

DILATOMETRIC STUDY OF Si<sub>3</sub>N<sub>4</sub>–LAS SYSTEMBRANKO MATOVIC, ALEKSANDRA SAPONJIC, MILICA POSARAC, ADELA EGELJA,  
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*The possibility of using Li-exchanged zeolite (LAS) as additive for densification of Si<sub>3</sub>N<sub>4</sub> ceramic was studied. Dilatometry was used to measure the shrinkage behavior of green bodies prepared from zeolitic precursor and Si<sub>3</sub>N<sub>4</sub> powder under a nitrogen atmosphere from room temperature to 1500°C. The first liquid forms as low as 1080°C, resulting in a significant reduction of sintering temperature. XRD data reveal that phase transformation from α- to β-Si<sub>3</sub>N<sub>4</sub> takes place after the second phase has been completely converted into a glassy phase. The results show that the Li-exchanged zeolite is a very effective low temperature sintering additive for silicon nitride.*

## INTRODUCTION

Silicon nitride is known for its high strength, good thermal shock resistance and relatively good resistance to oxidation compared to other high-temperature structural materials [1]. In spite of this, the application of Si<sub>3</sub>N<sub>4</sub> based ceramics is still limited among other things, due to high cost of additives as well as high sintering temperatures [2,3]. Therefore, there is a continuous search for production process of both low-cost Si<sub>3</sub>N<sub>4</sub> starting powder and sintering additives, which are equally inexpensive and enable low sintering temperatures.

Lithium aluminosilicate is known to melt at relatively low temperatures and it is a low cost material. Moreover, Li<sub>2</sub>O Al<sub>2</sub>O<sub>3</sub> nSiO<sub>2</sub> (LAS) glasses can be crystallized easily [4] being a base for the development of good mechanical properties. LAS can be prepared from different sources, but the synthesis route starting from ion-exchanged zeolites offers several advantages [5]. This route is a low-cost method and leads to an amorphous phase with high chemical reactivity compared to crystalline phases. Some reports on the use of LAS as sintering additives for Si<sub>3</sub>N<sub>4</sub> exist in the literature [6]. However, no work has yet been done on dilatometric study of Si<sub>3</sub>N<sub>4</sub>–LAS system. Thus, the purpose of this paper is to investigate the dilatometric behaviour of a mixture of Si<sub>3</sub>N<sub>4</sub> and LAS and to understand the sintering phenomena in this system.

## EXPERIMENTAL

The starting powders were commercial Si<sub>3</sub>N<sub>4</sub> (Silzot HQ with a mean particle size D<sub>50</sub> = 1.7 μm, specific surface area of 3.2 m<sup>2</sup>/g, O = 0.5 wt.%, N > 38.5 wt.%,

free Si < 0.5 wt.%, SiC < 0.4 wt.%, α/(α + β) = 0.8) and LAS powder with D<sub>50</sub> = 0.6 μm. The latter was synthesized by ion exchange using 0.1 M water solution of LiCl. The procedure was repeated eight times to ensure complete substitution of Li for Na in A-zeolite (Birach Co., Bosnia and Hercegovina) [7]. The product was heated thereafter, at 800°C to obtain an amorphous powder that was confirmed by X-ray diffraction (Figure 1). However, during thermal treatment of zeolitic precursor at 1000°C the amorphous powder completely crystallizes to crystalline phase β-eucryptite (Figure 1). Thus, obtained additive (zeolitic precursor) has a composition correspond to β-eucryptite (Li<sub>2</sub>O Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>). The powders (85 wt.% Si<sub>3</sub>N<sub>4</sub> and 15 wt.% LAS) were mixed for 4 h by attrition milling in isopropanol. After drying, the mixture was isostatically pressed into cylindrical sample with 10 mm height under 240 MPa. The green density reached about 57 % of the theoretical density (T.D.) as calculated from the starting powder composition by the rule of mixtures. The density values used for the calculation were 3.19 g/cm<sup>3</sup> for Si<sub>3</sub>N<sub>4</sub> and 2.76 g/cm<sup>3</sup> for β-eucryptite. A dilatometer was used to measure the shrinkage behavior over the temperature range from room temperature up to 1500°C under a flowing nitrogen atmosphere at a heating rate of 5 K/min. After dwell times of 5 and 480 min at the maximum temperature, the dilatometer furnace was switched off for rapid cooling. The densities and sample dimensions were measured after each experiment. The crystalline phases present in the raw powders, mixtures and sintered ceramics were identified by X-ray powder diffraction using a Siemens diffractometer model D5000 Kristalloflex (Ni-filtered Cu K<sub>α</sub> radiation; λ = 1.5406 Å). The X-ray tube was operated at 40 kV and 20 mA. Diffractographs of the samples were recorded over the 2θ range

