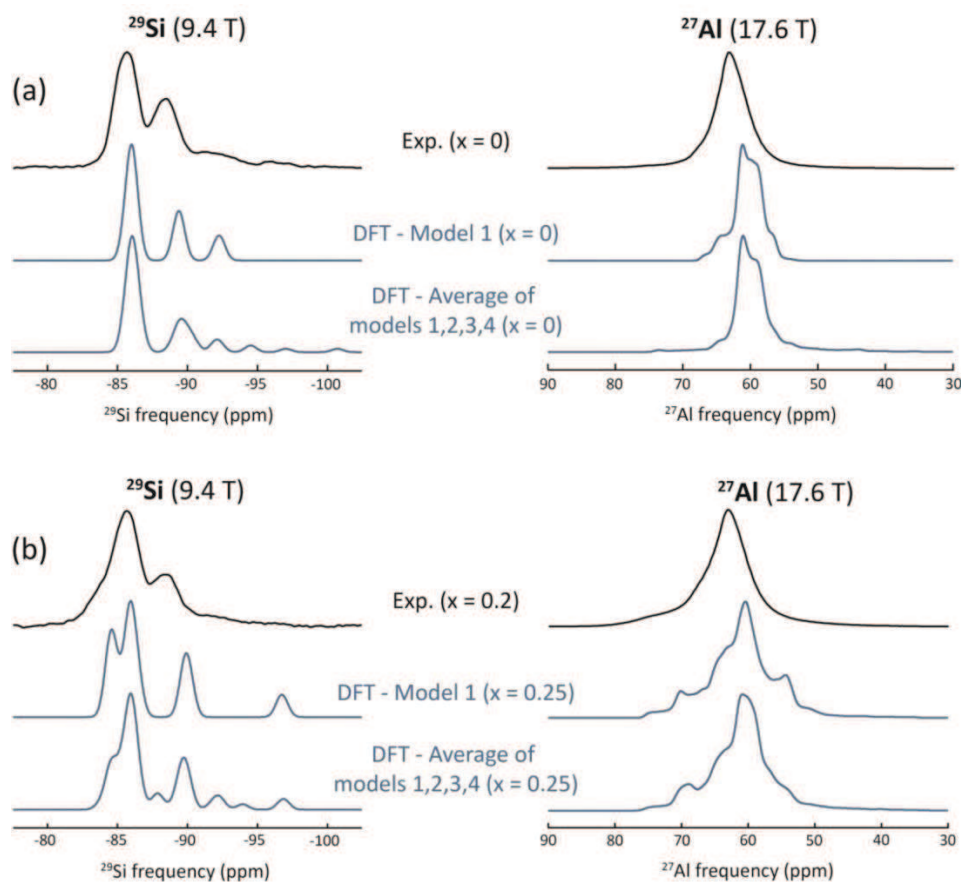


Figure 46 Comparison between the experimental MAS NMR spectra ($x = 0$ and 0.25) and those calculated by DFT for the modeled structures ($x = 0$ and 0.25)

The relatively good agreement between the DFT calculated ^{29}Si and ^{27}Al NMR spectra with the experimental ones as shown in Figure 46 reflects the reliability of the simplified structural models. These were subsequently used to calculate the birefringence (Figure 47).

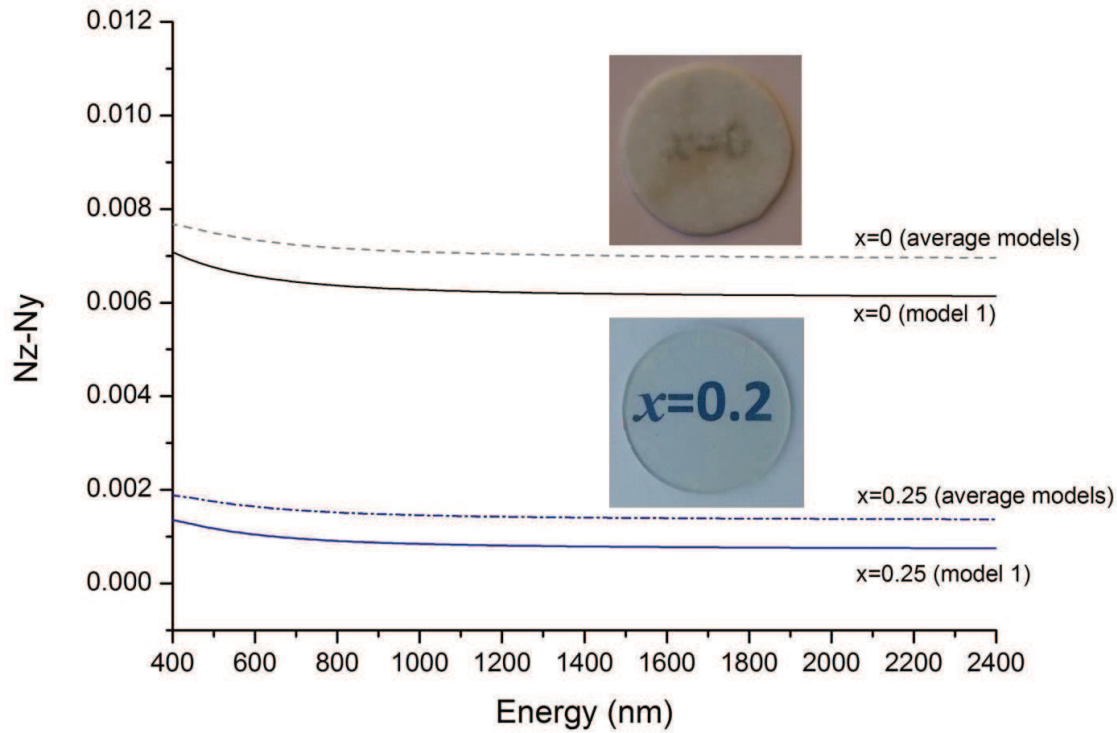


Figure 47 DFT calculated birefringence of the $x=0$ and $x=0.25$ sample compositions with their photograph in insert

Figure 47 shows the DFT-calculated birefringence where:

For $x=0$, the black line represents the DFT-calculated birefringence using the structural model 1, while the black dashed line represents that calculated using the average of the models 2,3 and 4. The birefringence of the $\text{SrAl}_2\text{Si}_2\text{O}_8$ sample is calculated and found to be equal to around 0.007.

For $x=0.25$ the black line represents the DFT-calculated birefringence using the structural model 1, while the black dashed line represents that calculated using the average of the models 2,3 and 4. The birefringence of the $x=0.25$ sample is calculated and found to have an almost null value of 0.001.

Based on the calculated birefringence values, we can observe that despite the presence of very large crystals and an anisotropic crystal structure, the transparency of the polycrystalline ceramics presented can thus be attributed to the combination of high density

(absence of pores), extremely thin grain boundaries and very weak birefringence. The birefringence appears to have a central role as the clear increase of the transparency level observed between $x=0$ and $x=0.25$ corresponds to a significant decrease of the calculated birefringence value, the microstructure characteristics (no porosity and thin grain boundaries) being the same for the two samples ($x=0$ and $x=0.25$).

This birefringence appears to be controlled by chemical composition through the amount of extra strontium Sr2 site in the structure. Computations for different structural models with a same composition show that the birefringence also depends on the Al/Si ordering configurations (Figure 48 and Figure 49).

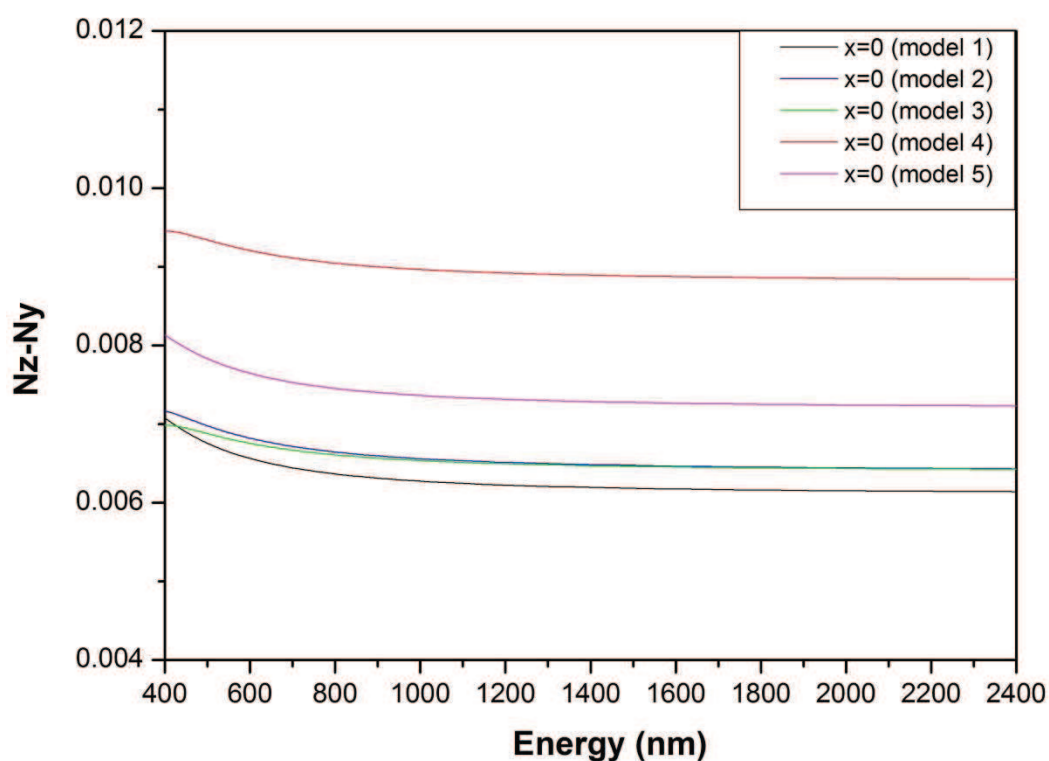


Figure 48 DFT-calculated birefringence for the structural models shown in figure 35 for $x=0$ composition

Figure 48 shows clearly the difference in the birefringence values for the different models of the same sample composition $x=0$. Model 5 with the highest degree of Al/Si order represents a higher birefringence value than that of model 1 (which accounts the most for the observed Al/Si ordering by NMR experiments). Model 4 although possessing a certain degree of Al/Si disorder, it presents a higher birefringence value among the other models.

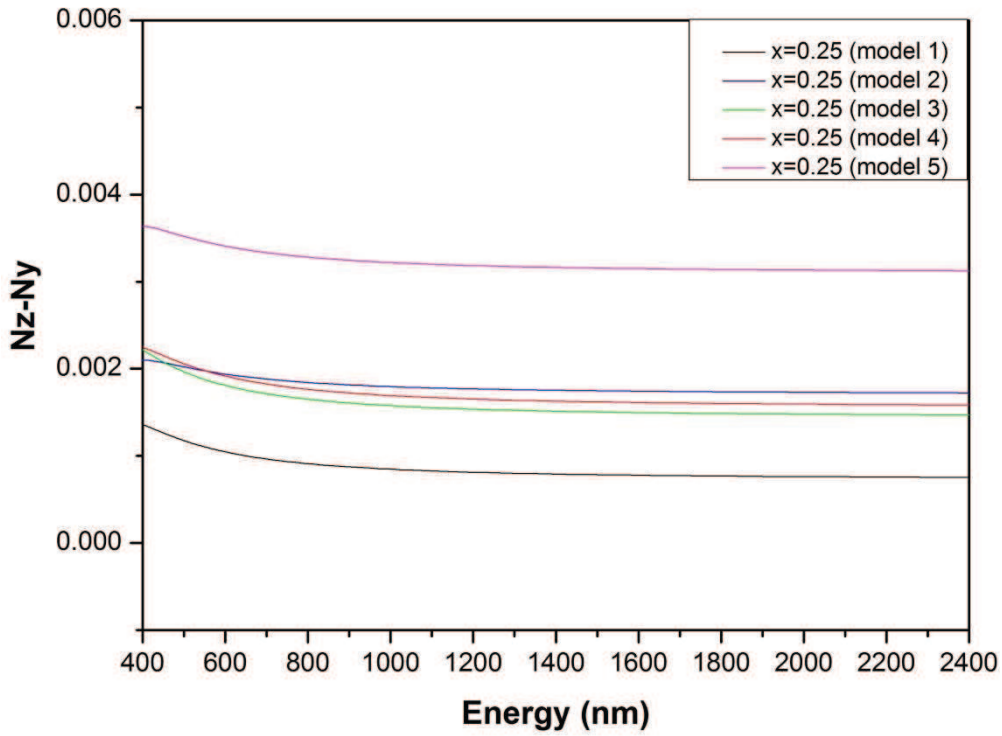


Figure 49 DFT-calculated birefringence for the structural models shown in figure 36 for $x=0.25$ composition

Figure 49 shows that model 5 with the most ordered structure presents the highest birefringence value, whereas the other models (1, 2, 3 and 4) with a certain degree of Al/Si disorder have lower birefringence.

Based on these simplified models, it appears clearly that the obtained birefringence is directly related to the structure of the polycrystalline ceramics, where a change of the Al/Si degree of order has resulted in different birefringence values. Therefore, it appears that a precise control of the birefringence can be achieved through the control of the strontium occupancy (chemical composition) and the Al/Si ordering (synthesis conditions),⁵³ the optimum birefringence (and thus transparency) being obtained for $x=0.2$.

IV.2.6.2 Controlled disorder and transparency: a new approach

In analogy with the multi-scale structure of glass⁵⁴, the obtained results suggest that an optical isotropy at the micrometer scale can be obtained in non-cubic crystalline material (with structural anisotropy at the nanometer scale) through the introduction of a controlled disorder. This would result in low birefringence values of the obtained ceramics, thus conserving their transparency even with micrometer scale crystallite size.

This new approach appears to be very promising in the transparent ceramic domain, where it could be applied to other compositions and observe its applicability with the various systems through a controlled induced disorder. The obtained transparent ceramics using this approach could then possess interesting applications and could hopefully be synthesized at an industrial scale due to enormous advantages of the glass crystallization route compared to other transparent ceramic sintering processes.

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General Conclusion

The objectives of this study were to elaborate and characterize large-scale new transparent polycrystalline ceramics with high transparency using a full and congruent glass crystallization approach. This synthetic route has been chosen due to its numerous advantages compared to already existing complex and time consuming sintering techniques running under pressure. Several systems have been studied: $\text{Sr}_3\text{Al}_2\text{O}_6$, $\text{Sr}_3\text{Ga}_2\text{O}_6$, and a series of solid solution compositions within the $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ternary diagram. Transparent strontium aluminosilicates polycrystalline ceramics with quasi-perfect transparency have been synthesized with remarkably large size samples. Different complementary techniques have been employed to probe the structure of these novel materials at long- and short-range scales.

In a first step, we have synthesized highly transparent cubic $\text{Sr}_3\text{Al}_2\text{O}_6$ and $\text{Sr}_3\text{Ga}_2\text{O}_6$ polycrystalline ceramics. As $\text{Sr}_3\text{Ga}_2\text{O}_6$ ceramics are slightly hygroscopic, the study has mainly been focused on the $\text{Sr}_3\text{Al}_2\text{O}_6$ composition. A high level of transparency ($\approx 87\%$) has been obtained in the visible and IR ranges (up to $6\mu\text{m}$), almost matching the maximum theoretical transmission (87.4%). This great transparency level has been explained through the specific microstructure inherent to the elaboration process. The light scattering is minimized because of the cubic symmetry of $\text{Sr}_3\text{Al}_2\text{O}_6$ material, which leads to optical isotropy (no birefringence). Moreover, the micrometer-scale $\text{Sr}_3\text{Al}_2\text{O}_6$ grains organization shows the absence of porosity and very thin grain boundaries, leading to an ultra-dense ceramic. The thermal and mechanical properties of the transparent $\text{Sr}_3\text{Al}_2\text{O}_6$ polycrystalline ceramic have also been measured. A considerable improvement of these properties has been observed when comparing the ceramic to the corresponding precursor glass. Luminescence and scintillation properties studies have revealed that $\text{Sr}_3\text{Al}_2\text{O}_6$ transparent polycrystalline ceramics can be considered as interesting candidates for photonic applications in the visible and IR ranges. The results of this study have been published in *Chemistry of Materials*.¹

In the second part of this work, the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 2$) compositions have been studied. This system can be divided into three solid solutions. For the first solid solution $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0.8 \leq x \leq 2$), highly transparent polycrystalline ceramics can be synthesized ($\varnothing \approx 3 - 5$ mm beads) especially for the $x=1.6$ composition. A structural study performed by powder diffraction has been conducted all along this solid solution. Strontium vacancies appeared in two of the five existing strontium crystallographic sites. The vacancy content increases when x decreases. For the second solid solution $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0.5 \leq x \leq 0.68$), glass compositions can be prepared using a commercialized electric furnace due to the lower melting temperature of the glass precursors ($1700-1750^\circ\text{C}$) compared to the first solid

solution. This is a direct consequence of the increased silica content in these compositions. Large scale samples can be easily elaborated, however the weak surface crystallization mechanism requires samples with a very small thickness (<0.3 mm) in order to prepare transparent polycrystalline ceramics. The ceramization of these solid solution compositions has led to a previously unreported orthorhombic crystalline phase (Pmc2₁ space group with $a=8.3$ Å, $b=10.2$ Å and $c=17.5$ Å). The structure has been determined *ab initio* based on a combined study using transmission electron microscopy with synchrotron and neutron powder diffraction data. For the third solid solution, $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0.4$), a detailed study has been realized. Five compositions have been studied ($x=0, 0.1, 0.2, 0.3$ and 0.4). Large-scale samples ($\varnothing \approx 4 - 5$ cm disks) can be easily prepared in a commercialized electric furnace due to the lower melting temperature of the glass precursor (increased silica content). Highly transparent polycrystalline ceramics have been synthesized throughout this solid solution. The $x=0.2$ composition ($\text{Sr}_{1.1}\text{Al}_{2.2}\text{Si}_{1.8}\text{O}_8$) presents an exceptional transparency which reaches the theoretical transmittance limit of 90% in the visible and near IR range, value which to the best of our knowledge has never been attained before for any transparent polycrystalline oxide ceramic. Structural refinements have been performed for each of the five compositions based on the well-known $\text{SrAl}_2\text{Si}_2\text{O}_8$ hexagonal structure (P63/mcm, $a=b=5.2$ Å, $c=15.2$ Å, one Sr site, two Al/Si sites and two oxygen sites). For $x \geq 0.1$, inspection of Fourier maps of these hexagonal crystalline phases shows the apparition of a new strontium site (Sr2) which occupancy increases with increasing x . ^{29}Si and ^{27}Al NMR experiments confirmed the existence of chemical disorder in our materials. When increasing x , the Al environment distribution become broader accompanied by the inclusion of q_4^4 unit and the proportions of q_2^4 , q_3^4 and q_4^4 units increase reflecting the formation of additional Al-O-Al bonds. These bonds reflecting a deviation from the Lowenstein rule are required for the local charge compensation in the vicinity of the additional Sr site. The birefringence of crystal structures from the solid solution have been calculated by DFT computations for two representative compositions ($x=0$ and $x=0.25$), using for each of them five optimized modeled structures. The modeled structures have different Al/Si ordering configurations which account differently for the real distributions of Al and Si environments observed by NMR. The results of these DFT computations have shown the enormous impact of the chemical disorder on minimizing the birefringence values. Despite the fact that these materials exhibit non-cubic symmetry and large crystallite sizes of several tens of microns, the maximum theoretical transmittance reached is achieved by (i) the absence of porosity, glassy and secondary phases and extremely thin grain boundaries (observed with high resolution TEM/STEM) resulting from the

elaboration process and (ii) a very weak DFT calculated birefringence (0.001 for $x=0.25$ composition) obtained from the introduction of a controlled chemical disorder (strontium occupancy and Al/Si ordering). The results of this third solid solution have been submitted for publication.² This study allows a new approach to be proposed for elaborating structurally anisotropic materials with an outstanding transparency: the introduction of a controlled chemical disorder can lead to optical isotropy. This new concept opens the way to large number of composition candidates to obtain transparent polycrystalline ceramics.

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Supplementary Information

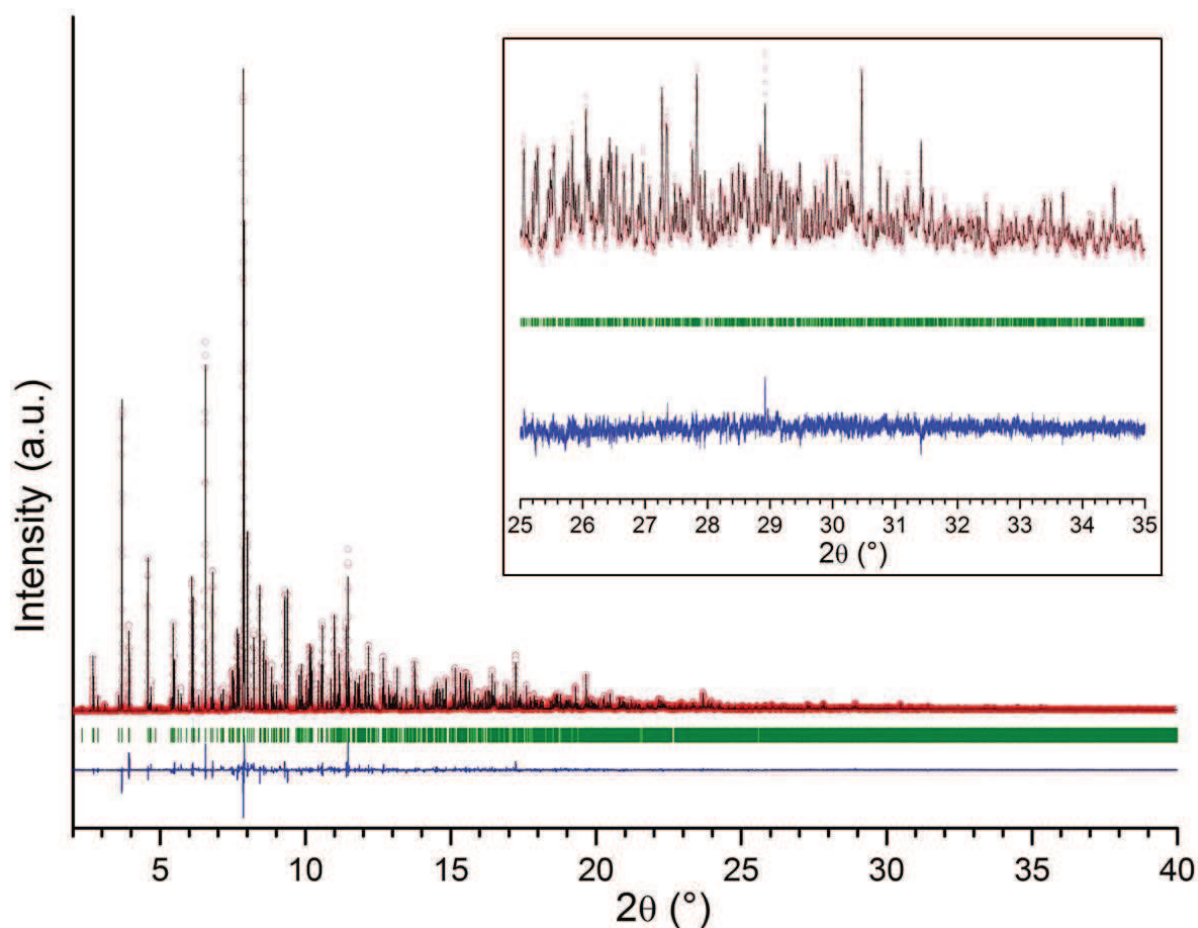


Figure S1. Rietveld refinement of the $\text{Sr}_{1.3}\text{Al}_{2.6}\text{Si}_{1.4}\text{O}_8$ ($x = 0.6$) synchrotron powder diffraction data collected at room temperature ($R_{wp} = 8.42\%$, $R_p = 6.85\%$, and $G.O.F = 1.55$). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines corresponds to the reflection positions. Enlargement of the $25 - 35^\circ$ angular range (2θ) is embedded.

Table S1. Atomic positions and selected inter-atomic distances of $\text{Sr}_{1.3}\text{Al}_{2.6}\text{Si}_{1.4}\text{O}_8$ ($x = 0.6$) obtained from room temperature Rietveld refinement of synchrotron powder diffraction data (cell parameters: $a = 8.289157(9)$ Å, $b = 10.22115(1)$ Å and $c = 17.48112(2)$ Å)

Atom	x	y	Z	Occupancy factor	Sites
Sr1	0.5	0.8172(1)	0.2403(3)	0.912(2)	2b
Sr2	0	0.5529(1)	-0.0103(3)	1	2a
Sr3	0	0.2671(1)	0.2642(3)	1	2a
Sr4	0.5	0.0409(1)	0.0136(3)	1	2b
Sr5	0	0.6793(1)	0.2789(3)	1	2a
Sr6	0	0.0446(17)	0.0060(9)	0.059(2)	2a
Sr7	0.5	0.4916(7)	0.0108(3)	0.195(2)	2b
Sr8	0.5	0.8396(34)	-0.1862(19)	0.031(2)	2b
(Al,Si)1	0.3129(2)	0.0817(2)	0.1753(3)	1	4c
(Al,Si)2	0.3012(3)	0.5311(2)	0.1703(3)	1	4c
(Al,Si)3	0.1842(3)	0.2974(2)	0.0722(3)	1	4c
(Al,Si)4	-0.3035(3)	0.2756(2)	-0.0902(3)	1	4c
(Al,Si)5	0.3008(3)	0.7853(2)	-0.0521(3)	1	4c
(Al,Si)6	-0.2998(2)	0.5501(2)	-0.1588(3)	1	4c
(Al,Si)7	0.1882(3)	0.8084(3)	0.1150(3)	1	4c
(Al,Si)8	0.1888(3)	0.9922(2)	0.3452(3)	1	4c

Al/Si tetrahedron (average)		Sr polyhedron (average)	
(Al/Si)1 – O	1.706	Sr1 – O (7)	2.743
(Al/Si)2 – O	1.722	Sr2 – O (7)	2.699
(Al/Si)3 – O	1.686	Sr3 – O (7)	2.646
(Al/Si)4 – O	1.730	Sr4 – O (7)	2.618
(Al/Si)5 – O	1.713	Sr5 – O (7)	2.702
(Al/Si)6 – O	1.679	Sr6 – O (7)	3.023
(Al/Si)7 – O	1.688	Sr7 – O (9)	2.977
(Al/Si)8 – O	1.680	Sr8 – O (9)	2.77

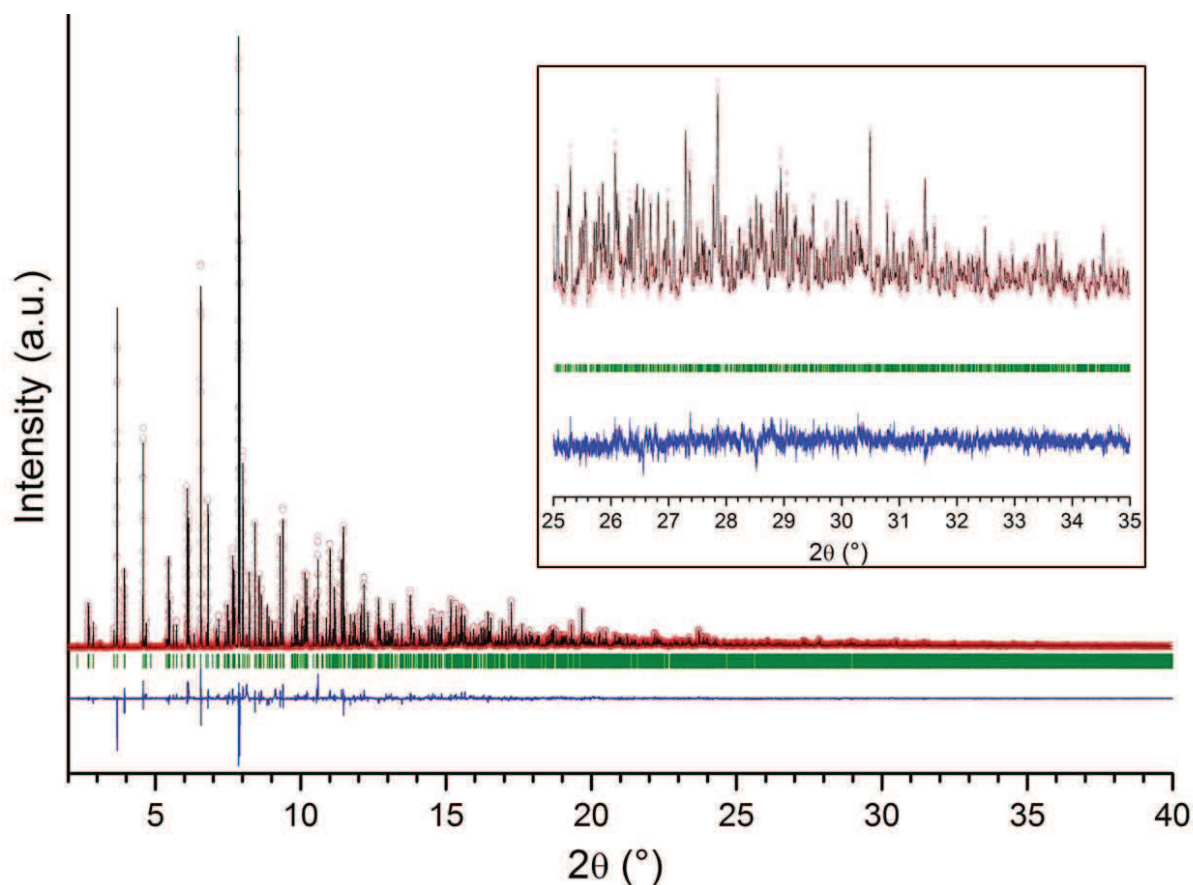


Figure S2. Rietveld refinement of the $\text{Sr}_{1.25}\text{Al}_{2.5}\text{Si}_{1.5}\text{O}_8$ ($x = 0.5$) synchrotron powder diffraction data collected at room temperature ($R_{wp} = 10.44\%$, $R_p = 8.25\%$, and $G.O.F=1.89$). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines corresponds to the reflection positions. Enlargement of the $25 - 35^\circ$ angular range (2θ) is embedded.

Table S2. Atomic positions and selected inter-atomic distances of $\text{Sr}_{1.25}\text{Al}_{2.5}\text{Si}_{1.5}\text{O}_8$ ($x = 0.5$) obtained from room temperature Rietveld refinement of synchrotron powder diffraction data (cell parameters: $a = 8.222837(11) \text{ \AA}$, $b = 10.21431(1) \text{ \AA}$ and $c = 17.46516(2) \text{ \AA}$)

Atom	x	y	Z	Occupancy factor	Sites
Sr1	0.5	0.8159(2)	0.2344(3)	0.842(2)	2b
Sr2	0	0.5533(1)	-0.0156(3)	1	2a
Sr3	0	0.2644(1)	0.2579(3)	1	2a
Sr4	0.5	0.0406(1)	0.0084(3)	1	2b
Sr5	0	0.6792(1)	0.2737(3)	1	2a
Sr6	0	0.0493(41)	-0.0115(20)	0.028(2)	2a
Sr7	0.5	0.4917(13)	0.0018(6)	0.107(1)	2b
Sr8	0.5	0.7641	-0.1219	0	2b
(Al/Si)1	0.3145(3)	0.0804(2)	0.1712(3)	1	4c
(Al/Si)2	0.3047(4)	0.5269(3)	0.1654(3)	1	4c
(Al/Si)3	0.1829(3)	0.2987(3)	0.0666(3)	1	4c
(Al/Si)4	-0.3065(4)	0.2760(3)	-0.0968(3)	1	4c
(Al/Si)5	0.3035(3)	0.7833(3)	-0.0567(3)	1	4c
(Al/Si)6	-0.2996(3)	0.5514(3)	-0.1644(3)	1	4c
(Al/Si)7	0.1869(4)	0.8074(3)	0.1101(3)	1	4c
(Al/Si)8	0.1899(4)	0.9901(3)	0.3402(3)	1	4c

Al/Si tetrahedron (average)		Sr polyhedron (average)	
(Al/Si)1 – O	1.729	Sr1 – O (7)	2.773
(Al/Si)2 – O	1.738	Sr2 – O (7)	2.722
(Al/Si)3 – O	1.650	Sr3 – O (7)	2.642
(Al/Si)4 – O	1.736	Sr4 – O (7)	2.595
(Al/Si)5 – O	1.712	Sr5 – O (9)	2.753
(Al/Si)6 – O	1.674	Sr6 – O (6)	2.902
(Al/Si)7 – O	1.691	Sr7 – O (9)	2.998
(Al/Si)8 – O	1.654	Sr8 – O	

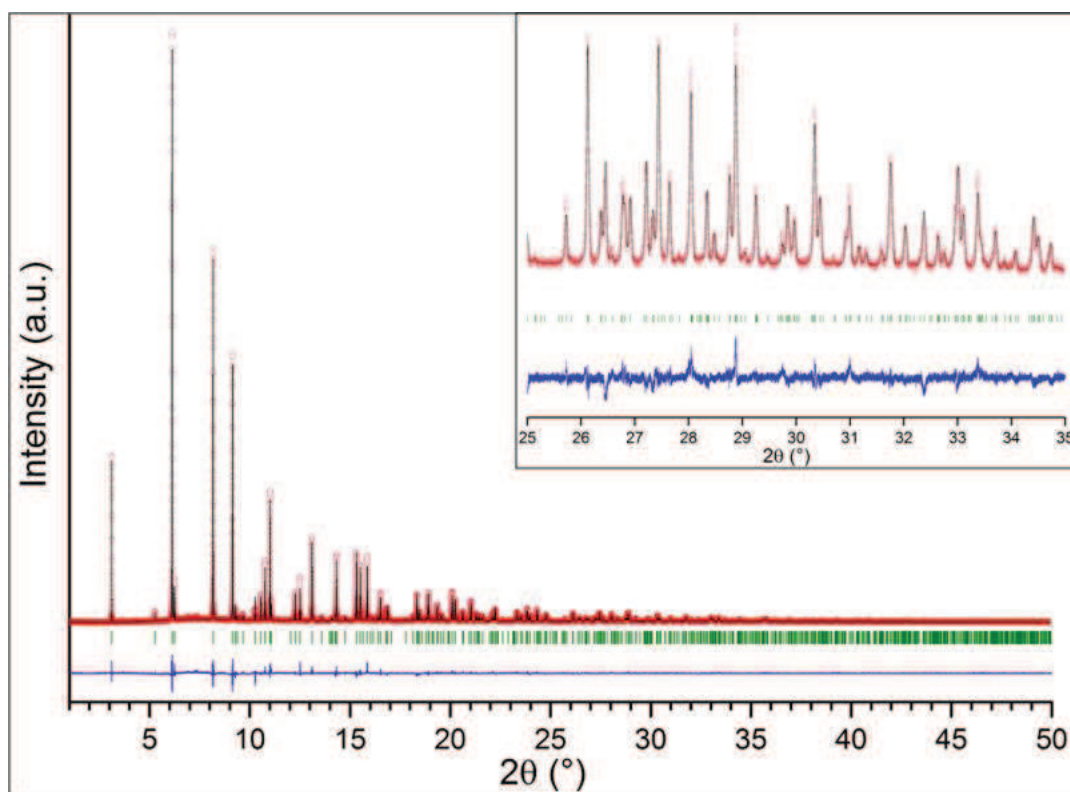


Figure S3. Rietveld refinement of the $\text{SrAl}_2\text{Si}_2\text{O}_8$ ($x = 0$) synchrotron powder diffraction data collected at room temperature ($R_{wp} = 7.99\%$, $R_p = 6.34\%$, and $G.O.F = 1.82$). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines corresponds to the reflection positions. Enlargement of the $25 - 35^\circ$ angular range (2θ) is embedded.

Table S3. Atomic positions and selected inter-atomic distances of $\text{SrAl}_2\text{Si}_2\text{O}_8$ ($x = 0$) obtained from room temperature Rietveld refinement of synchrotron powder diffraction data (cell parameters: $a = 5.19367(3) \text{ \AA}$ and $c = 15.1983(1) \text{ \AA}$)

Atom	Site	x	y	z	Uiso	Occ.
Sr1	2b	0	0	0	0.00972(7)	1
Al1	8h	0.33333	0.66667	0.14197(2)	0.00534(10)	0.5
Si1	8h	0.33333	0.66667	0.14197(2)	0.00534(10)	0.5
O1	4c	0.33333	0.66667	0.25	0.0113(3)	1
O2	12k	0.41633(17)	0	0.10121(6)	0.0246(4)	1

Sr1-O ($\text{\AA}$)		Al/Si-O ($\text{\AA}$)	
Sr1-O2 (x6)	3.4016(9)	Al/Si-O1	1.6426(3)
Sr1-O2 (x6)	2.6553(9)	Al/Si-O2 (x3)	1.6806(10)

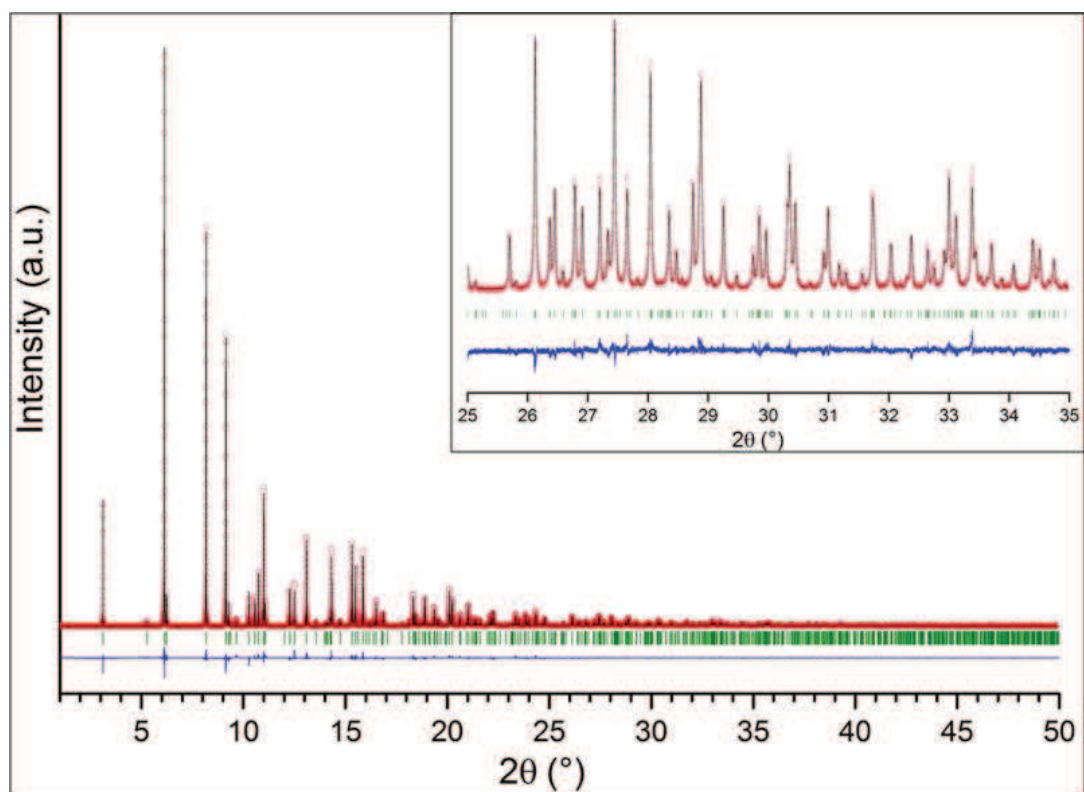


Figure S4. Rietveld refinement of the $\text{Sr}_{1.05}\text{Al}_{2.1}\text{Si}_{1.9}\text{O}_8$ ($x = 0.1$) synchrotron powder diffraction data collected at room temperature ($R_{wp} = 7.17\%$, $R_p = 5.55\%$, and $G.O.F = 1.62$). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines corresponds to the reflection positions. Enlargement of the 25 - 35° angular range (2θ) is embedded.

Table S4. Atomic positions and selected inter-atomic distances of $\text{Sr}_{1.05}\text{Al}_{2.1}\text{Si}_{1.9}\text{O}_8$ ($x = 0.1$) obtained from room temperature Rietveld refinement of synchrotron powder diffraction data (cell parameters: $a = 5.196294(5)$ Å and $c = 15.21997(2)$ Å)

Atom	Site	x	y	z	Uiso	Occ.
Sr1	2b	0	0	0	0.00824(5)	1
Sr2	2a	0	0	0.25	0.0054(10)	0.0306(4)
Al1	8h	0.33333	0.66667	0.1419(1)	0.00490(7)	0.515(1)*
Si1	8h	0.33333	0.66667	0.1419(1)	0.00490(7)	0.485(1)*
O1	4c	0.33333	0.66667	0.25	0.0139(2)	1
O2	12k	0.40670(10)	0	0.10149(4)	0.0136(2)	1

*: the Al/Si ratio was constrained using: (i) $\text{occ}(\text{Al}) = 0.5 + \text{occ}(\text{Sr2})/2$ for compensating the positive charge induced by Sr2 and (ii) $\text{occ}(\text{Al}) + \text{occ}(\text{Si}) = 1$ (full site occupancy).

Sr1-O (Å)		Sr2-O (Å)		Al/Si-O (Å)	
Sr1-O2 (x6)	3.4483(4)	Sr2-O1 (x6)	3.0001	Al/Si-O1	1.6447(2)
Sr1-O2 (x6)	2.6177(5)	Sr2-O2 (x6)	3.0943(5)	Al/Si-O2 (x3)	1.6923(3)

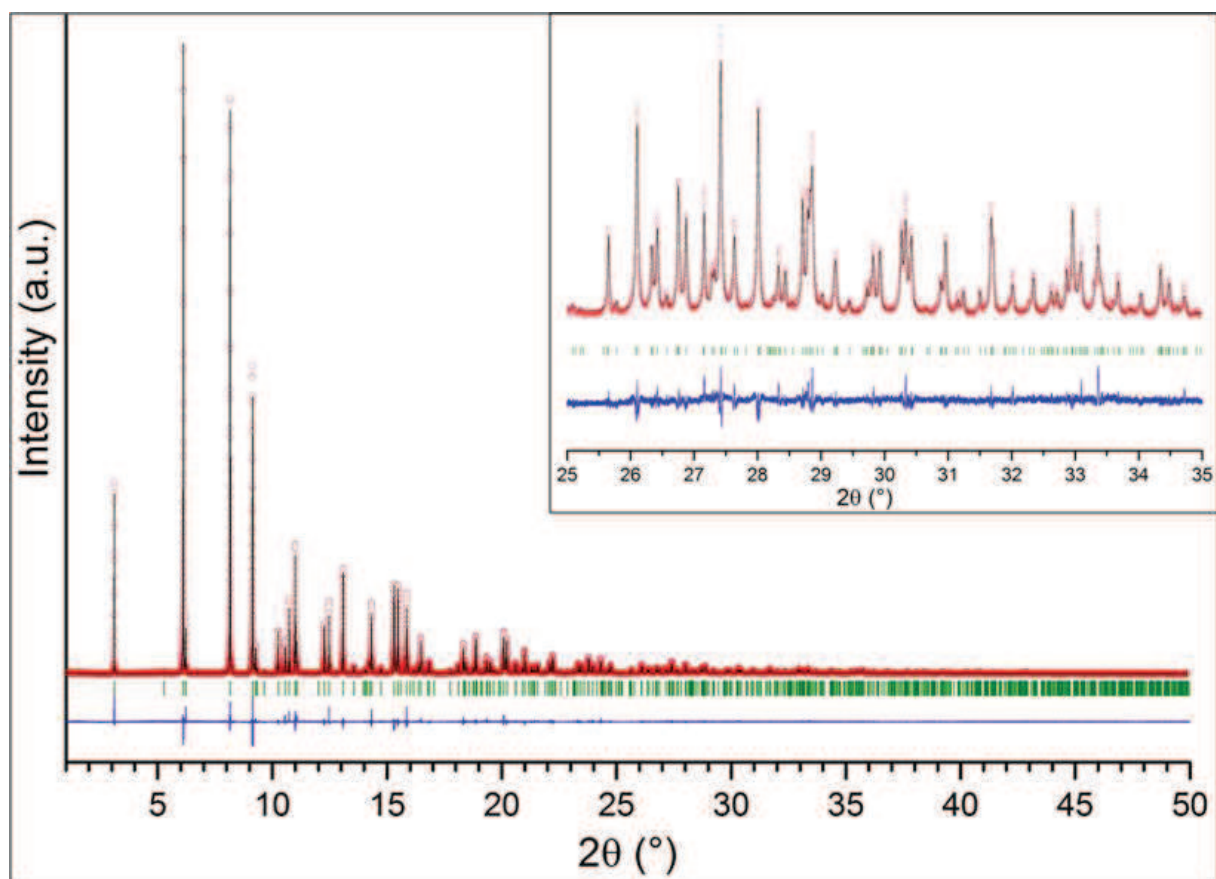


Figure S5. Rietveld refinement of the $\text{Sr}_{1.1}\text{Al}_{2.2}\text{Si}_{1.8}\text{O}_8$ ($x = 0.2$) synchrotron powder diffraction data collected at room temperature ($R_{wp} = 7.45\%$, $R_p = 6.24\%$, and $G.O.F = 1.67$). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines corresponds to the reflection positions. Enlargement of the $25 - 35^\circ$ angular range (2θ) is embedded.

