Spark Plasma Sintering of fine alpha-silicon nitride ceramics with LAS for spatial applications

Helen Reveron [a,*], Laurent Blanchard [b], Yann Vitupier [b], Emmanuelle Rivière [c], Guillaume Bonnefont [a], Gilbert Fantozzi [a]

[a] *Université de Lyon, Insa-Lyon, MATEIS CNRS UMR 5510, 20 Avenue Albert Einstein, F-69621 Villeurbanne Cedex, France*
[b] *Thales Alenia Space, 100 Bd du midi BP 99, 06156 Cannes La Bocca, France*
[c] *CNES, Service Structures et Mécanique, BP 1416, 18 Avenue Edouard Belin, 31401 Toulouse Cedex 4, France*

Abstract

Many space systems such as satellite mirrors and their supporting structures require to be made from very low-thermal expansion materials combining both high hydrostability and relatively high mechanical properties. In this study, we have applied the "composite concept" in order to explore the possibility of fabricating near zero thermal expansion silicon nitride based ceramics. Consequently, a negative thermal expansion material belonged to the lithium aluminosilicate family (LAS powder crystallized under de β-eucryptite structure) was introduced in an alpha-silicon nitride fine powder (5 and 20 vol% of LAS) and the resulting composite system was sintered by Spark Plasma Sintering (SPS) at 1400 and 1500 °C. In the case of 20 vol% LAS compositions, relatively well-densified ceramics (94.4% of the theoretical density) were produced without adding any further sintering additive. The addition of yttria and alumina oxides allowed enhancing the densification level up to 98.2% (20 vol% LAS compositions) or from 62.3% up to 96.7% of the theoretical density in 5 vol% LAS materials. Nevertheless, it was impossible to full consolidate silicon nitride/LAS composite ceramics at temperatures lower than the temperature at which β-eucryptite melts, even by using SPS technology. Moreover, because of the relatively low temperatures involved in SPS, the α to β-Si$_3$N$_4$ transformation was avoided, resulting in microstructures composed of fine equiaxed α-Si$_3$N$_4$ grains (<200 nm) and of a glassy phase. Even if the effect of having a very large negative thermal expansion material was lost during the sintering step (because of the β-eucryptite melting), ceramics containing only 20 vol% of LAS-based phase exhibited very interesting values as regards of mechanical properties (strength, hardness, toughness, and Young's modulus), thermal conductivity and thermal expansion coefficient. We discuss in this work why we are so interested in developing dense silicon nitride/LAS ceramics sintered without any further additive addition, even though β-eucryptite is melted during the process and the transformation to the β phase is avoided.
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1. Introduction

Silicon nitride (Si$_3$N$_4$) is a very interesting ceramic material for structural applications due to its excellent properties such as high creep resistance, fracture toughness and bending strength. This material crystallizes in the hexagonal system under two polymorphs called alpha (α at low temperatures) and beta (β at high temperatures). The α to β transformation takes place around 1400 °C and leads to the development of a rod-like or elongated β-Si$_3$N$_4$ microstructure.[1] This is one of the reasons why β-Si$_3$N$_4$ ceramics exhibit interesting mechanical properties explained on the base of crack bridging, pull out or crack deflection mechanisms. In addition to these conventional crystalline phases, a cubic-type structure (c-Si$_3$N$_4$) has been also observed but just at high pressure and temperature.[2] Moreover, silicon nitride material has a quite low thermal expansion coefficient or CTE ($\alpha = 3.1 \times 10^{-6}$/°C at 20 °C) and exhibits high dimensional stability under wet atmospheres. For all these reasons, silicon nitride ceramics could be used in some current space applications requiring both dimensional stability and good mechanical properties. However, in order to develop the future generation of silicon nitride based materials for optical and structural spatial systems, it is necessary to further reduce its thermal expansion, approaching null bulk expansion behaviour if possible.

* Corresponding author.
  E-mail address: helen.reveron@insa-lyon.fr (H. Reveron).

Since silicon and nitrogen atoms are strongly covalent linked, the silicon nitride densification is hard to be achieved by using conventional sintering processes. Therefore, an external additional sintering driving force must to be considered for sintering silicon nitride ceramics. Among all available methods allowing Si_3N_4 densification the most frequently used are: gas pressure sintering (GPS), hot pressing (HP), hot isostatic pressing (HIP) and natural sintering (NS). Regardless of the sintering method, sintering aids are commonly added to help densification by forming liquid phases at relatively low temperatures.[3–5] Nevertheless for economic reasons, GPS with sintering additives has become the most popular process used for preparing well-densified Si_3N_4 ceramics.[6] During sintering, sintering additives react with silica still present on the surface of silicon nitride particles, forming a silica-rich eutectic melt which allow the liquid phase sintering of the material. A mixing of alumina and yttria oxides is the most used sintering aid for silicon nitride.

In 1995, the Spark Plasma Sintering (SPS) method has been reported as a powerful tool for sintering silicon nitride ceramics at lower sintering temperatures and soaking times than conventional GPS or hot pressing methods. This decrease of temperature and time minimized the grain growth during sintering and allowed the fabrication of dense silicon nitride nano-ceramics as reported by Nishimura et al.[7] These authors showed that relative densities of 98.5% could be attained at 1550 °C in only 5.5 min and under 49 MPa by using β-Si_3N_4 nanopowders mixed with 5 wt% Y_2O_3 and 2 wt% MgO as sintering aids. The grain size in these first SPS sintered β-Si_3N_4 ceramics was about 200–300 nm. Nonetheless, this work also showed that fully dense α-Si_3N_4 nanoceramics cannot be prepared from commercial α-Si_3N_4 nanopowders even if SPS is applied because temperatures as high as 1650 °C are required to obtain at least 98.2% of density. Herein, the α to β transformation occurred partially and the final microstructure consisted of a mixing of elongated grains with a diameter <5 μm (most probably made of β-Si_3N_4) embedded in a nanosized matrix. Unfortunately, neither XRD analysis was performed on those SPS treated α-Si_3N_4 nanopowders nor the ratio of α to β phase was reported.

