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## **Thermal Conductivity of Pressureless Sintered Silicon Nitride Materials with LiYO<sub>2</sub> Additive**

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**Abstract:**

*Si<sub>3</sub>N<sub>4</sub> ceramics with different microstructures were prepared by pressureless sintering, using LiYO<sub>2</sub> as a sintering additive. The effect of microstructural parameters, such as grain size and volume of intergranular phase on thermal conductivity was studied. Materials with thermal conductivities of 26-38 W·(m·K)<sup>-1</sup> were obtained by changing the amount of sintering additive. The highest conductivity was measured for the material with the least amount of additive. Since the phase composition is the same for all sintered materials the difference in thermal conductivity is attributed to the amount of glassy phase in the grain-junctions.*

**Keywords:** *Si<sub>3</sub>N<sub>4</sub>, LiYO<sub>2</sub> additive, Sintering, Thermal conductivity.*

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### **1. Introduction**

Thermal conductivity is one interesting property of Si<sub>3</sub>N<sub>4</sub>, which combined with the excellent mechanical properties make it a serious candidate for high-performance substrates [1]. Si<sub>3</sub>N<sub>4</sub> was first pointed out by Haggerty and Lightfoot as a material with potentially high thermal conductivity at room temperature [2]. Calculations show that the intrinsic thermal conductivity of β-Si<sub>3</sub>N<sub>4</sub> single crystals is 320 W m<sup>-1</sup> K<sup>-1</sup>, which is similar to the thermal conductivity of SiC and AlN. Both materials have been successfully fabricated for commercial uses as high thermal conductivity substrates and heat sinks [3]. Thermal conductivity values ranging from 20 to 70 W m<sup>-1</sup> K<sup>-1</sup> were reported for Si<sub>3</sub>N<sub>4</sub> ceramics fabricated by reaction bonding [4], chemical vapor deposition [5], hot pressing and hot-isostatic pressing methods [6]. Very recently, Watari fabricated a Si<sub>3</sub>N<sub>4</sub> material with a thermal conductivity value of 155 W (m K)<sup>-1</sup> by a novel processing technique termed grain-orientation technology [3].

It has been postulated that heat flow in hexagonal β-Si<sub>3</sub>N<sub>4</sub> is different depending on the crystal axis. In single crystal measurements it was shown that the conductivity along the c-axis is about three times higher than that along the a-axis [7].

The thermal conductivity of Si<sub>3</sub>N<sub>4</sub> ceramics depends strongly on the amount of Al impurities and/or sintering additives because the incorporation of Al and O in the β-Si<sub>3</sub>N<sub>4</sub> structure reduces the thermal conductivity of the grains due to the reduced free path of phonons. Thus, Al-free sintering additives are a precondition for the production of Si<sub>3</sub>N<sub>4</sub> ceramics with high thermal conductivity [8]. Lattice defects in the grains [9] and increasing grain boundary thickness were also found to decrease the thermal conductivity [10].

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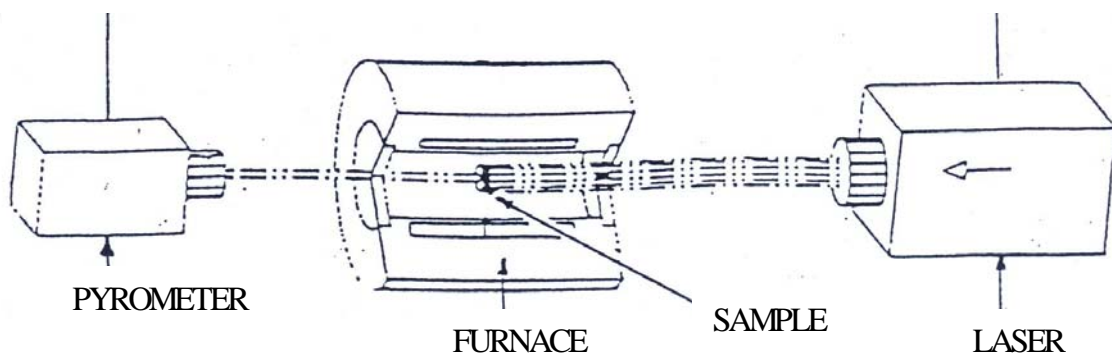
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From a commercial point of view, it is very important to fabricate high thermal conductivity  $\text{Si}_3\text{N}_4$  ceramics by a conventional sintering technique such as pressureless sintering. Seeding combined with careful control of grain boundary composition can be one processing strategy for this purpose. In addition, microstructure design for harmonising high thermal conductivity with good mechanical and electrical properties is also very important for the widespread use of  $\text{Si}_3\text{N}_4$  ceramics as high thermal conductivity materials [1].