Table S5. Atomic positions and selected inter-atomic distances of $\text{Sr}_{1.1}\text{Al}_{2.2}\text{Si}_{1.8}\text{O}_8$ ($x = 0.2$) obtained from room temperature Rietveld refinement of synchrotron powder diffraction data (cell parameters: $a = 5.19956(12)$ Å and $c = 15.24875(5)$ Å)

Atom	Site	x	y	z	Uiso	Occ.
Sr1	2b	0	0	0	0.01217(9)	1
Sr2	2a	0	0	0.25	0.0098(8)	0.090(1)
Al1	8h	0.33333	0.66667	0.1417(1)	0.00621(12)	0.545(1)*
Si1	8h	0.33333	0.66667	0.1417(1)	0.00621(12)	0.455(1)*
O1	4c	0.33333	0.66667	0.25	0.0159(4)	1
O2	12k	0.4020(1)	0	0.10149(1)	0.0107(3)	1

*: the Al/Si ratio was constrained using: (i) $\text{occ}(\text{Al}) = 0.5 + \text{occ}(\text{Sr2})/2$ for compensating the positive charge induced by Sr2 and (ii) $\text{occ}(\text{Al}) + \text{occ}(\text{Si}) = 1$ (full site occupancy).

Sr1-O (Å)		Sr2-O (Å)		Al/Si-O (Å)	
Sr1-O2 (x6)	3.4730(8)	Sr2-O1 (x6)	3.0022	Al/Si-O1	1.6517(4)
Sr1-O2 (x6)	2.6000(8)	Sr2-O2 (x6)	3.0827(8)	Al/Si-O2 (x3)	1.7001(4)

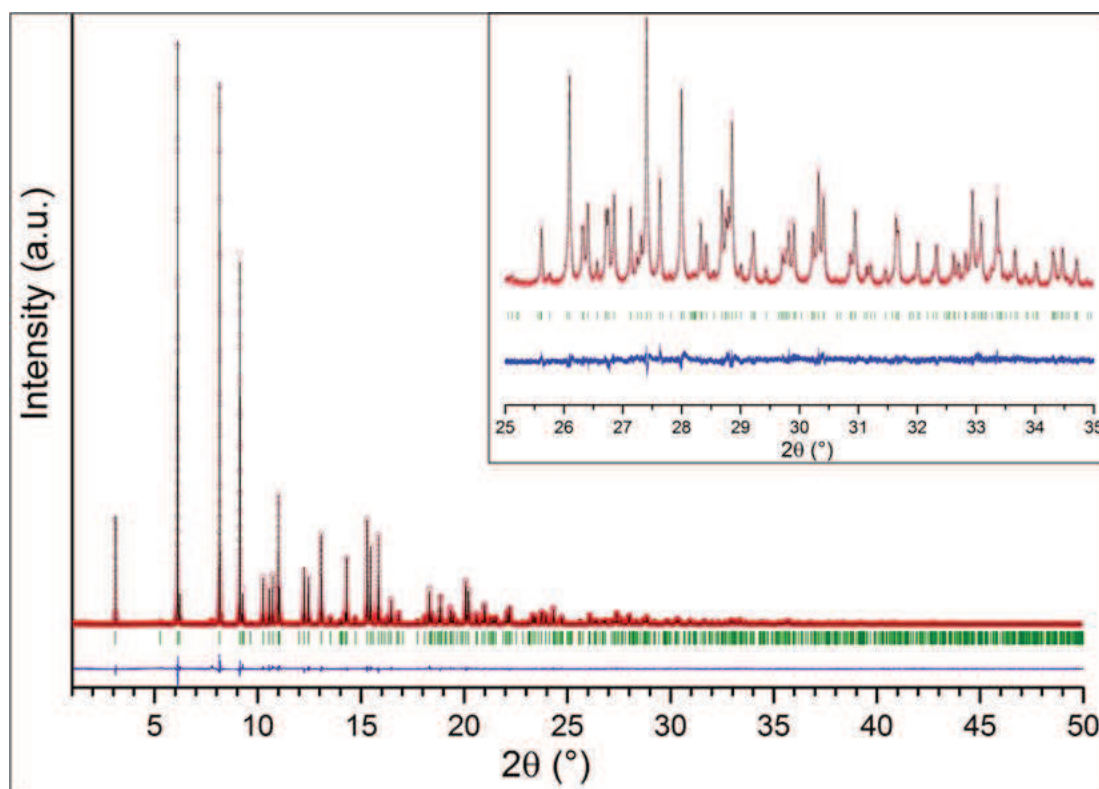


Figure S6. Rietveld refinement of the $\text{Sr}_{1.15}\text{Al}_{2.3}\text{Si}_{1.7}\text{O}_8$ ($x = 0.3$) synchrotron powder diffraction data collected at room temperature ($R_{wp} = 7.46\%$, $R_p = 5.65\%$, and $G.O.F = 1.65$). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines corresponds to the reflection positions. Enlargement of the 25 - 35° angular range (2θ) is embedded.

Table S6. Atomic positions and selected inter-atomic distances of $Sr_{1.15}Al_{2.3}Si_{1.7}O_8$ ($x = 0.3$) obtained from room temperature Rietveld refinement of synchrotron powder diffraction data (cell parameters: $a = 5.200894(6)$ Å and $c = 15.26844(3)$ Å)

Atom	Site	x	y	z	Uiso	Occ.
Sr1	2b	0	0	0	0.01192(6)	1
Sr2	2a	0	0	0.25	0.0193(4)	0.143(1)
Al1	8h	0.33333	0.66667	0.1416(1)	0.00620(8)	0.571(1)*
Si1	8h	0.33333	0.66667	0.1416(1)	0.00620(8)	0.429(1)*
O1	4c	0.33333	0.66667	0.25	0.0172(3)	1
O2	12k	0.3996(1)	0	0.1017(1)	0.0120(2)	1

*: the Al/Si ratio was constrained using: (i) $occ(Al)=0.5+occ(Sr2)/2$ for compensating the positive charge induced by Sr2 and (ii) $occ(Al) + occ(Si) = 1$ (full site occupancy).

Sr1-O (Å)		Sr2-O (Å)		Al/Si-O (Å)	
Sr1-O2 (x6)	3.4878(6)	Sr2-O1 (x6)	3.0027	Al/Si-O1	1.6517(3)
Sr1-O2 (x6)	2.5946(6)	Sr2-O2 (x6)	3.0729(6)	Al/Si-O2 (x3)	1.7023(3)

Table S7. Structural parameters of the different geometry-optimized model structures with $x = 0$ ($\text{SrAl}_2\text{Si}_2\text{O}_8$). The space group, the total energy relative to that of the lowest energy structure, the types and relative amounts of Si and Al environment and the corresponding Si-O and Al-O average bond length are reported

2x2x1 supercell model	Space group	Energy (eV)	Sites	Local environment	Proporti on (%)	Average bond length
Model 1	C2	+0.96	Q_4^4	$\text{Si}(\text{OAl})_4$	62.5	Si-O: 1.627
			Q_3^4	$\text{Si}(\text{OAl})_3(\text{OSi})$	25	Si-O: 1.630
			Q_2^4	$\text{Si}(\text{OAl})_2(\text{OSi})_2$	12.5	Si-O: 1.631
			q_0^4	$\text{Al}(\text{OSi})_4$	62.5	Al-O: 1.750
			q_1^4	$\text{Al}(\text{OSi})_3(\text{OAl})$	25	Al-O: 1.747
			q_2^4	$\text{Al}(\text{OSi})_2(\text{OAl})_2$	12.5	Al-O: 1.748
Model 2	P1	+1.05	Q_4^4	$\text{Si}(\text{OAl})_4$	75	Si-O: 1.628
			Q_3^4	$\text{Si}(\text{OAl})_3(\text{OSi})$	18.75	Si-O: 1.629
			Q_3^4	$\text{Si}(\text{OAl})(\text{OSi})_3$	6.25	Si-O: 1.632
			q_0^4	$\text{Al}(\text{OSi})_4$	75	Al-O: 1.749
			q_1^4	$\text{Al}(\text{OSi})_3(\text{OAl})$	18.75	Al-O: 1.751
			q_3^4	$\text{Al}(\text{OSi})(\text{OAl})_3$	6.25	Al-O: 1.745
Model 3	P1	+1.56	Q_4^4	$\text{Si}(\text{OAl})_4$	68.75	Si-O: 1.628
			Q_3^4	$\text{Si}(\text{OAl})_3(\text{OSi})$	25	Si-O: 1.629
			Q_4^4	$\text{Si}(\text{OSi})_4$	6.25	Si-O: 1.631
			q_0^4	$\text{Al}(\text{OSi})_4$	68.75	Al-O: 1.749
			q_1^4	$\text{Al}(\text{OSi})_3(\text{OAl})$	25	Al-O: 1.750
			q_4^4	$\text{Al}(\text{OAl})_4$	6.25	Al-O: 1.740
Model 4	P1	+2.00	Q_4^4	$\text{Si}(\text{OAl})_4$	50	Si-O: 1.628
			Q_3^4	$\text{Si}(\text{OAl})_3(\text{OSi})$	25	Si-O: 1.633

			Q^4_2	$Si(OAl)_2(OSi)_2$	25	Si-O: 1.631
			q^4_0	$Al(OSi)_4$	50	Al-O: 1.750
			q^4_1	$Al(OSi)_3(OAl)$	25	Al-O: 1.745
			q^4_2	$Al(OSi)_2(OAl)_2$	25	Al-O: 1.748
Model 5	P-3C1	0	Q^4_4	$Si(OAl)_4$	100	Si-O: 1.628
			q^4_0	$Al(OSi)_4$	100	Al-O: 1.750

Table S8. Structural parameters of the different geometry-optimized model structures with $x = 0.25$ ($\text{Sr}_{1.125}\text{Al}_{2.25}\text{Si}_{1.75}\text{O}_8$). The space group, the total energy relative to that of the lowest energy structure, the types and relative amounts of Si and Al environment and the corresponding Si-O and Al-O average bond length are reported

2x2x1 supercell model	Space group	Energy (eV)	Sites	Local environment	Proportion (%)	Average bond length
Model 1	P1	+0.99	Q_4^4	$\text{Si}(\text{OAl})_4$	71.45	Si-O: 1.629
			Q_3^4	$\text{Si}(\text{OAl})_3(\text{OSi})$	21.45	Si-O: 1.632
			Q_1^4	$\text{Si}(\text{OAl})(\text{OSi})_3$	7.1	Si-O: 1.634
			q_0^4	$\text{Al}(\text{OSi})_4$	33.3	Al-O: 1.752
			q_1^4	$\text{Al}(\text{OSi})_3(\text{OAl})$	38.9	Al-O: 1.750
			q_2^4	$\text{Al}(\text{OSi})_2(\text{OAl})_2$	11.1	Al-O: 1.756
			q_3^4	$\text{Al}(\text{OSi})(\text{OAl})_3$	5.6	Al-O: 1.742
			q_4^4	$\text{Al}(\text{OAl})_4$	11.1	Al-O: 1.754
Model 2	C2	+0.01	Q_4^4	$\text{Si}(\text{OAl})_4$	100.0	Si-O: 1.629
			q_0^4	$\text{Al}(\text{OSi})_4$	55.6	Al-O: 1.751
			q_1^4	$\text{Al}(\text{OSi})_3(\text{OAl})$	22.2	Al-O: 1.754
			q_2^4	$\text{Al}(\text{OSi})_2(\text{OAl})_2$	11.1	Al-O: 1.757
			q_4^4	$\text{Al}(\text{OAl})_4$	11.1	Al-O: 1.754
Model 3	P1	+1.12	Q_4^4	$\text{Si}(\text{OAl})_4$	57.1	Si-O: 1.630
			Q_3^4	$\text{Si}(\text{OAl})_3(\text{OSi})$	28.6	Si-O: 1.630
			Q_2^4	$\text{Si}(\text{OAl})_2(\text{OSi})_2$	14.3	Si-O: 1.631
			q_0^4	$\text{Al}(\text{OSi})_4$	22.2	Al-O: 1.753
			q_1^4	$\text{Al}(\text{OSi})_3(\text{OAl})$	44.5	Al-O: 1.751
			q_2^4	$\text{Al}(\text{OSi})_2(\text{OAl})_2$	22.2	Al-O: 1.750
			q_4^4	$\text{Al}(\text{OAl})_4$	11.1	Al-O: 1.750
Model 4	P1	+1.88	Q_4^4	$\text{Si}(\text{OAl})_4$	28.6	Si-O: 1.626
			Q_3^4	$\text{Si}(\text{OAl})_3(\text{OSi})$	50.0	Si-O: 1.632
			Q_2^4	$\text{Si}(\text{OAl})_2(\text{OSi})_2$	14.3	Si-O: 1.635

			Q^4_1	Si(OAl)(OSi) ₃	7.1	Si-O: 1.632
			q^4_0	Al(OSi) ₄	22.2	Al-O: 1.750
			q^4_1	Al(OSi) ₃ (OAl)	16.7	Al-O: 1.746
			q^4_2	Al(OSi) ₂ (OAl) ₂	33.3	Al-O: 1.754
			q^4_3	Al(OSi)(OAl) ₃	27.8	Al-O: 1.750
Model 5	C2	0	Q^4_4	Si(OAl) ₄	100.0	Si-O: 1.629
			q^4_0	Al(OSi) ₄	44.45	Al-O: 1.749
			q^4_1	Al(OSi) ₃ (OAl)	44.45	Al-O: 1.755
			q^4_4	Al(OAl) ₄	11.1	Al-O: 1.753

Atom	Core states	r_{loc} (a.u.)	r_{nonloc} (a.u.)	r_{aug} (a.u.)	Pseudopotential projectors
O	1s	1.3	1.3	0.9	2x2s, 2x2p
Si	1s, 2s, 2p	1.8	1.8	1.3	2x3s, 2x3p
Al	1s, 2s, 2p	2.0	2.0	1.4	2x3s, 2x3p
Sr	1s, 2s, 2p, 3s, 3d, 3d	2.0	2.0	1.2	4s, 4p, 5s

The corresponding Materials Studio Castep “on-the-fly” strings used to generate these potentials are:

O 2|1.3|16.537|18.375|20.212|20UU:21UU (qc=7.5) []

Si 2|2|3.675|5.512|7.717|30UU:31UU:32LGG []

Al 2|1.8|3.675|5.512|7.35|30UU:31UU:32LGG []

Sr 3|2|2|1.2|7.4|9.2|11|40U:50U:41UU:42UU []

Table S9. Description of pseudopotentials used for planewave DFT calculations. r_{loc} is the pseudisation radius for the local component of the pseudopotential, r_{nonloc} is the pseudisation radius for the non-local components of the pseudopotential, and r_{aug} is the pseudisation radius for the charge augmentation functions

Résumé de thèse en Français

Introduction Générale

Ce manuscrit représente la synthèse du travail effectué pendant trois ans sur l'élaboration et la caractérisation de céramiques polycristallines transparentes obtenues par cristallisation complète et congruente du verre.

L'intérêt des céramiques polycristallines transparentes réside dans leur capacité à remplacer les monocristaux dans des domaines tels que l'optique, les armures transparentes, l'électronique et les scintillateurs.¹⁻³ Les céramiques polycristallines sont intéressantes en raison d'un large domaine de composition chimique accessible, de leur souplesse de mise en forme, de taux de dopage élevés et de la possibilité d'une production en grande quantité, ces différentes caractéristiques n'étant pas envisageables pour les monocristaux.⁴⁻⁷ La transparence dans ces matériaux polycristallins avancés est assurée soit par une isotropie optique (cas de la symétrie cubique), soit par une très petite taille de cristallites^{2, 4} (beaucoup plus petite que la longueur d'onde de la lumière incidente telle que décrite par la théorie de la diffusion de particules de Rayleigh-Ganz⁸) et l'absence de sites de diffusion de la lumière (pores, phase secondaire ...).⁴ Plusieurs matériaux ont été développés, tels que le spinelle cubique MgAl_2O_4 utilisé dans des applications d'armure transparente⁹, les céramiques sesquioxides¹⁰ et Nd:YAG pour application laser^{7, 11}, les céramiques ZrO_2 et Lu_3NbO_7 pour lentilles optiques et l'alumine rhomboédrique nanométrique.^{12, 13} Il existe différentes méthodes de synthèse, par pression à chaud, sous vide, par micro-ondes ou frittage par SPS de précurseurs nanométriques. Cependant, tous ces procédés nécessitent des conditions de frittage complexes, et il reste difficile d'éliminer complètement la présence de pores résiduels qui atténuent fortement la transparence.⁵

La cristallisation complète et congruente d'un verre massif, conduisant à des matériaux polycristallins denses, est une alternative prometteuse qui permettrait de surmonter les inconvénients du monocristal et de matériaux céramiques frittés.

Sur la base de cette approche de cristallisation complète du verre, une étude précédente réalisée par S. Alahrache au laboratoire CEMHTI avait porté sur la synthèse de céramiques polycristallines transparentes de BaAl_4O_7 .¹⁴⁻¹⁷ Ces nouvelles céramiques peuvent exister sous la forme de deux polymorphes orthorhombiques (α - BaAl_4O_7 et β - BaAl_4O_7).

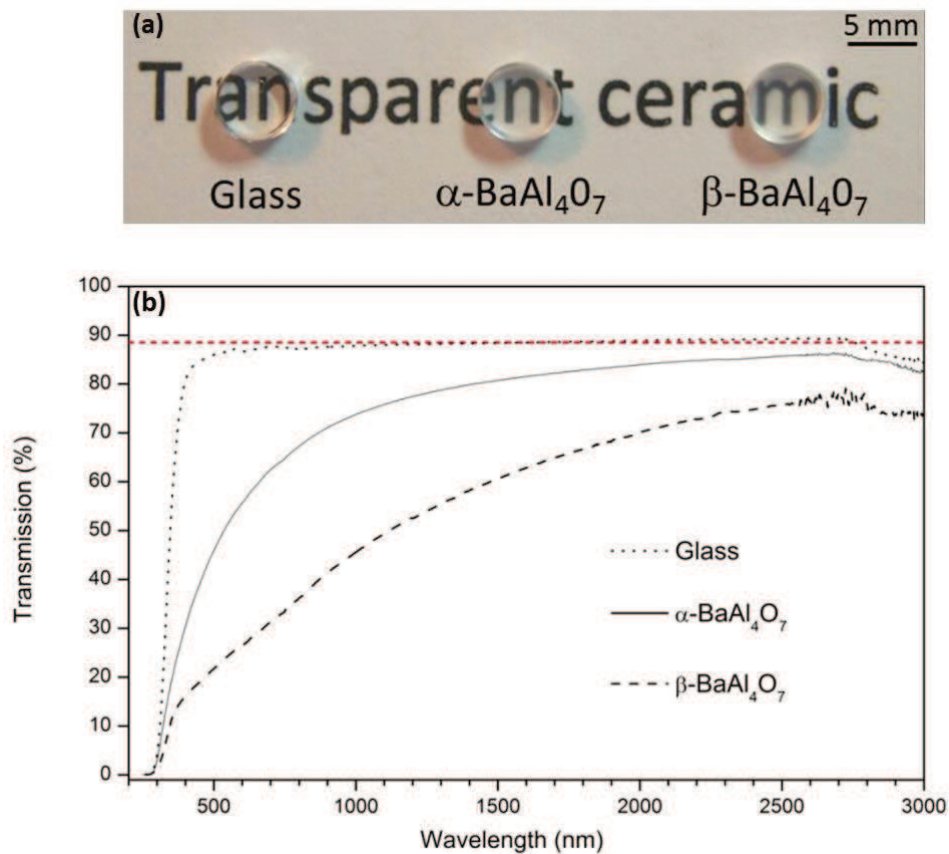


Figure 1 (a) verre $BaAl_4O_7$ et céramiques polycristallines transparentes polymorphe α , et polymorphe β . (b) spectre de transmission des trois échantillons: verre $BaAl_4O_7$, -polymorphe α et polymorphe β

Néanmoins, ces céramiques polycristallines transparentes présentent les limitations suivantes: i) température de fusion élevée du précurseur verre ($\approx 2100^\circ\text{C}$), ii) petites dimensions des échantillons (billes de verre, $\varnothing \approx 3 - 5\text{ mm}$) inhérentes à la méthode de synthèse du verre utilisée iii) transparence limitée ($\approx 60\%$ et 40% de transmission à 633 nm pour les polymorphes α et β respectivement) associée à une faible biréfringence. Par conséquent, deux objectifs principaux ont été identifiés pour notre étude:

- L'élaboration de matériaux céramiques polycristallins avec un maximum de transparence, si possible égale à la transmission maximale théorique. Dans ce but, nous avons cherché des matériaux présentant une isotropie optique.
- La recherche de céramiques polycristallines transparentes pouvant être élaborées à grande échelle.

Ce manuscrit est divisé en quatre chapitres.

Le chapitre I présente un rapport bibliographique sur la cristallisation complète du verre, ses avantages par rapport à d'autres techniques de frittage classiques pour la préparation des céramiques polycristallines transparentes. Un bref aperçu de la technologie vitrocéramique/céramique transparentes et des dernières avancées dans ce domaine sont également présentés.

Dans le chapitre II, nous décrivons les différentes méthodes de synthèse utilisées pour l'élaboration des précurseurs de verre dans ce travail (lévitation aérodynamique et fusion /trempe classique), puis les différentes techniques de caractérisation complémentaires de nos matériaux. Il s'agit notamment de la caractérisation de la microstructure (microscopie électronique à balayage (MEB), microscopie électronique en transmission (MET)), de la caractérisation de l'ordre à longue distance (diffraction sur poudre des rayons X, synchrotron et neutrons) qui donne des informations sur la périodicité et la structure moyenne de nos matériaux, de l'étude de l'ordre local (spectroscopie de Résonance Magnétique Nucléaire (RMN)), de calculs par DFT (density functional theory), ainsi que de mesures de transmission, de luminescence, thermiques et mécaniques.

Dans le chapitre III, l'élaboration de la céramique polycristalline transparente $\text{Sr}_3\text{Al}_2\text{O}_6$ et de son analogue $\text{Sr}_3\text{Ga}_2\text{O}_6$ est présentée. Le but de ce travail est d'élaborer des céramiques polycristallines avec une symétrie cubique (isotropie optique) afin d'atteindre un niveau de transparence plus élevé pour des propriétés photoniques améliorées. Ce résultat correspond au premier objectif de la thèse suite à l'obtention de la céramique polycristalline transparente BaAl_4O_7 , pour laquelle la biréfringence résultant de l'anisotropie optique (symétrie orthorhombique) a abouti à une perte de transmission par diffusion aux joints de grains. La synthèse de ces matériaux est décrite, suivie par la caractérisation de leur microstructure et de leurs propriétés mécaniques, thermiques et optiques.

Dans le chapitre IV, une étude sur le système $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 2$) est effectuée. Ce système se divise en trois solutions solides. En ce qui concerne la première ($0,8 \leq x \leq 2$) et la seconde ($0,5 \leq x \leq 0,68$), des céramiques polycristallines transparentes peuvent être élaborées. La résolution structurale de ces nouvelles phases cristallisées est réalisée sur la base des données de diffraction sur poudre (synchrotron et neutrons). Mais c'est la troisième solution solide $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0,4$) qui semble être la plus intéressante en termes d'échantillons de grande dimension et de niveau de transparence remarquable pour les céramiques polycristallines élaborées. Le protocole de synthèse de ces céramiques polycristallines transparentes ainsi que tous les problèmes rencontrés (et comment ils sont

surmontés) sont discutés en détails. L'évolution structurale de la solution solide est étudiée sur la base d'affinements Rietveld (synchrotron et neutrons). La microstructure (taille des cristaux, porosité, joints de grains) de ces céramiques polycristallines transparentes est déterminée par MEB, MET haute résolution et STEM. L'ordre Al/Si dans ces matériaux est étudié et quantifié à l'état local sur toute la solution solide en utilisant la spectroscopie de résonance magnétique nucléaire. Des calculs DFT sont effectués pour deux compositions de la solution solide. Les informations complémentaires fournies par les différentes études sont utilisées pour expliquer la transparence observée dans nos matériaux céramiques polycristallins.

A la fin de ce manuscrit, nous présentons une conclusion générale de ce travail sur la base des résultats obtenus en utilisant l'approche cristallisation complète du verre de même composition. Ces résultats servent de base pour proposer une nouvelle méthode de synthèse pour l'élaboration des céramiques polycristallines transparentes, ouvrant ainsi la voie au développement des céramiques polycristallines transparentes.

Chapitre I La cristallisation du verre: état de l'art

I.1 Cristallisation du verre

Céramiques et vitrocéramiques sont des matériaux élaborés par cristallisation complète ou partielle d'un verre respectivement. La nature et la microstructure de la phase cristalline influence directement les propriétés spécifiques de ces matériaux (thermique, mécanique, électrique, biologique, photonique ...). Par conséquent, la maîtrise du phénomène de cristallisation conduit à l'élaboration de matériaux céramiques et vitrocéramiques ayant diverses propriétés et par conséquent une large gamme d'applications techniques. Cette maîtrise est obtenue par le contrôle de la composition chimique initiale du verre, de la nature de la phase cristalline et de sa microstructure (taille des cristaux, morphologie) pendant la cristallisation.

La cristallisation s'effectue en deux étapes: nucléation et croissance cristalline. Les deux étapes peuvent avoir lieu séparément, mais un chevauchement de ces deux étapes peut également se produire. Il existe deux types de nucléation, la nucléation homogène (développement spontané de la phase cristallisée) et la nucléation hétérogène (initiée par des sites de nucléation spécifiques telles que des bulles, des impuretés, des défauts de surface ou des interfaces). Comme la nucléation hétérogène est beaucoup plus fréquente que la nucléation homogène, des agents de nucléation, généralement des éléments métalliques (Au, Ag, Pt, Pd) ou certains oxydes (ZrO_2 , TiO_2 , P_2O_5 , CeO_2 , ZnO_2 , etc), peuvent être ajoutés pour initier la nucléation hétérogène au sein du volume.¹⁸⁻²² Leur addition augmente le taux de nucléation et conduit à l'obtention de matériaux ayant les propriétés souhaitées avec un meilleur contrôle.²³⁻²⁵

I.2 Vitrocéramiques transparentes

Les vitrocéramiques sont élaborées par cristallisation contrôlée du verre parent. Elles sont composées de cristaux dispersés dans une matrice de verre, avec un pourcentage en volume de phase cristalline allant généralement de quelques % à plus de 90%. Une vitrocéramique peut être constituée d'une ou de plusieurs phases cristallines et vitreuses. Les cristaux formés peuvent avoir la même composition que le verre parent (cristallisation

congruente), ou une composition différente. Les avantages des vitrocéramiques sur les verres et les céramiques se situent dans le couplage des propriétés du verre et de la céramique. Certaines propriétés souhaitées ne peuvent être obtenues pour le verre ou pour la céramique de manière indépendante, comme la résistance thermique couplée à la transparence (vitrrocéramiques pour ustensiles de cuisine). Un autre avantage important est la grande variété de microstructures possibles des vitrocéramiques. Les phases de verre peuvent avoir des microstructures différentes, et les phases cristallines peuvent également présenter une plus grande variété de microstructures qui influencent les propriétés de la vitrocéramique obtenue. En conséquence, en faisant varier la composition du verre initial et la microstructure des phases cristallines, une grande variété de vitrocéramiques peut être mise au point avec des propriétés et des applications diverses. Les techniques de frittage sont également largement utilisées pour l'élaboration des vitrocéramiques.²⁶⁻³⁰

Pour les vitrocéramiques, leur microstructure constituée de micro- ou nano-cristallites dispersées dans une matrice vitreuse provoque une atténuation de l'intensité lumineuse. Deux modèles existent dans la littérature pour expliquer les deux types de diffusion élastique de la lumière dans les vitrocéramiques selon la taille des cristallites: i) le modèle de Rayleigh³¹ appliqué aux vitrocéramiques avec des cristallites ayant des tailles plus petites que la longueur d'onde de la lumière, ii) le modèle de Mie³² appliqué aux vitrocéramiques pour lesquelles la taille des cristallites est plus grande que la longueur d'onde de lumière. Toutefois, dans le cas des vitrocéramiques transparentes, les cristallites sont habituellement de taille nanométrique et c'est donc le modèle de Rayleigh qui est utilisé.

Sur la base du modèle de Rayleigh, deux conditions doivent être vérifiées pour obtenir une diffusion minimale: i) un indice de réfraction similaire pour la phase amorphe et la phase cristalline conduisant à un milieu " homogène optiquement " (différence de $\approx 0,1$), ii) une taille des cristallites beaucoup plus petite que la longueur d'onde de la lumière (≈ 15 nm).

Malgré les énormes progrès réalisés dans le domaine des vitrocéramiques transparentes et une large gamme d'applications, la cristallisation complète de ces vitrocéramiques représente un défi majeur. Dans les vitrocéramiques, la transparence peut être obtenue que par une cristallisation partielle et la formation de cristallites nanométriques (taille des cristallites beaucoup plus petite que la longueur d'onde de la lumière incidente, tel que décrit par la théorie de la diffusion de particules de Rayleigh-Ganz³³) et/ou une différence négligeable d'indice de réfraction entre les cristallites et la matrice vitreuse.³⁴ Pour surmonter ces obstacles, la cristallisation complète du verre semble être une approche intéressante.

I.3 Technologie "céramique transparente "

Avec la demande croissante de matériaux pour des applications photoniques, tels que les lasers de haute énergie, les scintillateurs, les lentilles optiques et les armures transparentes et le souhait de remplacer les monocristaux très coûteux, la technologie des céramiques polycristallines transparentes a vu le jour.

Les monocristaux, avec leur structure cristalline continue (absence de joints de grains et de défauts), présentent des propriétés uniques pour des applications dans des domaines de haute technologie en particulier de l'optique et de l'électronique.^{35, 36} Les monocristaux requis pour des applications de haute technologie nécessitent souvent des conditions extrêmes d'élaboration (haute température...), ce qui constitue un défi économique, parallèlement à d'autres inconvénients, dont le niveau de dopage restreint, une faible flexibilité de mise en forme et surtout un domaine limité de compositions chimiques pour ces monocristaux.³⁷ Au contraire, les céramiques polycristallines transparentes offrent plusieurs avantages comme la large gamme de compositions accessibles, les taux de dopage homogènes et élevés, la facilité de mise en forme et le coût réduit par rapport aux monocristaux.

I.3.1 Conditions de transparence dans les céramiques polycristallines

Les céramiques polycristallines transparentes présentent des centres de diffusion qui provoquent une perte significative de la transmission maximale théorique (T_{th}).

$$T_{th} = \frac{1 - R}{1 + R}$$

$$\text{Avec } R = \frac{(n-1)^2}{(n+1)^2}$$

$$T_{th} = \frac{2n}{n^2+1}$$

R représente la réflexion de la lumière (sur les faces d'entrée et de sortie du matériau) et n l'indice de réfraction.^{38, 39}

Pour les céramiques polycristallines transparentes, ces centres de diffusion sont constitués par les joints de grains, les pores résiduels, les phases secondaires, la double réfraction, les inclusions et la rugosité de surface. Ces centres de diffusion sont illustrés sur la Figure 2 donnée par Ikesue *et al.*³⁷

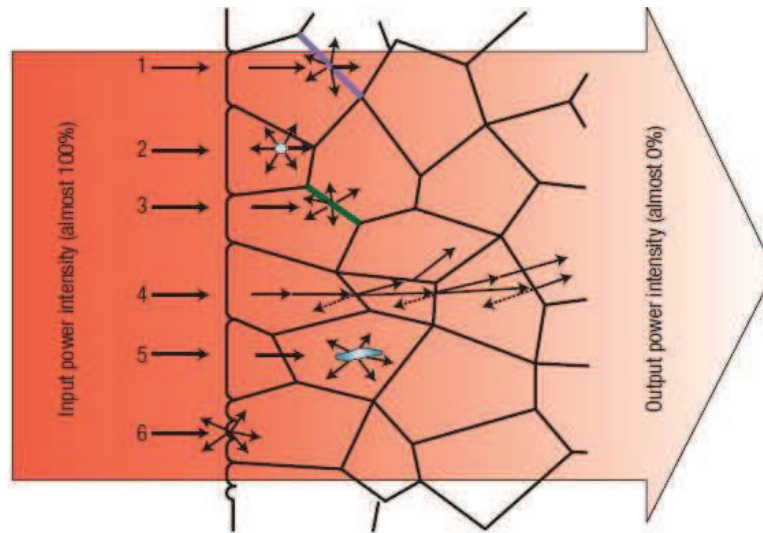


Figure 2 Représentation schématique des différents centres de diffusion de la microstructure conventionnelle d'une céramique transparente. Forte diffusion due à (1) un joint de grain, (2) les pores résiduels, (3) la phase secondaire, (4) la double réfraction, (5) les inclusions et (6) la rugosité de surface de la céramique (Ikesue et al.³⁷)

Pour une céramique polycristalline transparente cubique (isotrope optiquement), les sources de diffusion sont présentées p

ar les joints de grains, les phases secondaires et les pores résiduels essentiellement.

En ce qui concerne les céramiques polycristallines transparentes non-cubiques (anisotropes optiquement), la diffusion est provoquée par la biréfringence au niveau des joints de grains et la diffusion au niveau des pores résiduels et des phases secondaires. L'indice de réfraction du matériau devient très dépendant des axes cristallographiques, d'où un changement de direction du rayon lumineux au niveau de chaque joint de grain entre deux cristallites.

Pour l'élaboration des céramiques polycristallines transparentes, la stratégie classique réside dans l'élimination de toutes les sources de diffusion de la lumière, les pores résiduels, les phases secondaires aux joints de grains, la biréfringence (pour les matériaux non-cubiques) et les tailles de cristallites trop grandes.

I.3.2 Techniques de frittage des céramiques polycristallines transparentes

Le frittage est un procédé de conversion d'une poudre en un solide très dense, sous pression et température relativement élevées. Cette technique est souvent adoptée en raison du

point de fusion élevé de la matière première. Elle a été largement utilisée par les céramistes pour développer des céramiques polycristallines transparentes avec une porosité résiduelle la plus faible possible^{40, 41} Des approches diverses de frittage, soit par pression à chaud, sous vide, micro-ondes ou frittage par SPS de précurseurs nanométriques peuvent être utilisées. Cependant, ces techniques de frittage nécessitent des conditions de frittage complexes et coûteuses (haute pression et température) en plus de précurseurs nanométriques spécifiques pour lesquels la distribution de taille des particules peut avoir des effets importants sur le frittage.⁴²⁻⁴⁴ Les pores résiduels, une source importante de diffusion de la lumière, sont également très difficiles à éviter.⁵ Ces techniques exigent un contrôle précis des taux de frittage et de l'atmosphère de frittage qui peuvent avoir un effet énorme sur la densification du matériau.^{5, 45, 46} Pour la technique SPS, un inconvénient majeur est le risque de contamination par le carbone et de ségrégation (provoqué par l'utilisation de la matrice en graphite) qui peut dégrader les propriétés optiques des matériaux.⁴⁷ Ces inconvénients des techniques de frittage ont limité le nombre de céramiques polycristallines transparentes produites.⁵

I.3.3 La cristallisation complète du verre

La cristallisation complète du verre est une voie de synthèse innovante ouvrant la voie à l'élaboration de céramiques polycristallines transparentes denses. Elle consiste à élaborer le verre puis à le cristalliser totalement par un traitement thermique adapté. Si l'on utilise cette méthode, deux difficultés doivent être surmontées: (i) la synthèse d'un verre de même composition que la céramique visée (pour assurer la cristallisation congruente) et (ii) le maintien de la transparence au cours de la cristallisation.

En 2012, Allix et al.^{16, 17, 48} ont rapporté la synthèse des nouvelles céramiques polycristallines transparentes de BaAl_4O_7 synthétisées par cristallisation à partir d'un verre de même composition (Figure 3a). L'originalité de cette approche réside dans le traitement thermique relativement simple du verre pour obtenir des céramiques polycristallines transparentes sans nécessité de haute pression, ni de techniques de frittage complexes et coûteuses. Ces céramiques peuvent exister sous deux formes (polymorphes orthorhombiques). Même si elles présentent des cristaux de taille micrométrique et une anisotropie optique (biréfringence), leur transparence élevée est associée à l'absence totale de porosité, des joints de grains très fins et une faible biréfringence ($\sim 0,01$ obtenue à partir de calculs DFT). Le polymorphe α semble également être plus transparent que le polymorphe β en raison de

cristaux plus petits (0,5 - 2 μm pour le polymorphe α et 1-5 μm pour le polymorphe β) observés sur la Figure 3b-c.

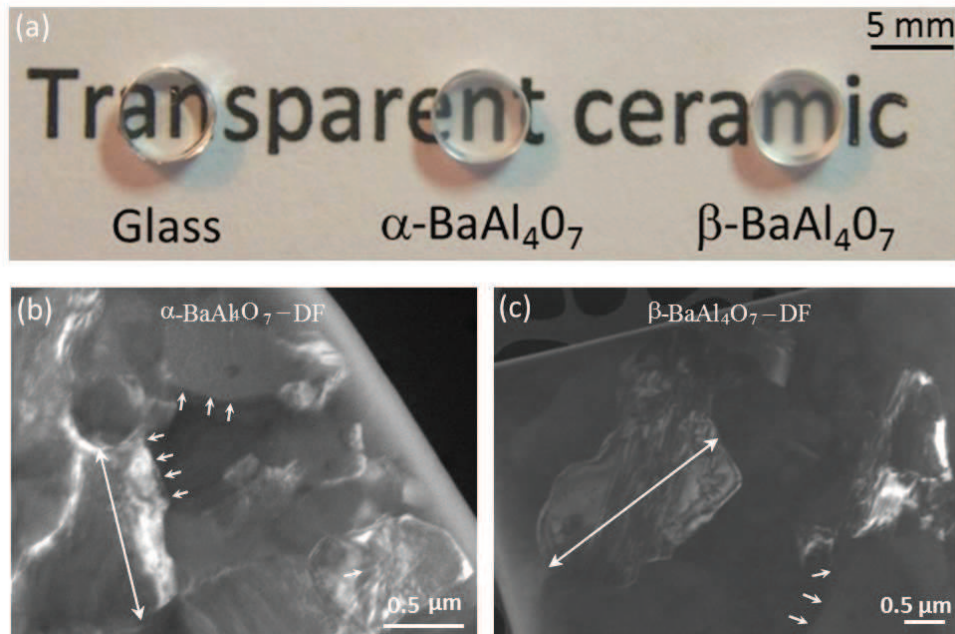


Figure 3 Céramiques polycristallines transparentes élaborées par cristallisation complète du verre: (a) de gauche à droite, BaAl_4O_7 verre et céramiques transparentes (polymorphes α et β respectivement). (b) et (c) micrographies en champ sombre des polymorphes α et β respectivement¹⁶

I.3.4 D'autres améliorations nécessaires

Malgré tous les avancements dans le domaine de la céramique polycristalline transparente, d'autres recherches sont encore nécessaires en raison de la demande croissante de céramiques transparentes pour différentes applications telles que lentilles optiques, armure transparente, scintillateurs et lasers. Les nombreux avantages (échantillons de grande taille, large gamme de compositions, flexibilité de mise en forme et taux de dopage élevés) offerts par la cristallisation complète du verre par rapport aux monocristaux et aux techniques de frittage font de cette approche une voie très prometteuse pour l'élaboration des céramiques polycristallines transparentes pour des applications photoniques.

Les céramiques BaAl_4O_7 présentent une faible biréfringence qui élimine leur niveau de transparence. Une autre limitation de cette composition est sa température de fusion élevée (2000 - 2200 $^{\circ}\text{C}$), ce qui nécessite l'utilisation d'un système de fusion particulier qui limite l'application à grande échelle du matériau. Un niveau plus élevé de transparence est fortement souhaitable pour des applications optiques et photoniques. A cet effet, la synthèse d'un

matériau présentant des propriétés optiques parfaitement isotropes (symétrie cubique) conduire à une transparence plus élevée, avec pour objectif a transmission théorique maximale. En outre, des céramiques transparentes qui pourraient être préparés à grande échelle par cette approche verrière relativement simple et peu coûteuse devraient être très intéressantes.

Les objectifs principaux de cette étude sont donc premièrement la synthèse de céramiques polycristallines transparentes isotropes optiquement pour une transparence améliorée, et deuxièmement d'élaborer des céramiques polycristallines transparentes de grandes dimensions par cristallisation complète du verre de même composition.

Chapitre II Méthodes et techniques **expérimentales**

Dans ce chapitre, nous présentons les différentes techniques expérimentales utilisées dans le cadre de nos travaux. Il s'agit principalement des procédures de synthèse des verres et des céramiques polycristallines, de leur caractérisation structurale à différentes échelles (moyenne et locale), par microscopie électronique (MEB et MET), diffraction sur poudre de rayons X, synchrotron et neutrons et spectroscopie de résonance magnétique nucléaire (RMN), de calculs DFT, et de techniques utilisées pour la caractérisation des propriétés physiques (transmission optique, luminescence et propriétés thermiques et mécaniques).

II.1 Synthèse des céramiques polycristallines transparentes

II.1.1 Synthèse du verre

L'élaboration de céramiques polycristallines transparentes commence par la synthèse du verre. Dans cette thèse, deux techniques d'élaboration du verre différentes ont été utilisées: le procédé classique de fusion/trempe réalisé dans un four électrique commercial ($T_{\text{max}} = 1750\text{ }^{\circ}\text{C}$) et la lévitation aérodynamique couplée à un système de chauffage laser ($T_{\text{max}} = 3000\text{ }^{\circ}\text{C}$, vitesse de refroidissement = $300\text{ }^{\circ}\text{C/s}$). Le choix entre ces deux techniques dépend de deux critères distincts: la température de fusion du mélange d'oxydes et la vitesse de refroidissement nécessaire pour éviter une cristallisation incontrôlée.

II.1.2 Cristallisation du verre

Après la synthèse du verre, un traitement thermique est nécessaire pour faire cristalliser le verre. Le choix des paramètres de traitement thermique dépend essentiellement de l'information (températures de transition vitreuse et de cristallisation) obtenue par calorimétrie à balayage différentiel (DSC).