Since this first study, further works have reported the use of SPS on sintering β-silicon nitride based ceramics; few works have used the SPS technology for obtaining silicon nitride ceramics containing the α-phase. Belonging to the first category (that is β-Si_3N_4 based ceramics), we quote here the only three existing works involving: (1) the use of the "rapid" SPS sintering (1600 °C–5 min–30 MPa) of β-Si_3N_4 high-energy mechanical milled powders with Y_2O_3 and Al_2O_3 additives done by Xu et al. in 2005[8] which resulted in fully dense 100% β-Si_3N_4 nano-ceramics with an average grain size of about 70 nm; (2) the rod-like micrometer-sized β-Si_3N_4 powders synthesized by Bai et al. in 2007[9] and sintered by SPS (1500 °C–5 min–20 MPa with Y_2O_3 and Al_2O_3 as sintering additives) that developed rod-like β-Si_3N_4 micrometer-sized microstructures; and finally (3) the 30 wt%BAS/Si_3N_4 composite fabricated via SPS (1800 °C–5 min–25 MPa) by Ye et al. in 2008[10] and characterized by a microstructure composed of rod-like micrometer-sized β-silicon nitride grains randomly oriented in a continuous BAS matrix.

Referring to the second category and in particular to ceramics containing both α/β-Si_3N_4 prepared by SPS, no more than two works dating from 2009 (Peng et al.[11,12]) have reported that very hard α/β composites were prepared by SPS using 5 wt% $MgSiN_2$ as sintering additive and α-Si_3N_4 as starting powder. A treatment at 1450 °C–6 min–60 MPa allowed full densification of very hard 79 wt% α-Si_3N_4 materials (Vickers hardness of 21.4 GPa). Regarding silicon nitride ceramics formed mainly by fine α-Si_3N_4 grains, only one work published by Chen et al. in 2008[13] has reported the use of 4 wt%MgO–16 wt%AlPO$_4$ as sintering additives for SPS sintering (1500 °C–5 min–30 MPa) of α-Si_3N_4 powders which reached 98% of density and grain sizes of about 500 nm. The sintering mechanism in these α-Si_3N_4 based ceramics is supposed to be governed by both reaction between MgO and SiO_2 present on the powders (which promotes the powders adherence) and the solid state sintering of AlPO$_4$. Based on XRD diffraction patterns, authors have stated in a qualitative way that the major phase was α-Si_3N_4 when the sintering was performed at 1300 °C but that at higher temperatures, a little conversion from α to β-Si_3N_4 was took place.

In the frame of these previous results, here we report for the first time the use of LAS (β-eucryptite) for the SPS sintering of the finer α-Si_3N_4 based ceramic never before prepared. As we explain below, the final goal of our work will be to recrystallize the LAS based melt onto the β-eucryptite phase. Nevertheless, these fine α-Si_3N_4 ceramics could be very interesting for dielectric applications. In fact, it is reported that alpha silicon nitride phase has lower dielectric constant than beta which could have a promising application. For instance, α-Si_3N_4 ceramic (dielectric constant $\varepsilon = 5.6$ and dielectric loss $tg\delta = 0.003$ at room temperature, compared to β-Si_3N_4 properties of $\varepsilon = 7.9$ and $tg\delta = 0.005$) can be utilized as an electromagnetic wave-penetrating material.[14]

To date, the system Li_2O–Al_2O_3–SiO_2 (LAS) has been successfully used in conventional sintering of silicon carbide at very low temperatures (<1177 °C for compositions containing 40 vol% of LAS) but to our knowledge, no work in the literature has reported the use of LAS powders and SPS for sintering silicon nitride ceramics. In this context, some advantages could be derived from the use of only LAS based powder for sintering fine α-Si_3N_4 ceramics: (1) since LAS (for example crystallized under β-eucryptite structure) melts at relatively low temperatures (about 1250 °C), α-Si_3N_4 liquid-phase sintering may begin at lower temperatures compared to liquid-phase sintering driven by conventional additives addition (metal oxides such as alumina, yttria, silica, lithia, magnesia or their mixing); (2) after sintering, LAS amorphous melt can be recrystallized by applying specific heat treatments into β-eucryptite (which has a negative thermal expansion coefficient), thus enhancing the composite final mechanical properties and decreasing the thermal expansion coefficient of silicon nitride (this is the principal reason why the further additive addition is not suitable, with the purpose of keep as much as possible the same β-eucryptite composition in the melt); (3) the use of Spark Plasma

Sintering allows reduction in time and sintering temperatures (compared with more classical HP, HIP, GPS or natural sintering methods), avoiding in this manner the α to β silicon nitride transformation[7] (particularly interesting for dielectric applications), the grain growth (enhancing the mechanical properties) and the crystallization of secondary phases (which could also modify the composition of the LAS melt). The no use of further sintering additives besides LAS phase with the β-eucryptite composition and preventing secondary phase crystallization from the melt are the two main important facts which would govern the final composition of the melt and consequently the possibility of recrystallize the β-eucryptite phase during a second thermal treatment.