## 2. Experimental work

The starting powders were commercial  $\text{Si}_3\text{N}_4$  (Silzot HQ with a mean particle size of  $D_{50} = 1.7 \mu\text{m}$ , specific surface area of  $3.2 \text{ m}^2/\text{g}$ , O = 0.5 wt%, N > 38.5 wt%, free Si < 0.5 wt%, SiC < 0.4 wt%,  $\alpha/(\alpha+\beta) = 0.8$ ) and  $\text{LiYO}_2$  powder with  $D_{50} = 1.2 \mu\text{m}$ . The latter was synthesised by mixing as-received  $\text{Y}_2\text{O}_3$  and  $\text{Li}_2\text{CO}_3$  powders and calcining the mixture at  $1400^\circ\text{C}$  for 4 h.  $\text{Si}_3\text{N}_4$  powders were mixed with 5, 10, 15 and 20 wt%  $\text{LiYO}_2$  for 4 h by attrition milling in isopropanol. After drying, the mixture was isostatically pressed under 240 MPa. The green density of the pellets was about 57% of the theoretical density. Sintering was accomplished in a graphite-heated furnace (FCT, Germany) under 0.1 MPa nitrogen atmosphere at temperatures between  $1550^\circ\text{C}$  and  $1650^\circ\text{C}$  for 8 h. The densities, weights and sample dimensions were measured after each experiment. XRD was used for the evaluation of the weight fraction of the  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$  phases, by calculation on the basis of the method proposed by Gazzara and Messier [11]. Scanning electron microscopy (SEM) analyses were carried out on polished and plasma etched surfaces of samples using a JEOL 6300F microscope at 3 kV accelerating voltage.

The laser-flash method was used for measuring the thermal diffusivity of  $\text{Si}_3\text{N}_4$  materials. Disk samples (diameter 12 mm and thickness 0.5 mm) were tested in in-house constructed laser-flash equipment. On the front face of the sample an Nd-YAG laser pulse ( $1.06 \mu\text{m}$  wavelength and pulse duration 1 ms) is homogeneously absorbed. The time-dependence of the temperature rise on the rear face is measured by an In-Sb IR detector and allows the determination of the thermal diffusivity. For this purpose, the amplified temperature response signal is evaluated by computer software. The method has a standard deviation of 3% for reference materials. The experimental set up is given in Fig. 1.



**Fig. 1** Experimental setup for measuring thermal diffusivity.

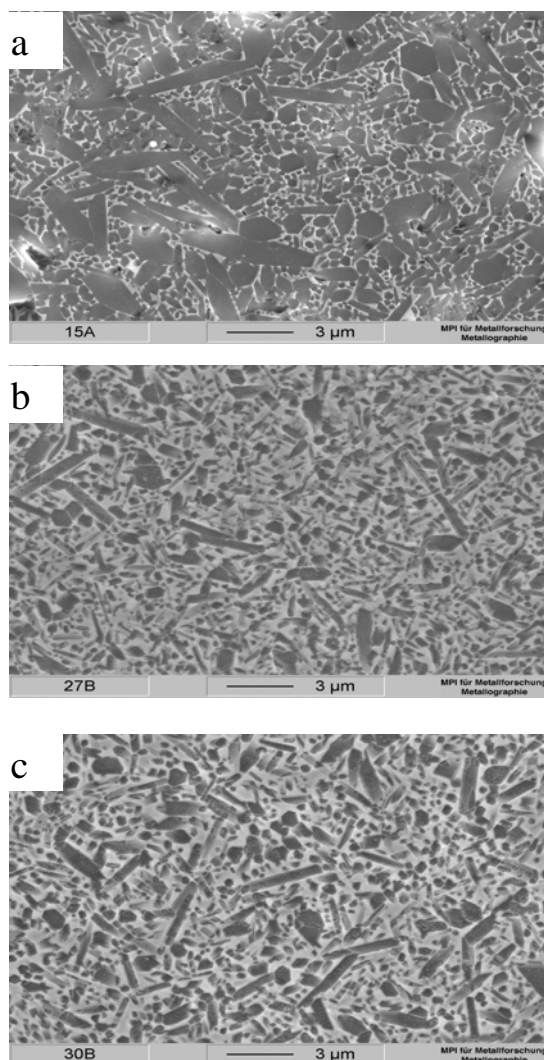
To protect the sample against heat loss, the specimen holder is installed in a vacuum chamber ( $p < 10^{-1} \text{ Pa}$ ). A Mo-furnace allows measurements between RT and 2000 K.