II.2 Caractérisation de la microstructure

II.2.1 La microscopie électronique à balayage (MEB)

La microscopie électronique à balayage couplée à la spectroscopie X à dispersion d'énergie est utilisée pour obtenir des informations sur la morphologie de surface des échantillons, l'homogénéité chimique, la composition chimique qualitative et quantitative à l'échelle du micromètre à travers les signaux obtenus en utilisant les électrons secondaires, les électrons rétrodiffusés et les rayons X. Dans le cadre de notre travail, la microscopie électronique à balayage a été utilisée principalement pour la caractérisation de la microstructure cristalline en mosaïque de nos céramiques polycristallines transparentes et l'étude de l'orientation des cristallites.

II.2.2 La microscopie électronique en transmission (MET)

La microscopie électronique en transmission à travers trois modes de fonctionnement différents (imagerie, diffraction et spectroscopie d'analyse dispersive en énergie(EDS)) donne des informations sur la structure cristalline et la composition chimique du matériau étudié. La MET a été utilisée dans cette étude pour examiner la microstructure des céramiques polycristallines transparentes (joints de grains, porosité et taille des cristaux). Elle a également été utilisée dans la détermination de la structure des nouvelles phases d'aluminosilicate de strontium dans le chapitre IV (via le mode de diffraction d'électrons) et pour l'analyse de la composition chimique (via le mode EDS).

II.3 Caractérisation structurale

II.3.1 Diffraction sur poudre

La diffraction sur poudre est une technique clé pour obtenir des informations sur la structure moyenne. La diffraction sur poudre peut être réalisée par des techniques diverses : rayons X de laboratoire, synchrotron et neutrons.

La diffraction par rayonnement synchrotron a été utilisée pour obtenir une résolution plus élevée que celle d'un spectromètre de RX de laboratoire.

La diffraction des neutrons fournit une information complémentaire de celle accessible par diffraction sur poudre des rayons X. Ses avantages sont les intensités importantes

obtenues à des angles de diffraction élevés et l'indépendance de l'intensité de la diffraction des neutrons par rapport au numéro atomique Z des éléments (intérêt pour les éléments légers).

II.3.2 Détermination de la structure et de l'affinement structural à partir de diffraction sur poudre

Les déterminations structurales et les affinements structuraux ont été effectués à partir de données de diffraction sur poudre suivant les méthodes de Le Bail et Rietveld⁴⁹⁻⁵¹ en utilisant un logiciel Jana2006.⁵² La résolution structurale *ab initio* de nouvelles structures cristallines a été réalisée par la méthode de charge flipping^{53, 54} à l'aide du logiciel SUPERFLIP⁵⁵ implémenté dans Jana.

II.3.3 La résonance magnétique nucléaire (RMN)

La spectroscopie de résonance magnétique nucléaire (RMN) à l'état solide est une technique pour sonder l'environnement du noyau. Elle a été utilisée dans notre étude pour fournir des informations sur la structure locale de nos matériaux céramiques.

Différents types d'interactions agissent sur un noyau placé dans un champ magnétique. Celles-ci varient et peuvent apporter des informations sur l'environnement du noyau. Ces informations, une fois extraites, peuvent apporter une meilleure compréhension de la structure moléculaire. Ces interactions comprennent les interactions de déplacement chimique, interaction directe dipôle-dipôle, le couplage dipolaire indirect et l'interaction quadripolaire (pour les noyaux avec un spin $I > 1/2$).

Dans cette thèse deux types de noyaux ont été étudiés par RMN : ^{29}Si ($I = 1/2$) et ^{27}Al ($I = 5/2$). Pour les spectres ^{27}Al MAS-RMN, le premier ordre de l'interaction quadripolaire n'est pas totalement éliminé et le second ordre n'est pas éliminé par l'angle magique. Cependant, d'autres expériences peuvent être appliquées à cette fin, comme l'expérience MQ-MAS (Multiple Quanta Magic Angle-Spinning). Cette technique conduit à un spectre 2D composé d'une dimension horizontale, équivalente au spectre MAS et d'une dimension verticale isotrope mieux résolue, dans laquelle on s'est affranchi de l'effet quadripolaire de second ordre.

Toutes les simulations des spectres RMN ^{29}Si et ^{27}Al ont été effectuées à l'aide du logiciel Dmfit qui permet leur interprétation. Dmfit est un programme développé dans le laboratoire CEMHTI par Dominique Massiot et collègues.⁵⁶

II.3.4 Théorie de la fonctionnelle de la densité (DFT)

La théorie de la fonctionnelle de la densité est considérée comme un outil utilisé pour la modélisation informatique des états quantiques de systèmes multi-électrons afin d'étudier leurs propriétés structurales, magnétiques et électroniques.

Les calculs DFT dans cette étude ont été effectués pour prédire la biréfringence par le calcul des indices de réfraction (suivant les différents axes cristallographiques) de la céramique polycristalline transparente. Des structures périodiques modélisées sont utilisées pour effectuer les calculs DFT des parties imaginaires et réelles de la fonction diélectrique à partir du logiciel CASTEP.^{57, 58} L'indice de réfraction peut donc être déterminé à partir de la relation suivante:

$$n = \left(\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} + \epsilon_1}{2} \right)^{1/2}$$

II.4 Caractérisation des propriétés

Après la caractérisation structurale et microstructurale des céramiques polycristallines transparentes, leurs propriétés optiques (transmission, luminescence et scintillation) et mécaniques ont été également déterminées en utilisant des techniques adaptées qui ont été expliquées en détails dans le manuscrit..

Chapitre III $Sr_3Al_2O_6$ et $Sr_3Ga_2O_6$: de nouvelles céramiques polycristallines transparentes

Dans ce chapitre, nous décrivons l'élaboration et la caractérisation de céramiques polycristallines très transparentes, optiquement isotropes (symétrie cubique). L'isotropie optique résout le problème de l'une des sources de diffusion de la lumière, la biréfringence. Cela rend le contrôle de la taille des cristaux moins crucial pour la transparence.

La synthèse du verre et le procédé de cristallisation congruente de verre sont décrits. La transparence de la céramique polycristalline obtenue est examinée en fonction de sa microstructure (taille des cristaux, joints de grains, porosité et isotropie). Nous avons également mesuré la dureté, le module d'élasticité et le coefficient de dilatation thermique de la céramique polycristalline transparente. D'un point de vue de l'application, les taux de dopages élevés et homogènes offerts par la voie de synthèse employée permettent l'utilisation de différents agents de dopage selon l'application souhaitée. Ainsi, des céramiques avec des dopages différents sont étudiées, montrant des possibilités d'application comme matériaux phosphorescents dans le visible et l'infra-rouge.

III.1 Elaboration du verre et de la céramique polycristalline transparente

Les compositions $Sr_3Al_2O_6$ et $Sr_3Ga_2O_6$ ont été choisies pour trois raisons principales:

- i. Elles se situent dans les domaines de vitrification de $SrO-Al_2O_3$.
- ii. Elles présentent une symétrie cubique (Pa-3, $a=15.85 \text{ \AA}$ pour $Sr_3Al_2O_6$ ⁵⁹ et $a=16.10 \text{ \AA}$ pour $Sr_3Ga_2O_6$ ⁶⁰).
- iii. Les aluminates de strontium sont connus pour leurs propriétés de photoluminescence persistante. $SrAl_2O_4$ co-dopé avec Dy^{3+}/Eu^{2+} préparé par la voie solide montre une luminescence verte très longue (plusieurs heures dans l'obscurité). $Sr_3Al_2O_6: Eu^{3+}$ synthétisé par voie sol-gel assistée par micro-ondes présente une forte luminescence rouge.⁶¹

Les verres $\text{Sr}_3\text{Al}_2\text{O}_6$ et $\text{Sr}_3\text{Ga}_2\text{O}_6$ ont été élaborés en utilisant la lévitation aérodynamique couplée à un dispositif de chauffage de laser. Synthèse sans contact et trempe rapide sont essentielles pour assurer la vitrification des deux compositions.⁶²

Le comportement thermique du verre de $\text{Sr}_3\text{Al}_2\text{O}_6$ a été étudié par DSC (calorimétrie différentielle à balayage). Le thermogramme (Figure 4) montre une transition vitreuse faible à 685(1) °C et un seul pic exothermique intense à 762(1) °C correspondant à la cristallisation de la phase unique $\text{Sr}_3\text{Al}_2\text{O}_6$ cubique (ICSD 71860, PDF 00-024-1187).

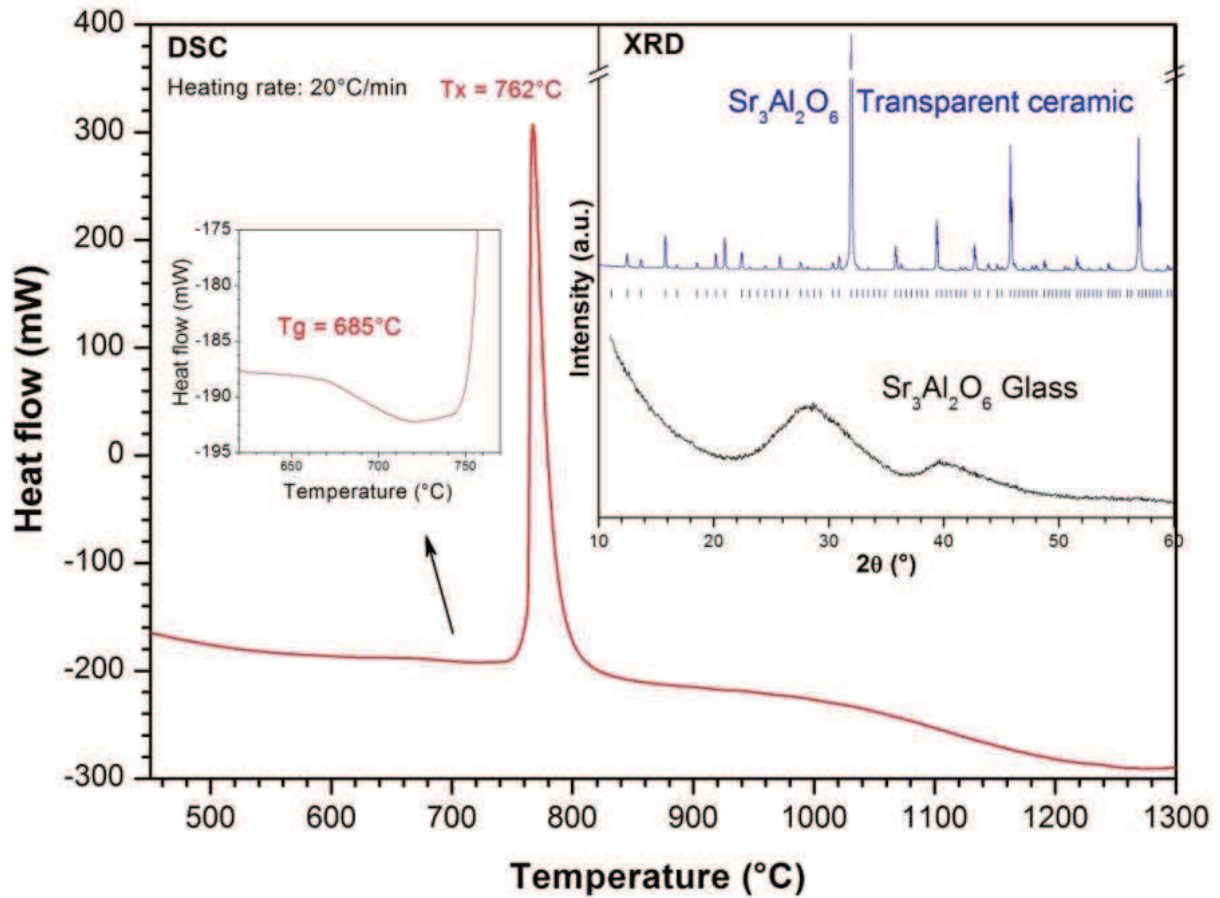


Figure 4 DSC du verre de $\text{Sr}_3\text{Al}_2\text{O}_6$. L'encart montre les diffractogrammes de RX du verre et de la céramique $\text{Sr}_3\text{Al}_2\text{O}_6$ polycristalline transparente obtenus. L'indexation correspond à la structure cubique de $\text{Sr}_3\text{Al}_2\text{O}_6$

De même pour le thermogramme de $Sr_3Ga_2O_6$ (Figure 5), une transition vitreuse à 698(1) °C et un seul pic exothermique à 749 (1) °C correspondant à la cristallisation de la phase cubique de $Sr_3Ga_2O_6$ (ICSD 93803 - PDF 01-070-7937) ont été enregistrés.

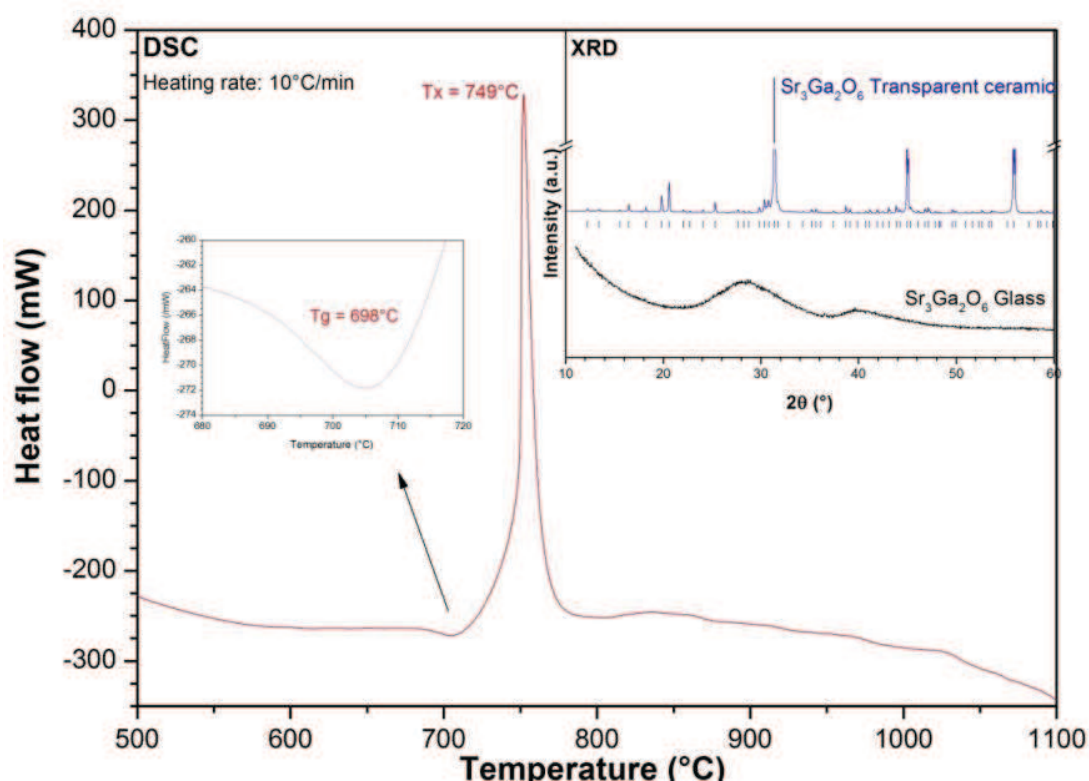


Figure 5 DSC du verre de $Sr_3Ga_2O_6$. L'encart montre les diffractogrammes de RX du verre et de la céramique $Sr_3Ga_2O_6$ polycristalline transparente obtenus. L'indexation correspond à la structure cubique de $Sr_3Ga_2O_6$

A partir de ces paramètres thermiques obtenus par les mesures de DSC, un traitement thermique simple de cristallisation, à 840 °C pendant 5 heures, a été utilisé pour faire cristalliser entièrement le verre de $Sr_3Al_2O_6$ (Figure 6).



Figure 6 Verre de $Sr_3Al_2O_6$ et sa céramique polycristalline transparente correspondante obtenue par un recuit du verre à 840 °C pendant 5 heures

De même, un traitement de cristallisation simple, à 750 °C pendant 2 heures et 30 minutes, a été utilisé pour faire cristalliser entièrement le verre de $Sr_3Ga_2O_6$ (Figure 7).



Figure 7 Verre de $Sr_3Ga_2O_6$ et sa céramique polycristalline transparente correspondante obtenue par un recuit du verre à 750 °C pendant 2 heures et 30 minutes

Cependant le verre et la céramique de gallate sont légèrement hygroscopiques. Une altération de la surface de l'échantillon est observée au bout de quelques heures dans l'atmosphère ambiante. Cette détérioration ne permet pas la conservation de la transparence, ce qui constitue un inconvénient majeur pour des applications commerciales. Cette sensibilité à l'humidité a été rapportée pour plusieurs luminophores d'aluminate alcalino-terreux tels que $SrAl_2O_4:Eu^{2+}, Dy^{3+}$.⁶³ Cependant, différentes méthodes ont été proposées pour protéger ces luminophores de l'humidité tels que des revêtements à l'aide de matières organiques ou inorganiques (fluorure de strontium, nitrures, SiO_2).⁶⁴⁻⁶⁷ Par conséquent l'utilisation de $Sr_3Ga_2O_6$ exigerait une encapsulation ou une passivation.^{63, 68}

III.2 Caractérisation des céramiques polycristallines transparentes

La céramique polycristalline de $Sr_3Al_2O_6$ présente une transparence exceptionnelle comme le montre la Figure 8. Cette transparence couvre une large gamme de longueur d'onde, du visible à l'infrarouge (de 300 nm jusqu'à 6 μm).

L'indice de réfraction moyen de la céramique polycristalline transparente de $Sr_3Al_2O_6$ a été mesuré : 1.70 ± 0.02 . Sur cette base, la transmission maximale théorique a été calculée : $87.4 \pm 0.5 \%$.

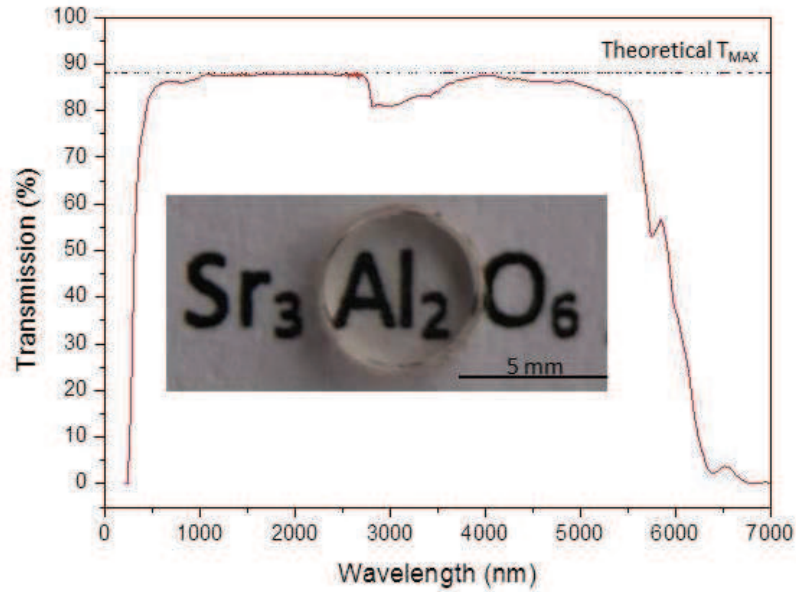


Figure 8 Spectre de transmission de la céramique polycristalline transparente de $Sr_3Al_2O_6$ (échantillon de 1,5 mm d'épaisseur). La ligne pointillée représente la transmission maximale théorique calculée ($87,4 \pm 0,5\%$) pour un indice de réfraction moyen de $1,70 \pm 0,02$. Egalement sur la figure, une photographie de la céramique polycristalline transparente $Sr_3Al_2O_6$

En ce qui concerne la courbe de transmission, on peut remarquer que la différence entre la transmission mesurée et la valeur théorique calculée est très faible, ce qui indique qu'une très faible quantité de centres de diffusion sont présents au sein de la céramique polycristalline transparente de $Sr_3Al_2O_6$.

Afin d'expliquer la transparence exceptionnelle de la céramique polycristalline de $Sr_3Al_2O_6$, la microstructure du matériau a été étudiée. A cet effet, les images de MET ont été enregistrées sur un échantillon préparé par FIB (Figure 9).

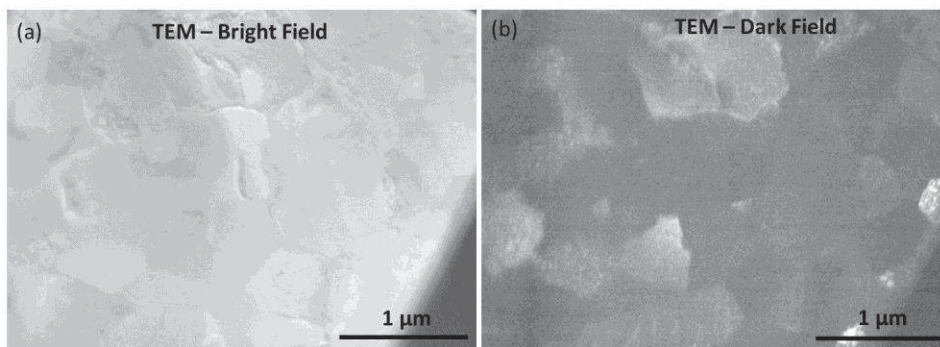


Figure 9 Imagerie en champ clair (a) et champ sombre (b) de la céramique polycristalline transparente $Sr_3Al_2O_6$ en microscopie électronique en transmission

Les images présentent une microstructure en mosaïque très dense avec une granulométrie micrométrique, similaire aux images observées pour des céramiques polycristallines transparentes obtenues par frittage sous une pression élevée.^{7, 69-71} Aucune porosité n'a été détectée et les joints de grains apparaissent très fins, ce qui prouve l'intérêt de la cristallisation à partir de verre plutôt que la réaction à l'état solide / frittage pour obtenir des céramiques polycristallines entièrement denses. La taille moyenne des cristaux est comprise entre 0,5 et 2 μm . A partir de ces observations de la microstructure, il s'avère que la réalisation d'une telle céramique hautement transparente est rendue possible grâce à la combinaison d'une densité élevée (absence de pores) et de joints de grains très fins. Ces excellentes caractéristiques de la microstructure obtenues par cristallisation du verre s'ajoutent à l'isotropie optique (pas de biréfringence) inhérente à la structure cubique de $Sr_3Al_2O_6$.

III.3 Caractérisation des propriétés des céramiques polycristallines transparentes

La dureté et le module d'élasticité réduite ont été mesurés à la fois sur les échantillons de verre et de céramique de $Sr_3Al_2O_6$ par nano-indentation. On a observé une augmentation significative à la fois de la dureté ($H_{\text{glass}} = 7$ et $H_{\text{ceramic}} = 10,5$ GPa), et du module d'élasticité réduite (105 à 150 GPa) pour la céramique.

Les mesures de coefficient de dilatation thermique ont été réalisées à partir des expériences in situ de diffraction des rayons X à haute température. Selon l'équation de Sun *et al.*⁷², tracer $\ln(V-V_0)$ en fonction de $(T-T_0)$ conduit au coefficient volumétrique d'expansion thermique (β_0). Par conséquent, le coefficient linéaire de dilatation thermique peut être calculé, sachant que nous avons une symétrie cubique ($\beta_0/3$). Le coefficient de dilatation thermique volumique obtenu est égal à $28.9(2) \cdot 10^{-6} K^{-1}$, d'où le coefficient de dilatation thermique linéaire égal à $9.6(1) \cdot 10^{-6} K^{-1}$.

D'un point de vue de l'application, les propriétés de luminescence et de scintillation de la céramique polycristalline $Sr_3Al_2O_6$ ont été étudiées en utilisant des dopages différents.

Pour la céramique polycristalline dopée $Sr_3Al_2O_6:Eu^{3+}$, le spectre d'émission présente deux bandes à deux longueurs d'onde, 393 et 272 nm. L'intensité des émissions est sensiblement plus élevée pour une excitation à 272 nm. Les émissions les plus intenses sont observées dans la gamme 580-620 nm et sont à l'origine de la luminescence rouge.

Les céramique polycristallines dopées $Sr_3Al_2O_6:Ho^{3+}$ et $Sr_3Al_2O_6:Er^{3+}$ possèdent à la fois des émissions infrarouges caractéristiques à 1,5 et 1,2 μm respectivement, en plus d'autres émissions dans la gamme visible et proche IR.

Chapitre IV Céramiques polycristallines **transparentes $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ de grandes** **dimensions**

Pour la préparation d'échantillons de grandes dimensions, un agent de vitrification doit être ajouté dans les compositions nominales afin d'abaisser la température de fusion et d'améliorer l'aptitude à la vitrification de mélanges d'oxydes contenant de l' Al_2O_3 . Notre recherche s'est donc tournée vers la synthèse de céramiques d'aluminosilicates. Ces dernières sont largement utilisées dans les applications d'ingénierie comme les matériaux réfractaires^{73, 74}, où la céramique à haute teneur en Al_2O_3 présente une résistance mécanique remarquable. Si la présence de SiO_2 dans les aluminosilicates affaiblit cette résistance par rapport aux aluminates, elle apporte par contre de nombreux avantages tels que l'abaissement de température de frittage et donc des coûts de production.⁷⁵ En outre, ces deux oxydes (alumine et silice) lorsqu'ils sont combinés avec d'autres oxydes (strontium, baryum, lithium, calcium, magnésium) conduisent à des matériaux céramiques ou vitrocéramiques ayant des propriétés thermiques, mécaniques et optiques intéressantes.⁷⁶⁻⁸² Ce chapitre porte sur l'élaboration de céramiques polycristallines transparentes d'aluminosilicate de strontium. Le point de départ de cette étude est la composition $SrAl_2O_4$ bien connue, un des meilleurs matériaux phosphorescents (phosphorescence de longue durée dans le vert en cas de codopage à l' Eu^{2+} et au Dy^{3+}). Toutefois, cette composition présente une température de fusion élevée. Nous nous sommes donc intéressés à un domaine du système triple $SrO-Al_2O_3-SiO_2$, en partant de $SrAl_2O_4$ auquel nous nous avons ajouté SiO_2 .

Le domaine étudié est représenté par la formule suivante $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 2$) qui se situe entre les compositions $SrAl_2O_4$ et $SrAl_2Si_2O_8$. Sur cette ligne de composition, la plus grande teneur en silice devait permettre d'abaisser la température de fusion du mélange d'oxydes et d'améliorer le processus de vitrification. L'aptitude à la vitrification d'une série de compositions a été étudiée, suivie par l'élaboration de céramiques polycristallines

transparentes par cristallisation complète du verre. Les propriétés structurales et physico-chimiques de ces céramiques transparentes ont été étudiées par une approche multi-échelle.

IV.1 Le système $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 2$)

Des essais de vitrification ont été effectués sur 12 compositions différentes à partir de $SrAl_2O_4$ par additions successives de SiO_2 , jusqu'à atteindre la composition $SrAl_2Si_2O_8$. Les compositions répondent à la formule générale $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ où $x = 2; 1,6; 1,2; 0,8; 0,68; 0,6; 0,5; 0,4; 0,3; 0,2; 0,1$ et 0 .

Pour la composition $x = 2$ ($SrAl_2O_4$), la synthèse du verre ne peut pas être réalisée, même en utilisant la lévitation aérodynamique couplée au système de chauffage laser. Il cristallise directement lors du refroidissement, malgré une vitesse de trempe très élevée, sous la forme monoclinique de $SrAl_2O_4$ ($P2_1$).

Pour les autres compositions, elles peuvent toutes être vitrifiées sous forme d'échantillons massifs de grande taille ($x = 0,4; 0,3; 0,2; 0,1$ et 0).

Après la synthèse de verre, la cristallisation complète des onze compositions différentes a été réalisée par des traitements thermiques simples du verre, chacun correspondant à une température et une durée données. Les conditions de cristallisation (température (T) et temps (t)) ont été déterminées pour chaque composition après de nombreux essais de cristallisation à différentes T et t . Les diffractogrammes des céramiques polycristallines obtenues sont présentés dans la Figure 10.

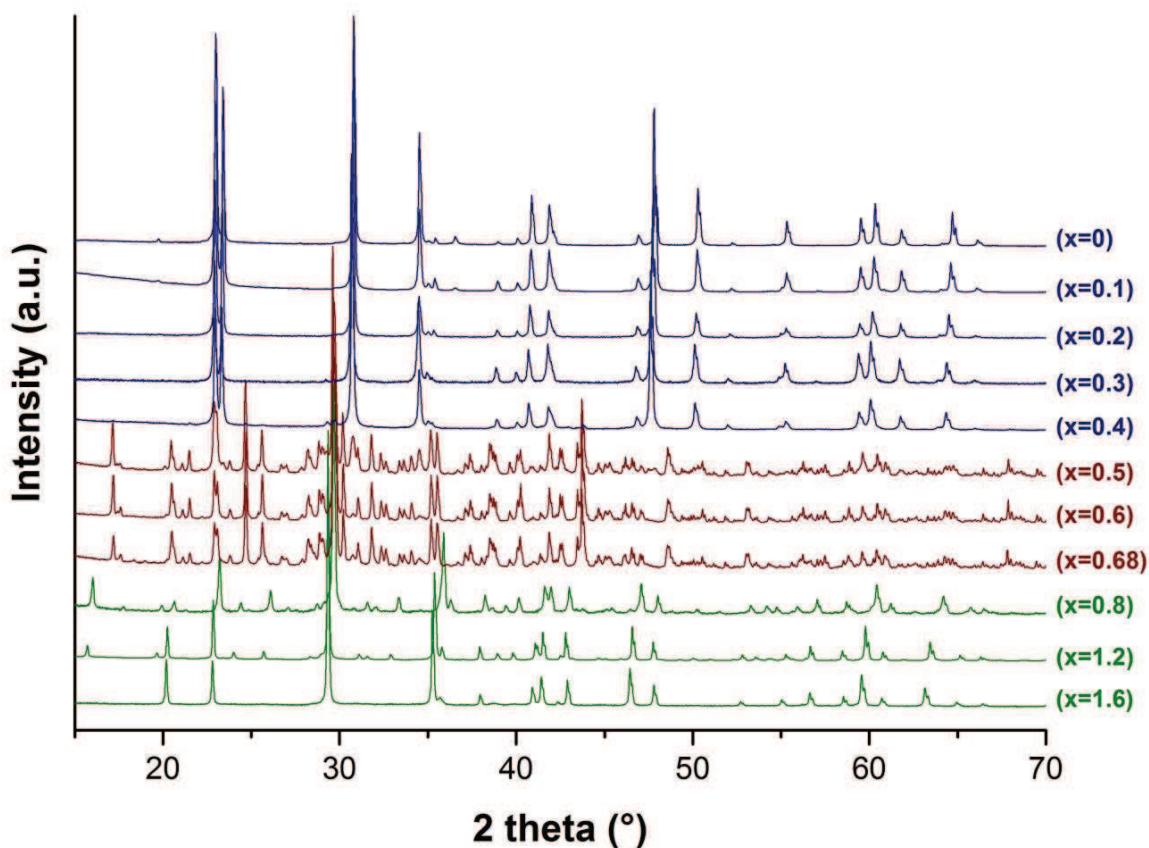


Figure 10 Diffractogrammes normalisés des céramiques polycristallines obtenues $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 2$) par diffraction des rayons X (spectromètre du laboratoire)

Le système $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 2$) peut être divisé en trois solutions solides:

1. La première solution solide $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0.8 \leq x \leq 2$)
2. La deuxième solution solide $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0.5 \leq x \leq 0.68$)
3. La troisième solution solide $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 0.4$)

Une étude détaillée de la structure a été effectuée pour les deux premières solutions solides. Mais l'essentiel du travail a été consacré à la troisième solution solide qui semblait être la plus intéressante en termes de transparence et de taille des échantillons élaborés.

IV.2 Céramiques polycristallines transparentes de $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 0.4$)

IV.2.1 Elaboration de céramiques polycristallines transparentes

Après la préparation des mélanges de précurseurs en proportions stœchiométriques, ceux-ci sont placés dans des creusets de platine, introduits dans un four électrique pré-chauffé

à 1700 °C, laissés pendant 10 minutes, chauffés jusqu'à 1750 °C pendant 10 min puis à nouveau à 1700 °C pendant 30 min. De grands échantillons de verre clair et transparent ont été obtenus par simple trempe à l'air des creusets.

Un traitement thermique de 3 heures à 1020 °C a été suffisant pour assurer la cristallisation complète des échantillons de verre d'après les données de diffraction sur poudre obtenues au synchrotron (Figure 11) et les observations au MET. Les diffractogrammes de ces céramiques présentent une seule phase polycristalline (Figure 11) pour chacune des cinq compositions ($x=0$; 0,1; 0,2; 0,3 et 0,4). Ils correspondent à l'indexation du $SrAl_2Si_2O_8$ hexagonal (ICSD 416598, PDF 01-077-5105).⁸³

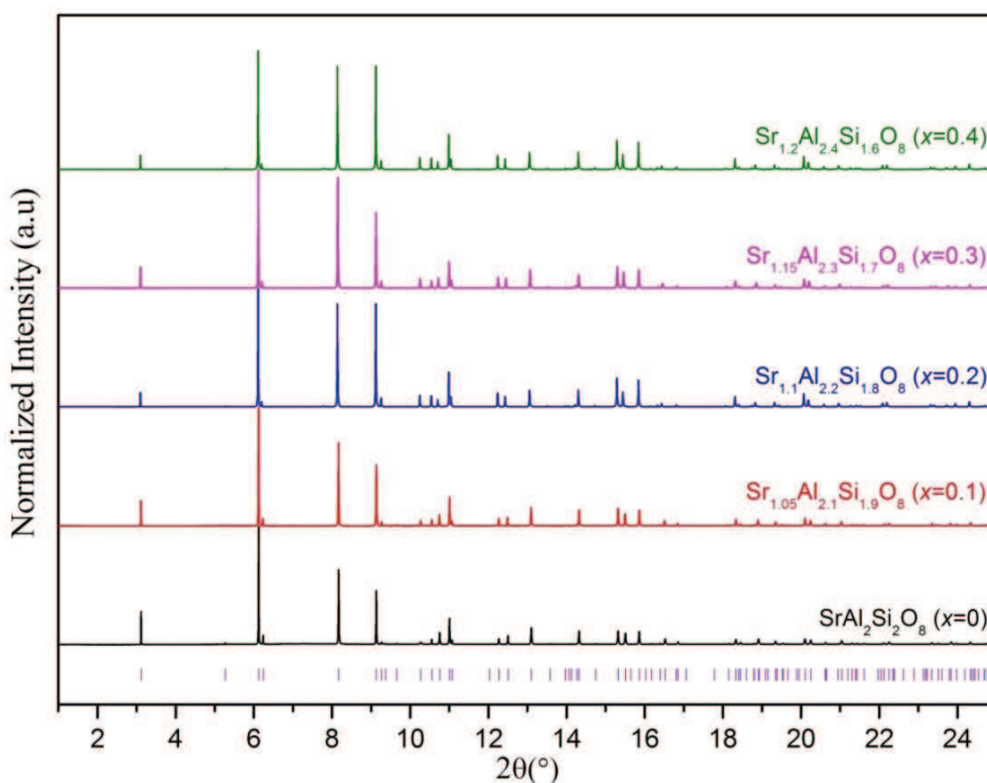


Figure 11 Diffractogrammes normalisés des céramiques polycristallines obtenues $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x = 0$; 0,1; 0,2; 0,3 et 0,4) par diffraction (synchrotron). L'indexation en bas de figure correspond à la structure hexagonale de $SrAl_2Si_2O_8$ (ICSD 416598, PDF 01-077-5105)

Des céramiques polycristallines homogènes très transparentes ont été obtenues, notamment pour la composition $x = 0,2$. Les valeurs de transmission optique mesurées pour la composition $x = 0,2$ (épaisseur 1,5 mm) sont proches de 90% pour tout le domaine visible et proche infra-rouge (Figure 12a). Ce résultat exceptionnel correspond presque à la transmission maximale théorique de 90,1% calculée à partir de l'indice de réfraction mesuré

($n = 1,59$), ce qui indique une quasi-absence de centres de diffusion au sein de la céramique polycristalline.

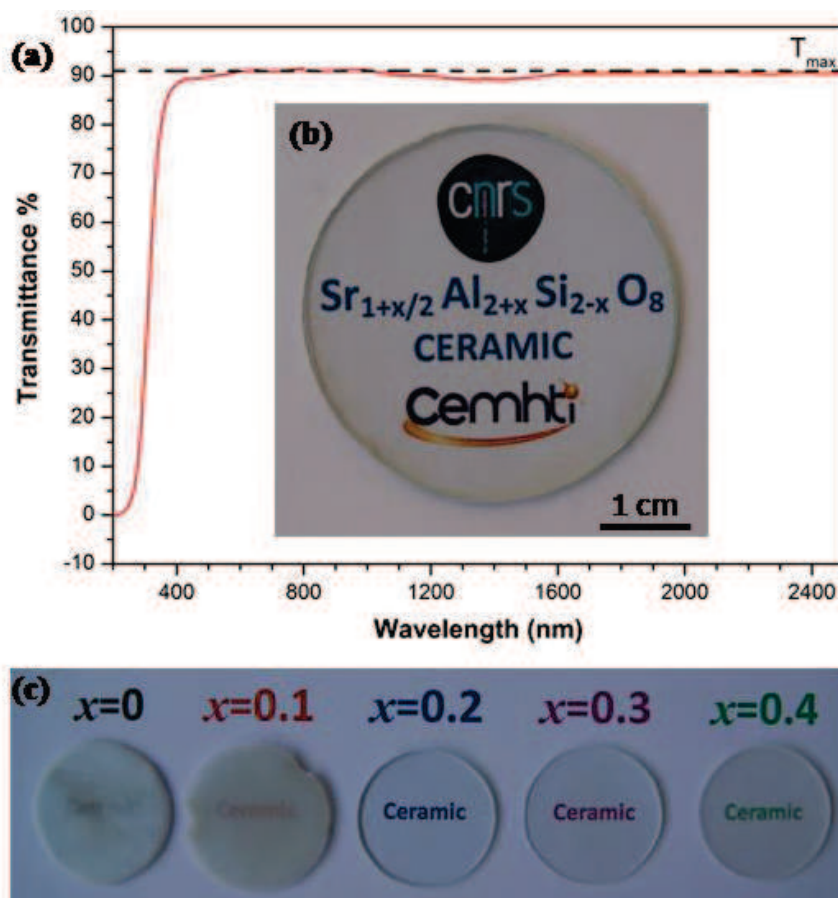


Figure 12 (a) Spectre de transmission mesuré sur l'échantillon $Sr_{1.1}Al_{2.2}Si_{1.8}O_8$ ($x = 0,2$). L'indice de réfraction $n = 1,59$ implique une transmission maximale théorique de 90,1% (ligne pointillée). (b) Photo de la céramique polycristalline $x=0,2$. (c) Photo des céramiques polycristallines $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($x = 0; 0,1; 0,2; 0,3$ et $0,4$) montrant l'évolution de la transparence.

IV.2.2 Etude structurale des céramiques polycristallines transparentes

L'élucidation de la structure de la solution solide $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 < x \leq 0,4$) a été effectuée en utilisant une combinaison de données de microscopie électronique en transmission (mode diffraction d'électrons) et de données de diffraction sur poudre (synchrotron et neutrons).

Les clichés de diffraction électronique et l'indexation de diagrammes de diffraction sur poudre confirment la structure hexagonale (groupe d'espace $P6_3/mcm$, $a \approx 5,2 \text{ \AA}$ et $c \approx 15,2 \text{ \AA}$) de $SrAl_2Si_2O_8$. Les affinements des données synchrotron révèlent une évolution linéaire des paramètres de maille le long de la solution solide. Les affinements Rietveld des données synchrotron ont ensuite été réalisés en utilisant la structure moyenne $P6_3/mcm$ de $SrAl_2Si_2O_8$.

comme base de départ (un site de Sr, un site mixte de Al/Si et deux sites de O, entièrement occupés), et en utilisant un modèle d'occupation statistique des sites tétraédriques Al/Si ainsi que les paramètres de maille déterminés précédemment. Un ajustement raisonnable a pu ainsi être obtenu. Mais l'examen des cartes de Fourier a révélé une augmentation de la densité de diffusion sur un nouveau site cristallographique 2a (0, 0, $\frac{1}{4}$) (Figure 2). Cette densité a été attribuée à un site supplémentaire de strontium (Sr2). Le taux d'occupation de Sr2 a ensuite été affiné, il augmente de manière continue tout au long du processus de substitution. Les affinements des données neutrons ne montrent pas de sites d'oxygène supplémentaire lié à Sr2, confirmant que la charge positive supplémentaire induite par le strontium supplémentaire est compensée par un rapport conséquent Al/Si.

La présence de désordre chimique Al/Si dans les structures de composés $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 \leq x \leq 0.4$) a été clairement confirmée par les expériences de ^{29}Si et ^{27}Al MAS et MQ-MAS RMN (Figure 13). Celles-ci mettent en évidence un éventail d'environnements chimiques des tétraèdres de Si et Al qui peuvent être décrits à l'aide des notations Q^n_m et q^n_m respectivement, où n est le nombre des atomes d'oxygène pontant et m est le nombre d'unités AlO_4 liées, ($0 \leq m \leq n \leq 4$). Pour $SrAl_2Si_2O_8$, la distribution des atomes Si et Al dans les sites tétraédriques conduit à quatre types d'environnements de Si (Q^4_m , $m = 4, 3, 2, 1$) et de Al (q^4_m , $m = 3, 2, 1, 0$) qui ne peuvent pas être différenciés dans la structure moyenne déterminée par RX et neutron. La proportion de ces différents environnements de Si ou Al reflète directement la dérogation à la règle de Loewenstein⁸⁴ qui indique que les liaisons entre les unités AlO_4 sont énergétiquement défavorables dans les matériaux d'aluminosilicates. Lorsque x augmente, la distribution d'environnements Al s'élargit pour inclure des entités q^4_4 et l'augmentation des unités q^4_4 , q^4_3 , q^4_2 reflète la formation de liaisons Al-O-Al supplémentaires requises par la compensation de charge locale du site de strontium supplémentaire dans la structure.

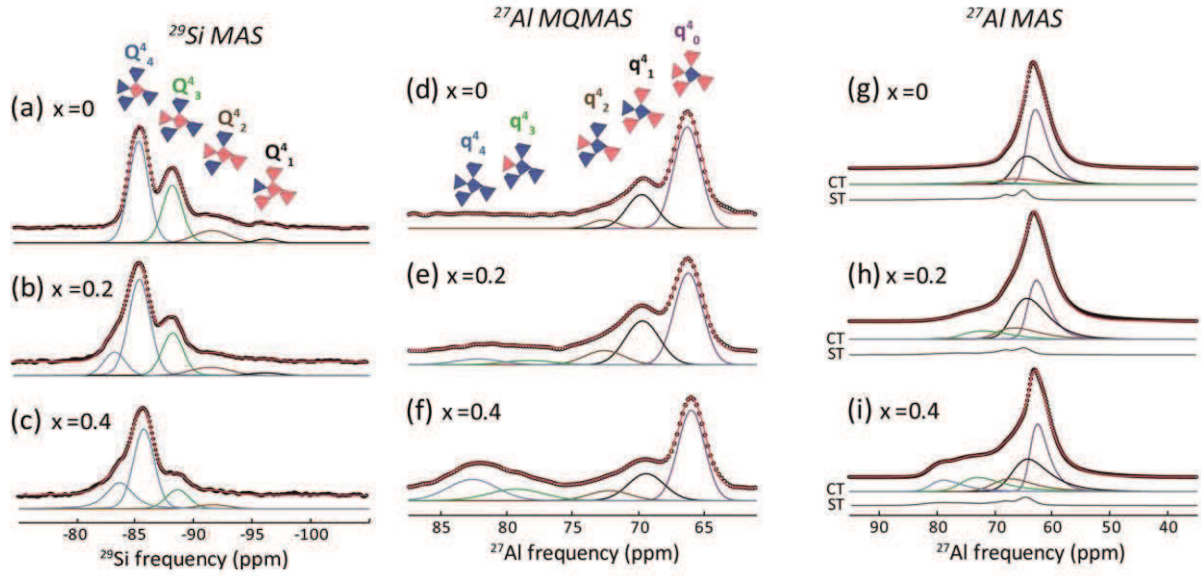


Figure 13 (a-c) Spectres MAS-RMN quantitatifs de ^{29}Si et spectres simulés, (d-e) Spectres MQMAS isotropiques de ^{27}Al et spectres simulés, (g-h) Spectres MAS-RMN quantitatifs de ^{27}Al et spectres simulés

IV.2.3 Etude de microstructure

L'analyse de la microstructure de la céramique $Sr_{1.1}Al_{2.2}Si_{1.8}O_8$ examinée par MEB a révélé une microstructure en mosaïque dense, avec des cristallites de taille micronique (5-20 pm) et aucune porosité (Figure 14a). L'image STEM-HAADF de l'interface de deux cristallites a montré un joint de grain très mince, aucune phase amorphe ou secondaire n'étant détectée (Figure 14b). En outre, une forte orientation des cristallites perpendiculaires à la surface a été mise en évidence par les images MEB de la section transversale de l'échantillon (Figure 14c) et par les données de diffraction des rayons X obtenues sur des échantillons massifs et en poudre (Figure 14d).