β-Eucryptite is the most anisotropic negative thermal expansion phase in the lithium aluminosilicate system or LAS (LiAlSiO$_4$), with coefficients of thermal expansion in the *a* and *c* crystallographic directions of 8.2 and −17.6 × 10^{-6}/°C, respectively.[15] Because of its high anisotropic structure, the volume expansion coefficient of the β-eucryptite unit cell is very slightly negative. Nevertheless, in the case of polycrystals, this anisotropy leads to thermal residual stresses which cause spontaneous microcracking. Therefore, the thermal expansion of sintered β-eucryptite polycrystals can tend toward the value given for the *c* crystallographic direction (i.e. large negative thermal expansion).

The guiding principle for this work is to apply the "composite concept" in order to prepare well densified silicon nitride-β eucryptite based composites with very low or null bulk thermal expansion. In this paper we report the possibility of processing dense silicon nitride ceramics from fine α-silicon nitride powders and β-eucryptite particles (5 and 20 vol%) by using SPS. A maximum β-eucryptite content of 20 vol% was fixed on the base of the negative thermal expansion coefficient measured on sintered β-eucryptite ceramics. Moreover, additional samples with identical β-eucryptite contents but with further addition of sintering aid oxides (Y$_2$O$_3$, Al$_2$O$_3$) were sintered as well, in order to study its effect on enhancing the final density. The SPS sintering behaviour, phase composition, microstructure, Vickers hardness, Young's modulus, flexural strength, fracture toughness, thermal conductivity and thermal expansion of selected 5 and 20 vol%LAS-Si$_3$N$_4$ materials were here investigate. The choice for study only these two selected samples was based on their potentiality to be applied in spatial applications such mirrors and its structural supports. The post-sintering thermal treatment of crystallization that must to be realized in 20 vol% LAS samples to further reduce thermal expansion coefficient will be covered in a forthcoming paper.

2. Experimental procedure

2.1. Starting materials

The silicon nitride powder used in the present study was the α-Si$_3$N$_4$ grade SN-E10 from Ube Industries Ltd. of Tokyo, Japan. This powder is equiaxed, has a mean particle size of about 0.2 μm, a specific surface area of 0.8 m^2/g and is 99.5%

crystalline, with less than 5% crystallized under the β-phase (in accordance with UBE specifications). The composition of Si$_3$N$_4$ is: N > 38.0 wt%; O = 1.30 wt%; Fe and Cl < 100 ppm each; Ca and Al < 50 ppm each; and C < 0.2 wt%. High purity powders of Al$_2$O$_3$ (grade CR1-Baikowski) and Y$_2$O$_3$ (Alfa-Aesar) were used as sintering aids (noted "*sa*" by the following) and of LiAlO$_2$ (Sigma–Aldrich) and SiO$_2$ (Sigma–Aldrich) for preparing LAS powders.

2.2. Ceramic preparation

LAS powder was prepared by mixing lithium aluminate and silica in order to have a molar ratio of Li:Al:Si = 1:1:1. This mixing was first ball-milled in water for 24 h, dried and then calcined at 1050 °C in air. After calcination, the LAS powder is composed of only well crystallized β-eucryptite phase. For the preparation of silicon nitride based compositions, Si$_3$N$_4$, LAS powder and in some cases sintering additives (yttria + alumina powders) were used as shown in Table 1. For ceramic processing, powder mixtures were ball-milled in distilled water for 16 h, using an anionic commercial dispersant (0.15 wt% of Darvan C with respect of silicon nitride), 55 wt% of solid loadings and alumina balls as grinding media (2 mm in diameter). After ball-milling, the slurries were dried, passed through a 140 mesh sieve and thermal treated at 1 °C/min up to 600 °C for 1 h (air). Finally, powders were loaded in a graphite die (inner diameter of 40 mm) and sintered by SPS (FCT System GmbH HP D-25/1) at 1400 and 1500 °C, using 5 min of holding time and applied pressures of 50 or 75 MPa (for all experiments the heating rate was fixed at 160 °C/min). Pressure was applied from the start of the thermal cycle until reaching a temperature of 1100 °C during cooling. Throughout the SPS treatment; the temperature was measured by means of an optical pyrometer focused on the upper graphite punch, at about 4 mm from the sample.

2.3. Ceramic characterization

Bulk densities were determined by Archimedes method using distilled water and three different weight measurements (dried mass, mass in water and mass imbedded in water) by following the C373-88(2006) ASTM standard test method. The relative density was obtained by correlating the bulk density with the theoretical density of mixtures. Phase identification on sintered samples was performed by means of X-ray diffraction (X-ray Bruker D8 diffractometer) using Ni-filtered Cu Kα radiation (0.1541 nm) between 20° and 80° (step width of 0.05° and an exposure time of 1 s). The α and β Si$_3$N$_4$ phase content was quantitatively evaluated using the relative peak intensity method described by Dai et al.[16] Microstructural features were examined by SEM (ESEM-FEG XL-30 FEI apparatus) on fractured surfaces. For hardness measurements, indentations were made on polished surfaces using a Vickers Hardness Tester (Type FV-7) with a load of 49 N during 10 s. The indentation fracture toughness (K_{IC}) was determined from indentation fracture lengths by applying the equation proposed by Anstis et al.[17] Flexural strength and Young's modulus were measured at room

Table 1
Ceramic compositions (vol%) prepared using sintering aids (sa) and without sintering aids.