The thermal conductivity was calculated from the tabulated heat capacity of  $\text{Si}_3\text{N}_4$ ,  $C_p$  [12], the thermal diffusivity as measured by the laser-flash technique,  $\alpha$ , and the bulk density of the material,  $\rho$ , according to the equation:

$$K = C_p \cdot \alpha \cdot \rho \quad (1)$$

### 3. Results and discussion

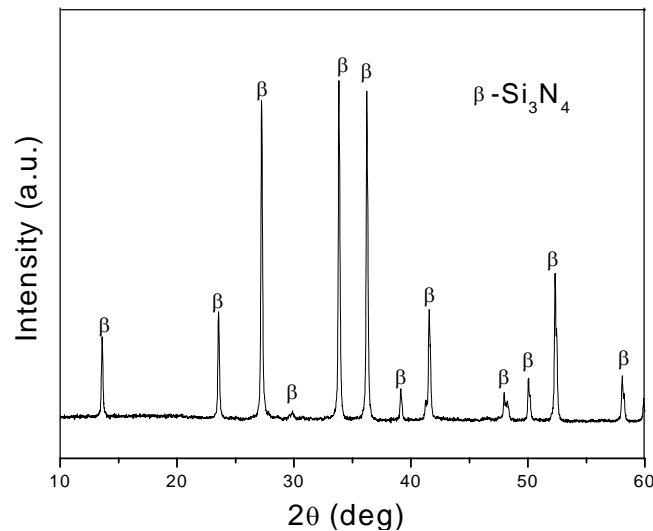
Since densification, as well as the phase transformation from  $\alpha\text{-Si}_3\text{N}_4$  to  $\beta\text{-Si}_3\text{N}_4$ , is influenced by the additive content, the same has to be true for the microstructure development. Fig. 2 shows SEM micrographs with varying additive content. It can be seen that the number and aspect ratio of elongated  $\beta$ -grains increases with increasing  $\text{LiYO}_2$  content.



**Fig. 2** SEM microstructure of  $\text{Si}_3\text{N}_4$  ceramics with total  $\text{LiYO}_2$  additive content of (a) 5 wt%, (b) 15 wt%, (c) 20 wt%. The samples were sintered at  $1600^\circ\text{C}$  for 4 h.

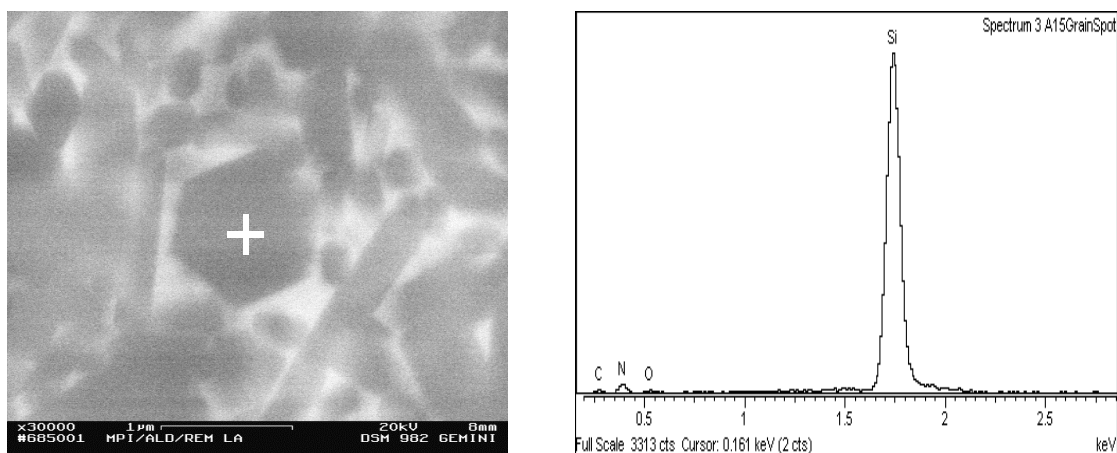
The materials with a large additive content are mainly composed of elongated grains. In contrast, for a small additive content, the microstructure consists of coarse  $\beta$ -grains within a fine-grained matrix. Thus, with increasing additive content, the aspect ratio distribution is shifted to higher values.