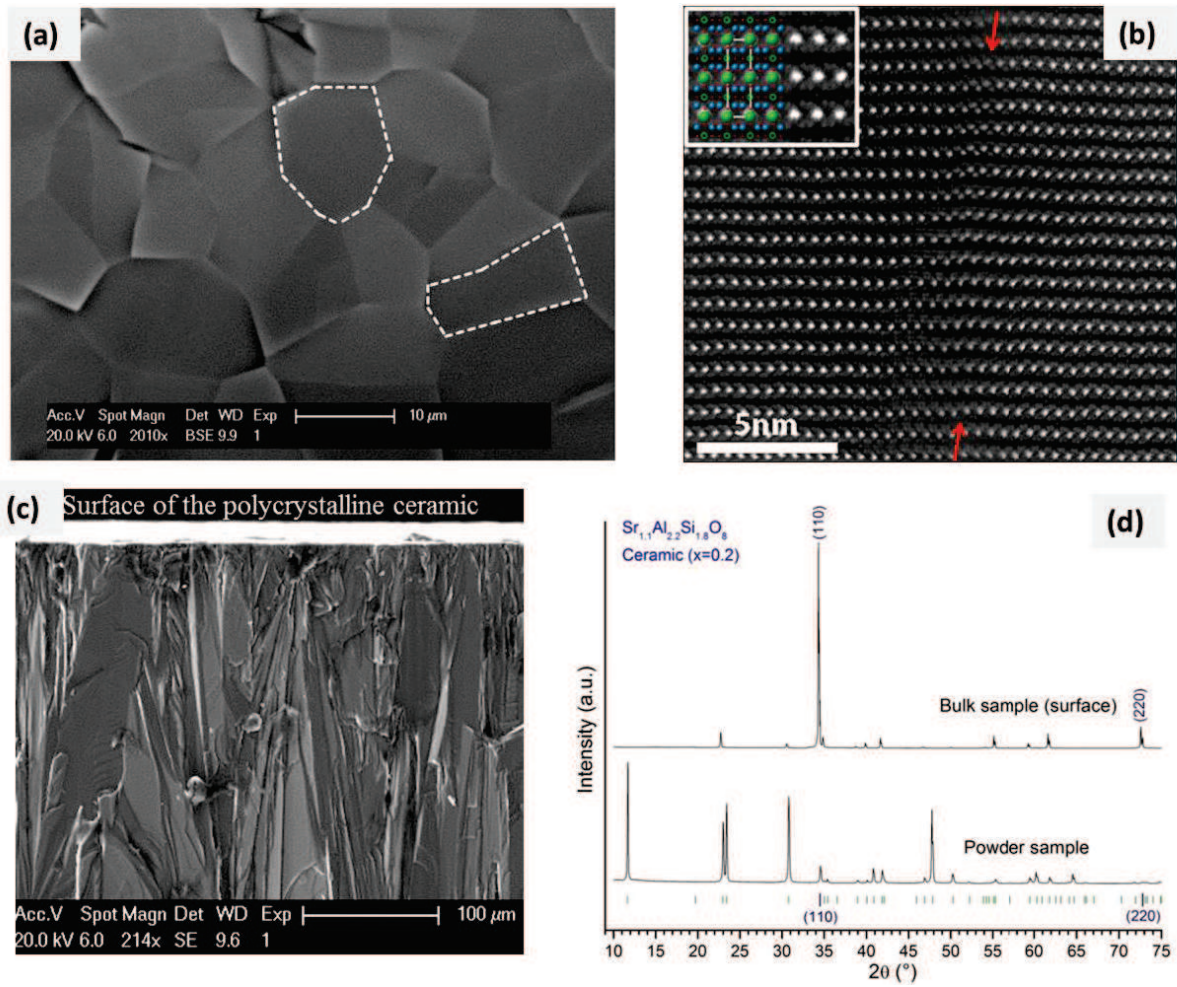


Figure 14 (a) Image en microscopie électronique à balayage de la céramique la plus transparente ($x=0,2$). (b) $[010]$ image haute résolution STEM HAADF-(contraste proportionnel au nombre atomique Z) de l'interface entre deux grains légèrement désorientés. (c) Image MEB enregistré sur une section de l'échantillon de $Sr_{1,1}Al_{2,2}Si_{1,8}O_8$ ($x=0,2$). (d) En haut: diffractogramme enregistrée sur la surface de l'échantillon de $Sr_{1,1}Al_{2,2}Si_{1,8}O_8$ ($x=0,2$); En bas: diffractogramme enregistré sur le même échantillon en forme de poudre.

Les céramiques polycristallines $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ($0 < x \leq 0.4$) combinent une structure hexagonale anisotrope et un alignement non parfait de cristallites microscopiques qui n'entraînent pas habituellement une transparence exceptionnelle. La biréfringence a alors été évaluée grâce à des calculs de DFT pour les compositions $x = 0$ et $x = 0,25$. Cinq structures périodiques différentes, comprenant des supercellules $2 \times 2 \times 1$ contenant 0 et 1 atome de strontium supplémentaire (Sr2) respectivement, ont été considérées pour $x = 0$ et $x = 0,25$. Les modèles structuraux présentent un ordre d'Al/Si qui représente les distributions observées pour les environnements chimiques de Si et Al. Les composantes de l'indice de réfraction ont été obtenues à partir du calcul des parties réelle et imaginaire de la fonction diélectrique $\epsilon(\omega)$ correspondant aux structures périodiques modélisées. Une faible valeur de biréfringence

d'environ 0,007 a été calculée pour $SrAl_2Si_2O_8$ ($x = 0$), alors que $Sr_{1.125}Al_{2.25}Si_{1.75}O_8$ ($x = 0,25$) présente une biréfringence encore plus faible, voire presque nulle (d'environ 0,001) sur tout le domaine visible (Figure 15).

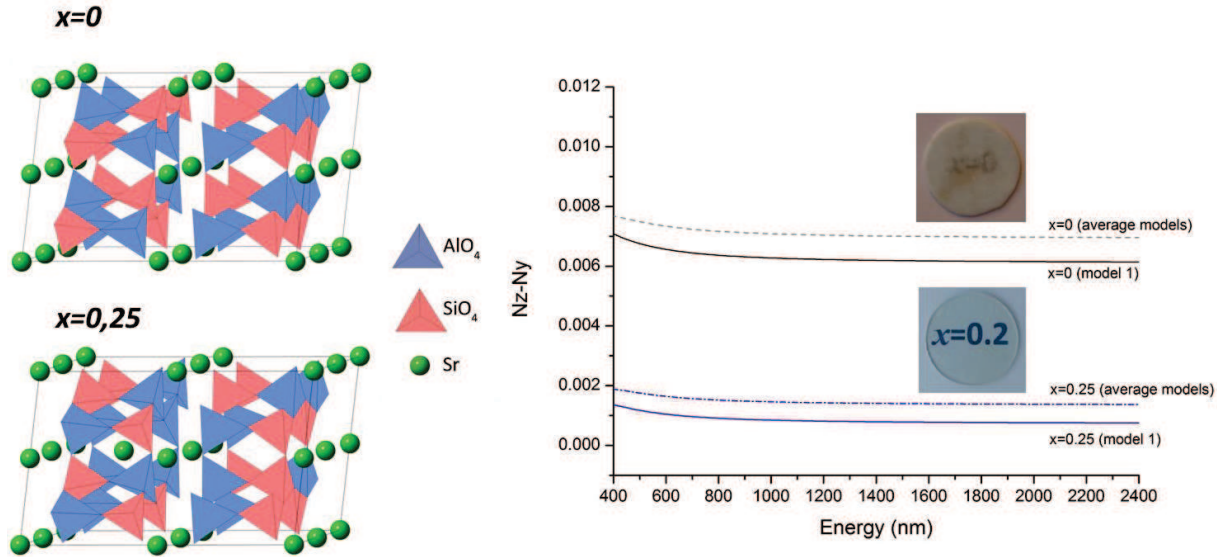


Figure 15 Biréfringence calculée par DFT pour les deux modèles structuraux correspondant aux compositions $x=0$ et $x=0,25$

Malgré la présence de gros cristaux et une structure cristalline anisotrope, la transparence de la céramique présentée en Figure 12 peut donc être attribuée à la combinaison d'une forte densité (absence de pores), de joints de grains très fins et d'une très faible biréfringence. La biréfringence semble avoir un rôle majeur pour l'augmentation du niveau de transparence observée entre $x=0$ et $0,25$ qui correspond à une diminution significative des valeurs de biréfringence calculées. Cette biréfringence est contrôlée par la composition chimique à travers l'occupation du site supplémentaire de strontium Sr2 dans la structure. Les calculs pour différents modèles structuraux avec une même composition montrent que la biréfringence dépend également de l'ordre Al/Si. Par conséquent, il apparaît qu'un contrôle précis de la biréfringence peut être obtenu par le contrôle de l'occupation du site du strontium (composition chimique) et la mise en ordre Al/Si (conditions de synthèse), la biréfringence optimale (et donc la transparence) étant obtenue pour $x = 0,2$.

Par analogie avec la structure multi-échelle de verre⁸⁵, ces résultats suggèrent que l'isotropie optique à l'échelle du micromètre peut être obtenue dans un matériau cristallin non cubique (avec une anisotropie structurale à l'échelle nanométrique) par l'introduction d'un désordre contrôlé. Il en résulterait des valeurs de biréfringence faibles de la céramique

correspondante, conservant ainsi une bonne transparence, même avec une taille de cristallite de l'ordre du micromètre.

Cette nouvelle approche semble être très prometteuse dans le domaine des céramiques transparentes, où elle pourrait être appliquée à d'autres compositions. Les céramiques transparentes obtenues en utilisant cette approche pourraient alors avoir des applications intéressantes et pourraient être synthétisée à l'échelle industrielle en raison des énormes avantages de la voie verrière (cristallisation du verre) par rapport aux autres procédés basés sur le frittage.

Conclusion Générale

Le principal objectif de cette étude était d'élaborer et de caractériser de nouvelles céramiques polycristallines avec une transparence élevée, obtenues par un procédé de cristallisation complète et congruente du verre. Le deuxième objectif était de pouvoir produire ces céramiques transparentes à grande échelle (échantillons de grandes dimensions et quantités importantes). Cette voie de synthèse verrière a été choisie en raison de ses nombreux avantages par rapport aux techniques de frittage sous pression déjà existantes, complexes et coûteuses. Plusieurs systèmes ont été étudiés: $\text{Sr}_3\text{Al}_2\text{O}_6$, $\text{Sr}_3\text{Ga}_2\text{O}_6$, et une série de solutions solides au sein du diagramme ternaire $\text{SrO-Al}_2\text{O}_3\text{-SiO}_2$. Des céramiques d'aluminosilicate de strontium polycristallines avec une transparence quasi parfaite ont été synthétisées sous forme d'échantillons de taille importante. Différentes techniques de caractérisation complémentaires ont été utilisées pour sonder la structure multi-échelle de ces nouveaux matériaux.

Dans un premier temps, nous avons élaboré des céramiques de $\text{Sr}_3\text{Al}_2\text{O}_6$ et $\text{Sr}_3\text{Ga}_2\text{O}_6$ cubiques polycristallines très transparentes. Comme les céramiques $\text{Sr}_3\text{Ga}_2\text{O}_6$ étaient légèrement hygroscopiques, l'étude a été axée principalement sur la composition $\text{Sr}_3\text{Al}_2\text{O}_6$. Un niveau élevé de transparence ($\approx 87\%$) a été obtenu dans le visible et le proche IR (jusqu'à 6 microns), presque la transmission maximale théorique (87,4%). Ce niveau de transparence élevé a été expliqué par la microstructure spécifique inhérente au processus d'élaboration. La diffusion de la lumière est réduite au minimum en raison de la symétrie cubique de $\text{Sr}_3\text{Al}_2\text{O}_6$, ce qui conduit à une isotropie optique (pas de biréfringence). Par ailleurs, l'organisation des grains de $\text{Sr}_3\text{Al}_2\text{O}_6$, de taille micrométrique, montre l'absence de porosité et des joints de grains très fins, ce qui conduit à une céramique ultra-dense. Les propriétés thermiques et mécaniques de la céramique polycristalline transparente $\text{Sr}_3\text{Al}_2\text{O}_6$ ont également été mesurées. Une amélioration considérable de ces propriétés a été observée lorsque l'on compare la céramique avec le verre précurseur correspondant. L'étude des propriétés de luminescence et de scintillation a révélé que la céramique polycristalline transparente $\text{Sr}_3\text{Al}_2\text{O}_6$ peut être considérée comme un candidat intéressant pour des applications photoniques dans le visible et l'infrarouge. Les résultats de cette étude ont été publiés dans *Chemistry of Materials*.⁸⁶

La deuxième partie de ce travail a porté sur les compositions $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 2$). Ce système peut être divisé en trois solutions solides. Pour la première solution solide, $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0,8 \leq x \leq 2$), une céramique polycristalline très transparente peut être synthétisée (billes de $\varnothing \approx 3 - 5$ mm), en particulier pour la composition $x = 1,6$. Une étude structurale par diffraction de poudre a été menée pour toute cette solution solide. Des lacunes de strontium sont apparues dans deux des cinq sites cristallographiques existants du strontium. Les lacunes de strontium augmentent lorsque x diminue. Pour la deuxième solution solide, $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0,5 \leq x \leq 0,68$), les verres peuvent être préparés en utilisant un four électrique commercial en raison de la température de fusion plus basse des précurseurs du verre (1700-1750 °C) par rapport à la première solution solide. Ceci est une conséquence directe de l'augmentation de la teneur en silice de ces compositions. Des échantillons de grandes dimensions peuvent être facilement élaborés, mais le mécanisme de cristallisation de surface observé nécessite des échantillons avec une très faible épaisseur ($< 0,3$ mm) pour pouvoir préparer des céramiques polycristallines transparentes. La céramisation de ces compositions a conduit à une phase orthorhombique cristalline non répertoriée précédemment (groupe d'espace $\text{Pmc}2_1$, $a=8,3$ Å, $b=10,2$ Å et $c=17,5$ Å). La structure a été déterminée *ab initio* sur la base d'une étude combinée associant microscopie électronique à transmission et données de diffraction (synchrotron et neutrons). Pour la troisième solution solide, $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0,4$), une étude détaillée a été réalisée. Cinq compositions ont été étudiées ($x = 0; 0,1; 0,2; 0,3$ et $0,4$). Des échantillons de grandes dimensions (disques de $\varnothing \approx 4 - 5$ cm) peuvent être facilement préparés dans un four électrique commercial en raison de la température de fusion relativement basse du précurseur de verre (augmentation de la teneur en silice). Des céramiques polycristallines ultra-transparentes ont été élaborées tout au long de cette solution solide. La composition $x=0,2$ ($\text{Sr}_{1,1}\text{Al}_{2,2}\text{Si}_{1,8}\text{O}_8$) présente une transparence exceptionnelle qui atteint la transmission théorique limite de 90% dans le domaine visible et proche IR, valeur qui, à notre connaissance, n'a jamais été atteinte jusqu'à présent pour une céramique polycristalline transparente à base d'oxydes. Des affinements structuraux ont été réalisés pour chacune des cinq compositions de structure hexagonale de type $\text{SrAl}_2\text{Si}_2\text{O}_8$ ($\text{P}6_3/\text{mcm}$, $a=b=5,2$ Å, $c=15,2$ Å, un site de Sr, deux sites Al/Si et deux sites d'O). Pour $x \geq 0,1$, l'examen des cartes de Fourier de ces phases cristallines hexagonales montre l'apparition d'un nouveau site de strontium (Sr2) dont le taux d'occupation augmente avec x . Les expériences de RMN de ^{29}Si et ^{27}Al ont confirmé l'existence d'un certain désordre structural dans nos matériaux. Lorsque x augmente, la distribution de l'environnement d'Al s'élargit à des unités de type q^4_4 et les proportions de q^4_2 , q^4_3 et q^4_4 augmentent, reflétant la formation de

liaisons Al-O-Al supplémentaires. Ces liaisons qui correspondent à une dérogation à la règle de Lowenstein sont nécessaires pour la compensation de charge locale dans le voisinage du site Sr supplémentaire. La biréfringence des structures cristallines de la solution solide ont été calculées par DFT pour deux compositions représentatives ($x=0$ et $x=0,25$), en utilisant pour chacune d'elles cinq structures modélisées optimisées. Les structures modélisées correspondent à des configurations avec différents arrangements Al/Si qui représentent les différents environnements Al et Si observés par RMN. Les résultats de ces calculs DFT ont montré l'énorme impact du désordre chimique/structural sur les valeurs de biréfringence. En dépit du fait que ces matériaux présentent une symétrie non cubique et des tailles de cristallites de quelques dizaines de microns, la transmittance théorique maximale est atteinte grâce à (i) l'absence de porosité, de phases vitreuses et secondaires, des joints de grains extrêmement fins (observés avec une haute résolution MET/STEM) résultant du processus d'élaboration et (ii) une biréfringence très faible (0,001 pour la composition $x = 0,25$) calculée par DFT et obtenue par introduction d'un désordre chimique contrôlé (taux d'occupation du strontium et ordre Al / Si). Les résultats obtenus pour cette troisième solution solide ont été soumis pour publication.⁸⁷

Cette étude permet donc de valider une nouvelle approche pour l'élaboration de matériaux de structure anisotrope avec une transparence exceptionnelle: l'introduction d'un désordre chimique contrôlé peut conduire à une isotropie optique. Ce nouveau concept ouvre la voie à de nouvelles compositions pour obtenir des céramiques polycristallines transparentes.

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Perfectly Transparent $\text{Sr}_3\text{Al}_2\text{O}_6$ Polycrystalline Ceramic Elaborated from Glass Crystallization

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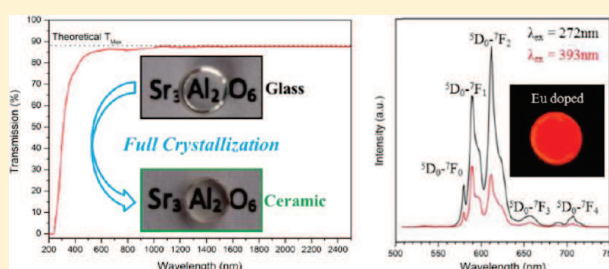
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Supporting Information

ABSTRACT: The highly visible and infrared (up to 6 μm) transparent $\text{Sr}_3\text{Al}_2\text{O}_6$ polycrystalline ceramic was obtained by full crystallization of the corresponding glass composition. The glass synthesis and the direct congruent crystallization processes are described, and the material transparency is discussed in light of its microstructure. This new transparent ceramic exhibits a high density (i.e., complete absence of porosity) and micrometer-scale crystallites with very thin grain boundaries. These microstructural characteristics, inherent to the preparation method, minimize light scattering and demonstrate the advantages of this synthesis route compared to the high-pressure process used for the few reported transparent polycrystalline materials. This $\text{Sr}_3\text{Al}_2\text{O}_6$ ceramic shows a $H = 10.5$ GPa hardness, a $E_r = 150$ GPa reduced elasticity modulus, and a $9.6 \times 10^{-6} \text{ K}^{-1}$ thermal expansion coefficient. Such a transparent strontium aluminate ceramic opens the way to a wide range of applications, especially photonics when doped by various doping agents. As examples, the luminescence of $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Eu}^{3+}$ and $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Er}^{3+}$, which show strong emissions in the visible and infrared ranges, respectively, is presented. Moreover, the $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Ce}^{3+}$ material was found to exhibit scintillation properties under X-ray excitation. Interestingly, the analogous $\text{Sr}_3\text{Ga}_2\text{O}_6$ transparent polycrystalline ceramic material could equally be prepared using the same elaboration method, although its hygroscopicity prevents the preservation of its high transparency under normal conditions. The establishment of the key factors for the transparency of this economical and innovative synthesis method should enable the prediction of new classes of technologically relevant transparent ceramics.

KEYWORDS: transparent polycrystalline ceramic, $\text{Sr}_3\text{Al}_2\text{O}_6$, $\text{Sr}_3\text{Ga}_2\text{O}_6$, glass, crystallization, luminescent materials



1. INTRODUCTION

In the rapidly evolving and challenging world of optical research and engineering, polycrystalline transparent ceramics are a promising class of photonic-quality materials.¹ Since the discovery of synthetic ruby ($\text{Cr}:\text{Al}_2\text{O}_3$)² in the 1960s, these materials, which combine transparency and a crystalline structure, have found commercial applications mainly as gain media for solid-state laser amplifiers³ ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Nd}$, $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$, $\text{Y}_2\text{O}_3:\text{Yb}$, $\text{Lu}_2\text{O}_3:(\text{Eu} \text{ or } \text{Yb})$, and $\text{Sc}_2\text{O}_3:\text{Yb}$), scintillators,⁴ optical lenses (Lu_3NbO_7 ⁵ and ZrO_2 ⁶), and transparent armor (MgAl_2O_4).⁷ Compared to other competitive materials for optical applications (e.g., single crystals),

polycrystalline transparent ceramics are characterized by their relatively low cost, ease of shaping, and possibility to be heavily and homogeneously doped,⁸ even though some segregation remains.⁹ Because of their important applications and characteristics, a considerable focus was given to their elaboration procedure. Over time, various synthesis methods emerged (hot pressing,¹⁰ spark plasma sintering (SPS),¹¹ and magnetic-field-assisted slip-casting¹²). However, the number of discovered

Received: June 16, 2013

Revised: September 24, 2013

Published: September 27, 2013

transparent polycrystalline ceramics remains restrained because of the complexity of avoiding light-scattering sources (in particular from the residual pores) during the synthesis.¹³ Furthermore, the required nanometer-scale raw materials and high-pressure/temperature elaboration conditions by these methods complicate and increase the cost of the synthesis process.

Crystallization from glass appears to be an interesting alternative. In principle, such an approach must produce dense and chemically homogeneous materials. In recent decades, much attention has been devoted to transparent glass ceramics, with applications in cooking ware, radomes, reinforced windows, telescope mirrors, and dental prosthesis.¹⁴ Glass ceramics are easily processed and can be shaped as desired. However, as described by the Rayleigh–Ganz¹⁵ particle-scattering theory, transparency in these materials is achieved only through a careful partial crystallization of nanometer-scale microstructure precipitates (crystallite sizes much smaller than the incident wavelength and/or a minimized difference in the refractive index between the crystallites and the glass matrix).¹⁶

To overcome these obstacles, complete crystallization from glass appears to be an interesting solution. We have recently reported the elaboration of the first highly transparent polycrystalline ceramic, BaAl_4O_7 , obtained by full crystallization from glass (congruent crystallization).¹⁷ Using this novel and promising method, this material exhibits two orthorhombic polymorphs, both transparent, showing micrometer grain size. The transparency, maintained throughout the crystallization process, is explained by the crystalline microstructure, which shows very thin grain boundaries, the absence of porosity inherent to the preparation method, and weak birefringence (determined by DFT calculation). Thus, the transparency of this polycrystalline ceramic prepared by complete crystallization from glass has been evidenced in the case of a material exhibiting structural anisotropy (orthorhombic polymorphs). The consequent optical anisotropy (birefringence) led to a limited level of transparency, although it reached up to 70% in the visible range. A greater level of transparency is highly desirable for efficient optical and even photonic applications. For this purpose, the synthesis of a material similarly prepared but exhibiting perfectly isotropic optical properties (cubic structural symmetry) should demonstrate higher transparency and would probably achieve the maximum theoretical transmission.

Here, we report the elaboration of a new highly transparent strontium aluminate ceramic, $\text{Sr}_3\text{Al}_2\text{O}_6$, using the same promising method that relies on a simple single heat treatment under ambient pressure, leading to the full crystallization from glass. The as-prepared strontium aluminate ceramic exhibits a very high transparency that is equivalent to the best values observed in commercial polycrystalline materials. No particular treatment for avoiding the formation of pores (light-scattering sources) is necessary. The synthesis method is described, and the transmission in both the visible and IR ranges is measured and discussed in light of the microstructure (crystals size, porosity, and grain boundaries thickness) determined by SEM and TEM. The thermal expansion coefficient of the $\text{Sr}_3\text{Al}_2\text{O}_6$ ceramic has been measured up to 900 K along with the mechanical hardness and the reduced elasticity modulus that were determined on both glass and ceramic by nanoindentation experiments. A wide range of optical applications can be sought, especially for use in luminescence and scintillation properties

because the transparency allows emission from the whole volume compared to opaque classic polycrystalline ceramics that are only surface efficient. Furthermore, strontium aluminates are particularly known for their great photoluminescence and persistent afterglow properties¹⁸ ($\text{Sr}_3\text{Al}_2\text{O}_6$,¹⁹ SrAl_2O_4 ,²⁰ $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$,²¹ and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$).²²). To illustrate the potential optical properties, $\text{Sr}_3\text{Al}_2\text{O}_6\cdot\text{Eu}^{3+}$, $\text{Sr}_3\text{Al}_2\text{O}_6\cdot\text{Er}^{3+}$, and $\text{Sr}_3\text{Al}_2\text{O}_6\cdot\text{Ho}^{3+}$, which show strong emissions in the visible (Eu^{3+}) and the infrared ranges (Er^{3+} and Ho^{3+}), are presented. Moreover, as a proof of concept, we show that $\text{Sr}_3\text{Al}_2\text{O}_6\cdot\text{Ce}^{3+}$ can exhibit scintillation properties. In addition to $\text{Sr}_3\text{Al}_2\text{O}_6$, an analogous gallate material, $\text{Sr}_3\text{Ga}_2\text{O}_6$, can be prepared by the same method, although its hygroscopicity prevents high transparency from being perdurable. Finally, the key points required to achieve transparency using this economical and promising new elaboration route are discussed so that new potential classes of technologically relevant transparent ceramics prepared by full crystallization from glass can be predicted.

2. EXPERIMENTAL SECTION

2.1. Glass and Transparent Polycrystalline Ceramic Synthesis. The $\text{Sr}_3\text{Al}_2\text{O}_6$ and $\text{Sr}_3\text{Ga}_2\text{O}_6$ glasses were synthesized from high purity SrCO_3 (99.99%), Al_2O_3 (99.98%), and Ga_2O_3 (99.99%) oxides using an aerodynamic levitator equipped with two CO_2 lasers.²³ In the case of the doped samples, Eu_2O_3 , Er_2O_3 , Ho_2O_3 , and CeO_2 oxides were used. The starting materials were first weighed in stoichiometric amounts, mixed, and pressed into pellets. To elaborate a glass bead, a piece of the pellet was placed in the levitator system's conical nozzle and melted, at around 1800 °C, using two CO_2 lasers (see Supporting Information, Figure S1). The melt was levitated by an argon flow, and glass beads were obtained by quenching (realized by cutting off the two laser beams with a cooling rate of approximately 300 °C/s). Full crystallization of the glass was then performed by a single and simple heat treatment at 840 °C for 5 h in an open-air tubular furnace.

2.2. Characterization Methods. A Setaram Multi HTC 1600 DSC instrument was used to determine the glass transition (T_g) and the crystallization (T_{onset}) temperatures of the studied glasses. These measurements were performed on a 300 mg glass powder sample with a heating rate of 20 K/min. Dry nitrogen was flowed in the sample chamber as the purge gas.

Laboratory X-ray diffraction (XRD) measurements were performed on a D8 Advance Bruker Bragg–Brentano diffractometer (Cu $K\alpha$ radiation) equipped with a Vantec-1 linear detector. Data were collected between 10° and 130° (2 θ) at room temperature with a 0.0164° step size. The coefficient of thermal expansion (CTE) of $\text{Sr}_3\text{Al}_2\text{O}_6$ was studied by in situ high-temperature XRD using a HTK1200N Anton Paar oven Chamber based on a Kanthal resistive-heating attachment. The powder sample was placed in a corundum crucible covered by platinum foil to minimize interaction with the sample. The set up temperature was previously calibrated using the thermal expansion of Al_2O_3 .²⁴ The sample was heated from 300 to 925 K at 10 K/min, and the ramp was stopped for each diffractogram to avoid any change during the data collection. The collected patterns were refined using the Rietveld method²⁵ with the TOPAS software (Bruker AXS TOPAS, version 3). Coefficients of thermal expansion were calculated following the method described by Sun et al.²⁶

Transmission electron microscopy (TEM) data were collected on a Philips CM20 microscope fitted with an Oxford energy dispersive spectrometry (EDS) analyzer. For the microstructure observations, a 10 × 15 μm^2 specimen was prepared using a focused ion beam (FIB) sample preparation system.

Density measurements were carried out at room temperature using the Archimedes method with absolute alcohol as the immersion fluid. The accuracy of the density measurement is $\pm 0.02 \text{ g cm}^{-3}$.

The transmission measurements were collected over the range from 200 to 7000 nm using a double-beam commercial spectrophotometer (Cary 5000) equipped with a photomultiplier and a PbS photocell for visible and infrared detection, respectively. An aperture of 1 mm was used for the reference and detection arm in accordance with the sample diameter. The average refractive index of the polycrystalline material was determined by fitting the reflectivity spectrum measured with a Bruker Vertex 80 V spectrometer in the infrared range (2–200 μm). From this analysis, an accurate estimation of the refractive index in the visible range is obtained by evaluating at visible wavelengths the physical dielectric function model optimized in the infrared range. The method is insensitive to scattering effects that can appear at shorter wavelengths.

Mechanical properties (i.e., reduced modulus and hardness) were measured with a nano mechanical testing system, Ti950 Triboindenter, Hysitron Inc. A number of 100 Berkovich indents were performed on optically polished surfaces at a 10 mN load. The loading and unloading rates were kept constant and equal to 1 mN/s, with a dwell time of 10 s at maximum load. The loading versus displacement curves were recorded, and the Oliver–Pharr method²⁷ was used to compute the reduced modulus. The hardness value was computed from the area function of the indenter tip and the maximum penetration depth at maximum load.

Excitation and emission spectra of the 5% Eu-doped $\text{Sr}_3\text{Al}_2\text{O}_6$ ($\text{Sr}_{2.85}\text{Eu}_{0.15}\text{Al}_2\text{O}_6$) transparent polycrystalline ceramics were recorded in a Horiba Jobin-Yvon Fluorolog spectrofluorometer. The picture showing the luminescence of the transparent doped sample was recorded under illumination with ultraviolet radiation ($\lambda = 254 \text{ nm}$).

The optical absorption spectra of the Er- and Ho-doped systems were measured using a PerkinElmer Lambda 1050 spectrophotometer, whereas their photoluminescence spectra were obtained under constant wavelength excitation using the 488 nm emission of an Ar^+ laser (National Laser Company NLC800, 250 mW). The emission was dispersed and selected with a monochromator (Princeton Instruments Acton SP2500) and then detected with a PMT (Thorn Emi QB9558) for the visible range or an InGaAs photodiode (Judson G5883) for the near-IR range.

For radioluminescence spectra, X-ray excitation was performed using a Philips X-ray tube equipped with a W anode. The high voltage (HV) was set at 35 kV, and the current was set at 30 mA. Collection of the emitted light was ensured by an optical fiber coupled to a monochromator (Shamrock 500) and a EMCCD camera (Newton, Andor). For scintillation decay time measurements, the 100 ps X-ray pulse width was produced with an X-ray tube triggered by a pulsed laser (Hamamatsu PLP10 and S20 cathode type). Scintillation photons detection was realized by a PMA165 photomultiplier tube and a PicoHarp 300 time correlated single-photon counting system, both from PicoQuant, ensuring a time resolution inferior to 150 ps.

3. RESULTS AND DISCUSSION

3.1. Synthesis of the $\text{Sr}_3\text{Al}_2\text{O}_6$ Transparent Ceramic.

Glass beads of 3–5 mm in diameter have been synthesized using an aerodynamic levitation system coupled to a double-laser heating device. Such a contactless setup allowed not only a high temperature (1800 $^\circ\text{C}$) to be reached but also a rapid quenching rate of several hundreds of degrees celsius per second. Both features are required to ensure vitrification of this composition.²⁸ It is expected that the production of larger quantities of glass sample could be performed using a conventional induction or electric-arc high-temperature melting industrial process. The sample's amorphousness has been checked by XRD (Figure 1, inset) and electron diffraction.

The thermal behavior of the as-elaborated $\text{Sr}_3\text{Al}_2\text{O}_6$ glass was recorded by DSC. The thermogram shows a weak glass transition at 685(1) $^\circ\text{C}$ and an intense single exothermic peak at 762(1) $^\circ\text{C}$ corresponding to the unique crystallization of the cubic $\text{Sr}_3\text{Al}_2\text{O}_6$ material (ICSD 71860, PDF 00-024-1187), as

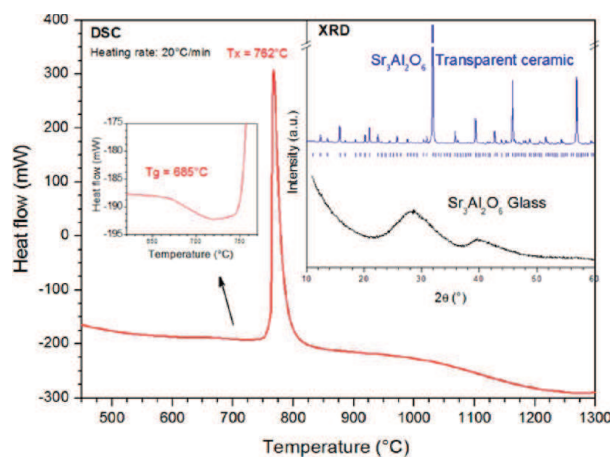


Figure 1. DSC thermogram of the $\text{Sr}_3\text{Al}_2\text{O}_6$ glass showing T_g at 685(1) $^\circ\text{C}$ and crystallization at 762(1) $^\circ\text{C}$. The inset shows the X-ray powder diffraction patterns of the $\text{Sr}_3\text{Al}_2\text{O}_6$ glass and transparent polycrystalline ceramic obtained after annealing the glass at 850 $^\circ\text{C}$ for 4 h. The indexation corresponds to the $\text{Sr}_3\text{Al}_2\text{O}_6$ reported structure (ICSD 71860, PDF 01-081-0506).²⁹

shown by XRD (Figure 1, inset). It should be noted that an exact 3:1 stoichiometric amount of the SrCO_3 and Al_2O_3 starting oxides is required to avoid the formation of secondary phases that prevent transparency during crystallization.

From these thermal parameters, full crystallization of the $\text{Sr}_3\text{Al}_2\text{O}_6$ glass was simply and directly performed using a single thermal treatment at 840 $^\circ\text{C}$ for 5 h, leading to a highly transparent polycrystalline ceramic hardly distinguishable from the glass by the naked eye (Figure 2). No amorphous area

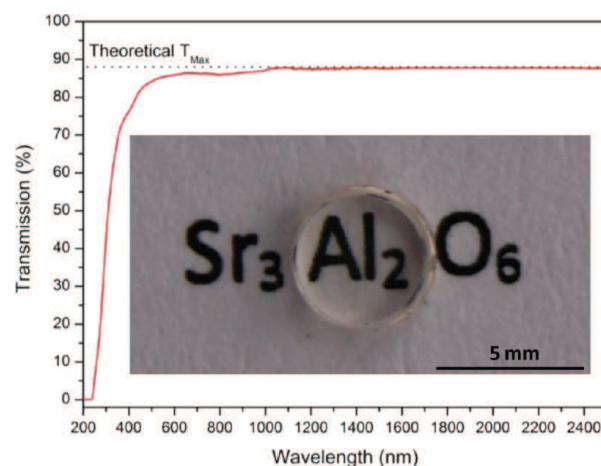


Figure 2. Transmission spectra of the $\text{Sr}_3\text{Al}_2\text{O}_6$ transparent polycrystalline ceramic (obtained from a 1.5 mm thick sample). The dotted black line corresponds to the theoretical maximum transmission calculated as 87.4% for an average refractive index of 1.70. A photograph of the $\text{Sr}_3\text{Al}_2\text{O}_6$ material is also shown.

could be detected under TEM examination, and longer annealing treatments at this temperature did not modify the transparency behavior or improve the crystallinity of the sample, demonstrating the full crystallization of the parent glass. Actually, the ceramization can be performed over a wide lower temperature range, with the use of a lower temperature only implying longer annealing times. However, annealing at

higher temperatures led to less transparent materials, most probably because of the strong thermal expansion constraints affecting the sample and thus inducing porosity or constraints (i.e., defects being diffusion centers).

As shown in Figure 2, the $\text{Sr}_3\text{Al}_2\text{O}_6$ polycrystalline ceramic obtained by full crystallization from glass displays an outstanding transparency in the visible range. Moreover, this transparency covers a wide optical range from the visible to infrared ranges (from 300 nm up to more than 6 μm). The full wavelength range transparency is presented in Figure S2. The absorption below 300 nm corresponds to the optical band gap absorption of the strontium aluminate sample, whereas the absorption observed around 3 μm corresponds to moisture in the sample (O–H bonds). The difference between the measured transparency and the theoretical maximum value calculated as $87.4 \pm 0.5\%$ for an average refractive index of 1.70 ± 0.02 is very small in the visible range and is negligible in the IR range. This indicates that a very small amount of scattering centers within the polycrystalline ceramic.

The high transmission value remains constant in the IR region up to 6 μm because of the relatively low phonon energy, especially compared to silicate compositions commonly used in glass-ceramic technology.^{14d} With alkaline earth aluminates being famous for their luminescence properties,^{18,19,20a,b,30} the elaboration of such a transparent ceramic is of technological interest because the excitation radiation and the light-emission response would be enhanced by orders of magnitude compared to common opaque bulk ceramics prepared from solid-state synthesis (with only their surface being active). Such a transparent polycrystalline material could thus compete with single-crystal technology by having a much lower cost and greater compositional flexibility (less or even no segregation of the doping agents during crystallization).

To explain the high transparency observed in the $\text{Sr}_3\text{Al}_2\text{O}_6$ transparent polycrystalline ceramic, the microstructure has been investigated in more detail.

3.2. Microstructure Study. TEM images of the $\text{Sr}_3\text{Al}_2\text{O}_6$ transparent polycrystalline ceramic recorded on a sample prepared by focused-ion-beam lift out are presented in Figure 3. A typical bright-field transmission electron microscopy image is shown in Figure 3a, and the corresponding dark-field pattern presented Figure 3b reveals a selection of crystals, allowing the grains morphology to be distinguished more clearly. The patterns show a very dense mosaic microstructure with micrometric grain size, similar to the images observed in previous transparent polycrystalline ceramics obtained from a solid-state reaction under high pressure.^{3d,31} No porosity could be detected, and the grain boundaries appear very narrow, proving the strong advantage and ease of using crystallization from glass rather than solid-state reaction/sintering to obtain fully dense polycrystalline ceramics. An average crystal size between 0.5 and 2 μm can be estimated.

From these microstructure observations, it appears that the achievement of such a highly transparent ceramic is made possible through the combination of the high density (absence of pores) and very thin grain boundaries, both achieved by the crystallization from glass elaboration method, as well as the structural and optical isotropy (no birefringence) inherent to the cubic $\text{Sr}_3\text{Al}_2\text{O}_6$ structure. The absence of porosity in the crystalline sample can be explained by the very similar density values of both glass and ceramic samples measured using the Archimedes's method (4.11(2) and 4.13(2) g cm^{-3} , respectively). A congruent crystallization with a weak density

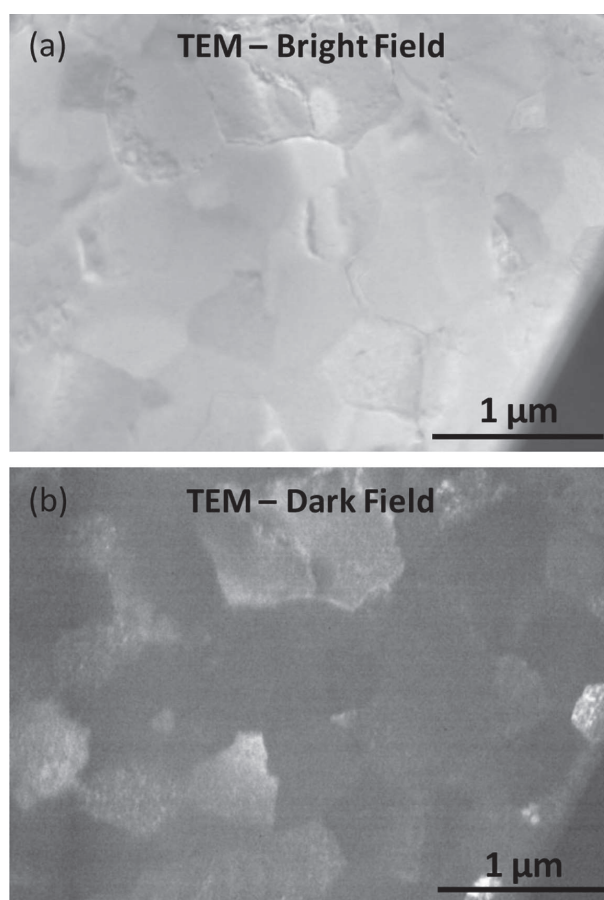


Figure 3. (a) Bright-field transmission electron microscopy image of the $\text{Sr}_3\text{Al}_2\text{O}_6$ transparent polycrystalline ceramic showing high density, narrow grain boundaries, and fine microstructures ($\sim 0.5\text{--}2\ \mu\text{m}$ grain size). (b) Dark-field pattern recorded on the same area clearly reveals the grain morphology.

difference between the glass and crystalline phases seems to be a key factor to obtain transparent polycrystalline ceramics by full crystallization from glass.