Sample[a]	Sintering aids	Si_3N_4	LAS	Y_2O_3[b]	Al_2O_3[b]	$LAS + Y_2O_3 + Al_2O_3$
5%LAS-sa	$\checkmark$	89.5	4.7	4.7	1.1	10.5
5%LAS	$\times$	95.0	5.0	–	–	5.0
20%LAS-sa	$\checkmark$	76.1	19.0	4.0	0.9	23.9
20%LAS	$\times$	80.0	20.0	–	–	20.0

[a] The ratio of LAS phase was fixed at 5 and 20 vol% according to Si_3N_4.
[b] Sintering aids: 8 wt% Y_2O_3 + 1.5 wt% Al_2O_3 based on Si_3N_4 mass.

temperature on bar specimens (4 mm × 4 mm × 30 mm) using a four-point bend fixture with an inner and outer span of 10 and 20 mm, respectively. The thermal conductivity was evaluated using the steady-state conductivity setup shown in Fig. 1. It consisted of one hot and one cold plate placed inside a structure working under vacuum. Eight thermocouples were used to monitor and to identify the steady-state temperatures, among which four were used for calculating the thermal conductivity by applying the following relation:

$$\lambda = \frac{P \cdot L}{S \cdot \Delta T} (W\ m^{-1}\ K^{-1}), \tag{1}$$

where P is the powder applied to one of the end of the sample, L and S are the cross-sectional area and tested length of the sample respectively and ΔT is the temperature difference between the two tested points of the sample. We used rectangular section samples (4 × 2 × 30 mm), a powder of 0.17 W and a vacuum of

1.5×10^{-6} mbar. Under these conditions, the uncertainty of the measure was estimated to 0.6 W m^{-1} K^{-1}.

A dilatometer (ADAMEL DI20) was used for thermal expansion coefficient measurements.

2.4. Sample abbreviation

Throughout this paper, samples will be identified as follows: %LAS(vol of β-eucryptite added to the system)-sintering aids (sa)/or not-SPS applied pressure (MPa)-soaking time(min)-sintering temperature (°C). For example, a sample containing 5 vol% of LAS, with sintering aids and SPS treated under 50 MPa for 5 min up to 1500 °C will be indicated as 5%LAS-sa-50-5-1500; the same composition but without any sintering additive will be: 5%LAS-50-5-1500 if the SPS experimental conditions are kept the same.
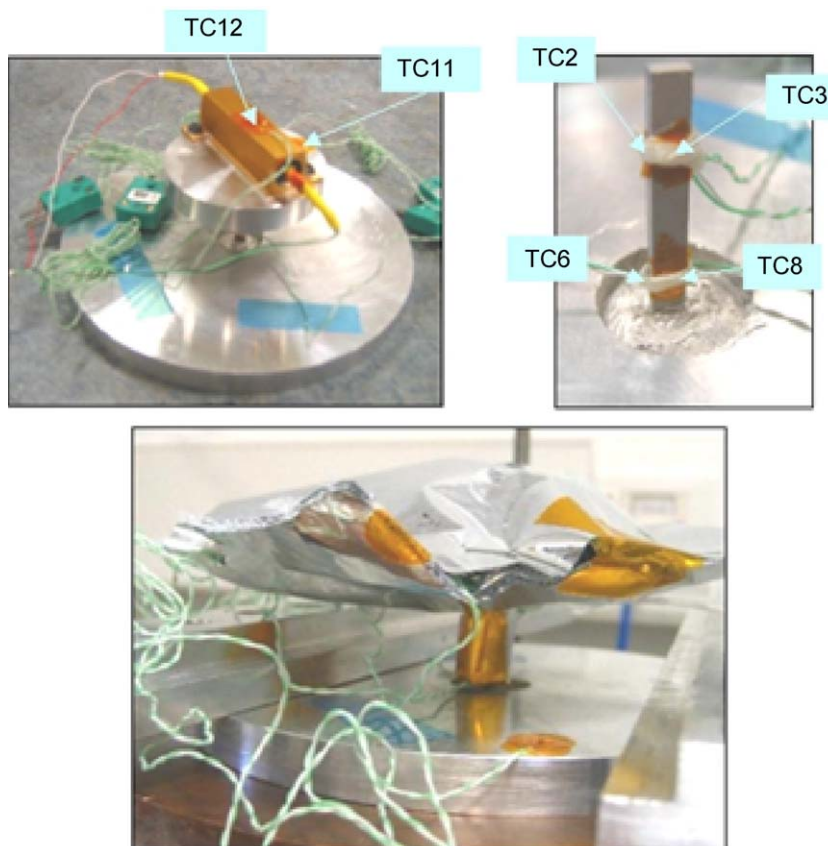

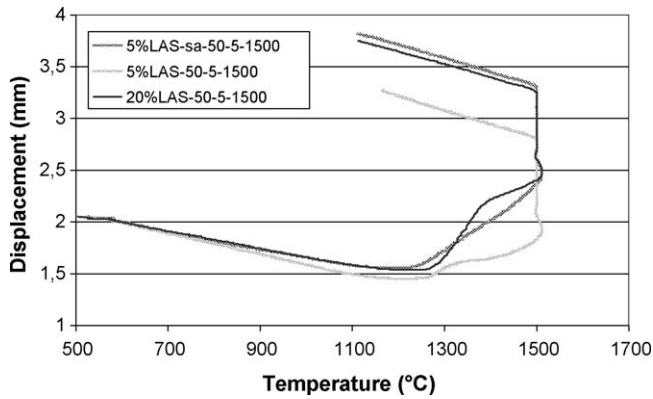Fig. 1. Setup for the measurement of thermal conductivity.

Fig. 2. Shrinkage sintering behaviour under a 50 MPa applied load as a function of the sample composition (heating rate 160 °C/min, $T = 1500$ °C–5 min).