X-ray diffraction patterns of samples sintered at 1600°C for 8 h show only the presence of  $\beta$ - $\text{Si}_3\text{N}_4$  and no other crystalline phases (Fig. 3). This indicates that the remainder of the secondary phase, after evaporation of virtually all of the lithium originally present in the sample [13], has been completely converted into a glass and that total conversion of  $\alpha$ - $\text{Si}_3\text{N}_4$  to  $\beta$ - $\text{Si}_3\text{N}_4$  has taken place.

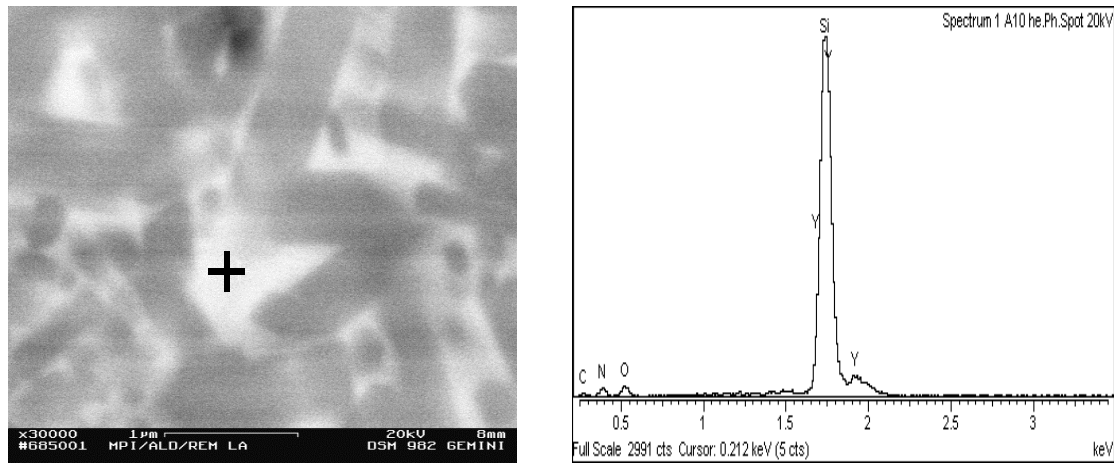


**Fig. 3** XRD pattern of a sample with 15 wt% of additive sintered at 1600°C for 8 h.

The amorphous phase in  $\text{Si}_3\text{N}_4$  materials is well established to remain as a stable film at the grain boundaries [14], with an increasing additive content only causing an enlargement of multi-grain junctions. For the present materials, the chemistry of the intergranular phase and  $\beta$ -grains was analyzed by energy dispersive microanalysis (EDX) with SEM (Fig. 4a and Fig. 4b). Backscattered electron (BSE) images are shown for reference. EDX analysis on the basal plane of a  $\beta$ - $\text{Si}_3\text{N}_4$  grain (denoted by a cross) shows Si and N, but no Y. This is because Y is insoluble in  $\text{Si}_3\text{N}_4$  [15]. Consequently,  $\text{Y}_2\text{O}_3$  is localized in the grain-boundary glassy phase.