3.3. $\text{Sr}_3\text{Ga}_2\text{O}_6$ Transparent Polycrystalline Ceramic. Using a similar preparation method, we have been able to synthesize an analogous gallate transparent polycrystalline ceramic, namely, $\text{Sr}_3\text{Ga}_2\text{O}_6$. DSC measurements presented in Figure S3 show thermal parameters ($T_g = 698(1)\ ^\circ\text{C}$ and $T_c = 749(1)\ ^\circ\text{C}$) close to those of the aluminate sample analogue. The crystallization peak corresponds to the single crystallization of $\text{Sr}_3\text{Ga}_2\text{O}_6$, as proved by XRD (Figure S3, inset). Consequently, the $\text{Sr}_3\text{Ga}_2\text{O}_6$ transparent polycrystalline ceramic has been prepared by annealing the glass at 750 $^\circ\text{C}$ for 2 h 30 min. Both the $\text{Sr}_3\text{Ga}_2\text{O}_6$ glass and ceramic are presented in Figure 4. A high transparency level, similar to the $\text{Sr}_3\text{Al}_2\text{O}_6$ material, can be attained. However, both the glass and ceramic are slightly hygroscopic. An alteration of the sample surface can be observed after a few hours under ambient conditions. This deterioration prevents the high transparency from being maintained, which may be a strong drawback for commercial applications. Utilization of this material would require encapsulation or passivation.³²

3.4. Mechanical and Thermal Properties. The hardness and the reduced elasticity modulus values measured on both

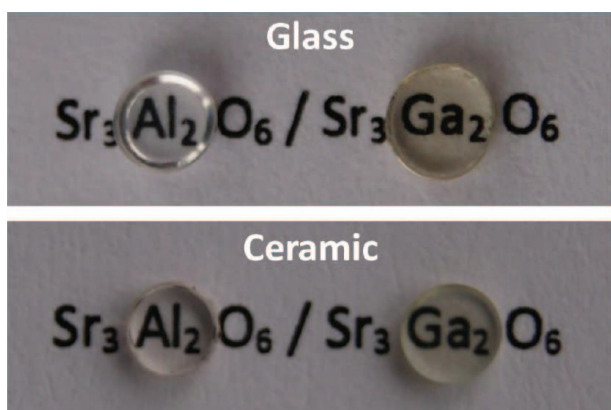


Figure 4. Pictures of both $\text{Sr}_3\text{Ga}_2\text{O}_6$ and $\text{Sr}_3\text{Al}_2\text{O}_6$ glass (top) and transparent polycrystalline ceramic (bottom).

the $\text{Sr}_3\text{Al}_2\text{O}_6$ glass and ceramic samples by nanoindentation were quite reproducible from one batch to another (Figure S4). A significant increase of both the hardness, $H_{\text{glass}} = 7$ and $H_{\text{ceramic}} = 10.5$ GPa, and the reduced elasticity modulus (from 105 to 150 GPa) was observed.

Because the thermal expansion can be an important characteristic for many applications, CTE measurements have been performed from in situ high-temperature XRD experiments. The unit-cell parameters evolution versus temperature for $\text{Sr}_3\text{Al}_2\text{O}_6$ is shown in Figure S5a. According to Sun et al.,²⁶ the volumetric CTE is defined by the following expression

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right) \text{ or } V(T) = V_0 \exp \left[\int \beta(T) dT \right]$$

where V_0 is the measured volume at T_0 (room temperature) and $\beta(T)$ is a temperature-dependent thermal expansion. Linear fitting of $\ln(V/V_0)$ versus $(T - T_0)$ up to 925 K (see Figure S5b) leads to the volumetric thermal expansion coefficient of $\text{Sr}_3\text{Al}_2\text{O}_6$ ($\beta_0 = (28.9(2) \times 10^{-6} \text{ K}^{-1})$) and a linear thermal expansion coefficient calculated as $9.6(1) \times 10^{-6} \text{ K}^{-1}$ (cubic symmetry) from rt to 925 K. Given the fully dense (pore free) polycrystalline microstructure of our $\text{Sr}_3\text{Al}_2\text{O}_6$ material, the linear CTE obtained by HTXRD can be directly compared to values measured by dilatometry. The $\text{Sr}_3\text{Al}_2\text{O}_6$ CTE is then close to the value reported for the SrAl_2O_4 ceramic ($7.8 \times 10^{-6} \text{ K}^{-1}$).³³

3.5. Optical Properties. Alkaline earth aluminates have been widely studied for their optical properties, particularly for their promising phosphorescent properties.^{18,20a,b,30,34} Here, we show that the $\text{Sr}_3\text{Al}_2\text{O}_6$ material may be used as a matrix for doping with various related applications. Eu^{3+} , Er^{3+} , and Ho^{3+} single-doping agents have been chosen to show visible (for Eu^{3+}) and infrared (for Er^{3+} and Ho^{3+}) luminescence. Remarkably, scintillation properties can be equally demonstrated using Ce^{3+} doping.

To confirm the incorporation of europium within the $\text{Sr}_3\text{Al}_2\text{O}_6$ structure, we performed $\text{Eu}:\text{Sr}_3\text{Al}_2\text{O}_6$ cell parameters refinements from XRD data on different doping contents (0, 2.5, and 5%). The results (Figure S6 and Table S1) clearly show a continuous decrease of the cell parameter, as expected from the ionic radius of Eu^{3+} (0.890 Å in VI coordination) being smaller than that of Sr^{2+} (1.180 Å in VI coordination).³⁵ As a consequence, the Eu^{3+} doping must induce some structural rearrangement to accommodate the charge difference. Previous

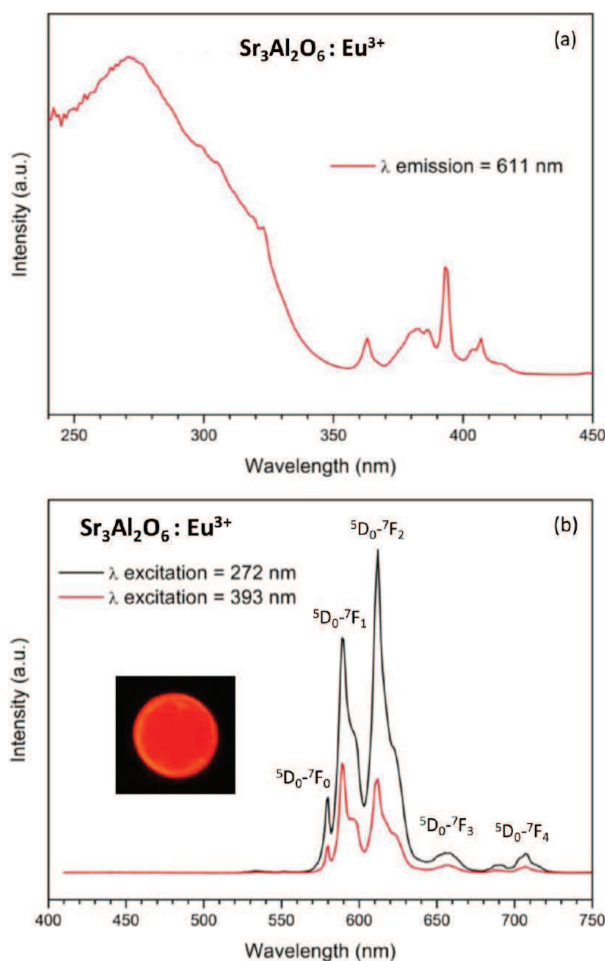


Figure 5. (a) Excitation ($\lambda_{\text{em}} = 611 \text{ nm}$) and (b) emission ($\lambda_{\text{ex}} = 272$ and 393 nm) spectra of the 5% Eu^{3+} -doped $\text{Sr}_3\text{Al}_2\text{O}_6$ sample. The inset shows a picture of the $\text{Eu}:\text{Sr}_3\text{Al}_2\text{O}_6$ sample recorded under UV excitation.

computational work showed that strontium vacancies may compensate for the excess of charge.^{19d} Figure 5a shows the excitation spectrum for the 5% Eu -doped $\text{Sr}_3\text{Al}_2\text{O}_6$ ($\text{Sr}_{2.85}\text{Eu}_{0.15}\text{Al}_2\text{O}_6$) ceramic monitored at 611 nm. This spectrum consists of several typical bands in the 200–450 nm range similar to those previously reported earlier on $\text{Sr}_3\text{Ga}_2\text{O}_6:\text{Eu}^{3+}$ powder ceramics,^{19e} which were attributed to an $\text{Eu}^{3+}/\text{O}^{2-}$ charge-transfer band (CTB; broad feature centered at 272 nm) and to the direct excitation of the Eu^{3+} cations from the ground state to higher levels of the 4f manifold (weaker bands at $>300 \text{ nm}$).

The emission spectrum of this Eu^{3+} doped sample (Figure 5b) obtained either using an excitation wavelength of 272 (CTB) or 393 nm (the most intense Eu^{3+} excitation band corresponds to the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition) displayed similar emissions, with most of them at $\lambda > 570 \text{ nm}$ because of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($j = 1, 2, 3$, and 4) electronic transitions characteristic of the Eu^{3+} cations. However, the intensity of these emissions was noticeably higher when exciting at 272 nm, indicating that the most efficient excitation of Eu^{3+} occurs through the charge transfer band. It can also be observed that the most intense emissions appeared in the 580–620 nm range. These are responsible for the strong red luminescence observed for this

sample (Figure 5b, inset). Finally, it is important to mention that the relative intensity of the $^5D_0 \rightarrow ^7F_2$ emission band was higher than that associated with the $^5D_0 \rightarrow ^7F_1$ transition, which is expected for Eu^{3+} cations located in crystallographic sites without an inversion center, as is the case for the Sr polyhedra in the $\text{Sr}_3\text{Al}_2\text{O}_6$ structure.

Figures 6a and S7a show the absorption spectra of Er- and Ho-doped ceramics. The spectra consist of several absorption

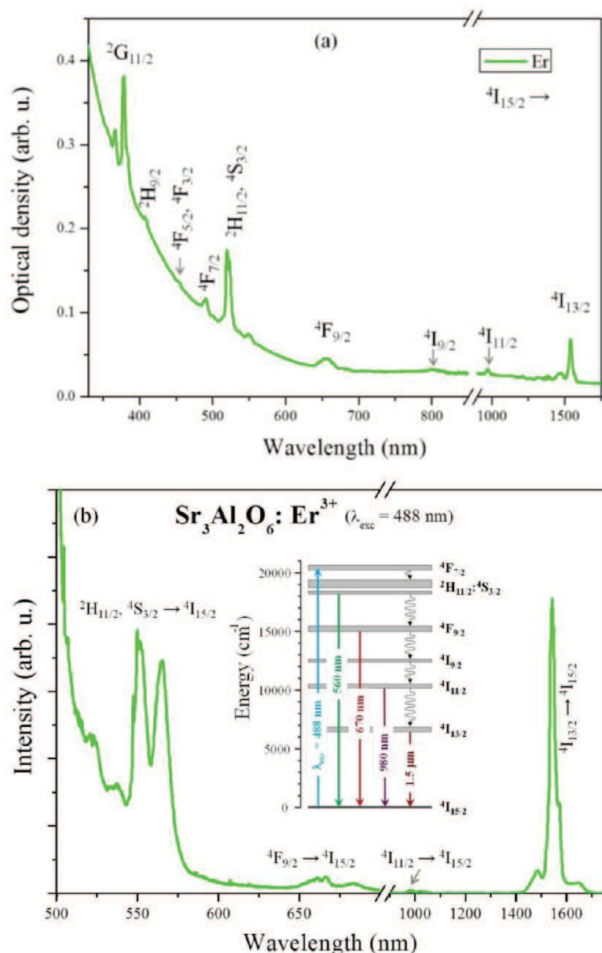


Figure 6. (a) Optical density and (b) emission ($\lambda_{\text{ex}} = 488$ nm) spectra of the 1% Er^{3+} -doped $\text{Sr}_3\text{Al}_2\text{O}_6$ ceramic.

bands, which are clearly identified over a background that increases toward the shortest wavelength region of the spectra. This background may be associated with light scattering in the ceramic.³⁶ The different absorption bands of the rare-earth ions are clearly visible and correspond to transitions from the ground state, $^4I_{15/2}$ for Er^{3+} and 5I_8 for Ho^{3+} , to the different excited state multiplets that are labeled in the figure.

Figures 6b and S7b show the luminescence spectra of the transparent Er- and Ho-doped polycrystalline ceramics after 488 nm laser excitation. The insets include the energy-level structure together with the relevant transitions for each cation. In the case of Er^{3+} (Figure 6b), the excitation reaches the $^4F_{7/2}$ multiplet, which relaxes to the $^2H_{11/2}$, $^4S_{3/2}$ levels, from which an intense green emission (550 nm, $^2H_{11/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$) takes place. The excitation also partially relaxes non radiatively to lower-lying excited-state multiplets, giving rise to a cascade of

different emissions in the visible and near-infrared range: ~ 670 nm, ($^2F_{9/2} \rightarrow ^4I_{15/2}$), ~ 980 nm ($^4I_{11/2} \rightarrow ^4I_{15/2}$), and the characteristic IR emission at $1.5 \mu\text{m}$ from the lowest excited-state multiplet ($^4I_{13/2} \rightarrow ^4I_{15/2}$). In the case of Ho^{3+} (Figure S7), the excitation reaches the 5F_3 multiplet, which relaxes to the 5F_4 , 5S_2 levels first and then to other lower-lying multiplets, giving rise to several characteristic emissions in the visible and near IR range, which are also labeled in the figure. The observed emissions are in accordance with those observed in other Er- and Ho-doped hosts.³⁷

Scintillating materials (e.g., single crystals, powders, thin films, and ceramics) have the capacity to emit visible or UV photons under ionizing radiation. Having a scalable synthesis route to produce transparent bulk material with scintillating properties is of high interest because of its low cost (compared to single crystal). Depending on the application, a compromise between the two important parameters for scintillation (i.e., yield and the timing response) has to be made. For counting technique applications, having a rather fast time response is mandatory to avoid pile-up (submicrosecond). In this view, most common activators are Ce^{3+} and Eu^{2+} , which exhibit a fast and efficient radiative electric dipole transition from $5d^14f^0$ to $4f^n$ configurations. Nevertheless, because of the complex relaxation processes prior to the emission of light, having a fast and efficient luminescence under intracenter excitation does not guaranty the efficiency and fast timing response under ionizing radiation. In this regard, photoluminescence spectroscopy and radioluminescence spectra of the cerium-doped samples as well as luminescence decay under pulsed X-ray excitation have been performed and are presented in Figure 7.

In the glass sample, the cerium emission spectrum peaks at 415 nm, and the two related excitation bands observed are typical for cerium in a low-symmetry site (Figure 7a). In the crystallized form, the emission spectra recorded under UV excitation (365 nm) is red-shifted (centered at 470 nm), indicating a stronger crystal field. The excitation spectrum of the emission at 500 nm consists of several unresolved bands. These spectral behaviors are quite similar to the ones previously observed in the same material prepared by solid-state reaction.^{19f} However, a small red shift in the emission spectrum is observed, and the ratio intensity in the excitation bands is not identical. Because the process of the full crystallization from glass does not follow the same thermodynamic pathway as compared to the solid-state reaction, a different distribution of cerium on the crystallographic sites of the $\text{Sr}_3\text{Al}_2\text{O}_6$ may be considered for the transparent ceramics. Some differences in the charge compensation ($\text{Sr}^{2+}-\text{Ce}^{3+}$), which have a significant effect on the excitation bands as pointed out by the authors using additional codopants, may be considered as well. Under X-ray excitation, the emission spectrum of the crystallized compound is similar to that observed under UV excitation, whereas under the same excitation and light-collection conditions, no scintillation is detected in the glass material. This corresponds to the general tendency of scintillating materials to exhibit a better efficiency when crystallized as compared to when in amorphous phases. Under pulsed X-ray excitation (100 ps timing resolution), the scintillation decay time can be fitted with a two exponential decay, with decay constants of 5.8 and 66 ns (the fit presented Figure 7c). The short decay clearly indicates a quenching process, which is in good agreement with the rather weak scintillation yield observed as compared to the standard cerium-doped crystals such as $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ (a rough comparison gives around 50 to

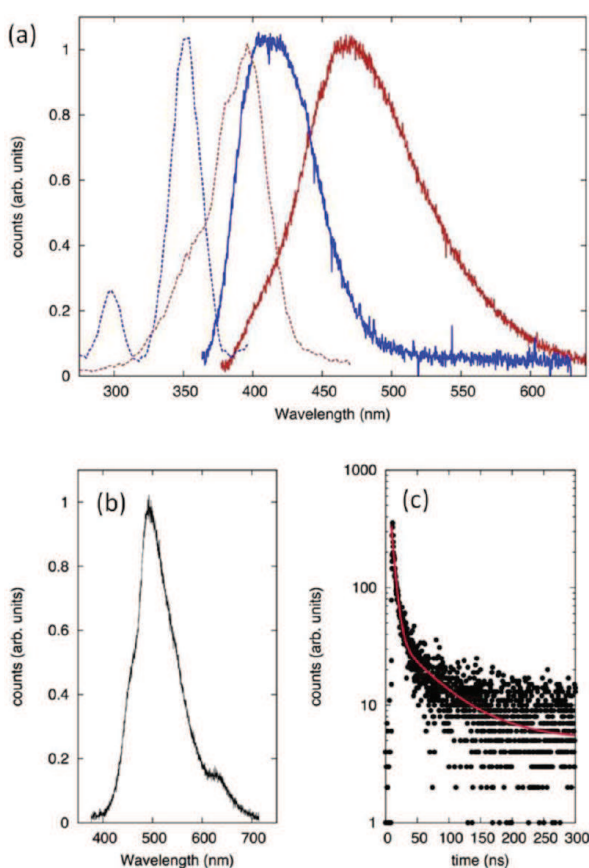


Figure 7. (a) Room-temperature luminescence (solid line) and excitation spectra (dashed line) of the $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Ce}^{3+}$ glass (blue spectra, excitation recorded at 350 nm and emission at 420 nm) and the $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Ce}^{3+}$ transparent ceramic (red spectra, excitation recorded at 365 nm and emission at 500 nm). (b) Room-temperature radioluminescence spectrum of the $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Ce}^{3+}$ transparent ceramic (excitation conditions: W anode, HT35 kV, $I = 25$ mA). (c) Scintillation decay time under pulsed X-ray excitation (W anode, HV 30 kV).

100 times lower). Nevertheless, it indicates that this synthesis route enables the production of scintillating material, which can be applied to other compositions exhibiting higher scintillation yield.

4. CONCLUSIONS

We have synthesized a new transparent polycrystalline ceramic, namely, $\text{Sr}_3\text{Al}_2\text{O}_6$, by congruent full crystallization from glass. The high level of transparency, almost matching the maximum theoretical value throughout the visible and IR (up to 6 μm) ranges, is explained through the specific microstructure inherent to the elaboration process. The micrometer-scale $\text{Sr}_3\text{Al}_2\text{O}_6$ grains organization shows no porosity and very thin grain boundaries, leading to an ultra-dense ceramic. Moreover, the light scattering is minimized because of the cubic symmetry of this material, which leads to optical isotropy (no birefringence). Along with the thermal and mechanical properties improvement, the transparent $\text{Sr}_3\text{Al}_2\text{O}_6$ ceramic appears to be an interesting candidate for various photonic applications, such as luminescence and scintillation, either in the visible or IR ranges.

Full congruent crystallization from glass appears to be a simple and effective way to elaborate transparent polycrystalline ceramics. This process overcomes the porosity problem that is the main drawback to the development of transparent polycrystalline ceramic by widely used sintering techniques. As a proof of concept, we have equally elaborated a highly transparent $\text{Sr}_3\text{Ga}_2\text{O}_6$ polycrystalline ceramic, which turned out to be slightly hygroscopic. We believe that the cost-effective and simple method described in this article proposes an alternative that is likely to stimulate the development of new transparent ceramic materials with designable optical properties.

■ ASSOCIATED CONTENT

Supporting Information

Scheme of the aerodynamic levitator equipped with two CO_2 lasers. Transmission spectra of the $\text{Sr}_3\text{Al}_2\text{O}_6$ transparent polycrystalline ceramic. DSC thermogram of the $\text{Sr}_3\text{Ga}_2\text{O}_6$ glass and X-ray powder diffraction patterns of the $\text{Sr}_3\text{Ga}_2\text{O}_6$ glass and transparent polycrystalline ceramic. Scanning probe microscopy images of 10 mN Berkovich indentation imprints on the $\text{Sr}_3\text{Al}_2\text{O}_6$ glass and ceramic. Hardness and reduced modulus values of the glass and the ceramic. Normalized unit cell parameters for $\text{Sr}_3\text{Al}_2\text{O}_6$ as a function of temperature and plot of $\ln(V/V_0)$ versus $(T - T_0)$ from rt to 925 K for $\text{Sr}_3\text{Al}_2\text{O}_6$. X-ray powder diffraction patterns of the europium doped transparent polycrystalline ceramics samples showing the cell parameter decrease along the strontium for europium substitution process. Optical density and emission spectra of the Er^{3+} -doped $\text{Sr}_3\text{Al}_2\text{O}_6$ sample. Evolution of the $\text{Eu}:\text{Sr}_3\text{Al}_2\text{O}_6$ cell parameters as a function of the Europium substitution content. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was partly funded by the French ANR under the project CrystOG ANR-12-JS08-0002-01, by Junta de Andalucía (Grant FQM6090) and by the Spanish MINECO (MAT2012-34919). The authors thank the CRMD (Orléans, France) laboratory for access to the TEM.

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■ NOTE ADDED AFTER ASAP PUBLICATION

There were errors in the text of this paper published October 11, 2013. The correct version published October 22, 2013.

Perfectly transparent $\text{Sr}_3\text{Al}_2\text{O}_6$ polycrystalline ceramic elaborated from glass crystallization

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Supporting Information

Figure S1. Scheme of the aerodynamic levitator equipped with two CO_2 lasers.

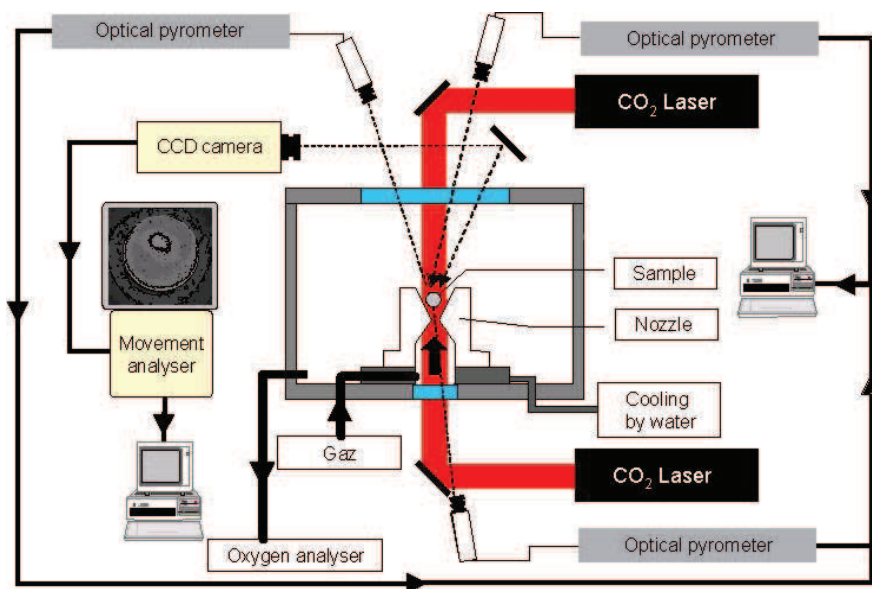


Figure S2. Transmission spectra of the $\text{Sr}_3\text{Al}_2\text{O}_6$ transparent polycrystalline ceramic (obtained from a 1.5mm thick sample). The dotted black line corresponds to the theoretical maximum transmission calculated as 87.4 % for an average refractive index of 1.70.

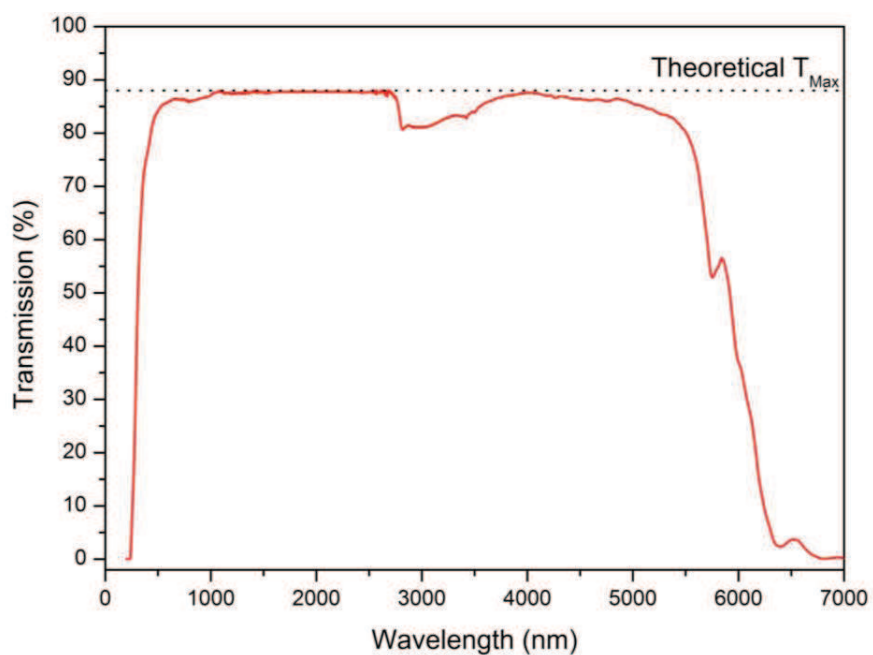


Figure S3. DSC thermogram of the $\text{Sr}_3\text{Ga}_2\text{O}_6$ glass showing T_g at 698(1) $^\circ\text{C}$ and crystallization at 749(1) $^\circ\text{C}$. Inset: X-ray powder diffraction patterns of the $\text{Sr}_3\text{Ga}_2\text{O}_6$ glass and transparent polycrystalline ceramic obtained after annealing of the glass at 750 $^\circ\text{C}$ for 2 h 30 min. The indexation corresponds to the $\text{Sr}_3\text{Ga}_2\text{O}_6$ reported structure (ICSD 71860 - PDF 00-024-1187).

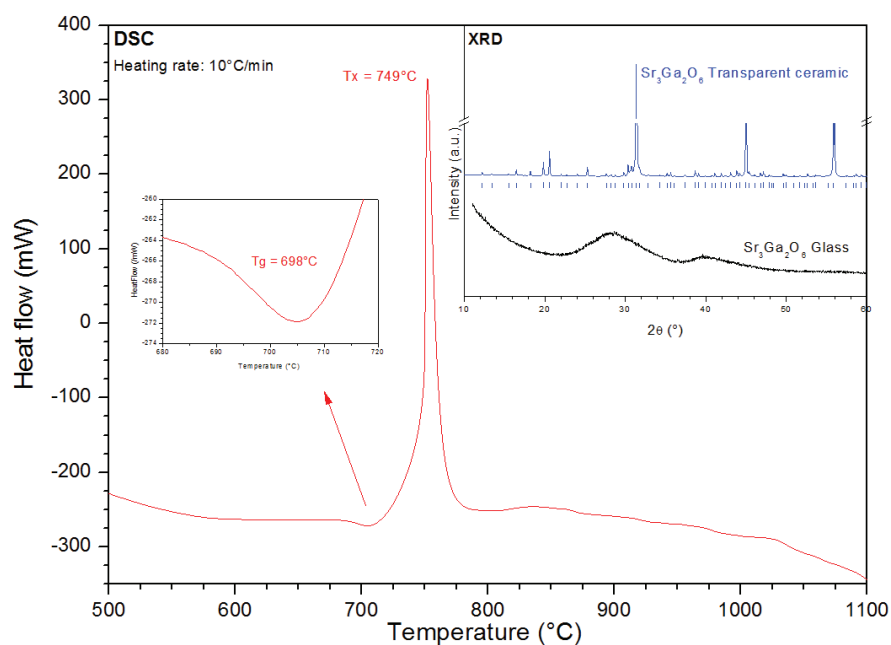


Figure S4. Scanning probe microscopy images (Hysitron TI-950) of 10 mN Berkovich indentation imprints on: a) the $\text{Sr}_3\text{Al}_2\text{O}_6$ glass and b) the $\text{Sr}_3\text{Al}_2\text{O}_6$ ceramic. c) Hardness and d) reduced modulus values of the $\text{Sr}_3\text{Al}_2\text{O}_6$ glass and ceramic. Two samples from two different batches (1 and 2) were tested. Each reported value is a mean value over at least 100 measurements, error bars are the respective standard deviation of the data set.

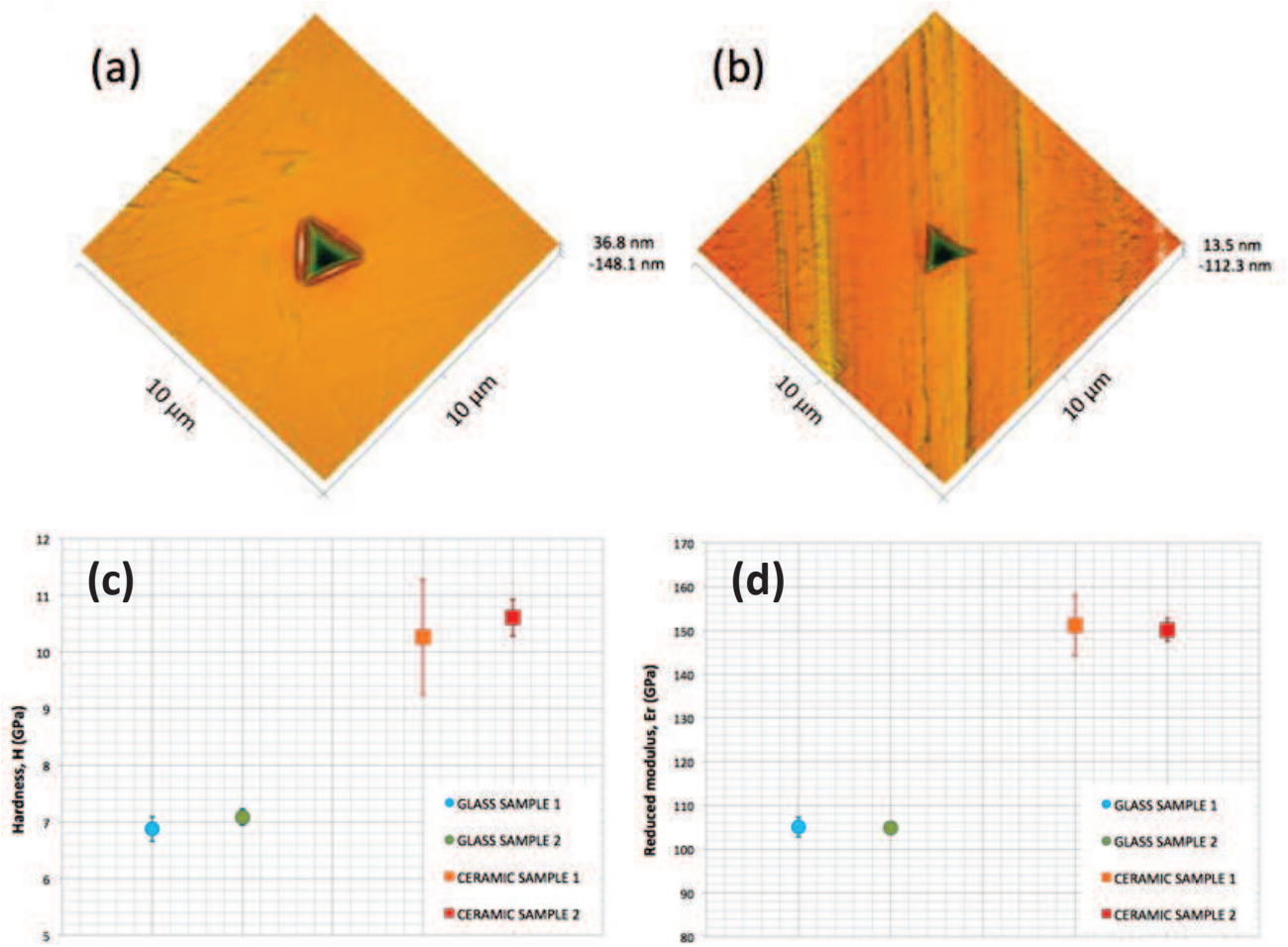


Figure S5. (a) Normalized unit cell parameters for $\text{Sr}_3\text{Al}_2\text{O}_6$ as a function of temperature. (b) Plot of $\ln(V/V_0)$ versus $(T-T_0)$ from RT to 925 K for $\text{Sr}_3\text{Al}_2\text{O}_6$.

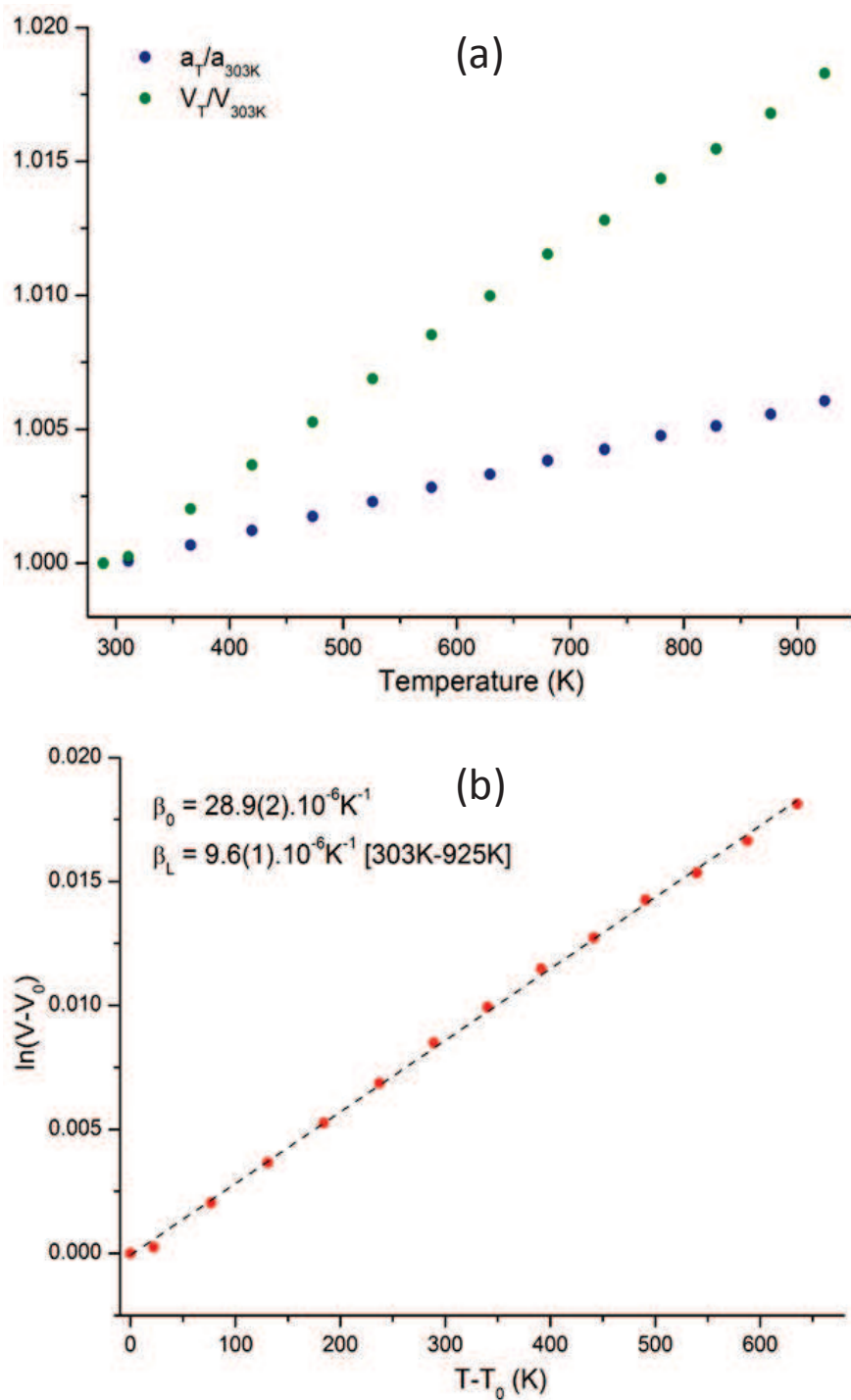


Figure S6. X-ray powder diffraction patterns of the europium doped transparent polycrystalline ceramics samples ($\text{Sr}_3\text{Al}_2\text{O}_6$ (0%), $\text{Sr}_{2.925}\text{Eu}_{0.075}\text{Al}_2\text{O}_6$ (2.5%) and $\text{Sr}_{2.85}\text{Eu}_{0.15}\text{Al}_2\text{O}_6$ (5%)). Inset: evolution of the $\text{Eu}:\text{Sr}_3\text{Al}_2\text{O}_6$ cell parameters as a function of the europium substitution level.

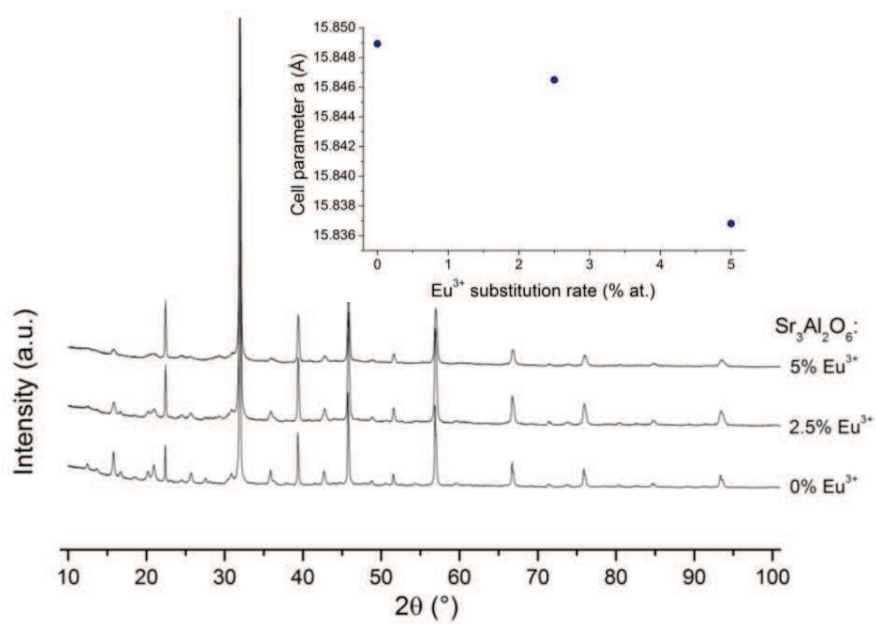


Figure S7. (a) Optical density and (b) emission ($\lambda_{\text{exc}} = 488$ nm) spectra of the 1% Er^{3+} -doped $\text{Sr}_3\text{Al}_2\text{O}_6$ sample.

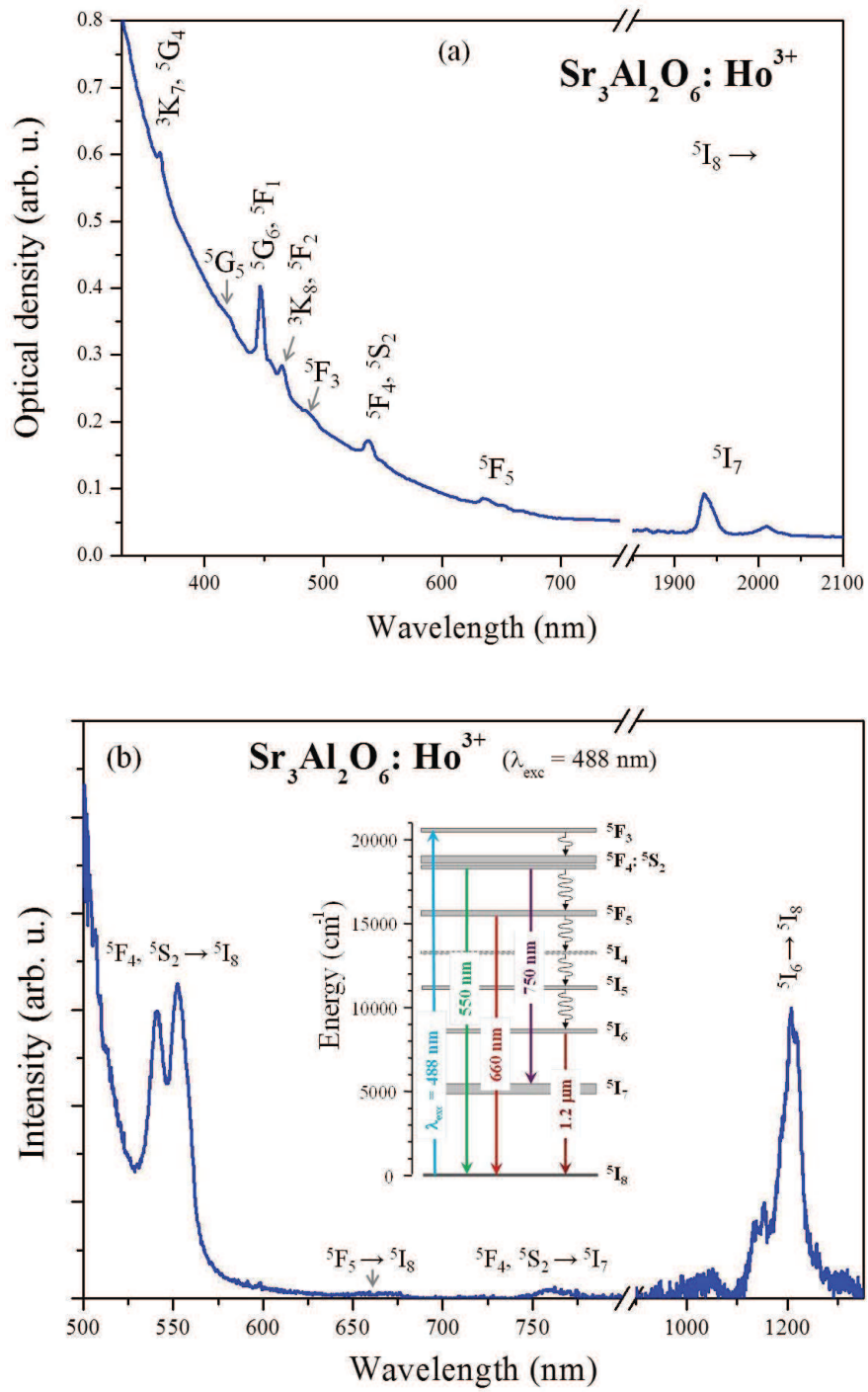


Table S1. Evolution of the $\text{Eu}:\text{Sr}_3\text{Al}_2\text{O}_6$ cell parameters as a function of the europium substitution content. The non doped, 2.5% doped and 5% doped samples correspond respectively to the $\text{Sr}_3\text{Al}_2\text{O}_6$, $\text{Sr}_{2.925}\text{Eu}_{0.075}\text{Al}_2\text{O}_6$ and $\text{Sr}_{2.85}\text{Eu}_{0.15}\text{Al}_2\text{O}_6$ formula.

$\text{Sr}_3\text{Al}_2\text{O}_6$	Cell parameter (Å)
Non doped	15.8489(1)
Eu^{3+} Doped (2.5%)	15.8465(1)
Eu^{3+} Doped (5%)	15.8368(1)

Transparency record through structural disorder: a new concept for innovative transparent ceramics

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KEYWORDS: *Transparent polycrystalline ceramic, Glass crystallization, strontium aluminosilicate, local disorder, DFT birefringence calculation.*

ABSTRACT: Transparent polycrystalline ceramics present significant economical and functional advantages over single crystal materials for optical, communication, and laser technologies. To date, transparency in these ceramics is ensured either by an optical isotropy (i.e. cubic symmetry) or a nanometric crystallite size, and the main challenge remains to eliminate porosity through complex high pressure-high temperature synthesis. Here we introduce a new concept to achieve ultimate transparency reaching the theoretical limit. We use a controlled degree of chemical disorder in the structure to obtain optical isotropy at the micrometer length scale. This approach can be applied in the case of anisotropic structures and micrometer scale crystal size ceramics. We thus report $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 < x \leq 0.4$) readily scalable polycrystalline ceramics elaborated by full and congruent crystallization from glass. These materials reach 90% transmittance, the highest reported value for polycrystalline oxide materials. This innovative method should drive the development of new highly transparent materials with technologically relevant applications.