3. Results and discussion

3.1. Densification kinetics

Fig. 2 shows the variation of the linear shrinkage for 5%LAS–Si$_3$N$_4$ based samples (with and without sintering aids) and for 20%LAS–Si$_3$N$_4$ based materials (without any further additive) during the SPS sintering treatment performed under 50 MPa with a soaking time of 5 min and up to 1500 °C.

From this figure it can be noticed that for 5% LAS composition, the densification starts at lower temperatures when alumina and yttria are added, i.e. the temperature of the shrinkage beginning is shifted from 1240 °C (5%LAS) to 1230 °C (5%LAS-sa). On the other hand, for 20%LAS composition, densification shrinkage starts at a temperature of 1265 °C. Moreover, whatever the composition studied, densification is not completed at the end of the soaking time and continues during cooling (curve recording was stopped at 1100 °C when pressure was released). We observe that for all samples, the beginning of the shrinkage occurs at temperatures lower than the expected temperature of liquid formation (i.e. around 1350 °C for β-eucrytite melting or 1370 °C for ternary Al$_2$O$_3$–Y$_2$O$_3$–SiO$_2$ melt). The expected enhancement of densification in materials containing 20%LAS did not take place. Only a faster consolidation rate was achieved between 1265 and 1400 °C, but after that, the densification rate decreased, resulting in lower final densification compared to 5%LAS-sa sample.

Table 2 provides the relative final density for samples treated by SPS at 1400° or 1500 °C for 5 min under 50 or 75 MPa

Table 2
Relative density of the Spark Plasma Sintered LAS-Si$_3$N$_4$ ceramics.

Sample	Density (%)
5%LAS-sa-75-5-1400	96.6
5%LAS-sa-75-5-1500	96.7
5%LAS-sa-50-5-1500	96.6
5%LAS-50-5-1500	62.3
20%LAS-sa-75-5-1400	96.6
20%LAS-sa-75-5-1500	98.2
20%LAS-sa-50-5-1500	97.3
20%LAS-50-5-1500	94.4

load. SPS treatments performed on 5%LAS-sa compositions gave relative densities of about 97% regardless of the sintering conditions when additional yttria and alumina were added as sintering aids. Nonetheless, the relative low densification achieved in pure 5%LAS ceramics (only ∼62%) suggests that for this LAS composition, the use of further sintering aids is strictly necessary for enhancing the quantity of liquid formed during sintering and thereby the liquid-phase sintering densification. It is known that the liquid phase is formed by means of a reaction taking place between the additives and the silica layer present in silicon nitride starting powders. Regarding our compositions containing yttria and alumina powders ("sa" compositions in Table 2), i.e. in the SiO$_2$–Al$_2$O$_3$–Y$_2$O$_3$ ternary system, the lowest liquid formation temperature (ternary eutectic temperature) predicted from the phase diagram was determined at 1371 ± 5 °C,[18] temperature from which the ceramic densification proceeds via a transient liquid-phase.[19] On the other hand, in samples containing 20%LAS phase, the densification takes place thanks to the LAS based melt formed during sintering. The effectiveness of LAS as sintering additive is moderate compared to yttria–silica–alumina ternary eutectic melt, since the densification in systems prepared with additives was always higher. Nonetheless, after SPS sintering at 1500 °C (5 min–50 MPa) of 20%LAS based compositions, densification was slightly decreased from 97.3% to 94.4% when no additional sintering aids were used. It means that for this LAS composition, it should be possible to well-densify silicon nitrides ceramics containing only LAS-based glassy phase.

In contrast with 5%LAS compositions, relative densities in 20%LAS compositions containing sintering additives depend on the sintering conditions in a traditional way: they can be increased by increasing the temperature and/or the pressure applied during the SPS treatment. Therefore, a maximum relative density of 98.2% was reached after sintering at 1500 °C for 5 min under 75 MPa.

3.2. Structural, mechanical and thermal characterization of selected samples

Among all the samples and compositions prepared by SPS, only two compositions and conditions were selected for the structural, mechanical and thermal characterization: 5%LAS-sa-50-5-1500 (96.6% theoretical density) and 20%LAS-50-5-1500 (94.4% theoretical density). As previously discussed, this choice was based on the potentiality of these materials to be used in current spatial applications, even without applying the β-eucryptite crystallization post-sintering thermal treatment. Although it is true that in the case of 5%LAS-sa we certainly have modified the composition of β-eucryptite melt because of the use of sintering additives, this material could shown superior mechanical properties compared to 20%LAS. In the following, the results to be discussed are just related to these two selected samples.

As shown in Fig. 3, X-ray diffraction patterns obtained on 5%LAS-sa and 20%LAS silicon nitride based ceramics sintered at 1500 °C for 5 min and under 50 MPa have shown the same characteristics: both sintered samples were characterized by the occurrence of mainly the α-Si$_3$N$_4$ form (identified from
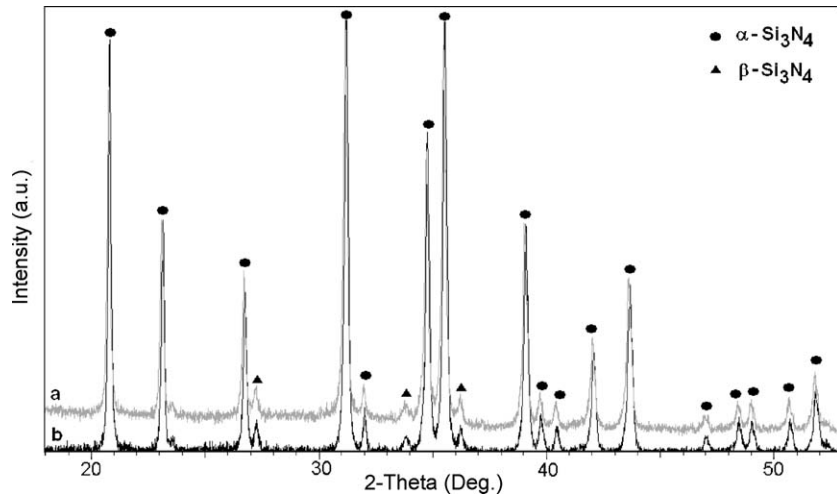
Fig. 3. X-ray diffraction patterns obtained on samples sintered by SPS: (a) 20%LAS-50-5-1500 and (b) 5%LAS-sa-50-5-1500.