from 10° up to 80° at a scanning rate of 2°/min using a position-sensitive detector with 8° acceptance angle. For phase analysis, the software Diffrac AT was used. XRD was also used for quantitative evaluation of the weight fraction of the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> and  $\beta$ -Si<sub>3</sub>N<sub>4</sub> phases by calculations based on of the method proposed by Gazzara and Messier [8].

## RESULTS AND DISCUSSION

Dilatometric study of sintering process is very useful because it can show the length change of green bodies during heat treatment which curve can show different phenomena. In the case of Si<sub>3</sub>N<sub>4</sub>, the dilatometric behavior is affected directly by the characteristic of the liquid phase present. Hence, it is very important to find the minimum liquid forming temperature; i. e. the effective densification temperature. The change in length and rate of shrinkage are shown in Figure 2. The peak at 800°C is associated with the collapse of the zeolite structure. The appearance of the liquid in the

sample starts at 1080°C (point 2) corresponding to the eutectic melting point in the Li<sub>2</sub>O-SiO<sub>2</sub> phase diagram [9]. This reaction sequence can be described by reaction between crystalline  $\beta$ -eucryptite and silica (SiO<sub>2</sub>) which is an inherent component of Si<sub>3</sub>N<sub>4</sub> powders. The shrinkage rate curve shows three maxima at 1180°C, 1275°C and 1490°C (points 3-5). The phase evolution after heat treatment at temperatures corresponding to characteristic shrinkage points are listed in Table 1.

The maximum at 1180°C (point 3) is related to an increasing amount of the liquid phase, which surrounds the silicon nitride particles completely, favoring grain rearrangement [9]. The XRD pattern of the sample quenched at this temperature exhibits  $\beta$ -eucryptite and silica phase. However, the intensity of  $\beta$ -eucryptite decreased in comparison on its intensity of sample quenched at 1080°C (point 2) which indicated its partially melting. This is also associated with excess silica (SiO<sub>2</sub>) which has crystallized from the liquid during cooling. The XRD pattern for the sample quenched at 1275°C (point 4), shows the disappearance of the  $\beta$ -eucryptite. At the same time the appearance of  $\beta$ -spodumen (LiAlSiO<sub>6</sub>) with the same (Li : Al) cation ratio as in LiAlSiO<sub>4</sub> but with higher amount of silica, is observed. In spite of the total conversion of LiAlSiO<sub>4</sub> additive into liquid phase the total amount of liquid phase does not increase significantly due to partial crystallization in to a new phase, spodumen (LiAlSiO<sub>6</sub>). This is agreeing with the phase diagram for the system Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> [10]. Melting of  $\beta$ -eucryptite in presence of excess silica leads to crystallization of spodumen. The maximum at 1490°C, which occurs together with a decrease in the XRD intensity of spodumen phase and an increase in the intensity of SiO<sub>2</sub> corresponds to increasing volume of the liquid phase.

Table 1. Phase contents of the samples quenched from different temperatures.

Temperature (°C)	Phase content (wt.%)	Remarks
1080	$\beta$ -Si <sub>3</sub> N <sub>4</sub> 20 %, $\beta$ -LiAlSiO <sub>4</sub>	onset of shrinkage
1180	$\beta$ -Si <sub>3</sub> N <sub>4</sub> 20 %, $\beta$ -LiAlSiO <sub>4</sub> , SiO <sub>2</sub>	1 <sup>st</sup> maximum of shrinkage velocity
1275	$\beta$ -Si <sub>3</sub> N <sub>4</sub> 20 %, $\beta$ -LiAlSi <sub>2</sub> O <sub>6</sub> , SiO <sub>2</sub>	2 <sup>nd</sup> maximum of shrinkage velocity
1490	$\beta$ -Si <sub>3</sub> N <sub>4</sub> 20 %, $\beta$ -LiAlSi <sub>2</sub> O <sub>6</sub> , SiO <sub>2</sub>	3 <sup>rd</sup> maximum of shrinkage velocity
1500	$\beta$ -Si <sub>3</sub> N <sub>4</sub> 20 %, $\beta$ -LiAlSi <sub>2</sub> O <sub>6</sub> , SiO <sub>2</sub>	after annealing for 5 min
1500	$\beta$ -Si <sub>3</sub> N <sub>4</sub> 35 %, SiO <sub>2</sub>	after annealing for 1 h