INTRODUCTION

Transparent inorganic materials are a key technology in modern technology; used for optical and lighting applications in electronic, aerospace, civil construction and defense industries.¹ Despite outstanding optical performance, single crystal materials are limited in size and geometry, restricted chemical doping level, and expensive synthesis requirements. Transparent polycrystalline ceramics have recently proved their ability to replace expensive single crystals in domains including optics, electronics, and scintillating devices.²⁻⁶ Polycrystalline ceramics are attractive due to geometric versatility, relatively swift scalable manufacturing, doping flexibility, and a wide range of accessible chemistries.^{2, 4, 6-9} To date, transparency in these advanced materials is ensured either by an optical isotropy (i.e. cubic symmetry) or a very small crystal size^{3, 10} (smaller than the wavelength of the incident light as described by the Rayleigh-Ganz particle scattering theory¹¹), and the absence of light scattering sites (pores, secondary phase...) to avoid energy dissipation within the material.¹⁰ Several materials have been developed such as the cubic MgAl_2O_4 spinel used in transparent armor applications¹², sesquioxides and Nd:YAG ceramics for laser application¹³, ZrO_2 and Lu_3NbO_7 ceramics for optical lenses^{14, 15} and the nanometric rhombohedral Al_2O_3 .¹⁶⁻¹⁸ Diverse synthetic approaches, either by hot pressure, vacuum, microwave or spark plasma sintering of specific

nanometer-scale raw materials are employed. However, all these processes require complex sintering conditions, and it remains difficult to completely eliminate the presence of residual pores which strongly attenuates transparency.⁷

To overcome the drawbacks of sintered ceramic materials, full and congruent crystallization from a massive glass precursor is a promising alternative leading to fully dense polycrystalline materials (i.e. showing complete absence of porosity and very thin grain boundaries). Based on this approach, the authors have recently reported on the BaAl_4O_7 and $\text{Sr}_3\text{Al}_2\text{O}_6$ transparent polycrystalline ceramic compositions.¹⁹⁻²¹ In these studies, glass precursors were prepared using a homemade aerodynamic levitator coupled to a CO_2 laser heating system²² which limited the synthesis scale to glass beads $\leq 5\text{mm}$ in diameter, thus hindering access to technological applications via industrial transfer. In such materials showing micrometer scale crystallites, the transparency is limited by the intrinsic birefringence of the material which gives rise to light scattering effects at the grain boundaries.

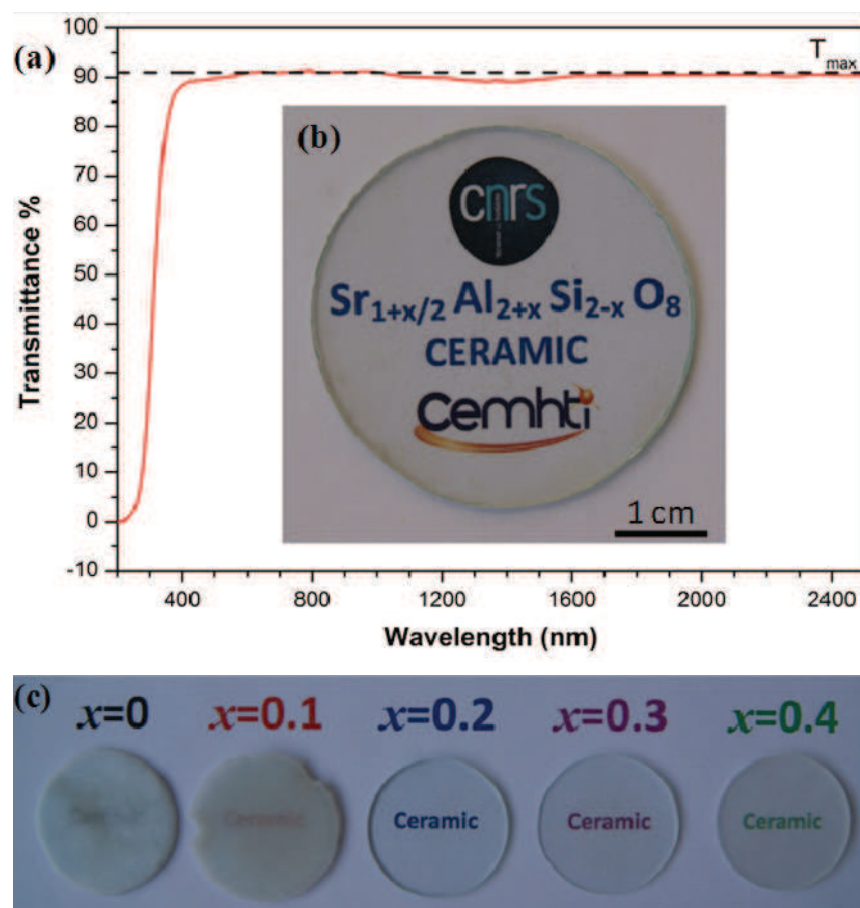


Figure 1. Transparency of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0.4$) polycrystalline ceramics. (a) Transmission spectrum measured on a $\text{Sr}_{1.1}\text{Al}_{2.2}\text{Si}_{1.8}\text{O}_8$ ($x = 0.2$) composition sample (1.5 mm thickness). The $n = 1.59$ refractive index implies a 90.1 % maximum theoretical transparency (dashed line). (b) Photograph of the same material illustrating the almost perfect 90% transparency. (c) Photograph of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($x=0, 0.1, 0.2, 0.3$ and 0.4) polycrystalline ceramics showing transparency evolution along the reported solid solution.

In this communication we report the possibility to elaborate innovative large scale and highly transparent polycrystalline ceramics (**Figure1**). These fully crystallized materials constitute a previously unreported $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 < x \leq 0.4$) solid solution localized along the tie line between $\text{SrAl}_2\text{Si}_2\text{O}_8$ and SrAl_2O_4 in the $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ternary diagram (**Figure2a**). The parent glass materials can be prepared at a large scale by a classic melt-quenching preparation method. A subsequent simple heat treatment leads to full and congruent crystallization of highly transparent polycrystalline ceramics (**Figure1**). The control of chemical disorder along this solid solution allows minimization of the birefringence in these non cubic materials exhibiting hexagonal symmetry and micrometer scale crystallite sizes, thus leading to optical isotropy. As a result, the transmittance reaches its theoretical limit, 90 % within the visible and near infrared ranges, which represents the highest reported value for microscale polycrystalline oxide materials (**TableS1**).

EXPERIMENTAL SECTION

Synthesis. The five $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($x = 0, 0.1, 0.2, 0.3$ and 0.4) polycrystalline ceramics were first prepared as

glass materials from high purity SrCO_3 (99.9%, Strem Chemicals), Al_2O_3 (99.98%, Alfa Aesar) and SiO_2 (99.8%, Alfa Aesar) precursors. Stoichiometric ratios for each composition were weighed and homogenized in an agate mortar. The samples were then placed in rhodium/platinum crucibles, introduced in a 1700°C pre-heated electric furnace, left for 10 min, heated up to 1750 °C for 10min and back to 1700 °C for 30 min. The samples were then cooled in air. A single heat treatment performed at 1020 °C for 3 hours in an open air-atmosphere furnace was then sufficient to ensure full congruent crystallization of the glass materials.

Structural characterization. Differential Scanning Calorimetry (DSC) measurements were realized on 475 mg samples using a MULTI HTC 1600 Setaram instrument and a 10 K/min heating rate. Electron diffraction was performed on a Philips CM20 transmission electron microscope operating at 200 keV. The sample was first crushed in ethanol, and a drop of the solution with the small crystallites in suspension was deposited onto a carbon-coated copper grid. High resolution STEM-HAADF imaging was realized on a JEOL ARM200F cold FEG S/TEM double corrected. The grid was prepared from a

sample first cut with a diamond wire saw, then mechanically polished with a tripod and inlaid diamond discs until 70 µm thickness. The foil was finally thinned by argon ion bombardment (PIPS). Scanning Electron Microscopy (SEM) images were acquired on a FEI ESEM XL 40 apparatus. Structure elucidation was performed using a combination of high-intensity and high-resolution synchrotron powder diffraction data (from 11-BM at the Advanced Photon Source, Argonne National Laboratory, US - data were collected on a spinning sample (60 Hz) over the 0.5 - 60 ° 2θ range with a 0.001 ° step size at room temperature using a $\lambda = 0.413978$ Å wavelength) with neutron powder diffraction data (from 3T2 station at the LLB, France - data were collected for 22h on a 5 g sample over the 4.5 - 121 ° 2θ range using a 0.05 ° step size and a 1.225 Å wavelength). The JANA2006 software²³ was used for Rietveld refinements. ²⁹Si and ²⁷Al NMR experiments were performed on Bruker Avance spectrometers at magnetic fields of 9.4 and 17.6 T, respectively. The ²⁹Si quantitative Magic Angle Spinning (MAS) NMR spectra were recorded with a spinning frequency of 7 kHz, a pulse duration of 1.05 µs (25° flip angle) and a recycle delay of 60s. The ²⁷Al quantitative MAS spectra were recorded with a spinning frequency of 30 kHz, a pulse duration of 0.36 µs (15° flip angle) and a recycle delay of 0.5s. The ²⁷Al 2D MQMAS spectra were acquired at a spinning frequency of 30 kHz.

DFT calculations. DFT calculations of the dielectric function $\epsilon(\omega)$ and the NMR spectra were performed with the CASTEP²⁴ code using periodic boundary conditions. The Perdew-Burke-Ernzerhof (PBE) functional was used for the exchange correlation kernel.²⁵ The core-valence interactions were described by ultrasoft pseudopotentials (USPP)²⁶ generated using the on-the-fly generator (OTF-USPP) included in CASTEP. The $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ structural models consisted of a supercell of 2x2x1 unit cells with 32 tetrahedral sites (occupied by Si or Al atoms) and a total of 104 atoms for $x = 0$ and 105 atoms for $x = 0.25$ (one of the extra strontium positions in the supercell being fully occupied). Computations were performed after DFT-PBE optimization of the atomic positions. The refractive index was determined from the following relationship:

$$n = \left(\frac{\epsilon_1^2 + \epsilon_2^2 + \epsilon_3}{2} \right)^{1/2}$$
 Full details about DFT calculations can be found in FigureS16.

Optical characterization. Transmission measurements were collected over the range 250 to 3000 nm using a double beam commercial spectrophotometer (Cary 5000) equipped with a Photomultiplier and a PbS photocell for visible and infrared detection, respectively. The transmittance measurement was confirmed using a collimated HeNe laser emitting at 632.8 nm and a powermeter placed at a distance of 15 cm from the sample. The average refractive index of the material was determined by fitting the reflectivity spectrum measured with a Bruker Vertex 80V spectrometer in the infrared range (2-200 µm). From this analysis, an accurate estimation (~ 0.01 error) of the refractive index in the visible range is obtained by evaluating at visible wavelengths the physical dielectric

function model optimized in the infrared range. The method is insensible to scattering effects that can appear at smaller wavelengths.

RESULTS AND DISCUSSION

A series of five clear transparent glass compositions ($x=0, 0.1, 0.2, 0.3$ and 0.4) have been prepared by conventional melt-quenching at 1700°C using a commercial electrical furnace. The quenching was performed in air, no fast or special quenching rate being required to avoid glass crystallization. The amorphousness of the as-prepared glasses was confirmed by powder X-ray diffraction (XRD) (FigureS1). This production route, combined with the high glass forming ability of this system, allows large scale samples to be prepared and shaped (50 g massive glass samples were easily obtained by simple cooling in air). It is anticipated that much larger samples can be synthesized using the same protocol. The DSC thermogram of each $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ glass composition shows glass transition temperatures around 905 ± 2 °C and single exothermic peaks ranging from 1050 ± 2 °C to 1090 ± 2 °C (FigureS2 and TableS2). A 3 hours treatment at 1020°C leads a complete crystallization of the sample. X-ray diffraction patterns show single phase polycrystalline ceramic which matches the hexagonal $\text{SrAl}_2\text{Si}_2\text{O}_8$ (ICSD 416598, PDF 01-077-5105) indexation²⁷ (FigureS3). Such elaborated $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0.4$) microscale polycrystalline ceramics exhibit evolving transparency behavior in the visible range (figure1c), the highest transmittance being obtained for $x \approx 0.2$. The optical transmission values measured at the $x=0.2$ composition (1.5 mm thickness) was found to be close to 90% all along the visible and near infra-red ranges (Figure1a). This outstanding result almost matches the maximum theoretical transmittance of 90.1% calculated from the measured refractive index of $n=1.59$, indicating that almost no scattering centers exist within the polycrystalline ceramic. Structure determination of this new solid solution and microstructure observations were then undertaken in order to explain this exceptional transparency.

The structure elucidation of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 < x \leq 0.4$) solid solution has been performed using a combination of synchrotron and neutron powder diffraction data. Both electron diffraction (FigureS4) and powder indexing agree with a hexagonal unit cell ($P6_3/mcm$ space group with $a \approx 5.2$ Å and $c \approx 15.2$ Å) matching the $\text{SrAl}_2\text{Si}_2\text{O}_8$ structure indexation. LeBail refinements of synchrotron powder diffraction data reveal a linear evolution of the cell parameters along the solid solution (FigureS5). It should be noted that in contrast to $\text{Sr}_{1-y/2}\text{Al}_{2-y}\text{Si}_{2+y}\text{O}_8$ ($0 < y \leq 0.3$)²⁷, the present $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 < x \leq 0.4$) solid solution cannot be synthesized by classic solid state reaction (FigureS6). Crystallization from glass affords unique synthetic access to the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ system.

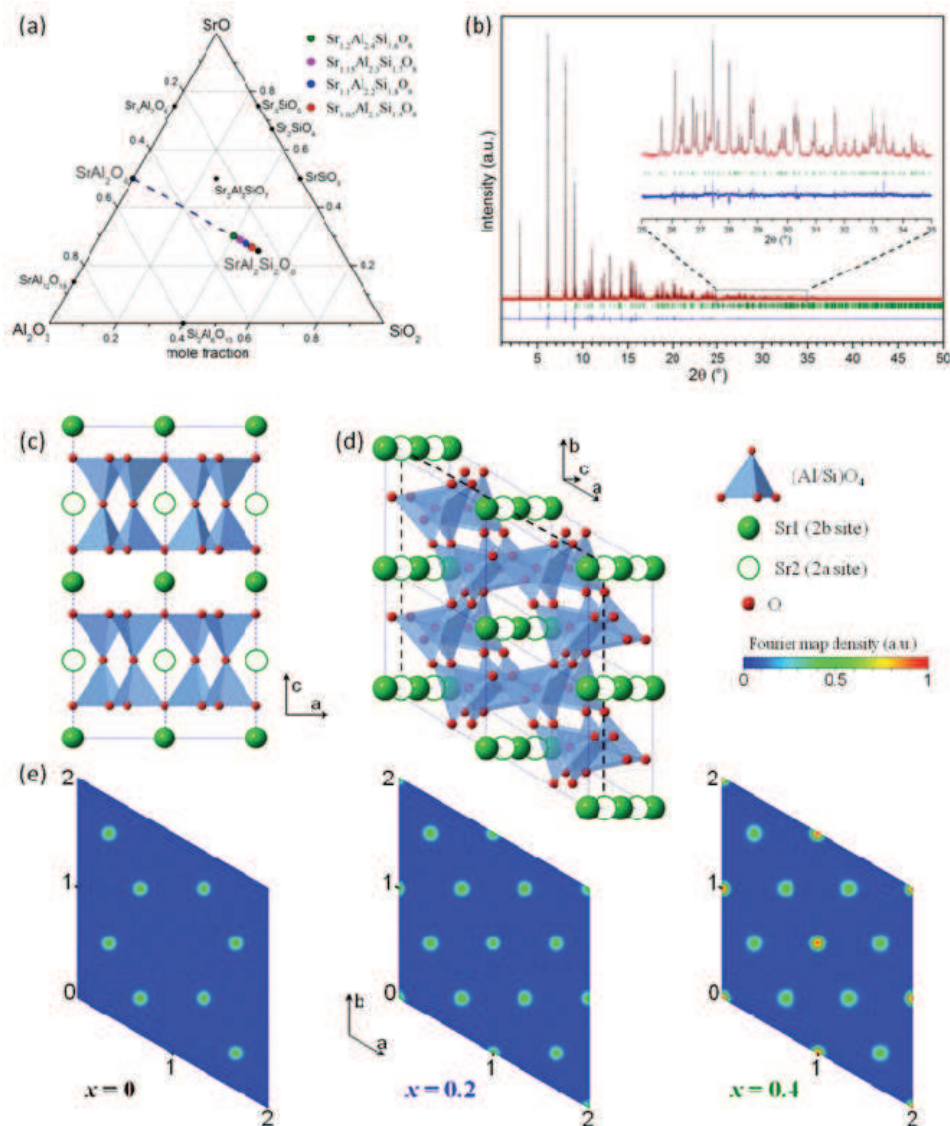


Figure 2. Crystal structure. (a) Localization of the new $\text{Sr}_{1-x}\text{Al}_2\text{Si}_x\text{O}_8$ ($0 < x \leq 0.4$) solid solution in the $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ternary system. The compositions studied in this work are represented by full circle colored symbols. (b) Rietveld refinement of the $\text{Sr}_{1-x}\text{Al}_2\text{Si}_x\text{O}_8$ ($x = 0.2$) synchrotron powder diffraction data collected at room temperature ($R_{\text{wp}} = 7.45\%$, $R_p = 6.24\%$, and $\chi^2 = 1.67$). (c) [010] view of the crystal structure showing AlO_4 and SiO_4 tetrahedra forming channels occupied by strontium atoms. (d) [001] perspective view and (e) corresponding observed Fourier maps of the $x = 0$, $x = 0.2$ and $x = 0.4$ compositions (section at $z = 0.25$). This section plan is dot drawn in the structure view presented figure 2d). The scattering density of Sr2 is clearly appearing and increasing as a function of x .

Rietveld refinements of synchrotron diffraction powder data were then performed using the $\text{P6}_3/\text{mcm}$ $\text{SrAl}_2\text{Si}_2\text{O}_8$ average structure as a starting model (one Sr site, one mixed Al/Si site and two O sites, all fully occupied) using a statistical Al/Si occupation of the tetrahedral sites and the cell parameters previously determined. A reasonable fit could then be obtained, allowing an inspection of Fourier maps which revealed an increasing scattering density on a new 2a (0 , 0 , $1/4$) crystallographic site (Figure 2). This scattering density was assigned to an extra strontium site (Sr2). The occupancy of Sr2 was then refined (the Al/Si ratio was constrained to compensate the extra positive charge induced by Sr2) and a continuous increase of its content is observed along the substitution process (Fig-

ure S7). Sr1 and Sr2 alternatively occupy channels formed by corner-sharing $(\text{Al/Si})\text{O}_4$ tetrahedra. Neutron powder diffraction refinements did not show any extra oxygen position related to Sr2, confirming that the extra positive charge induced by the extra strontium was compensated by a consequent Al/Si ratio. As reported previously, a fully ordered P-3c1 model with one Al and one Si distinct crystallographic sites can also be considered for $\text{SrAl}_2\text{Si}_2\text{O}_8$ (ICSD 416597).²⁷ However, our synchrotron and neutron powder diffraction refinements using this model did not show any improvement or any Al/Si differentiation that would have implied this structural description.

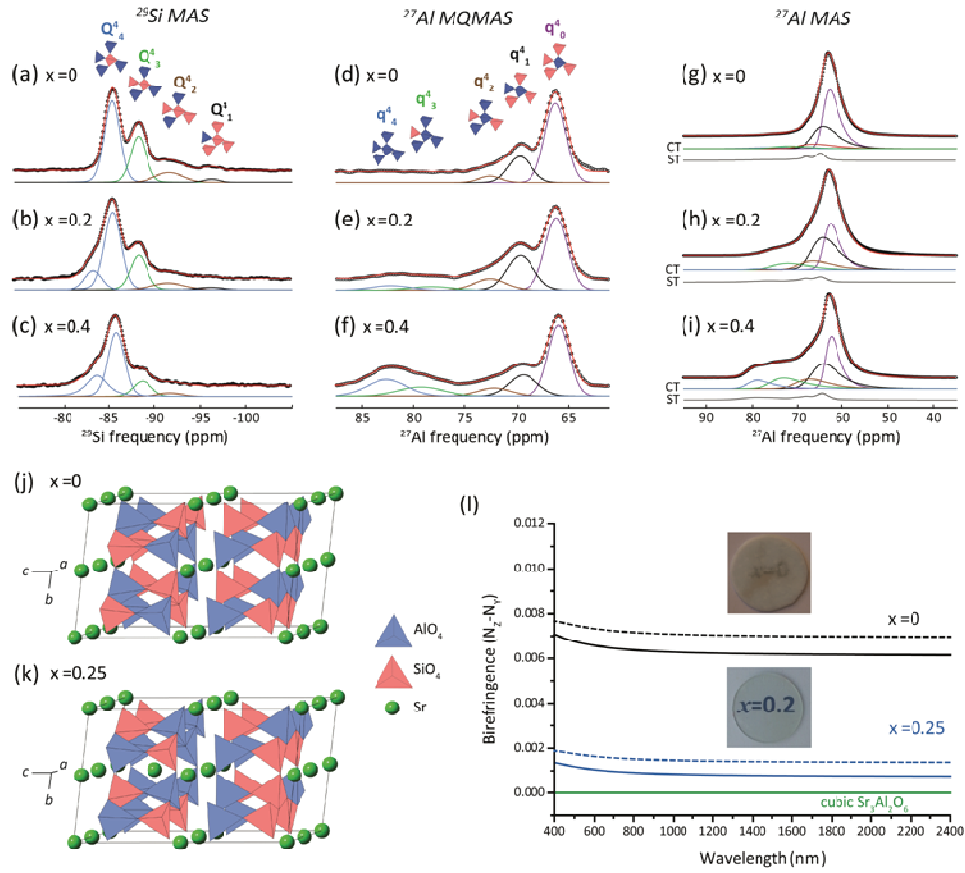


Figure 3. Local structure and birefringence. (a-c) Experimental ^{29}Si quantitative MAS NMR spectra (black circles) of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ samples and their fit (red lines). The individual contributions (with Gaussian line shape) corresponding to the distinct Q^n_m Si units are shown below the experimental spectra. For $x > 0$, the ^{29}Si spectra show an additional contribution associated to a distinct type of Q^4_4 units located in the vicinity of the extra Sr sites. (d-f) ^{27}Al isotropic MQMAS spectra (black circles) and their best fit (red lines). (g-i) Experimental ^{27}Al quantitative MAS NMR spectra (black circles) and their fit (red lines). The individual contributions (with (d-f) Gaussian line shapes and (g-i) second order quadrupolar broadened line shapes) associated to the distinct q^n_m Al units are shown below the experimental spectra. The composition are (a, d, g) $x = 0$, (b, e, h) $x = 0.2$ and (c, f, i) $x = 0.4$. The assignment of ^{29}Si and ^{27}Al resonances is fully supported by experimental data²⁵ and DFT computations of the ^{29}Si and ^{27}Al chemical shifts. (j-k) Modeled structures of the (j) $x = 0$ and (k) $x = 0.25$ compounds. These models consist of a supercell of $2 \times 2 \times 1$ unit cells with an Al/Si ordering closely accounting for the observed distributions of Al and Si environments. In (a, d, j, k), the red and blue tetrahedra correspond to SiO_4 and AlO_4 units, respectively, and green spheres are Sr atoms. (l) DFT-calculated birefringence of the $x = 0$ (black line) and $x = 0.25$ (blue line) samples using the modeled structures shown in (j) and (k). The dashed lines correspond to the birefringence deduced from the average refractive index values of four different structural models (effective medium approximation). These different models were selected such that the average distribution of Al and Si environments was close to the observed one (see figures S16 and S17 and table S11 and S12). The green line corresponds to the DFT-calculated birefringence of the $\text{Sr}_3\text{Al}_2\text{O}_6$ cubic structure.

The presence of Al/Si chemical disorder in the structures of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0.4$) compounds (**Figure 3**) was clearly confirmed by ^{29}Si and ^{27}Al MAS and MQMAS NMR experiments. These allow evidencing a range of Si and Al tetrahedral chemical environments which can be described using Q^n_m and q^n_m notations, respectively, where n is the number of bridging oxygen atoms and m is the number of bonded AlO_4 units ($0 \leq m \leq n \leq 4$). For $\text{SrAl}_2\text{Si}_2\text{O}_8$, the distribution of Si and Al atoms in the tetrahedral sites results in four types of both Si (Q^4_m , $m=4, 3, 2, 1$) and Al (q^4_m , $m=3, 2, 1, 0$) environments which cannot be disentangled in the average long-range structure. The proportion of these various Si or Al environments directly reflects the deviation from the

Loewenstein rule²⁸ stating that linkages between AlO_4 units are energetically unfavorable in aluminosilicate materials. When increasing x , the Al environment distribution becomes broader to include q^4_4 unit and the proportions of q^4_2 , q^4_3 and q^4_4 units increase reflecting the formation of additional Al-O-Al linkages required by the local charge compensation of the extra strontium site in the structure. The $\text{P6}_3/\text{mcm}$ average structure of the new $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0.4$) solid solution is presented Figure 2. Full details of all synchrotron powder diffraction refinements are given **Figures S8-S12** and **Tables S3-S7**. The neutron powder diffraction refinement of the $x=0.4$ member is shown **Figure S13**. The ^{29}Si and ^{27}Al NMR parameters and the relative proportions of the various Q^n_m

and q_m^4 sites are given in **Tables S8 and S9**. The ^{27}Al 2D MQMAS spectra and their simulations are shown in **Figure S14**.

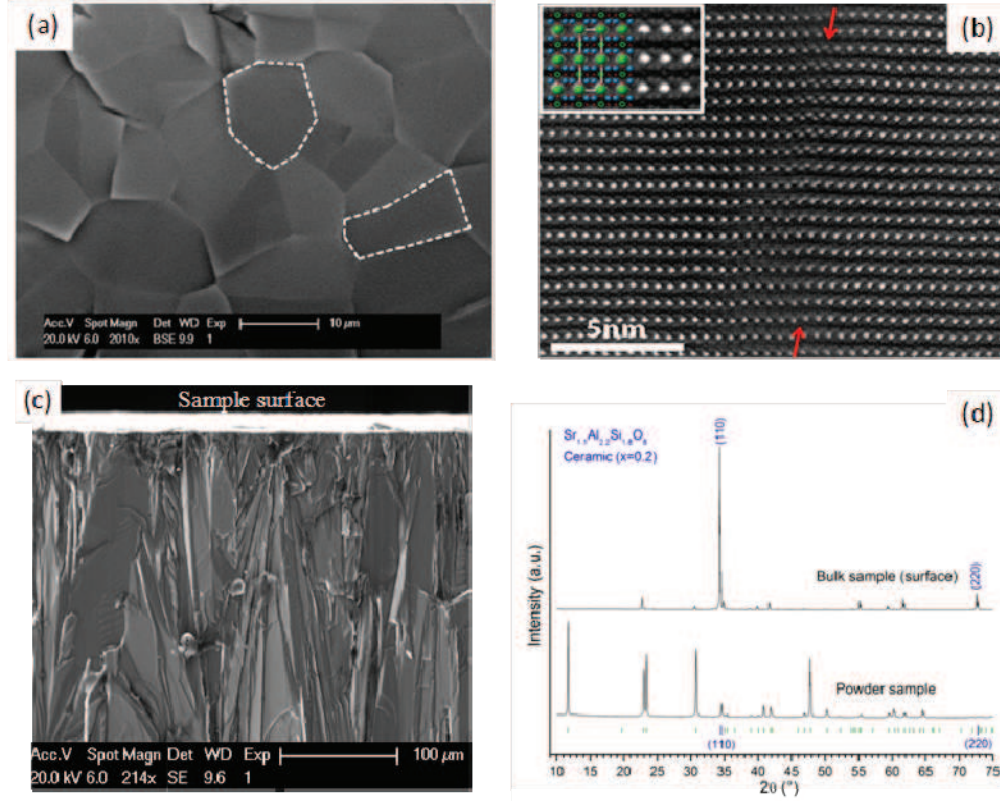


Figure 4. Microstructure. (a) Scanning electron microscopy image of the transparent bulk $x=0.2$ ceramic sample showing no porosity, thin grain boundaries, full dense structure and a crystal size of about 5–20 μm . (b) $[010]$ high resolution STEM-HAADF image (contrast proportional to the atomic number Z) of the interface between two slightly disoriented grains. The grain boundary (red arrows) appears extremely thin and free of glassy phase. Imbedded, the crystal structure obtained from powder diffraction perfectly matches the atomic resolution image (green Sr_1 site appears bright, blue Al/Si is gray and the partially occupied open green Sr_2 sites are dark gray. The red oxygen atoms are not visible due to their low atomic number). (c) SEM image recorded on a section of the $\text{Sr}_{1-x}\text{Al}_{2-x}\text{Si}_{2-x}\text{O}_8$ ($x=0.2$) sample showing the strong orientation of crystallization perpendicular to the surface due to the heterogeneous surface crystallization process. (d) Top: bulk X-ray diffraction pattern recorded on the surface of a $\text{Sr}_{1-x}\text{Al}_{2-x}\text{Si}_{2-x}\text{O}_8$ ($x=0.2$) sample; down: powder diffraction pattern recorded on the same crushed sample. The bulk pattern shows much enhanced hho reflection intensities compared to the powder sample.

The microstructure of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0.4$) transparent ceramics was first examined by Scanning Electron Microscopy (SEM) after a thermal etching step preparation (2 hours at 975°C). The image of the sample surface presented **figure 4a** displays a typical mosaic microstructure as usually observed for transparent polycrystalline ceramics obtained by high pressure/high temperature sintering processes.⁹ Large micron scale crystallites (5–20 μm) and the absence of porosity are evidenced. Moreover, no residual glass or secondary phases could be detected, even at the atomic scale on the STEM-HAADF image of a grain boundary interface (figure 4b). The grain boundary appears extremely thin and no amorphous phase is observed.

Interestingly, a strong orientation of the crystallites perpendicular to the surface can be observed, as evi-

denced on the SEM image recorded along the sample section (Figure 4c). This observation resulting from a heterogeneous surface nucleation crystallization process is confirmed by XRD data recorded on bulk material showing much enhanced hho reflection intensities compared to theoretical ones (Figure 4d). However the crystallization mechanism is not fully oriented as all hkl reflections can still be observed.

The combination of structural anisotropy of the hexagonal $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0.4$) structures, non perfect alignment of the crystallite orientations and micrometer-scale microstructure, would not typically result in the high optical transparency observed in these polycrystalline ceramics. To understand this seeming contradiction, the birefringence of the solid solution materials has been evaluated through density functional theory (DFT) com-

putation. The refractive index components were obtained from calculation of real and imaginary parts of the dielectric function $\varepsilon(\omega)$ carried out from modeled periodic structures. To account for the partial occupancy of the extra Sr site, the modeled structures consist of supercell of $2 \times 2 \times 1$ unit cells of the average structure and computations were performed for $x=0$ and 0.25 compositions for which the supercell contain 0 and 1 extra Sr atom, respectively. Considering structural models with an Al/Si ordering nearly accounting for the observed distributions of Si and Al chemical environments (figure3j,k), a small birefringence value of about 0.007 is calculated for $\text{SrAl}_2\text{Si}_2\text{O}_8$ ($x=0$) whereas the $\text{Sr}_{1.125}\text{Al}_{2.25}\text{Si}_{1.75}\text{O}_8$ ($x=0.25$) exhibits an even weaker and almost null birefringence of about 0.001 all along the visible range (figure3l). Similar trends were observed for the average birefringence calculated from four different structural models (effective medium approximation) selected such that the average distribution of Al and Si environments was close to the observed one. The reliability of the simplified model structures (with a limited number of atoms) used for the computations is confirmed by the relatively good agreement between their DFT-calculated ^{29}Si and ^{27}Al NMR spectra and the experimental ones (figureS15). Despite the presence of very large crystals and an anisotropic crystal structure, the transparency of the ceramics presented Figure1 can thus be attributed to the combination of high density (absence of pores), extremely thin grain boundaries and very weak birefringence. The birefringence appears to have a central role as the clear increase of the transparency level observed between $x=0$ and 0.25 corresponds to a significant decrease of the calculated birefringence values. This birefringence is controlled by chemical composition through the amount of the extra strontium Sr₂ site in the structure. Computations for different structural models with a same composition show that the birefringence also depends on the Al/Si ordering configurations (figuresS16-S17). Therefore, it appears that a precise control of the birefringence can be achieved through the control of the strontium occupancy (chemical composition) and the Al/Si ordering (synthesis conditions),²⁹ the optimum birefringence (and thus transparency) being obtained for $x=0.2$. In analogy with the multi-scale structure of glass,³⁰ this suggests that an optical isotropy at the micrometer scale can be obtained in non cubic crystalline material (with structural anisotropy at the nanometer scale) through the introduction of a controlled disorder.

CONCLUSION

The development of new $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 < x \leq 0.4$) perfectly transparent polycrystalline ceramics through full and congruent glass crystallization has been demonstrated for large scale shapeable samples. Despite the materials exhibit non cubic symmetry and large crystallite sizes of several tens of microns, the maximum theoretical transmittance can be reached. This is achieved by (i) the absence of porosity and extremely thin grain boundaries resulting from the elaboration process and (ii) a very weak birefringence obtained from the introduction of a

controlled chemical disorder (strontium occupancy and Al/Si ordering). It is anticipated that these new materials will generate follow-on optical and photonic applications and that the proposed concept of tailoring disorder to enhance transparency will considerably extend the development of transparent ceramics with specific applications.

ASSOCIATED CONTENT

X-ray diffraction data of the $x=0.2$ glass material. DSC thermograms of the different glass compositions. Synchrotron powder diffraction patterns of the ceramic compositions. Electron diffraction patterns of the new $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ solid solution. Unit cell parameters and volume of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ solid solution. X-ray diffraction patterns of unsuccessful solid state synthesis attempts to elaborate the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($x = 0.4$) solid solution. Occupancy of the Sr₂ crystallographic site as a function of x along the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ solid solution. Rietveld refinement of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ synchrotron and neutron powder diffraction data collected at room temperature. ^{27}Al experimental 2D MQMAS spectra of $\text{SrAl}_2\text{Si}_2\text{O}_8$ and (b) $\text{Sr}_{1.2}\text{Al}_{2.4}\text{Si}_1$ with their best fits. Comparison between the $^{29}\text{Si}/^{27}\text{Al}$ experimental MAS NMR and DFT calculated spectra. Modeled structures of the $\text{SrAl}_2\text{Si}_2\text{O}_8$ and $\text{Sr}_{1.125}\text{Al}_{2.25}\text{Si}_{1.75}\text{O}_8$ compounds and DFT-calculated birefringence for these structural models. Refractive index (n_∞) and maximum theoretical transmission values of transparent oxide ceramics reported in the literature. Glass transition and crystallization temperatures of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ glass materials. Atomic positions and selected inter-atomic distances of $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ new materials obtained from room temperature Rietveld refinement of synchrotron powder diffraction data. Isotropic chemical shifts δ_{ISO} , full width at half maximum Fwhm (± 0.2) and relative intensity I (± 2) of the ^{29}Si resonances corresponding to the different Si local environments in the structure of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ compounds determined from the fits of the ^{29}Si quantitative MAS spectra. Isotropic chemical shifts ($\delta_{\text{ISO}} \pm 0.2$), average quadrupolar coupling constant ($\bar{C}_Q \pm 0.10$), full width at half maximum of the Gaussian distribution of the quadrupolar coupling constant (Fwhm(C_Q) ± 0.20), asymmetry parameter of the quadrupolar tensor ($\eta_Q \pm 0.1$) and relative intensity ($I \pm 5$) of the ^{27}Al resonances corresponding to the different Al local environments in the structure of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ compounds. Description of pseudopotentials used for planewave DFT calculations. Structural parameters of the different geometry-optimized model structures with $x = 0$ ($\text{SrAl}_2\text{Si}_2\text{O}_8$). Structural parameters of the different geometry-optimized model structures with $x = 0.25$ ($\text{Sr}_{1.125}\text{Al}_{2.25}\text{Si}_{1.75}\text{O}_8$).

CRYSTALLOGRAPHIC INFORMATION.

Further details of the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD- 427089 ($x=0.4$), CSD-427090 ($x=0.3$), CSD-427091 ($x=0.2$), CSD-427092 ($x=0.1$) and CSD-427093 ($x=0$).

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Author Contributions

K.A.S. and S.C. synthesized the materials and contributed to the structural characterisations. M.A. wrote the manuscript and performed the structure determinations with E.V.. F.F. performed the NMR experiments, DFT calculations and contributed to the writing of the manuscript with M.S. C.G. performed the STEM-HAADF experiments. G.M. and D.M. contributed to result analysis and discussion. M.S. and F.P. respectively carried out the synchrotron and neutron powder diffraction experiments.

Notes

The authors declare no competing financial interest.

Funding Sources

This work was partially funded by the French ANR (project CrystOG ANR-12-JS08-0002).

ACKNOWLEDGMENT

The authors thank the ANR for its financial support to the project CrystOG ANR-12-JS08-0002 and both the CRMD and CRISMAT/CIMAP laboratories for TEM access. Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. Neutron experiments at the Laboratoire Léon Brillouin in Saclay (France). DFT computations have been performed at the “Centre de Calcul Scientifique en Région Centre” facility (CCRS – Orléans, France) under the CASCIMODOT program. Domingos De Sousa Meneses is acknowledged for refractive index measurement.

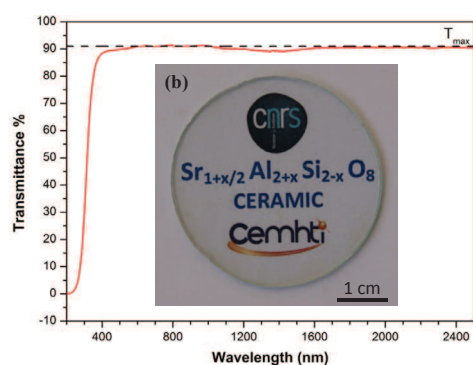
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SUPPLEMENTARY INFORMATION

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Figure S1. Laboratory X-ray diffraction data of the $x = 0.2$ member of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ solid solution showing the complete amorphousness of the glass materials.

Figure S2. DSC thermograms of the different $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($x = 0, 0.1, 0.2, 0.3, 0.4$) glass compositions.

Figure S3. Normalized synchrotron powder diffraction patterns of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($x = 0, 0.1, 0.2, 0.3, 0.4$) ceramic compositions ($\lambda = 0.413978 \text{ \AA}$).

Figure S4. Experimental $[001]^*$ and $[010]^*$ electron diffraction patterns characteristic of the new $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 \leq x \leq 0.4$) solid solution.

Figure S5. Variation of the unit cell (a) parameters and (b) volume of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ solid solution ($x = 0, 0.1, 0.2, 0.3$ and 0.4).

Figure S6. X-ray diffraction patterns of unsuccessful solid state synthesis attempts to elaborate the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($x = 0.4$) solid solution.

Figure S7. Occupancy of the Sr2 crystallographic site as a function of x along the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ solid solution.

Figure S8. Rietveld refinement of the $\text{SrAl}_2\text{Si}_2\text{O}_8$ ($x = 0$) synchrotron powder diffraction data collected at room temperature ($R_{\text{wp}} = 7.99\%$, $R_p = 6.34\%$, and $\chi^2 = 1.82$).

Figure S9. Rietveld refinement of the $\text{Sr}_{1.05}\text{Al}_{2.1}\text{Si}_{1.9}\text{O}_8$ ($x = 0.1$) synchrotron powder diffraction data collected at room temperature ($R_{\text{wp}} = 7.17\%$, $R_p = 5.55\%$, and $\chi^2 = 1.62$).

Figure S10. Rietveld refinement of the $\text{Sr}_{1.1}\text{Al}_{2.2}\text{Si}_{1.8}\text{O}_8$ ($x = 0.2$) synchrotron powder diffraction data collected at room temperature ($R_{\text{wp}} = 7.45\%$, $R_p = 6.24\%$, and $\chi^2 = 1.67$).

Figure S11. Rietveld refinement of the $\text{Sr}_{1.15}\text{Al}_{2.3}\text{Si}_{1.7}\text{O}_8$ ($x = 0.3$) synchrotron powder diffraction data collected at room temperature ($R_{\text{wp}} = 7.46\%$, $R_p = 5.65\%$, and $\chi^2 = 1.65$).

Figure S12. Rietveld refinement of the $\text{Sr}_{1.2}\text{Al}_{2.4}\text{Si}_{1.6}\text{O}_8$ ($x=0.4$) synchrotron powder diffraction data collected at room temperature ($R_{\text{wp}} = 8.06\%$, $R_p = 6.33\%$, and $\chi^2 = 1.67$).

Figure S13. Rietveld refinement of the $\text{Sr}_{1.2}\text{Al}_{2.4}\text{Si}_{1.6}\text{O}_8$ ($x = 0.4$) neutron powder diffraction data collected at room temperature ($R_{\text{wp}} = 2.40 \%$, $R_p = 1.65 \%$, and $\chi^2 = 2.00$).

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Figure S17. (a-e) Modeled structures of the $\text{Sr}_{1.125}\text{Al}_{2.25}\text{Si}_{1.75}\text{O}_8$ compound ($x = 0.25$). (f) DFT-calculated birefringence for the structural models shown in (a-e).

Table S1. Refractive index (n_∞) and maximum theoretical transmission values of transparent oxide ceramics reported in the literature.

Table S2. Glass transition and crystallization temperatures of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($x = 0, 0.1, 0.2, 0.3, 0.4$) glass materials obtained from Differential Scanning Calorimetry (DSC) measurements.

Table S3. Atomic positions and selected inter-atomic distances of $\text{SrAl}_2\text{Si}_2\text{O}_8$ ($x = 0$) obtained from room temperature Rietveld refinement of synchrotron powder diffraction data.

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Table S8. Isotropic chemical shifts δ_{ISO} (± 0.2), full width at half maximum Fwhm (± 0.2) and relative intensity I (± 2) of the ^{29}Si resonances corresponding to the different Si local environments in the structure of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ compounds determined from the fits of the ^{29}Si quantitative MAS spectra.

Table S9. Isotropic chemical shifts ($\delta_{\text{ISO}} \pm 0.2$), average quadrupolar coupling constant ($\bar{C}_Q \pm 0.10$), full width at half maximum of the Gaussian distribution of the quadrupolar coupling constant ($\text{Fwhm}(C_Q) \pm 0.20$), asymmetry parameter of the quadrupolar tensor ($\eta_Q \pm 0.1$) and relative intensity ($I \pm 5$) of the ^{27}Al resonances corresponding to the different Al local environments in the structure of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ compounds.

Table S10. Description of pseudopotentials used for planewave DFT calculations.

Table S11. Structural parameters of the different geometry-optimized model structures with $x = 0$ ($\text{SrAl}_2\text{Si}_2\text{O}_8$).

Table S12. Structural parameters of the different geometry-optimized model structures with $x = 0.25$ ($\text{Sr}_{1.125}\text{Al}_{2.25}\text{Si}_{1.75}\text{O}_8$).