JCPDS file 41-0360) and a little of β-Si$_3$N$_4$ (JCPDS file 33-1160). Peaks related to the sintering additives (Y$_2$O$_3$–Al$_2$O$_3$) or β-eucryptite phase are not visible, corroborating its melting during sintering. The amount of β phase ($\beta/(\alpha + \beta)$) on the starting silicon nitride powder was estimated from XRD peak intensities as 5.9%. This value is slightly higher to that given by UBE industries (<5%). After sintering, the β phase content was 9.1%

Fig. 4. SEM micrographs of SPS sintered samples: (a) 5%LAS-sa-50-5-1500 and (b) 20%LAS-50-5-1500.

(for 5%LAS-sa) and 11.2% (for 20%LAS). It means that SPS sintering occurred with reduced α to β transformation, certainly due to the low temperature and time here employed. Effectively, it is well known that in silicon nitride systems sintered conventionally with the help of conventional sintering additives, the conversion of α-Si$_3$N$_4$ to β-Si$_3$N$_4$ generally starts at temperatures above 1500 °C. For instance, it has been shown that this phase transformation occurred rapidly from 1550 to 1600 °C and ended at 1600 °C during the sintering of Si$_3$N$_4$–MgO–CeO$_2$ ceramics.[20] In the present study, since we used a sintering temperature below 1500 °C, the transformation was prevented. From a mechanical point of view, this fact must affect negatively the toughness of the ceramic. Nevertheless, our choice of working here at low temperatures is justified as regards of preventing second phase crystallization, which we know could modify the composition of the β-eucryptite melt and thereby complicate its recrystallization process.
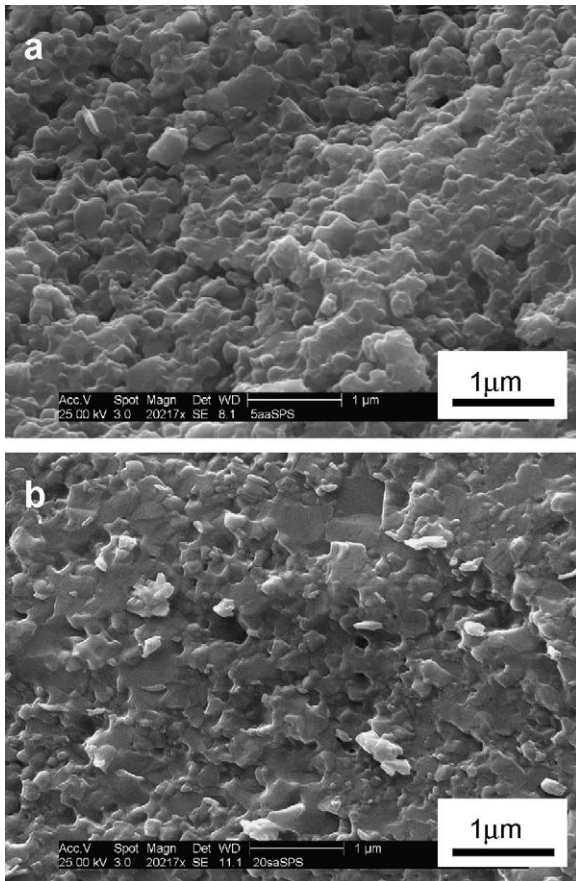
Fig. 4 shows the typical microstructure on the fractured surface of sintered materials. Both specimens exhibited a microstructure composed of small equiaxed grains having a mean size of about 160 nm (5%LAS-sa) or 166 nm (20%LAS). According to the XRD results, these equiaxed grains are mainly α-Si$_3$N$_4$ grains. Moreover, some elongated grains are also visible imbedded onto the matrix phase which could be related to the β-Si$_3$N$_4$ grains. The measured grain size indicates that densification took place with almost no grain growth. Since melting temperature of sintering additives (system Y$_2$O$_3$–Al$_2$O$_3$–SiO$_2$) and LAS phase are both far below 1500 °C, an intergranular amorphous phase should be present in both materials, a fact that could explain the smooth aspect of the fractured surfaces.

The mechanical and thermal properties of the selected 5% and 20%LAS-Si$_3$N$_4$ based ceramics are shown in Table 3. The Vickers hardness of the 5%LAS-sa and 20%LAS compositions were about 16 GPa and 14 GPa, respectively. These values are in good agreement with Vickers hardness values commonly measured on hot-pressed silicon nitride materials.[21,22] The decrease of Vickers hardness in samples containing 20%LAS could be related to both its relatively low densification and high content of amorphous phase.

Table 3
Summary of properties for 5% and 20% LAS-Si$_3$N$_4$ ceramics sintered by SPS.