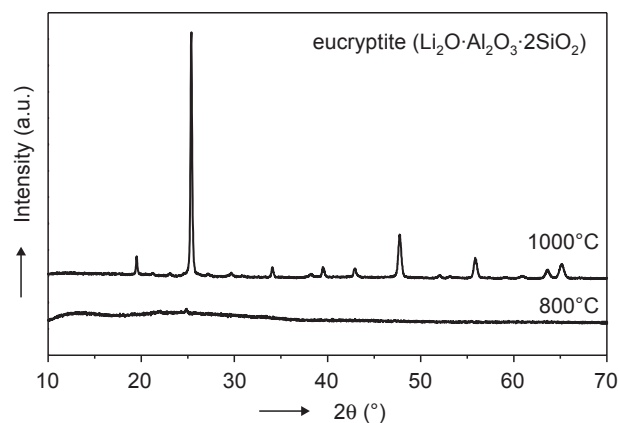


Figure 1. XRD pattern of Li-exchanged zeolite at 800° and 1000°C.

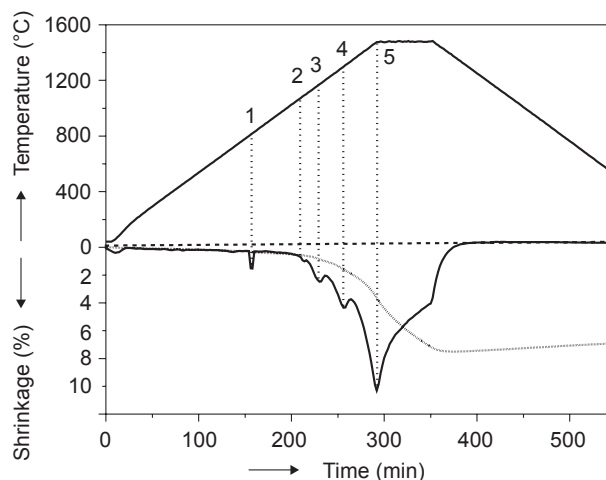


Figure 2. Shrinkage (dashed line) and shrinkage velocity (full line) of a silicon nitride green body with 15% LAS additive showing characteristic features at: 1 - 810°C; 2 - 1080°C; 3 - 1180°C; 4 - 1275°C; 5 - 1490°C.

However, the  $\alpha/\beta$ - $\text{Si}_3\text{N}_4$  ratio remains the same up to  $1500^\circ\text{C}$  indicating that no significant transformation takes place during the first stage of sintering. This means that the initial stage is related with the formation of the liquid phase and to the reaction between the sintering additive and the surface silica from  $\text{Si}_3\text{N}_4$  grains. It was found that the crystallization of the secondary phases from the melt can occur already during sintering especially for compositions situated on a tie line between one secondary phase and  $\text{Si}_3\text{N}_4$ . In this case, the volume fraction of the liquid phase is strongly reduced and complete densification is impossible [11]. According to the XRD patterns of the samples quenched at particular temperatures show that the amount of liquid phase increases only slowly with temperature due to the sequence of chemical reactions.

Hence, the densification may be assumed to take place with less particle rearrangement than is usual for the liquid phase sintering. In the liquid LAS system, the significant amount of additive is converted into liquid at  $1500^\circ\text{C}$ . Also an appreciable amount of  $\text{Si}_3\text{N}_4$  can be dissolved [12]. Thus, the degree of  $\alpha$ - $\beta$  phase transformation increases during prolonged sintering at  $1500^\circ\text{C}$ . It was found that the transformation from  $\alpha$ - $\text{Si}_3\text{N}_4$  to  $\beta$ - $\text{Si}_3\text{N}_4$  is over after 8 h of annealing (Figure 3).