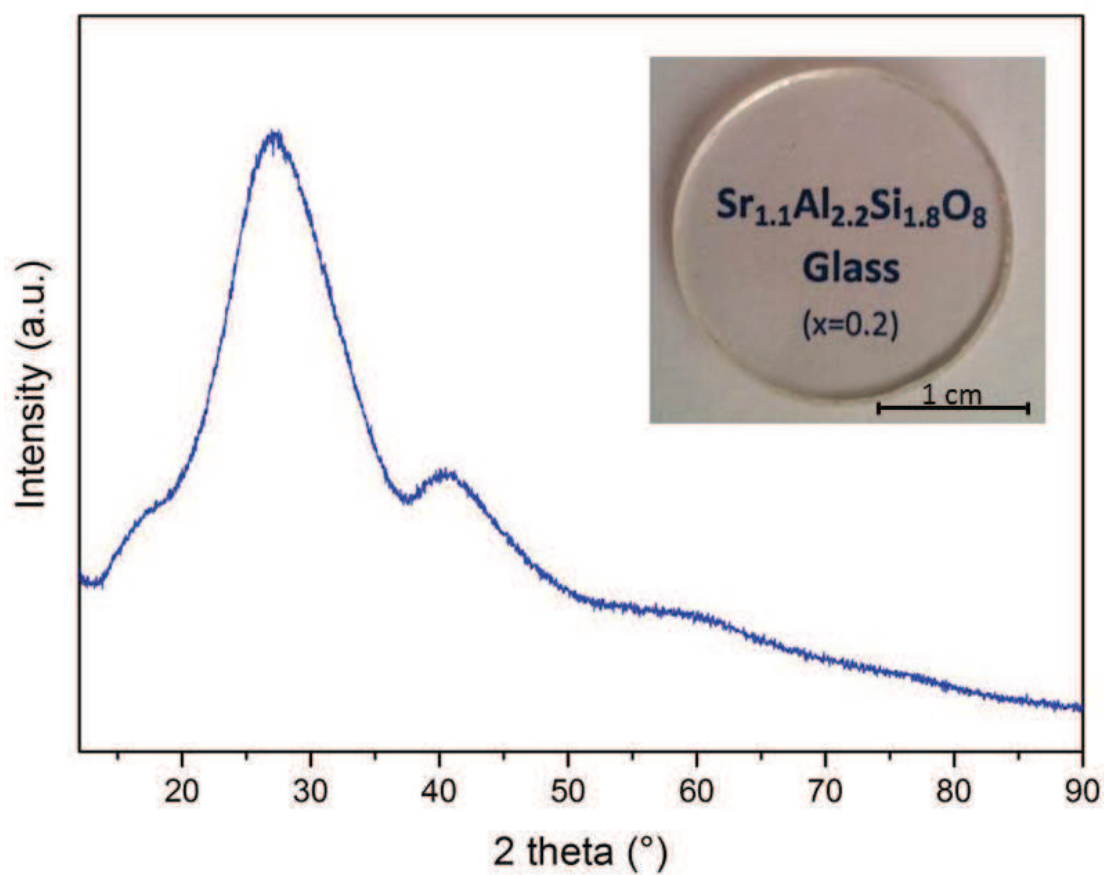


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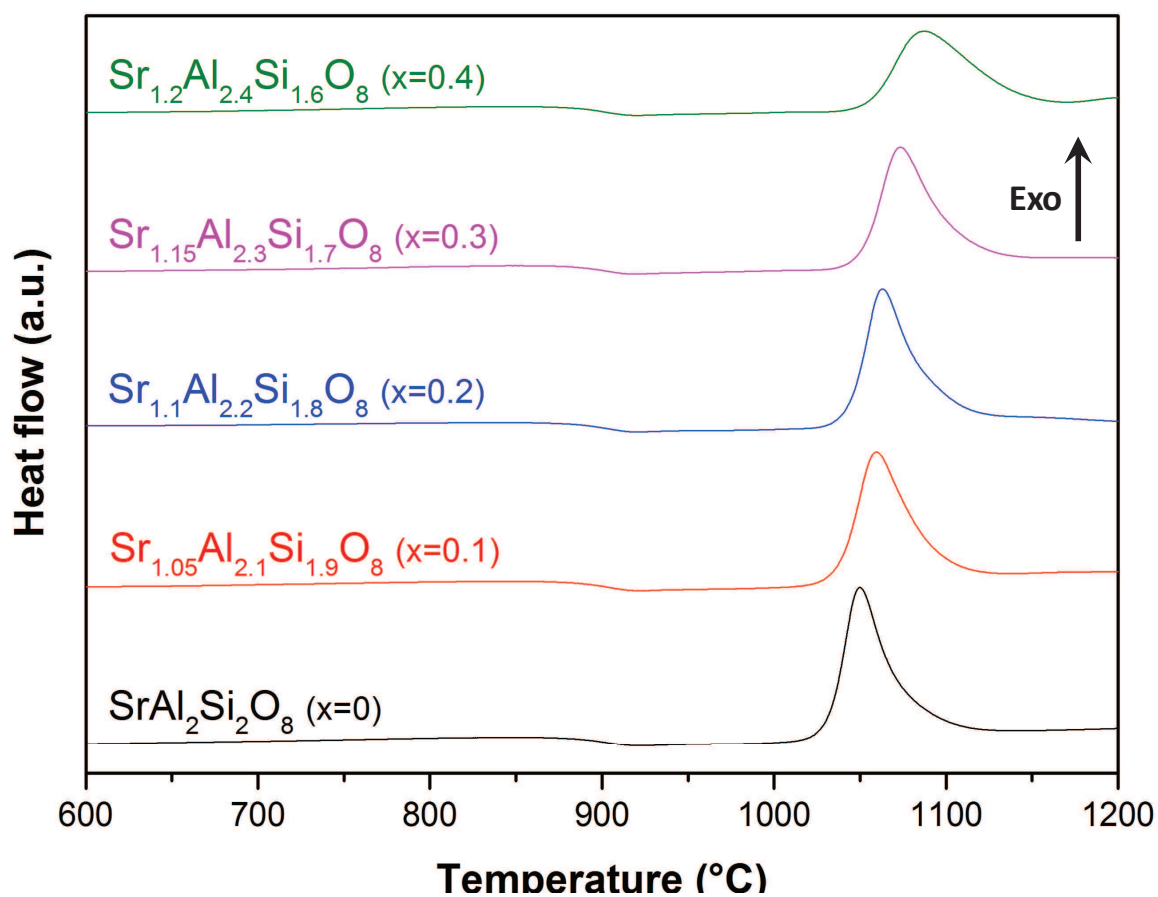


Figure S2 DSC thermograms of the different $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($x = 0, 0.1, 0.2, 0.3, 0.4$) glass compositions. The data have been recorded on powdered samples using a 10 K/min heating rate. The glass transition and crystallization temperatures are gathered in table S2.

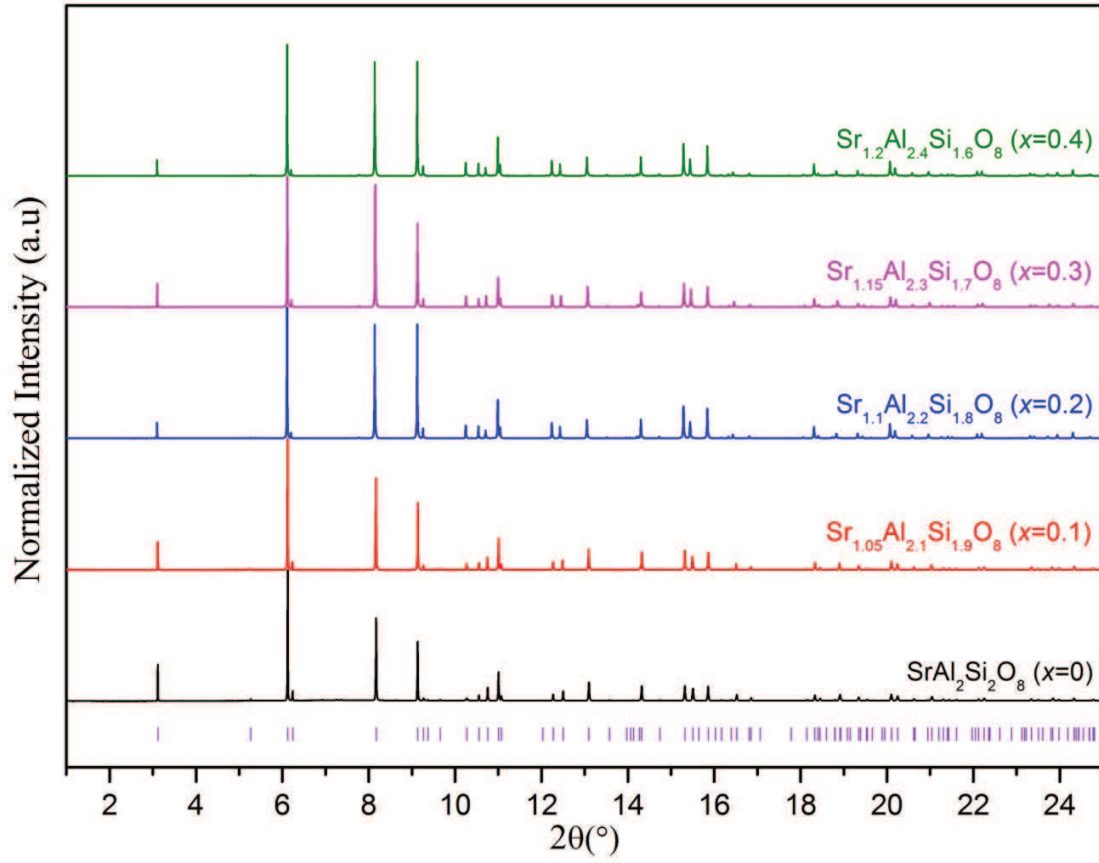


Figure S3 Normalized synchrotron powder diffraction patterns of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($x = 0, 0.1, 0.2, 0.3, 0.4$) ceramic compositions ($\lambda = 0.413978 \text{ \AA}$). The indexation at the bottom of the figure corresponds to the $\text{SrAl}_2\text{Si}_2\text{O}_8$ structure (ICSD 416598, PDF 01-077-5105).

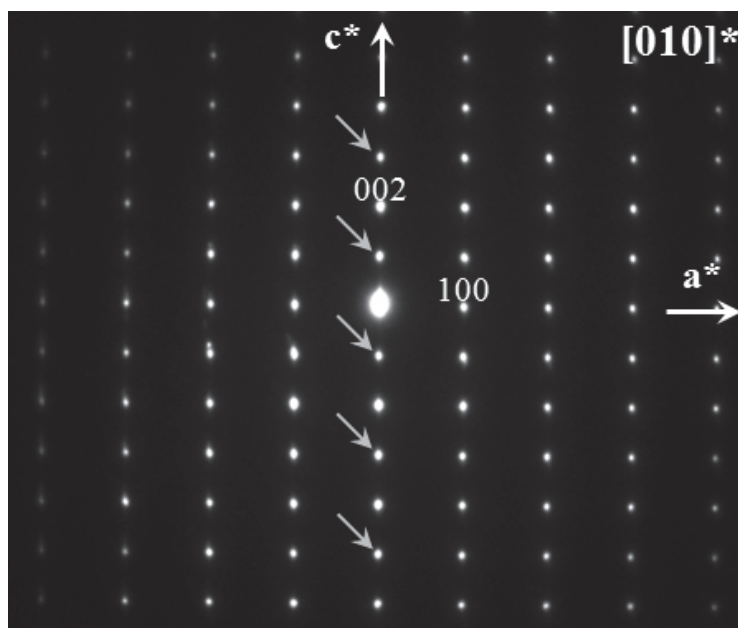
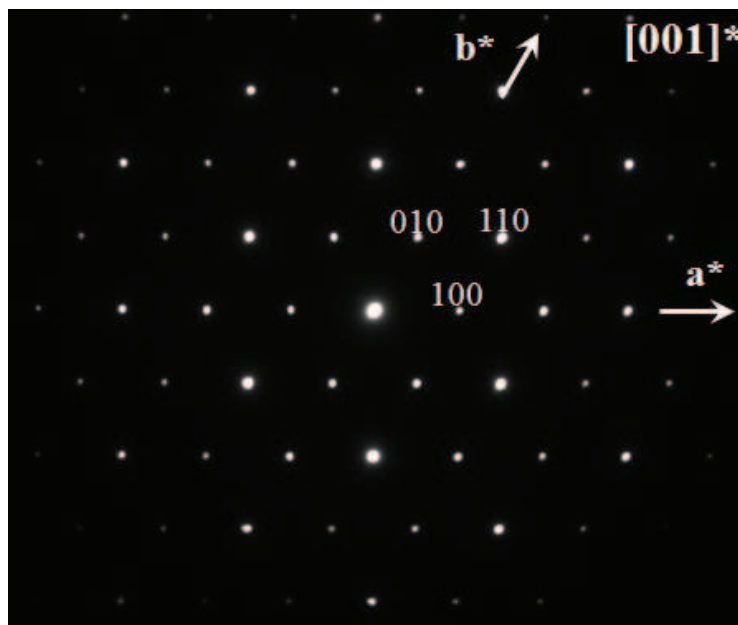


Figure S4 Experimental $[001]^*$ and $[010]^*$ electron diffraction patterns characteristic of the new $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 < x \leq 0.4$) solid solution. The patterns are indexed in a $P6_3/mcm$ hexagonal cell with $a \approx 5.2 \text{ \AA}$ and $c \approx 15.2 \text{ \AA}$ cell parameters. Small grey arrows point to double diffraction reflections. No extra reflections or streaks were observed during the electron diffraction study.

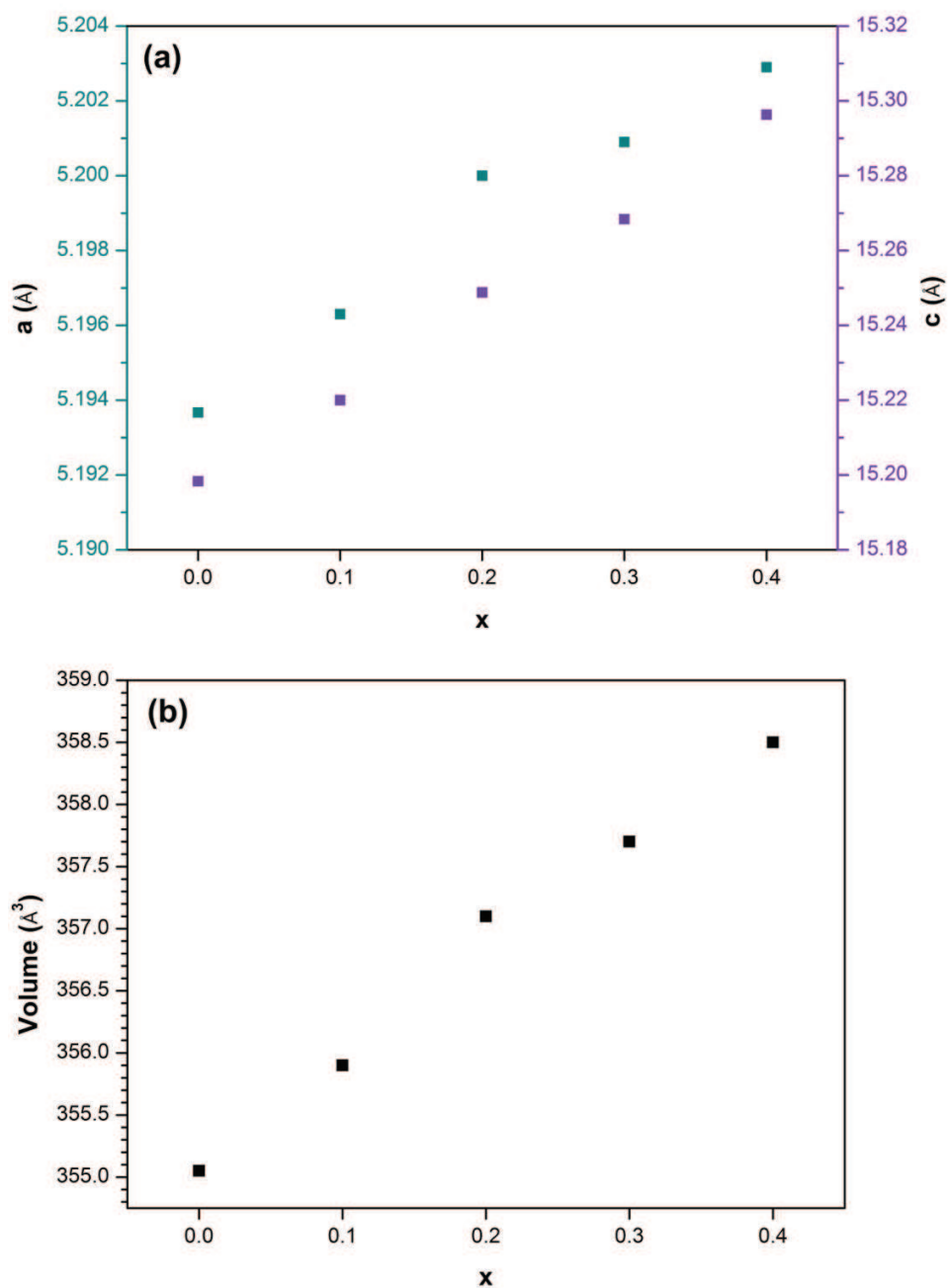


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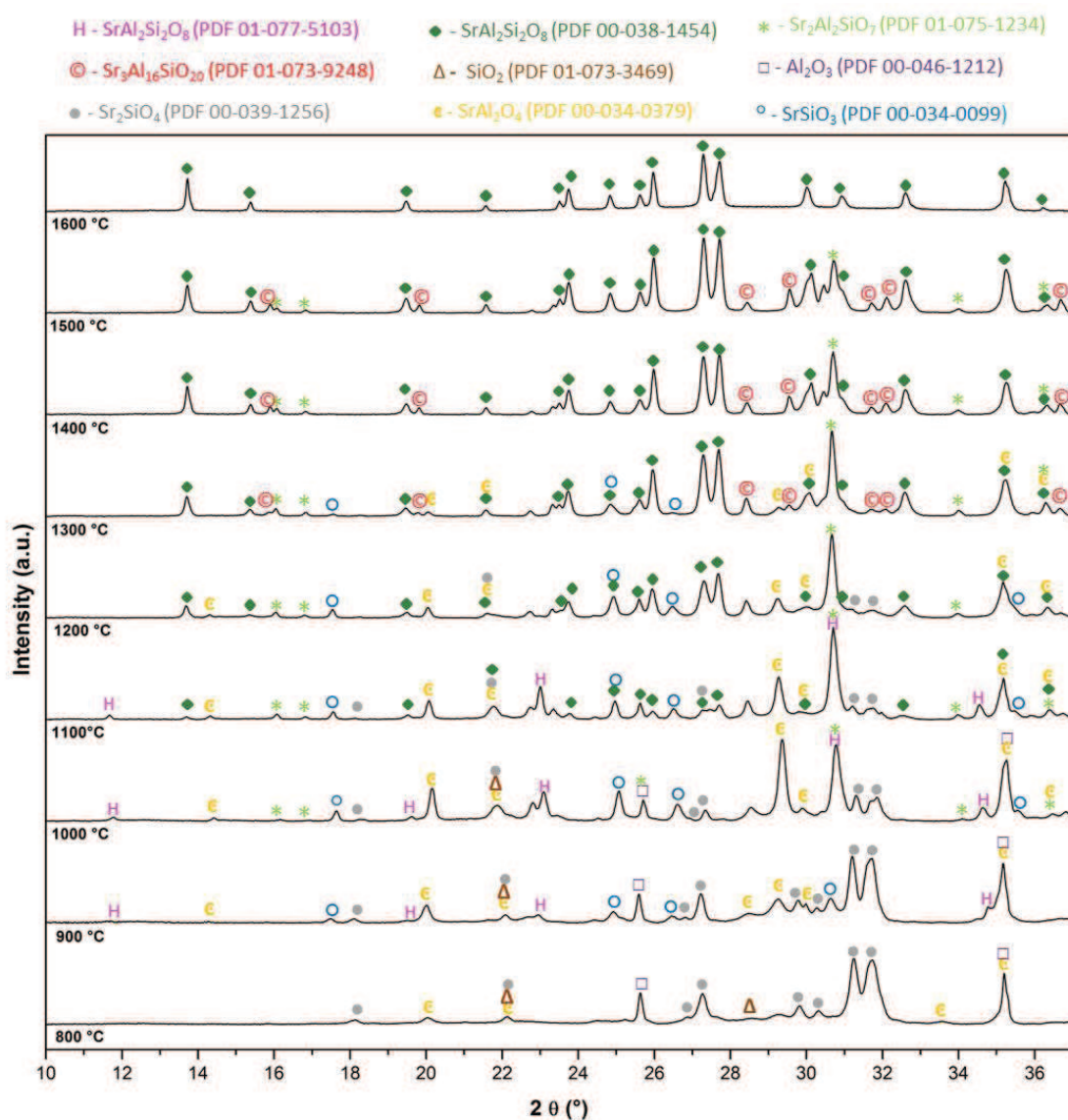


Figure S6 X-ray diffraction patterns of unsuccessful solid state synthesis attempts to elaborate the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($x = 0.4$) solid solution. The samples were heated at different temperatures but no $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ phase could be observed.

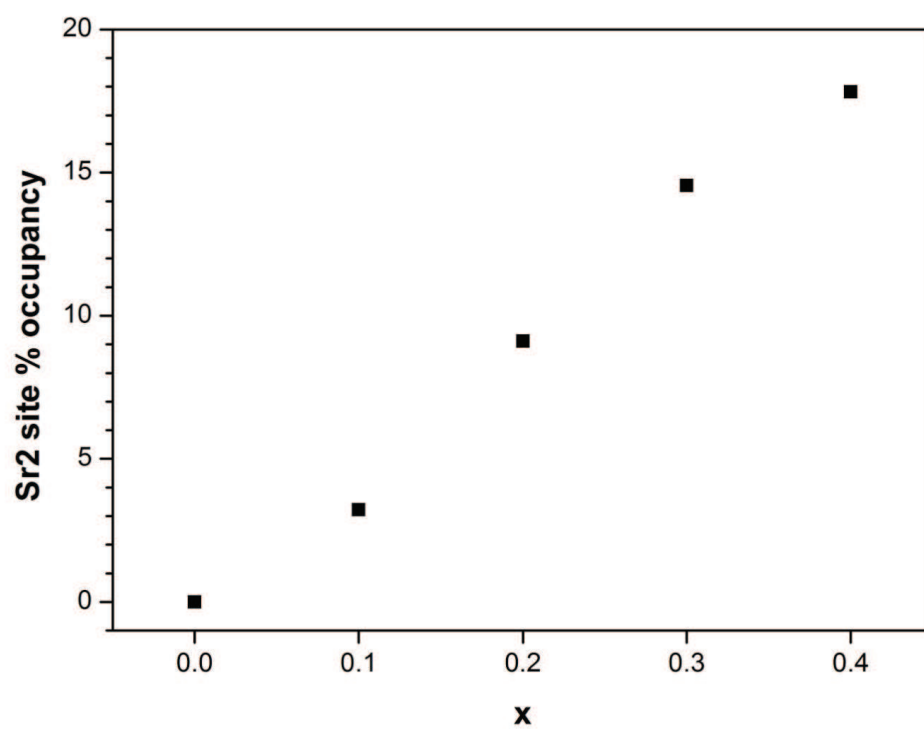


Figure S7. Refined occupancy of the Sr2 crystallographic site as a function of x along the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ solid solution.

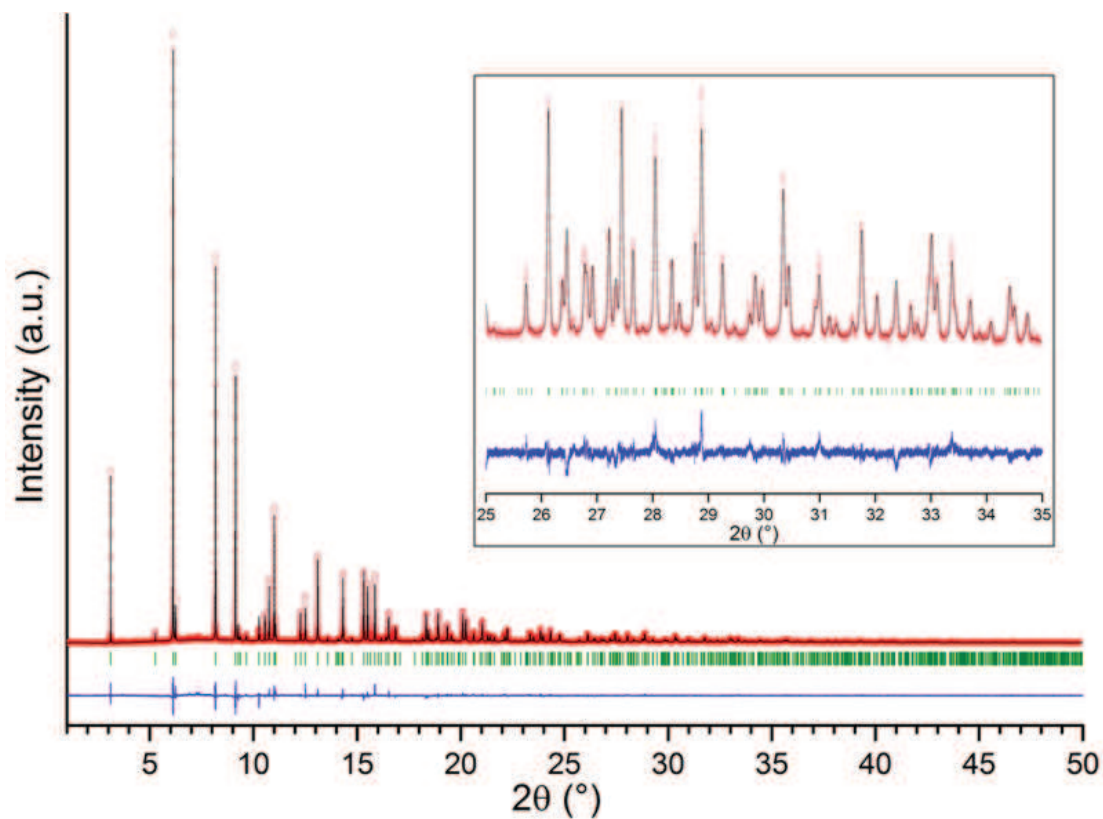


Figure S8. Rietveld refinement of the $\text{SrAl}_2\text{Si}_2\text{O}_8$ ($x = 0$) synchrotron powder diffraction data collected at room temperature ($R_{\text{wp}} = 7.99\%$, $R_p = 6.34\%$, and $\chi^2 = 1.82$). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines corresponds to the reflection positions. Enlargement of the 25 - 35° angular range (2θ) is embedded.

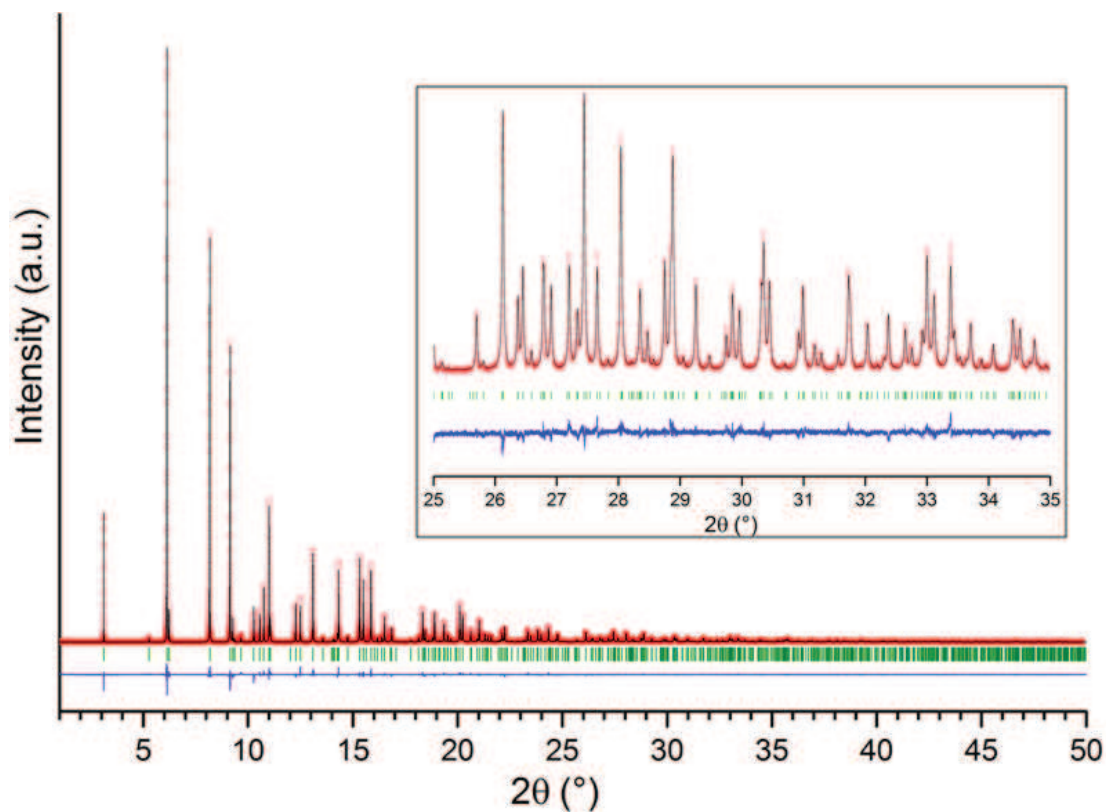


Figure S9. Rietveld refinement of the $\text{Sr}_{1.05}\text{Al}_{2.1}\text{Si}_{1.9}\text{O}_8$ ($x = 0.1$) synchrotron powder diffraction data collected at room temperature ($R_{\text{wp}} = 7.17\%$, $R_{\text{p}} = 5.55\%$, and $\chi^2 = 1.62$). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines corresponds to the reflection positions. Enlargement of the 25 - 35° angular range (2θ) is embedded.

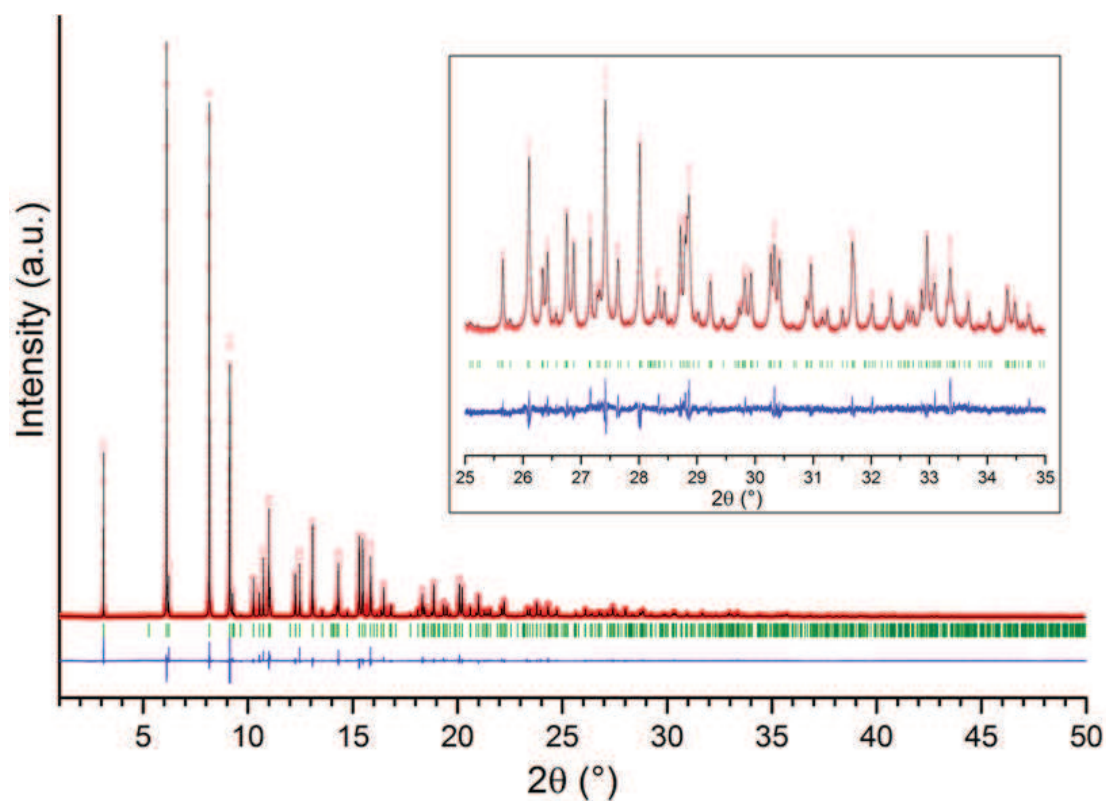


Figure S10. Rietveld refinement of the $\text{Sr}_{1.1}\text{Al}_{2.2}\text{Si}_{1.8}\text{O}_8$ ($x = 0.2$) synchrotron powder diffraction data collected at room temperature ($R_{\text{wp}} = 7.45\%$, $R_{\text{p}} = 6.24\%$, and $\chi^2 = 1.67$). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines corresponds to the reflection positions. Enlargement of the $25 - 35^\circ$ angular range (2θ) is embedded.

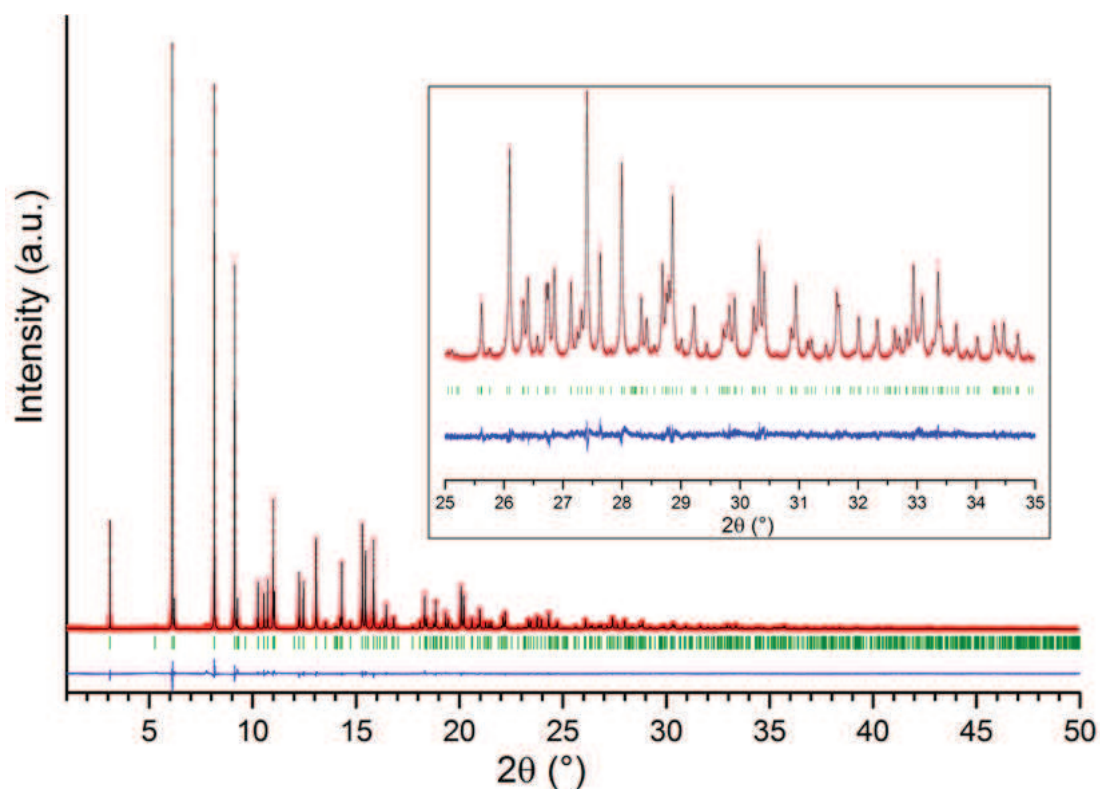


Figure S11. Rietveld refinement of the $\text{Sr}_{1.15}\text{Al}_{2.3}\text{Si}_{1.7}\text{O}_8$ ($x = 0.3$) synchrotron powder diffraction data collected at room temperature ($R_{\text{wp}} = 7.46\%$, $R_{\text{p}} = 5.65\%$, and $\chi^2 = 1.65$). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines corresponds to the reflection positions. Enlargement of the 25 - 35° angular range (2θ) is embedded.

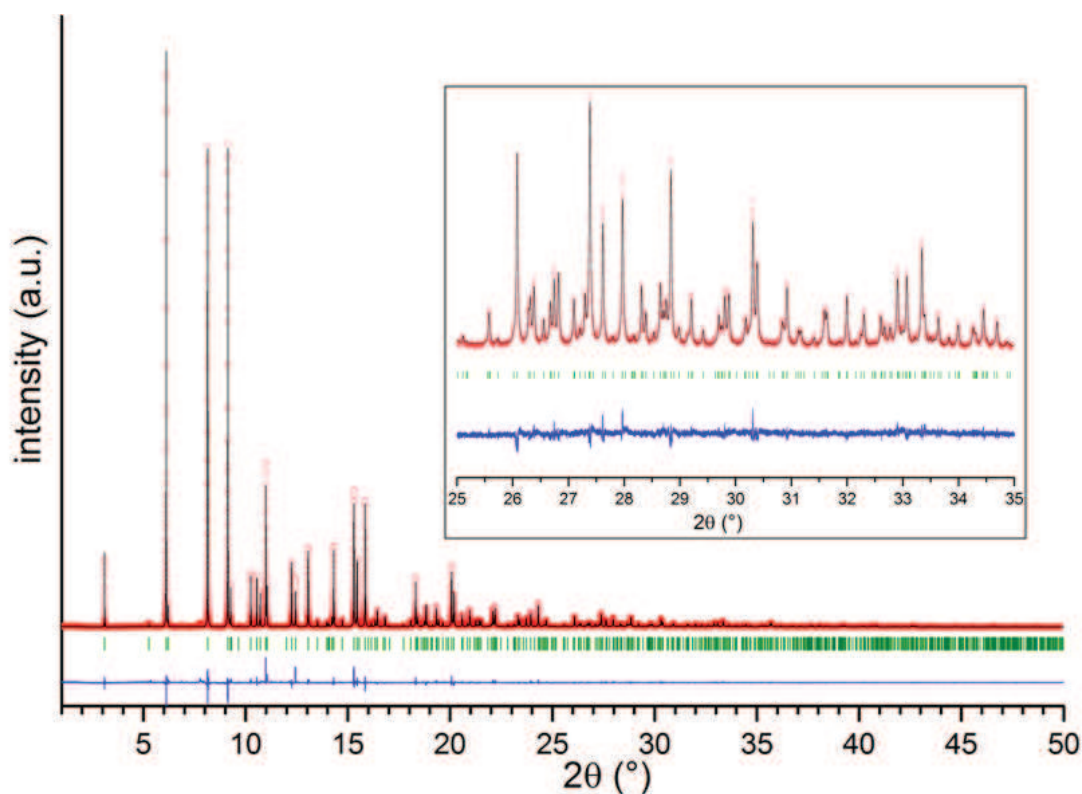


Figure S12 Rietveld refinement of the $\text{Sr}_{1.2}\text{Al}_{2.4}\text{Si}_{1.6}\text{O}_8$ ($x=0.4$) synchrotron powder diffraction data collected at room temperature ($R_{\text{wp}} = 8.06\%$, $R_p = 6.33\%$, and $\chi^2 = 1.67$). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines corresponds to the reflection positions. Enlargement of the $25 - 35^\circ$ angular range (2θ) is embedded.

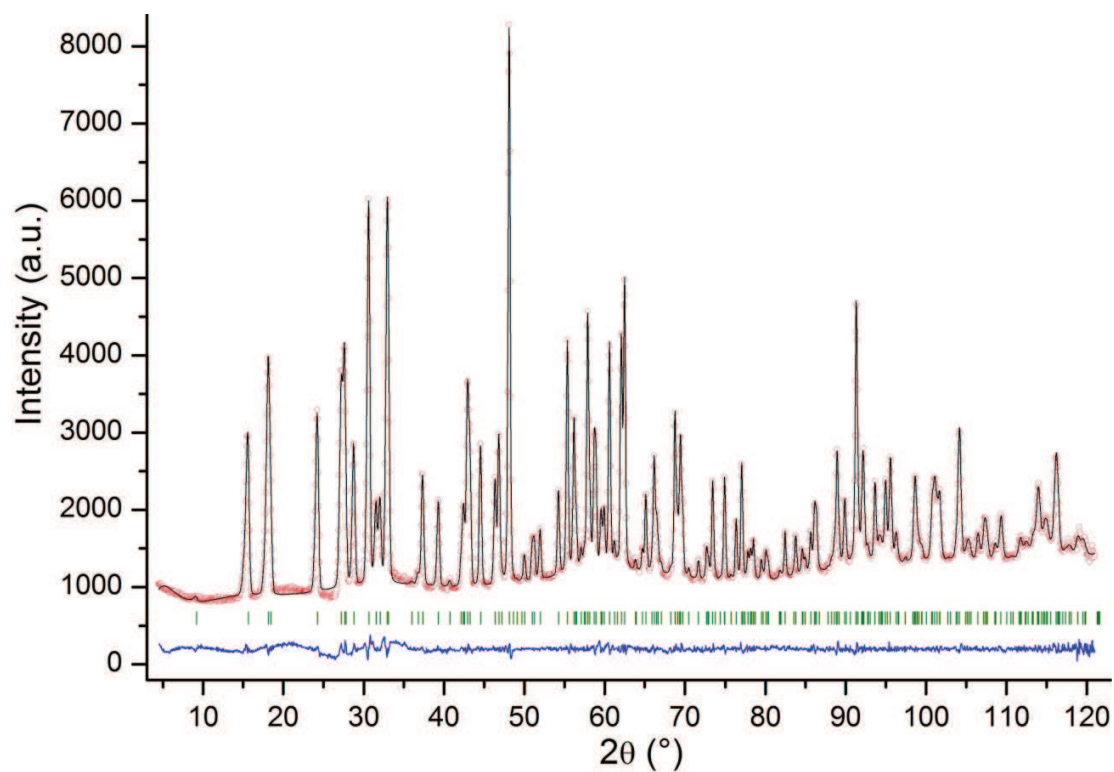


Figure S13 Rietveld refinement of the $\text{Sr}_{1.2}\text{Al}_{2.4}\text{Si}_{1.6}\text{O}_8$ ($x = 0.4$) neutron powder diffraction data collected at room temperature ($R_{\text{wp}} = 2.40\%$, $R_p = 1.65\%$, and $\chi^2 = 2.00$). Observed (red circles), calculated (black line) and difference (blue line) profiles are shown. The set of green vertical lines corresponds to the reflection positions.