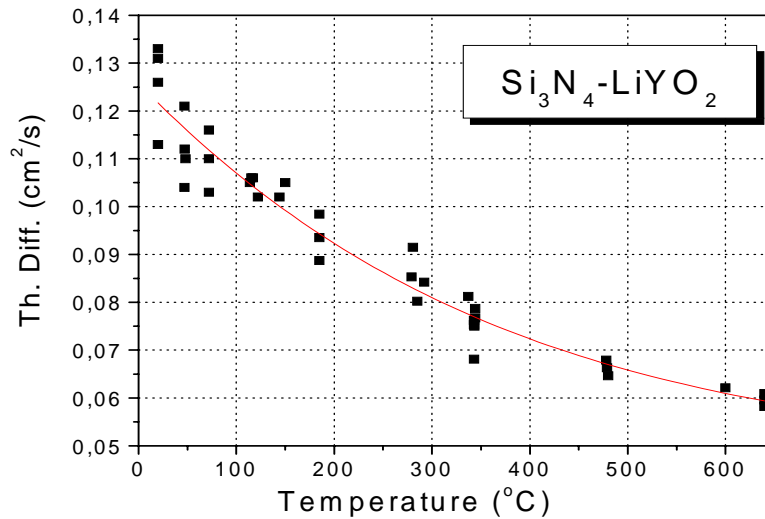


**Fig. 4a** Backscattered electron image and EDX of  $\beta$ - $\text{Si}_3\text{N}_4$  grain (+). Sample sintered at 1650°C for 1 h.



**Fig. 4b** Backscattered electron image and EDX of intergranular phase (+). Sample sintered at 1650°C for 1 h.

Since the thermal conductivity of covalent materials is mainly due to phonons, it is controlled by the type and amount of crystal defects inside the grains, porosity and grain boundary phases. The thermal diffusivity significantly decreases with increasing temperature in sintered materials (Fig. 5). The main reason is increased phonon scattering due to the higher degree of anharmonicity.



**Fig. 5** Temperature dependence of the thermal diffusivity of  $\text{Si}_3\text{N}_4$  ceramics sintered with 15 wt% of  $\text{LiYO}_2$ .

The effect of additive content on the thermal conductivity of  $\text{Si}_3\text{N}_4$  ceramics sintered with 5-20 wt% of  $\text{LiYO}_2$  additive at 1650°C for 4 h is shown in Table I.

In spite of the lower density (higher porosity), a higher value of thermal conductivity is obtained for materials sintered with only 5 wt% of additive. Increasing the additive content reduces the thermal conductivity. Since the phase composition and grain-boundary phase remain the same, the difference in thermal conductivity is attributed to microstructural variations.

**Table I** Effect of the amount of additive on the thermal conductivity of Si<sub>3</sub>N<sub>4</sub> ceramics sintered with LiYO<sub>2</sub> additive.

Additive content (wt%)	Density (g/cm <sup>3</sup> )	Thermal conductivity (W(m·K) <sup>-1</sup> )
5	2.85	38.6
10	3.12	29.1
15	3.21	29.7
20	3.20	26.8

Considering the thermal conductivity of SiO<sub>2</sub> based glasses, the thermal conductivity of the intergranular phase is much lower than that of Si<sub>3</sub>N<sub>4</sub> grains, ranging from 0.1 to 0.7 W(m·K)<sup>-1</sup> [16]. Thus, Si<sub>3</sub>N<sub>4</sub> ceramics can be considered as two-phase materials composed of Si<sub>3</sub>N<sub>4</sub> grains with high thermal conductivity and an intergranular phase with low thermal conductivity. The thermal conductivity of the two-phase material then depends on the individual thermal conductivity of the phases and on their distribution. In the case of higher additive contents, the amount of glassy phase in the grain-junctions is higher, which results in a decreasing overall thermal conductivity.

#### 4. Conclusion

Pressureless sintered Si<sub>3</sub>N<sub>4</sub> ceramics were prepared using LiYO<sub>2</sub> additives. The thermal conductivity increased up to 38 W·(m·K)<sup>-1</sup> for 5% of additive in comparison to 26 W·(m·K)<sup>-1</sup> for 20% of the additive. Sintered materials with less additive exhibit a coarser microstructure with a smaller volume of intergranular glassy phase. It seems therefore, that the amount of intergranular phase has a more pronounced influence on thermal conductivity than the higher residual porosity.