Sample	Density (%)	β_{transf} (%)	Grain size (nm)	Vickers hardness (GPa)	E (GPa)	σ_f (MPa)	K_{IC} (MPa m$^{1/2}$)	λ (W m^{-1} K^{-1})	$\alpha_{(20–40\,°C)}$ ($/°C$)
5%LAS-sa-50-5-1500	96.6	3.2	159 ± 48	16.2 ± 0.4	142	168	1.9	–	1.16×10^{-6}
20%LAS-50-5-1500	94.4	5.3	166 ± 52	13.8 ± 0.2	275	308	3.3	21.4 ± 0.6	1.11×10^{-6}

Despite of we expected based on the level of densification, the mechanical properties of 5%LAS-sa sample are significantly lower than that classically measured on hot-pressed or gas-pressure sintered silicon nitride materials, or even the values measured in 20%LAS material. Moreover, the Young's modulus of 275 MPa and the flexural strength of 308 MPa which characterized 20%LAS material can be enough for some current spatial applications. As expected, the fracture toughness remains too low (3.3 MPa m$^{1/2}$) and principally attributed to the development of a very fine equiaxed microstructure. It is recognized that the fracture toughness in silicon nitride is highly dependent on microstructure features.[10] For example, it can be increased in β-Si$_3$N$_4$ materials by increasing the diameter of the elongated β-grains (by means of crack bridging/pullout and/or crack deflection mechanisms) or by introducing residual stresses using secondary phases (Si$_3$N$_4$ under compression stress can promote grain bridging and pullout mechanisms). Fracture toughness values on well developed β-microstructures are usually located between 4 and 6 MPa m$^{1/2}$. In the present study, the fact of developing fine α-phase particles without either transformation or grain growth is detrimental to the development of high-toughness ceramics. Since the main goal of our approach is to develop near zero thermal expansion composites, the use of low sintering temperatures was here justified looking for the β-eucryptite recrystallization step, in which having a melt with almost the same β-eucryptite composition is essential. If necessary, toughness could be further increased by putting on another phase/material, for instance some carbon nanotubes that also could play a role in enhancing thermal conductivity.

For spatial applications such as mirrors or structural systems where high dimensional stability is needed, low thermal expansion and good mechanical properties are demanded together with high thermal conductivity. The thermal conductivity of silicon nitride ceramics sintered by GPS with oxide additives is around 25–30 W m^{-1} K^{-1}. The decrease on the thermal conductivity obtained for 20%LAS material can be related to the introduction of a further oxide-based glassy phase to the system. Nevertheless, the value of 21.4 W m^{-1} K^{-1} is certainly very low compared to previous reports done by Peng et al.[11,12] by using non-oxide additives (MgSiN$_2$). This reduction could be attributed to the presence of oxygen[23,24] in LAS or LAS/Y$_2$O$_3$–Al$_2$O$_3$ compositions and the development of very fine equiaxed α-phase microstructures instead of elongated β-grains.

The thermal expansion coefficient of silicon nitride/LAS based ceramics is decreased compared to the thermal expansion coefficient of pure silicon nitride ($3.1 \times 10^{-6}/°C$) and is in the range of classical silicon nitride ceramics sintered by GPS with additives. Based on these observations we can conclude that the oxide-based amorphous phase retained after SPS sintering (LAS–Y$_2$O$_3$–Al$_2$O$_3$–SiO$_2$ based or LAS based) can also contribute to reducing the thermal expansion of silicon nitride ceramics. With the aim of further decrease the thermal expansion coefficient on 20%LAS ceramic here prepared, a second thermal treatment could be applied in order to crystallized the large negative thermal expansion β-eucrytite phase within the α-Si$_3$N$_4$ matrix. This recrystallization treatment would be more easily controlled in samples containing only LAS powder.

4. Conclusions

This study confirmed the unique possibility of obtaining well densified and very fine α-Si$_3$N$_4$ based ceramics by using the Spark Plasma Sintering (SPS) technology and β-eucryptite powder (LAS). The use of SPS allows the densification of silicon nitride based compositions containing 5 vol%LAS with additives or 20 vol% of LAS based phases at relatively low temperatures (<1500 °C) and time (5 min of soaking time).

During SPS at temperatures <1500 °C, densification took place without silicon nitride grain growth or the α to β phase transformation. The SPS treatment promoted the development of well densified α-Si$_3$N$_4$ based ceramics composed of very fine α-Si$_3$N$_4$ equiaxed grains (mean size of 159 or 166 nm in ceramics with 5 vol%LAS-sa and 20 vol%LAS, respectively) and an intergranular oxide-based phase of amorphous nature.

The use of sintering additives such as Y$_2$O$_3$–Al$_2$O$_3$ in addition to LAS was necessary for sintering compositions containing 5 vol% of LAS. In contrast with that, in the case of 20 vol% of LAS system, the liquid phase formed from the LAS melting was enough to promote its densification. Moreover, sintering at relatively lower temperatures prevented the crystallization of other secondary phases.

In these SPS sintered silicon nitride materials, the fine equiaxed α-Si$_3$N$_4$ microstructure and the use of oxide had a detrimental effect on the thermal conductivity and toughness. Nonetheless, the thermal expansion coefficient of Si$_3$N$_4$–20%LAS based ceramic was reduced to $1.1 \times 10^{-6}/°C$ and could be further decreased by applying a second thermal treatment for β-eucryptite recrystallization. This topic will be the matter of a forthcoming paper.

Mechanical and thermal properties appeared highly dependent on sample compositions. The bending strength of 308 MPa, Young's modulus of 275 MPa and Vickers hardness of 14 GPa measured on Si$_3$N$_4$–20 vol%LAS system allow the use of this material in some existing spatial applications.