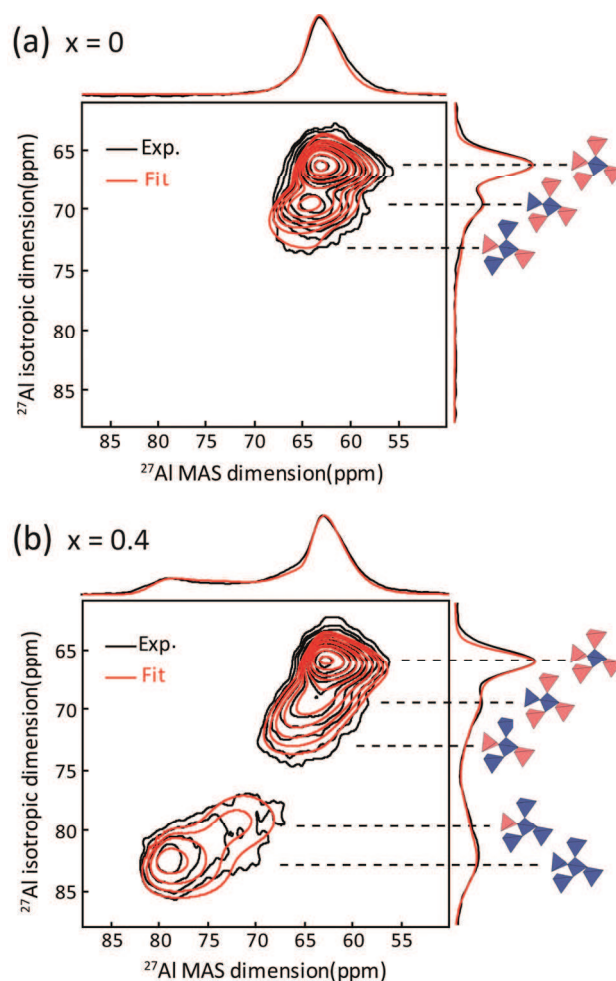


Figure S14. ^{27}Al experimental 2D MQMAS spectra (black lines) of (a) $\text{SrAl}_2\text{Si}_2\text{O}_8$ ($x = 0$) and (b) $\text{Sr}_{1.2}\text{Al}_{2.4}\text{Si}_{1.6}\text{O}_8$ ($x = 0.4$) with their best fits (red lines). The projection along the MAS dimension is shown on top of the 2D spectra. The projection along the isotropic dimension is shown on the right side of the 2D spectra with the different q^4_m structural motifs associated to the distinct ^{27}Al isotropic resonances (blue and red tetrahedra correspond to AlO_4 and SiO_4 units, respectively). The experimental MQMAS spectra were recorded at a magnetic field of 17.6 T and a spinning frequency of 30 kHz using a three pulse Z-filter sequence.¹ The pulse durations for the triple quantum coherence excitation and reconversion were of 3.2 and 1.2 μs , respectively, with a radio-frequency field strength of 116 kHz. The duration of the central transition selective pulse was of 4.3 μs . 20 t_1 increments of 133.3 μs (corresponding to four rotor periods) with 312 transients each were collected using a recycle delay of 1s. The experimental spectra were fitted using the DMFit software.² Second order quadrupolar broadened lineshapes with a Gaussian distribution of the quadrupolar coupling constant were used. Distributions of the ^{27}Al isotropic chemical shift were taken into account. The obtained quadrupolar and chemical shift parameters were used to fit the quantitative ^{27}Al 1D MAS spectra (shown in figure 3).

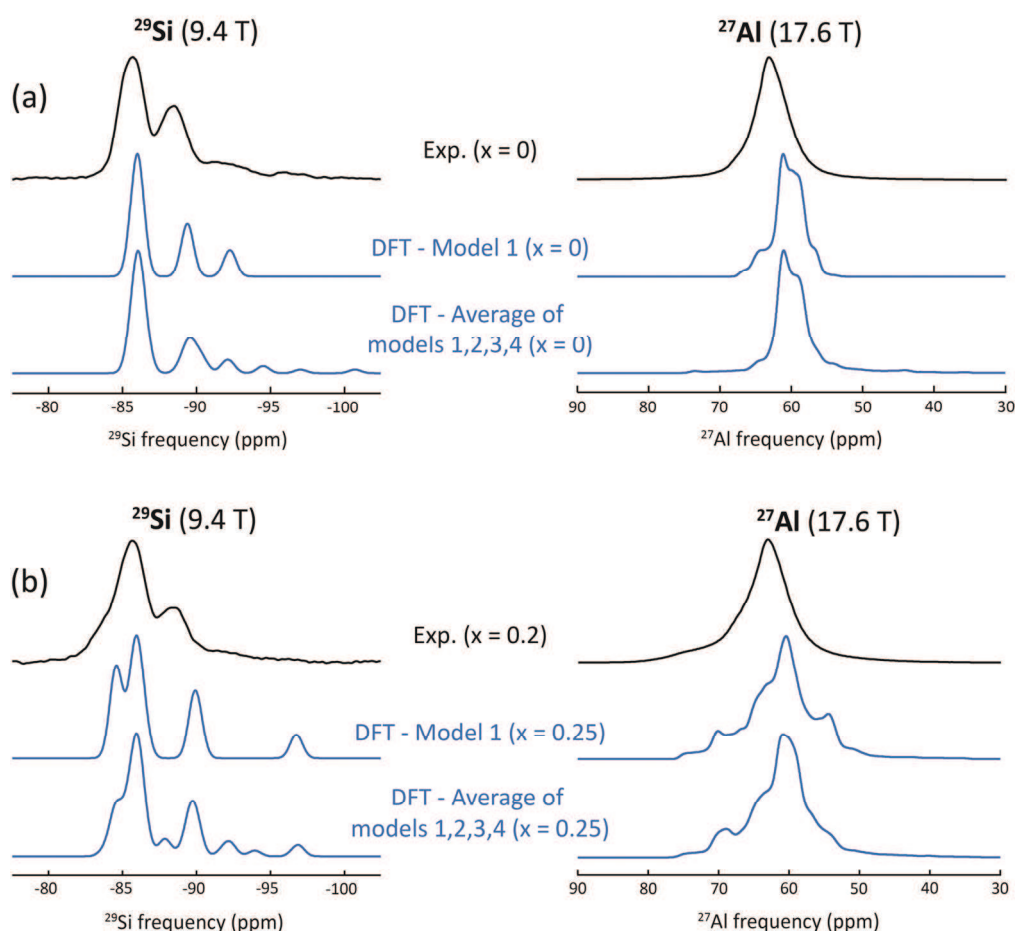


Figure S15. Comparison between the experimental MAS NMR spectra ($x = 0$ and 0.2) and those calculated by DFT for the modeled structures ($x = 0$ and 0.25). (a) Top, experimental ^{29}Si and ^{27}Al MAS spectra for $x = 0$. Middle, ^{29}Si and ^{27}Al DFT-calculated MAS spectra for the modeled structure with $x = 0$ shown in figure 3j (labeled model 1 in figure S15). Bottom, simulated ^{29}Si and ^{27}Al MAS spectra obtained by averaging the results of calculations on models 1 to 4 in figure S15 ($x = 0$). (b) Top, experimental ^{29}Si and ^{27}Al MAS spectra for $x = 0.2$. Middle, ^{29}Si and ^{27}Al DFT-calculated spectra for the modeled structure with $x = 0.25$ shown in figure 3k (labeled model 1 in figures S16). Bottom, simulated ^{29}Si and ^{27}Al MAS spectra obtained by averaging the results of calculations on models 1 to 4 in figure S16 ($x = 0.25$). DFT calculations of the NMR parameters were performed with the CASTEP code⁴ using the projector augmented waves^{5,6} (PAW) and gauge included projector augmented waves⁷ (GIPAW) methods for computing the EFG and NMR chemical shielding tensors, respectively. The ^{29}Si and ^{27}Al isotropic chemical shifts were deduced from the calculated ^{29}Si and ^{27}Al isotropic shielding using previously established linear relationships.⁸ The PBE functional was used for the exchange-correlation energy.³ The pseudopotentials were the same than those used for the geometry optimization and computation of $\epsilon(\omega)$ (ultrasoft pseudopotentials generated “on the fly”). The energy cutoff for the plane wave

basis set expansion was set to 600 eV and the Brillouin zone was sampled using a Monkhorst-Pack grid spacing of $0.04 \text{ \AA}^{-1}$.

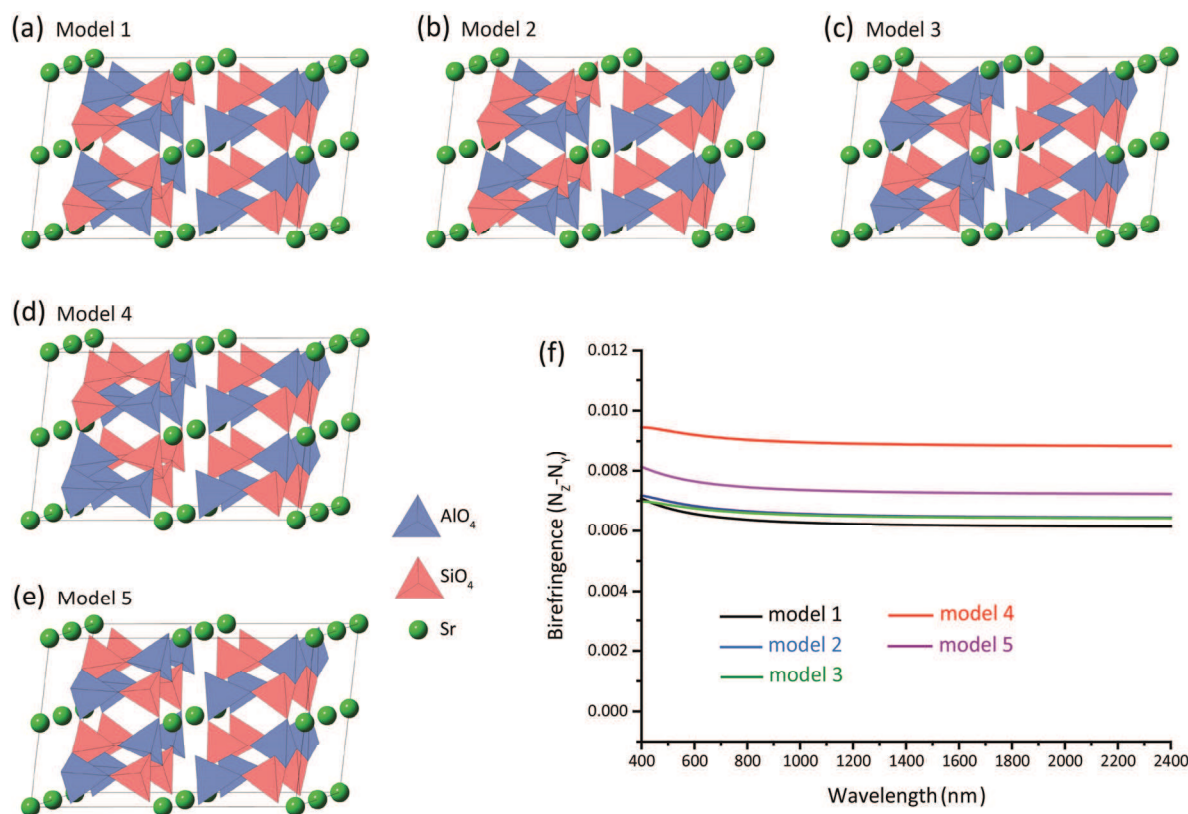


Figure S16. (a-e) Modeled structures of the $\text{SrAl}_2\text{Si}_2\text{O}_8$ compound ($x = 0$) which consist of a supercell of 2x2x1 unit cells of the average structure with different Al/Si ordering configurations. The supercell contains 32 tetrahedral sites (occupied by Si or Al atoms) and a total of 104 atoms. The red and blue tetrahedra correspond to SiO_4 and AlO_4 units, respectively, and green spheres to Sr atoms. In (a), the Al/Si ordering closely accounts for the distributions of Al and Si environments observed by NMR. Models 1 to 4 depicted in (a-d) were used to calculate the average birefringence value shown in figure 3 (dashed black line). The lowest energy structure is shown in (e). In all cases, DFT optimization of all atomic positions was performed by minimizing the residual forces on all atoms up to $|F|_{\text{max}}$ below $0.006 \text{ eV} \cdot \text{\AA}^{-1}$, fixing the cell parameters to the experimentally determined values. For the geometry optimization, an energy cutoff of 600 eV was used for the plane wave basis set expansion and the Brillouin zone was sampled using a Monkhorst-Pack grid spacing of $0.04 \text{ \AA}^{-1}$. Some structural parameters of the geometry optimized structures are reported in table S11. (f) DFT-calculated birefringence for the structural models shown in (a-e). The refractive index was determined from the real and imaginary part of the calculated dielectric function. DFT computations of the dielectric function $\epsilon(\omega)$ were performed using an energy cutoff of 600 eV for the plane wave basis set expansion. 96 empty bands were considered (total

number of bands of 384) and the Brillouin zone was sampled using a Monkhorst-Pack grid spacing of $0.02 \text{ \AA}^{-1}$. For both geometry optimization and computation of $\epsilon(\omega)$, the Perdew-Burke-Ernzerhof (PBE) functional was used in the generalized gradient approximation (GGA) for the exchange-correlation energy.³ The core-valence interactions were described by ultrasoft pseudopotentials generated using the on-the-fly generator included in CASTEP (details are provided in table S10).⁴

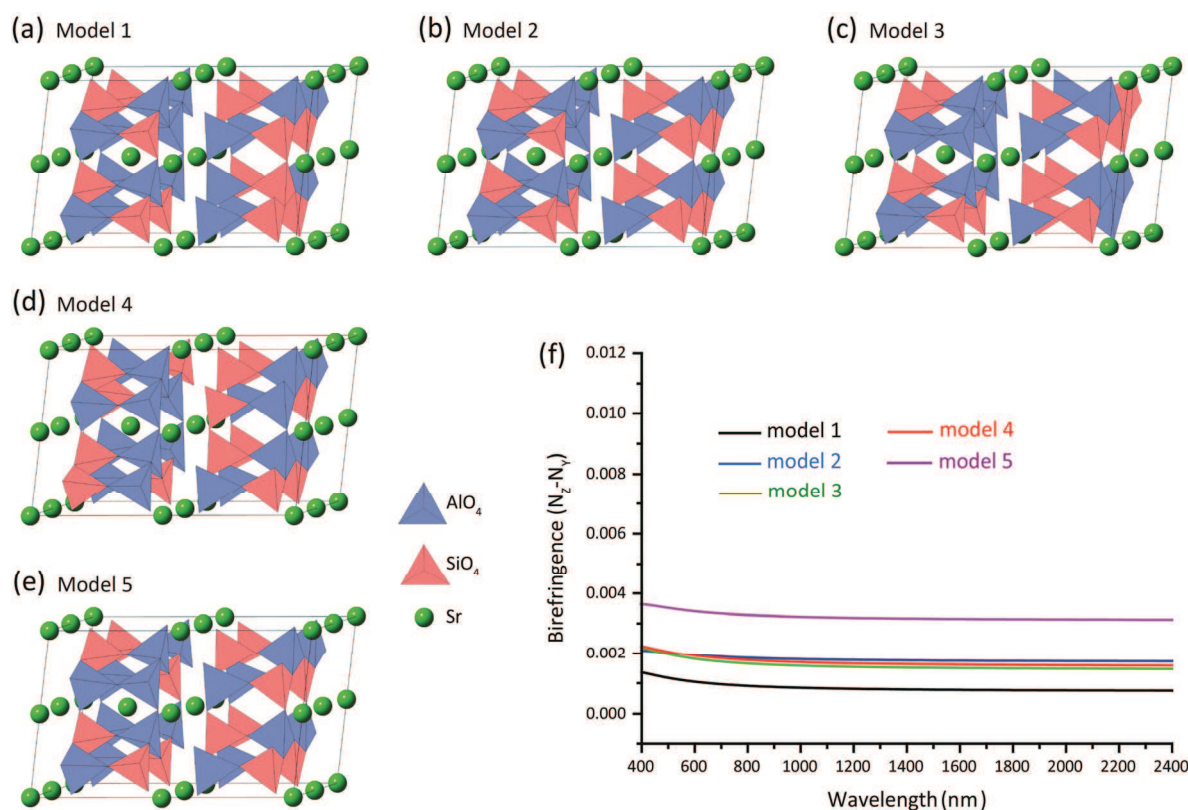


Figure S17. (a-e) Modeled structures of the $\text{Sr}_{1.125}\text{Al}_{2.25}\text{Si}_{1.75}\text{O}_8$ compound ($x = 0.25$) which consist of a supercell of 2x2x1 unit cells of the average structure with different Al/Si ordering. The supercell contains 32 tetrahedral sites (occupied by Si or Al atoms) and a total of 105 atoms (one of the extra strontium positions in the supercell being fully occupied). The red and blue tetrahedra correspond SiO_4 and AlO_4 units, respectively, and green spheres are Sr atoms. In (a), the Al/Si ordering closely accounts for the observed distributions of Al and Si environments. Models 1 to 4 depicted in (a-d) were used to calculate the average birefringence value shown in figure 3 (dashed blue line). The lowest energy structure is shown in (e). In all cases, DFT optimization of all atomic positions was performed by minimizing the residual forces on all atoms up to $|F|_{\text{max}}$ below $0.006 \text{ eV} \cdot \text{\AA}^{-1}$, fixing the cell parameters to the experimentally determined values. (f) DFT-calculated birefringence for the structural models shown in (a-e). The refractive index was determined from the real and imaginary part of the calculated dielectric function. The parameters used for the geometry optimization and the DFT computations of the dielectric function $\epsilon(\omega)$ were the same than those reported in figure S14.

Table S1. Refractive index (n_∞) and maximum theoretical transmission values of transparent oxide ceramics reported in the literature.

Composition	Refractive index (n_∞)	Maximum theoretical transmission (%)
MgAl₂O₄⁹	1.701	87.4
Y₃Al₅O₁₂⁹	1.812	84.6
Al₂O₃⁹	1.755	86.0
Lu₂O₃¹⁰	1.900	82.4
Y₂O₃⁹	1.892	82.6
Sc₂O₃¹⁰	1.954	81.1
ZrO₂⁹	2.113	77.3
LaGdZr₂O₇¹¹	2.08	78.1
Sr_{1+x/2}Al_{2+x}Si_{2-x}O₈	1.59	90.1

Table S2. Glass transition and crystallization temperatures of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($x = 0, 0.1, 0.2, 0.3, 0.4$) glass materials obtained from Differential Scanning Calorimetry (DSC) measurements. Each measurement was performed on a 475 mg glass powder sample using a heating rate of 10 K/min.

	Thermal characteristics	T _g (°C) ± 2	T _x (°C) ± 2
Glass Composition	SrAl₂Si₂O₈ (x=0)	907	1050
	Sr_{1.05}Al_{2.1}Si_{1.9}O₈ (x=0.1)	905	1060
	Sr_{1.1}Al_{2.2}Si_{1.8}O₈ (x=0.2)	904	1063
	Sr_{1.15}Al_{2.3}Si_{1.7}O₈ (x=0.3)	903	1073
	Sr_{1.2}Al_{2.4}Si_{1.6}O₈ (x=0.4)	904	1088

Table S3. Atomic positions and selected inter-atomic distances of $\text{SrAl}_2\text{Si}_2\text{O}_8$ ($x = 0$) obtained from room temperature Rietveld refinement of synchrotron powder diffraction data (cell parameters: $a = 5.19367(3)$ Å and $c = 15.1983(1)$ Å).

Atom	Site	x	y	z	Uiso	Occ.
Sr1	2b	0	0	0	0.00972(7)	1
Al1	8h	0.33333	0.66667	0.14197(2)	0.00534(10)	0.5
Si1	8h	0.33333	0.66667	0.14197(2)	0.00534(10)	0.5
O1	4c	0.33333	0.66667	0.25	0.0113(3)	1
O2	12k	0.41633(17)	0	0.10121(6)	0.0246(4)	1

Sr1-O (Å)		Al/Si-O (Å)	
Sr1-O2 (x6)	3.4016(9)	Al/Si-O1	1.6426(3)
Sr1-O2 (x6)	2.6553(9)	Al/Si-O2 (x3)	1.6806(10)

Table S4. Atomic positions and selected inter-atomic distances of $\text{Sr}_{1.05}\text{Al}_{2.1}\text{Si}_{1.9}\text{O}_8$ ($x = 0.1$) obtained from room temperature Rietveld refinement of synchrotron powder diffraction data (cell parameters: $a = 5.196294(5)$ Å and $c = 15.21997(2)$ Å).

Atom	Site	x	y	z	Uiso	Occ.
Sr1	2b	0	0	0	0.00824(5)	1
Sr2	2a	0	0	0.25	0.0054(10)	0.0306(4)
Al1	8h	0.33333	0.66667	0.1419(1)	0.00490(7)	0.515(1)*
Si1	8h	0.33333	0.66667	0.1419(1)	0.00490(7)	0.485(1)*
O1	4c	0.33333	0.66667	0.25	0.0139(2)	1
O2	12k	0.40670(10)	0	0.10149(4)	0.0136(2)	1

*: the Al/Si ratio was constrained using: (i) $\text{occ}(\text{Al}) = 0.5 + \text{occ}(\text{Sr2})/2$ for compensating the positive charge induced by Sr2 and (ii) $\text{occ}(\text{Al}) + \text{occ}(\text{Si}) = 1$ (full site occupancy).

Sr1-O (Å)		Sr2-O (Å)		Al/Si-O (Å)	
Sr1-O2 (x6)	3.4483(4)	Sr2-O1 (x6)	3.0001	Al/Si-O1	1.6447(2)
Sr1-O2 (x6)	2.6177(5)	Sr2-O2 (x6)	3.0943(5)	Al/Si-O2 (x3)	1.6923(3)

Table S5. Atomic positions and selected inter-atomic distances of $\text{Sr}_{1.1}\text{Al}_{2.2}\text{Si}_{1.8}\text{O}_8$ ($x = 0.2$) obtained from room temperature Rietveld refinement of synchrotron powder diffraction data (cell parameters: $a = 5.199956(12)$ Å and $c = 15.24875(5)$ Å).

Atom	Site	x	y	z	Uiso	Occ.
Sr1	2b	0	0	0	0.01217(9)	1
Sr2	2a	0	0	0.25	0.0098(8)	0.090(1)
Al1	8h	0.33333	0.66667	0.1417(1)	0.00621(12)	0.545(1)*
Si1	8h	0.33333	0.66667	0.1417(1)	0.00621(12)	0.455(1)*
O1	4c	0.33333	0.66667	0.25	0.0159(4)	1
O2	12k	0.4020(1)	0	0.1014(1)	0.0107(3)	1

*: the Al/Si ratio was constrained using: (i) $\text{occ}(\text{Al}) = 0.5 + \text{occ}(\text{Sr2})/2$ for compensating the positive charge induced by Sr2 and (ii) $\text{occ}(\text{Al}) + \text{occ}(\text{Si}) = 1$ (full site occupancy).

Sr1-O (Å)		Sr2-O (Å)		Al/Si-O (Å)	
Sr1-O2 (x6)	3.4730(8)	Sr2-O1 (x6)	3.0022	Al/Si-O1	1.6517(4)
Sr1-O2 (x6)	2.6000(8)	Sr2-O2 (x6)	3.0827(8)	Al/Si-O2 (x3)	1.7001(4)

Table S6. Atomic positions and selected inter-atomic distances of $\text{Sr}_{1.15}\text{Al}_{2.3}\text{Si}_{1.7}\text{O}_8$ ($x = 0.3$) obtained from room temperature Rietveld refinement of synchrotron powder diffraction data (cell parameters: $a = 5.200894(6)$ Å and $c = 15.26844(3)$ Å).

Atom	Site	x	y	z	Uiso	Occ.
Sr1	2b	0	0	0	0.01192(6)	1
Sr2	2a	0	0	0.25	0.0193(4)	0.143(1)
Al1	8h	0.33333	0.66667	0.1416(1)	0.00620(8)	0.571(1)*
Si1	8h	0.33333	0.66667	0.1416 (1)	0.00620(8)	0.429(1)*
O1	4c	0.33333	0.66667	0.25	0.0172(3)	1
O2	12k	0.3996(1)	0	0.1017(1)	0.0120(2)	1

*: the Al/Si ratio was constrained using: (i) $\text{occ}(\text{Al}) = 0.5 + \text{occ}(\text{Sr2})/2$ for compensating the positive charge induced by Sr2 and (ii) $\text{occ}(\text{Al}) + \text{occ}(\text{Si}) = 1$ (full site occupancy).

Sr1-O (Å)		Sr2-O (Å)		Al/Si-O (Å)	
Sr1-O2 (x6)	3.4878(6)	Sr2-O1 (x6)	3.0027	Al/Si-O1	1.6517(3)
Sr1-O2 (x6)	2.5946(6)	Sr2-O2 (x6)	3.0729(6)	Al/Si-O2 (x3)	1.7023(3)

Table S7. Atomic positions and selected inter-atomic distances of $\text{Sr}_{1.2}\text{Al}_{2.4}\text{Si}_{1.6}\text{O}_8$ ($x = 0.4$) obtained from room temperature Rietveld refinement of synchrotron powder diffraction data (cell parameters: $a = 5.202892(6)$ Å and $c = 15.29364(3)$ Å).

Atom	Site	x	y	z	Uiso	Occ.
Sr1	2b	0	0	0	0.01278(6)	1
Sr2	2a	0	0	0.25	0.0135(3)	0.174(1)
Al1	8h	0.33333	0.66667	0.1416(1)	0.00662(9)	0.587(1)*
Si1	8h	0.33333	0.66667	0.1416(1)	0.00662(9)	0.413(1)*
O1	4c	0.33333	0.66667	0.25	0.0213(4)	1
O2	12k	0.3973(1)	0	0.1022(1)	0.0135(3)	1

*: the Al/Si ratio was constrained using: (i) $\text{occ}(\text{Al}) = 0.5 + \text{occ}(\text{Sr2})/2$ for compensating the positive charge induced by Sr2 and (ii) $\text{occ}(\text{Al}) + \text{occ}(\text{Si}) = 1$ (full site occupancy).

Sr1-O (Å)		Sr2-O (Å)		Al/Si-O (Å)	
Sr1-O2 (x6)	3.5037(7)	Sr2-O1 (x6)	3.0039	Al/Si-O1	1.6583(3)
Sr1-O2 (x6)	2.5913 (7)	Sr2-O2 (x6)	3.0631(7)	Al/Si-O2 (x3)	1.7041(4)

Table S8. Isotropic chemical shifts δ_{ISO} (± 0.2), full width at half maximum Fwhm (± 0.2) and relative intensity I (± 2) of the ^{29}Si resonances corresponding to the different Si local environments in the structure of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ compounds determined from the fits of the ^{29}Si quantitative MAS spectra. ^{29}Si chemical shift were referenced relative to neat TMS ($\text{Si}(\text{CH}_3)_4$).

Sample	Unit	Label	δ_{ISO} (ppm)	Fwhm (ppm)	I (%)
x = 0	$\text{Si}(\text{OAl})_4$	Q^4_4	-85.6	2.0	54
	$\text{Si}(\text{OAl})_3(\text{OSi})$	Q^4_3	-88.4	2.0	31
	$\text{Si}(\text{OAl})_2(\text{OSi})_2$	Q^4_2	-91.7	3.5	12
	$\text{Si}(\text{OAl})(\text{OSi})_3$	Q^4_1	-96.3	2.1	3
x = 0.2	$\text{Si}(\text{OAl})_4$	Q^4_4	-83.5/-85.6	2.1/2.1	67
	$\text{Si}(\text{OAl})_3(\text{OSi})$	Q^4_3	-88.4	2.1	23
	$\text{Si}(\text{OAl})_2(\text{OSi})_2$	Q^4_2	-91.6	4.0	8
	$\text{Si}(\text{OAl})(\text{OSi})_3$	Q^4_1	-96.2	3.0	2
x = 0.4	$\text{Si}(\text{OAl})_4$	Q^4_4	-83.6/-85.7	2.7/2.1	82
	$\text{Si}(\text{OAl})_3(\text{OSi})$	Q^4_3	-88.3	2.3	14
	$\text{Si}(\text{OAl})_2(\text{OSi})_2$	Q^4_2	-91.6	3.2	4
	$\text{Si}(\text{OAl})(\text{OSi})_3$	Q^4_1	-	-	0

Table S9. Isotropic chemical shifts ($\delta_{\text{ISO}} \pm 0.2$), average quadrupolar coupling constant ($\bar{C}_Q \pm 0.10$), full width at half maximum of the Gaussian distribution of the quadrupolar coupling constant ($\text{Fwhm}(C_Q) \pm 0.20$), asymmetry parameter of the quadrupolar tensor ($\eta_Q \pm 0.1$) and relative intensity ($I \pm 5$) of the ^{27}Al resonances corresponding to the different Al local environments in the structure of the $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ compounds. The NMR parameters (δ_{ISO} , $\bar{C}_Q$, $\text{Fwhm}(C_Q)$ and η_Q) were determined from the fits of both 2D MQMAS and 1D MAS spectra. The relative intensities were determined from the fits of the ^{27}Al quantitative MAS spectra taking into account the contributions of the $\langle \pm 1/2, \pm 3/2 \rangle$ and $\langle \pm 3/2, \pm 5/2 \rangle$ satellite transitions. ^{27}Al chemical shift were referenced relative to 1.0 M $\text{Al}(\text{NO}_3)_3$ aqueous solution.

Sample	Unit	Label	δ_{ISO} (ppm)	$\bar{C}_Q$ (MHz)	$\text{Fwhm}(C_Q)$ (MHz)*	η_Q	I (%)
x = 0	$\text{Al}(\text{OSi})_4$	q^4_0	64.2	3.60	2.60	0.5	55
	$\text{Al}(\text{OSi})_3(\text{OAl})$	q^4_1	67.2	4.77	2.47	0.6	33
	$\text{Al}(\text{OSi})_2(\text{OAl})_2$	q^4_2	70.3	5.60	2.67	0.6	9
	$\text{Al}(\text{OSi})(\text{OAl})_3$	q^4_3	75.9	5.87	2.33	0.3	3
	$\text{Al}(\text{OAl})_4$	q^4_4	-	-	-	-	0
x = 0.2	$\text{Al}(\text{OSi})_4$	q^4_0	64.0	3.58	2.60	0.5	34
	$\text{Al}(\text{OSi})_3(\text{OAl})$	q^4_1	67.2	4.91	2.67	0.6	40
	$\text{Al}(\text{OSi})_2(\text{OAl})_2$	q^4_2	70.3	5.60	2.67	0.6	14
	$\text{Al}(\text{OSi})(\text{OAl})_3$	q^4_3	76.0	5.87	2.33	0.3	11
	$\text{Al}(\text{OAl})_4$	q^4_4	80.5	4.60	3.33	0.6	1
x = 0.4	$\text{Al}(\text{OSi})_4$	q^4_0	64.0	3.58	2.47	0.5	32
	$\text{Al}(\text{OSi})_3(\text{OAl})$	q^4_1	67.1	4.97	2.67	0.6	22

Al(OSi) ₂ (OAl) ₂	q ₂ ⁴	69.8	5.60	2.67	0.6	19
Al(OSi)(OAl) ₃	q ₃ ⁴	76.3	5.87	2.33	0.3	18
Al(OAl) ₄	q ₄ ⁴	81.0	4.60	3.33	0.6	9

* Fwhm(C_Q) = 2√2 ln2 σ, σ being the standard deviation of the Gaussian distribution of C_Q

Table S10. Description of pseudopotentials used for planewave DFT calculations. r_{loc} is the pseudisation radius for the local component of the pseudopotential, r_{nonloc} is the pseudisation radius for the non-local components of the pseudopotential, and r_{aug} is the pseudisation radius for the charge augmentation functions.

Atom	Core states	r_{loc} (a.u.)	r_{nonloc} (a.u.)	r_{aug} (a.u.)	Pseudopotential projectors
O	1s	1.3	1.3	0.9	2x2s, 2x2p
Si	1s, 2s, 2p	1.8	1.8	1.3	2x3s, 2x3p
Al	1s, 2s, 2p	2.0	2.0	1.4	2x3s, 2x3p
Sr	1s, 2s, 2p, 3s, 3d, 3d	2.0	2.0	1.2	4s, 4p, 5s

The corresponding Materials Studio Castep “on-the-fly” strings used to generate these potentials are:

O 2|1.3|16.537|18.375|20.212|20UU:21UU(qc=7.5) []
Si 2|2|3.675|5.512|7.717|30UU:31UU:32LGG []
Al 2|1.8|3.675|5.512|7.35|30UU:31UU:32LGG []
Sr 3|2|2|1.2|7.4|9.2|11|40U:50U:41UU:42UU []

Table S11. Structural parameters of the different geometry-optimized model structures with $x = 0$ ($\text{SrAl}_2\text{Si}_2\text{O}_8$). The space group, the total energy relative to that of the lowest energy structure, the types and relative amounts of Si and Al environment and the corresponding Si-O and Al-O average bond length are reported.

2x2x1 supercell model	Space group	Energy (eV)	Sites	Local envi- ronment	Proportion (%)	Average bond length
Model 1	C2	+0.96	Q^4_4	$\text{Si}(\text{OAl})_4$	62.5	Si-O: 1.627
			Q^4_3	$\text{Si}(\text{OAl})_3(\text{OSi})$	25	Si-O: 1.630
			Q^4_2	$\text{Si}(\text{OAl})_2(\text{OSi})_2$	12.5	Si-O: 1.631
			q^4_0	$\text{Al}(\text{OSi})_4$	62.5	Al-O: 1.750
			q^4_1	$\text{Al}(\text{OSi})_3(\text{OAl})$	25	Al-O: 1.747
			q^4_2	$\text{Al}(\text{OSi})_2(\text{OAl})$	12.5	Al-O: 1.748
Model 2	P1	+1.05	Q^4_4	$\text{Si}(\text{OAl})_4$	75	Si-O: 1.628
			Q^4_3	$\text{Si}(\text{OAl})_3(\text{OSi})$	18.75	Si-O: 1.629
			Q^4_3	$\text{Si}(\text{OAl})(\text{OSi})_3$	6.25	Si-O: 1.632
			q^4_0	$\text{Al}(\text{OSi})_4$	75	Al-O: 1.749
			q^4_1	$\text{Al}(\text{OSi})_3(\text{OAl})$	18.75	Al-O: 1.751
			q^4_3	$\text{Al}(\text{OSi})(\text{OAl})_3$	6.25	Al-O: 1.745
Model 3	P1	+1.56	Q^4_4	$\text{Si}(\text{OAl})_4$	68.75	Si-O: 1.628
			Q^4_3	$\text{Si}(\text{OAl})_3(\text{OSi})$	25	Si-O: 1.629
			Q^4_4	$\text{Si}(\text{OSi})_4$	6.25	Si-O: 1.631
			q^4_0	$\text{Al}(\text{OSi})_4$	68.75	Al-O: 1.749
			q^4_1	$\text{Al}(\text{OSi})_3(\text{OAl})$	25	Al-O: 1.750
			q^4_4	$\text{Al}(\text{OAl})_4$	6.25	Al-O: 1.740
Model 4	P1	+2.00	Q^4_4	$\text{Si}(\text{OAl})_4$	50	Si-O: 1.628

			Q^4_3	$Si(OAl)_3(OSi)$	25	Si-O: 1.633
			Q^4_2	$Si(OAl)_2(OSi)_2$	25	Si-O: 1.631
			q^4_0	$Al(OSi)_4$	50	Al-O: 1.750
			q^4_1	$Al(OSi)_3(OAl)$	25	Al-O: 1.745
			q^4_2	$Al(OSi)_2(OAl)_2$	25	Al-O: 1.748
Model 5	P-3C1	0	Q^4_4	$Si(OAl)_4$	100	Si-O: 1.628
			q^4_0	$Al(OSi)_4$	100	Al-O: 1.750

Table S12. Structural parameters of the different geometry-optimized model structures with $x = 0.25$ ($\text{Sr}_{1.125}\text{Al}_{2.25}\text{Si}_{1.75}\text{O}_8$). The space group, the total energy relative to that of the lowest energy structure, the types and relative amounts of Si and Al environment and the corresponding Si-O and Al-O average bond length are reported.

2x2x1 supercell model	Space group	Energy (eV)	Sites	Local envi- ronment	Proportion (%)	Average bond length
Model 1	P1	+0.99	Q^4_4	$\text{Si}(\text{OAl})_4$	71.45	Si-O: 1.629
			Q^4_3	$\text{Si}(\text{OAl})_3(\text{OSi})$	21.45	Si-O: 1.632
			Q^4_1	$\text{Si}(\text{OAl})(\text{OSi})_3$	7.1	Si-O: 1.634
			q^4_0	$\text{Al}(\text{OSi})_4$	33.3	Al-O: 1.752
			q^4_1	$\text{Al}(\text{OSi})_3(\text{OAl})$	38.9	Al-O: 1.750
			q^4_2	$\text{Al}(\text{OSi})_2(\text{OAl})$	11.1	Al-O: 1.756
			q^4_3	$\text{Al}(\text{OSi})_2(\text{OAl})^2$	5.6	Al-O: 1.742
			q^4_4	$\text{Al}(\text{OSi})(\text{OAl})_3$ $\text{Al}(\text{OAl})_4$	11.1	Al-O: 1.754
Model 2	C2	+0.01	Q^4_4	$\text{Si}(\text{OAl})_4$	100.0	Si-O: 1.629
			q^4_0	$\text{Al}(\text{OSi})_4$	55.6	Al-O: 1.751
			q^4_1	$\text{Al}(\text{OSi})_3(\text{OAl})$	22.2	Al-O: 1.754
			q^4_2	$\text{Al}(\text{OSi})_2(\text{OAl})$	11.1	Al-O: 1.757
			q^4_4	$\text{Al}(\text{OAl})_4^2$	11.1	Al-O: 1.754
Model 3	P1	+1.12	Q^4_4	$\text{Si}(\text{OAl})_4$	57.1	Si-O: 1.630
			Q^4_3	$\text{Si}(\text{OAl})_3(\text{OSi})$	28.6	Si-O: 1.630
			Q^4_2	$\text{Si}(\text{OAl})_2(\text{OSi})_2$	14.3	Si-O: 1.631
			q^4_0	$\text{Al}(\text{OSi})_4$	22.2	Al-O: 1.753
			q^4_1	$\text{Al}(\text{OSi})_3(\text{OAl})$	44.5	Al-O: 1.751
			q^4_2	$\text{Al}(\text{OSi})_2(\text{OAl})$	22.2	Al-O: 1.750
			q^4_4	$\text{Al}(\text{OAl})_4^2$	11.1	Al-O: 1.750

Al(OAl) ₄						
Model 4	P1	+1.88	Q ⁴ ₄	Si(OAl) ₄	28.6	Si-O: 1.626
			Q ⁴ ₃	Si(OAl) ₃ (OSi)	50.0	Si-O: 1.632
			Q ⁴ ₂	Si(OAl) ₂ (OSi) ₂	14.3	Si-O: 1.635
			Q ⁴ ₁	Si(OAl)(OSi) ₃	7.1	Si-O: 1.632
			q ⁴ ₀	Al(OSi) ₄	22.2	Al-O: 1.750
			q ⁴ ₁	Al(OSi) ₃ (OAl)	16.7	Al-O: 1.746
			q ⁴ ₂	Al(OSi) ₂ (OAl)	33.3	Al-O: 1.754
			q ⁴ ₃	² Al(OSi)(OAl) ₃	27.8	Al-O: 1.750
Model 5	C2	0	Q ⁴ ₄	Si(OAl) ₄	100.0	Si-O: 1.629
			q ⁴ ₀	Al(OSi) ₄	44.45	Al-O: 1.749
			q ⁴ ₁	Al(OSi) ₃ (OAl)	44.45	Al-O: 1.755
			q ⁴ ₄	Al(OAl) ₄	11.1	Al-O: 1.753

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Céramiques transparentes par cristallisation complète du verre : application aux aluminosilicates de strontium

Les céramiques transparentes élaborées par cristallisation complète du verre constituent une nouvelle famille de matériaux de qualité photonique en compétition avec la technologie des monocristaux pour les applications optiques. Cette approche verrière offre des avantages considérables par rapport aux monocristaux et aux céramiques polycristallines frittées : un coût réduit, la possibilité d'une production à grande échelle, une large gamme de compositions chimiques accessibles, une mise en forme plus souple et un taux de dopage élevé.

Dans le cadre de ce travail, nous avons synthétisé des céramiques polycristallines transparentes de $\text{Sr}_3\text{Al}_2\text{O}_6$ et $\text{Sr}_3\text{Ga}_2\text{O}_6$ (structures cubiques) par cristallisation complète du verre de même composition. Les verres d'aluminate de strontium ($75\text{SrO}-25\text{Al}_2\text{O}_3$) et de gallate de strontium ($75\text{SrO}-25\text{Ga}_2\text{O}_3$) sont élaborés par lévitation aérodynamique couplée à un dispositif de chauffage laser. La transparence de la céramique de $\text{Sr}_3\text{Al}_2\text{O}_6$ obtenue s'explique par son isotropie optique, ses joints de grains très fins et sa structure totalement dense (non poreuse).

Nous avons également développé une nouvelle famille de céramiques transparentes $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 < x \leq 0.4$) obtenues par cristallisation complète et congruente du verre. La transmission exceptionnelle de plus de 90% dans la gamme visible et proche infrarouge est expliquée grâce à des études microstructurales et structurales. Cette transparence qui atteint la limite théorique est associée à une biréfringence quasi nulle, des joints de grains très fins et une porosité nulle. Les études par RMN prouvent l'existence d'un désordre chimique qui est à l'origine de la valeur pratiquement nulle de la biréfringence calculée par DFT. Ces matériaux céramiques polycristallins évolutifs et hautement transparents sont des candidats prometteurs pour une large gamme d'applications optiques et photoniques dans les gammes IR et visible..

Cette étude a donc conduit à de nouvelles céramiques transparentes, avec des valeurs de transmission jamais atteintes jusqu'à présent pour des oxydes. Elle propose également une nouvelle approche pour l'obtention de céramiques transparentes dans le cas de matériaux anisotropes : introduire un désordre chimique contrôlé au sein du matériau afin d'induire une isotropie optique. Ce concept ouvre la voie à de nouvelles compositions, étendant ainsi le domaine des céramiques transparentes et de leurs applications.

Mots-clés: céramique transparente, vitrocéramique, verre, aluminate de strontium, aluminosilicate de strontium, cristallisation, diffraction sur poudre, résolution structurale, microstructure, RMN, calcul DFT, désordre, biréfringence, anisotropie, optique, photonique

Transparent ceramics by full crystallization from glass: application to strontium aluminosilicates

Transparent polycrystalline ceramics elaborated by full crystallization from glass are an emerging class of photonic quality materials competing with single crystal technology, especially for optical applications. This approach provides considerable advantages over single crystals and polycrystalline sintered ceramics represented by cost effectiveness, large scale production, wide range of accessible chemical compositions, easy shaping and high doping level hosting structure.

In this work, we show the preparation of transparent cubic $\text{Sr}_3\text{Al}_2\text{O}_6$ and $\text{Sr}_3\text{Ga}_2\text{O}_6$ polycrystalline ceramics by full crystallization from the parent strontium aluminate ($75\text{SrO}-25\text{Al}_2\text{O}_3$) and strontium gallate ($75\text{SrO}-25\text{Ga}_2\text{O}_3$) glasses elaborated by aerodynamic levitation coupled to laser heating system. The transparency of the obtained $\text{Sr}_3\text{Al}_2\text{O}_6$ ceramics is explained by their optical isotropy, thin grain boundaries and highly dense (non-porous) microstructure.

We also show a series of novel $\text{Sr}_{1+x/2}\text{Al}_{2+x}\text{Si}_{2-x}\text{O}_8$ ($0 < x \leq 0.4$) oxide compositions leading to highly transparent and readily scalable polycrystalline ceramics to be obtained by full congruent glass crystallization. The outstanding transparency exceeding 90% in the visible and near IR range is explained through different microstructural and structural (average and local) studies. This transparency, reaching the theoretical limit, is associated to the almost null birefringence, thin grain boundaries and non-porosity. NMR experiments prove the existence of chemical disorder which is at the origin of the relatively zero birefringence value calculated by DFT computations. These scalable and highly transparent polycrystalline ceramic materials are promising candidates for a wide range of optical and photonic applications in the IR and visible ranges.

This study besides revealing new ceramic compositions with previously unreported transmission values for micro-scale polycrystalline materials, proposes a new approach for obtaining transparent ceramics in anisotropic materials. This approach consists in inducing a controlled chemical disorder within the material in order to induce optical isotropy. It is anticipated that this proposed concept will open the way to different composition candidates to be elaborated as transparent polycrystalline ceramics, thus extending the ceramic technology domain and its applications.

Keywords: transparent ceramics, glass-ceramics, glass, strontium aluminate, strontium aluminosilicate, crystallization, powder diffraction, structural resolution, microstructure, NMR, DFT calculations, disorder, birefringence, anisotropy, optics, photonics