## CONCLUSION

Dilatometric study of the system  $\text{Si}_3\text{N}_4$  and a zeolite-derived lithium aluminum silicate (LAS) was investigated in this study. Onset of shrinkage first occurs at  $1080^\circ\text{C}$  what is related to liquid formation in the mixture compacts. The used additive forms a Li-Al silicate melt with a composition corresponding to  $\beta$ -eucryptite, which allows sintering temperatures to decrease at as low as  $1500^\circ\text{C}$ . It was found that the transformation

from  $\alpha$ - $\text{Si}_3\text{N}_4$  to  $\beta$ - $\text{Si}_3\text{N}_4$  does not take place before  $1500^\circ\text{C}$ . However, the amount of phase transformation increases during prolonged sintering and it is completed after 8 h of annealing. The results show that a significant improvement in the low-temperature, pressureless sinterability of  $\text{Si}_3\text{N}_4$  ceramics can be achieved by using Li-exchanged zeolite as sintering additive.

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## References

1. Ziegler G., Heinrich J., Wötting G.: *J.Mater.Sci.* 22, 3041 (1987).
2. Riley F.L. F.L.: *J.Am.Ceram.Soc.* 83, 245 (2000).
3. Hermann M., Schulz I., Hintermayer J. in: *Fourth Euro-Ceramics, Vol. 2*, p. 211, Ed. C. Galassi, C., 1995.
4. Zhien L., Yuihui S., Hijiang D., Jijian C.: *J.Mater.Sci.* 23, 390 (1995).
5. Boskovic S., Kosanovic D., Dondor V., Dimitrijevic R.: *Ceram.Int.* 26, 33 (2000).
6. Matovic B., Rixecker G., Boskovic S., Aldinger F.: *International Journal of Materials Research* 97, 1264 (2006).
7. Dimitrijevic R., Dondor V., Mioc U., Kremenovic A., Srejjic R.: *Advances in Science and Technology* 3, 687 (1995).
8. Gazzara C.P., D.R. Messier D.R.: *J.Am.Ceram.Soc.* 78, 1076 (1977).
9. Kim S., Sanders T.H.: *J.Am.Ceram.Soc.* 74, 1833 (1991).
10. Lewis E.M., Robbins C.R., McMurdie H.F. in: *Phase diagram for ceramists*, Ed. Reser M.K., American Ceramic Society, Westerville 1969.
11. Hoffman M.J.: *MRS Bull.* 2, 28 (1995).
12. Kim D., Greil P., Petzow G.: *Adv.Ceram.Mater.* 2, 817 (1987).

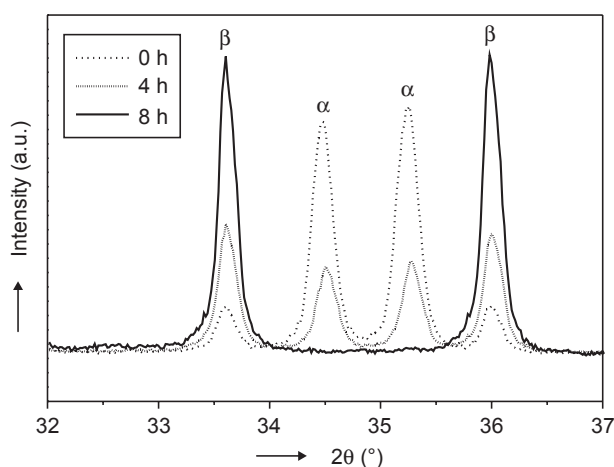


Figure 3. Evolution of phase transformation as a function of the dwell time temperature at  $1500^\circ\text{C}$ .

## DILATOMETRIČKÁ STUDIE SYSTÉMU $\text{Si}_3\text{N}_4$ -LAS

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Byla studována možnost použití litného zeolitu získaného iontovou výměnou (LAS) jako přísady pro zhuštění  $\text{Si}_3\text{N}_4$  keramiky. Chování vzorků připravených ze zeolitického prekurzoru a prášku  $\text{Si}_3\text{N}_4$  při bylo sledováno dilatometricky v teplotním rozmezí od pokojové teploty do  $1500^\circ\text{C}$ . První tavenina se začíná tvořit při  $1080^\circ\text{C}$ , což vede k výraznému poklesu slinovací teploty. Data RTG difrakční analýzy ukazují, že fázová transformace  $\alpha$ - $\beta$ - $\text{Si}_3\text{N}_4$  probíhá po přechodu druhé fáze do skelného stavu. Výsledky ukazují, že zeolit LAS je velmi účinnou slinovací přísadou nitridu křemíku.