Because of ceramics here prepared are mainly composed of fine equiaxed α-Si$_3$N$_4$ grains, they would be also interesting for dielectric applications.

Acknowledgments

References

[1]. Suematsu H, Mitomo M, Mitchell T, Petrovic J, Fukunaga O, Ohashi N. The alpha–beta transformation in Silicon Nitride Single Crystals. *J Am Ceram Soc* 1997;**80**:615–20.

[2]. Zerr A, Miehe G, Serghiou G, Schwarz M, Kroke E, Riedel R, et al. Synthesis of cubic silicon nitride. *Nature* 1999;**400**:340–2.

[3]. Zhu XW, Zhou Y, Hirao K. Effect of sintering additive composition on the processing and thermal conductivity of sintered reaction-bonded Si_3N_4. *J Am Ceram Soc* 2004;**87**:1398–400.

[4]. Lin Y, Ning X, Zhou H, Chen K, Peng R, Xu W. Study on the thermal conductivity of silicon nitride ceramics with magnesia and yttria as sintering additives. *Mater Lett* 2002;**57**:15–9.

[5]. Lee BT, Yoo JH, Kim HD. Microstructural characterization of GPSed-RBSN and GPSed-Si_3N_4 ceramics. *Mater Trans* 2000;**41**:312–6.

[6]. Okamoto Y, Hirosaki N, Ando M, Munakata F, Akimune Y. Effect of sintering additive composition on the thermal conductivity of silicon nitride. *J Mater Res* 1998;**13**:3473–4.

[7]. Nishimura T, Mitomo M, Hirotsuru H, Kawahara M. Fabrication of silicon nitride nano-ceramics by spark plasma sintering. *J Mater Sci Lett* 1995;**14**:1046–7.

[8]. Xu X, Nishimura T, Hirosaki N, Xie R, Zhu Y, Yamamoto Y, et al. New strategies for preparing nanosized silicon nitride ceramics. *J Am Ceram Soc* 2005;**88**:934–7.

[9]. Bai L, Mao X, Shen W, Ge C. Comparative study of β-Si_3N_4 powders prepared by SHS sintered by spark plasma sintering and hot pressing. *J Univ Sci Technol Beijing* 2007;**14**:271–5.

[10]. Ye F, Liu L, Zhang J, Meng Q. Synthesis of 30 wt%BAS/Si_3N_4 composite by spark plasma sintering. *Comp Sci Technol* 2008;**68**:1073–9.

[11]. Peng G, Li X, Liang M, Liang Z, Liu Q, Li W. Spark plasma sintered high hardness α/β Si_3N_4 composites with $MgSiN_2$ as additives. *Scripta Mater* 2009;**61**:347–50.

[12]. Peng G, Liang M, Liang Z, Li Q, Li W, Liu Q. Spark plasma sintered silicon nitride ceramics with high thermal conductivity using $MgSiN_2$ as additives. *J Am Ceram Soc* 2009;**92**:2122–4.

[13]. Chen F, Shen Q, Yan F, Zhang L. Spark plasma sintering of α-Si_3N_4 ceramics with MgO-$AlPO_4$ as sintering additives. *Mater Chem Phys* 2008;**107**:67–71.

[14]. Chen F, Shen Q, Yan F, Zhang L. Pressureless sintering of α-Si_3N_4 porous ceramics using a H_3PO_4 pore-forming agent. *J Am Ceram Soc* 2007;**90**:2379–83.

[15]. Gillery F, Bush E. Thermal contraction of β-eucryptite ($Li_2O·Al_2O_3·2SiO_2$) by X-ray and dilatometer methods. *J Am Ceram Soc* 1959;**42**:175–7.

[16]. Dai J, Li J, Yen Y. The phase transformation behaviour of Si_3N_4 with single Re_2O_3 (Re = Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb) additive. *Mater Chem Phys* 2003;**80**:356–9.

[17]. Anstis G, Chantikul P, Lawn BR, Marshall DB. A Critical evaluation of indentation techniques for measuring fracture toughness: I. Direct crack measurements. *J Am Ceram Soc* 1981;**64**:533–8.

[18]. Kolitsch U, Seifert HF, Ludwig T, Aldinger F. Phase equilibria and crystal chemistry in the Y_2O_3–Al_2O_3–SiO_2 system. *J Mater Res* 1999;**14**:447–55.

[19]. Ziegler G, Heinrich J, Wötting G. Relationships between processing, microstructure and properties of dense and reaction–bonded silicon nitride. *J Mater Res* 1987;**22**:3041–86.

[20]. Yang H, Yang G, Yuan R. Densification and α/β phase transformation of Si_3N_4 containing MgO and CeO_2 during sintering. *Mater Chem Phys* 1998;**55**:164–6.

[21]. Miyazaki H, Hyuga H, Yoshizawa Y, HiraoK, Ohji T. Crack profiles under a Vickers indent in silicon nitride ceramics with various microstructures. *Ceram Int* 2010;**36**:173–9.

[22]. Gong J, Wu J, Guan Z. Load dependence of the apparent hardness of silicon nitride in a wide range of loads. *Mater Lett* 1998;**35**:58–61.

[23]. Zhu X, Hayashi H, Zhou Y, Hirao K. Influence of additive composition on thermal and mechanical properties of ß–Si_3N_4 ceramics. *J Mater Res* 2004;**19**:3270–8.

[24]. Yokota H, Abe H, Ibukiyama M. Effect of lattice defects on the thermal conductivity of β-Si_3N_4. *J Eur Ceram Soc* 2003;**23**:1751–9.