Investigations of Si<sub>3</sub>N<sub>4</sub> ceramics with specially tailored microstructures have demonstrated the potential of Si<sub>3</sub>N<sub>4</sub> as a material with high thermal conductivity [3-7]. Optimising the sintered density for a low LiYO<sub>2</sub> additive content, together with dedicated post-densification annealing treatments to obtain a coarser grain structure, is expected to lead to comparable conductivity values in the present low-cost Si<sub>3</sub>N<sub>4</sub> ceramics.

#### References

- [1] K. Hirao, K. Watari, H. Hayashi and M. Kitayama, MRS Bulletin **6** (2001) 451.
- [2] S. Haggerty and A. Lightfoot, Ceram. Eng. Sci. Proc., **16** (1995) 475.
- [3] K. Watari, J. Ceram. Sci. Jpn., **109** (2001) 57.
- [4] G. Ziegler, J. Heinrich, G. Wötting, J. Mater. Sci., **22**, (1987) 3041.
- [5] T. Hirai, S. Hayashi and K. Niihara, Am. Ceram. Soc. Bull., **57** (1978) 1126.
- [6] K. Tsukama, M. Shimada and M. Koizumi, Am. Ceram. Soc. Bull., **60** (1981) 910.
- [7] K. Watari, L. Pottier, B. Li, D. Fournier and M. Toriyama, in Grain Boundary Engineering in Ceramics, ed. T. Sakuma, L. Sheppard and Y. Ikuhara, The American Ceramic Society, Westerville (2000) p. 341.
- [8] G. Petzow and M. Herrmann, Structure and Bonding, **Vol. 102**, Springer-Verlag, Berlin (2002) p. 51.

- [9] K. Watari, K. Hirao, M. Toriyama and K. Ishizaki, c., **82** (1999) 777.  
[10] M. Kitayama, K. Hirao, M. Toriyama and S. Kanzaki, J. Am. Ceram. Soc., **82** (1999) 3105.  
[11] C.P. Gazzara, D.R. Messier, J. Am. Ceram. Soc. **78** (1977) 1076.  
[12] M. Kitoyama, K. Hirao, A. Tsuge, K. Watari, M. Toriyama and S. Kauzaki, J. Am. Ceram. Soc., **83** (2000) 1985.  
[13] B. Matovic, G. Rixecker and F. Aldinger, J. Am. Ceram. Soc., accepted for publication.  
[14] H. J. Kleebe, J. Ceram. Soc. Jpn., **105** (1993) 453.  
[15] I. Tanaka, K. Niihara, S. Nasu and H. Adachi, J. Am. Ceram. Soc., **76** (1993) 2833.  
[16] D. Gerlich and G. A. Slack, J. Phys. Chem. Solids, **46** (1985) 433.

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**Резюме:** Керамики  $Si_3N_4$  с различными микроструктурами приготовлены спеканием без прессования и с использованием  $LiYO_2$  в качестве добавки. Исследовано влияние микроструктурных параметров: размер зерен и объем межзеренной фазы, на термическую проводимость. Материалы, термическая проводимость которых 26-38  $W (m \cdot K)^{-1}$ , получены при изменении количества добавок. Самая высокая проводимость измерена в материалах с наименьшим количеством добавок. Учитывая, что для всех спеченных материалов фазовый состав одинокий, ответственной для разницы в термической проводимости является количество стекловидной фазы в границах зерен.  
**Ключевые слова:**  $Si_3N_4$ , добавка  $LiYO_2$ , спекание, удельная теплопроводность.

**Садржај:**  $Si_3N_4$  керамике различитих микроструктура припремљене су синтеровањем без притиска коришћењем  $LiYO_2$  као додатка приликом синтеровања. Проучен је утицај микроструктурних параметара, као што су величина зрна и запремина међучестичне фазе на термичку проводност. Материјали са термичком проводношћу од 26-38  $W (m \cdot K)^{-1}$  добијени су променом количине додатка. Највећа проводност је измерена за материјал са најмањом количином додатка. Како је фазни састав исти за све синтероване материјале, разлика у термичкој проводности се приписује количини стакласте фазе у границама зрна.

**Кључне речи:**  $Si_3N_4$ ,  $LiYO_2$  додатак, синтеровање, термичка проводност

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