

Dielectric properties of silicon nitride ceramics prepared by low temperature spark plasma sintering technique

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In this study, α -Si₃N₄ ceramics were successfully prepared using MgO and AlPO₄ as the sintering additives and a low temperature spark plasma sintering (SPS) technique. The resultant α -Si₃N₄ ceramics sintered from 1300 °C to 1500 °C show a fine microstructure with nearly no grain growth and phase transformation. The dielectric properties of the sintered ceramics are investigated in detail. α -Si₃N₄ ceramics with a porosity of 5-36% show a dielectric constant of 4.5-7.4 and a dielectric loss of less than 10×10^{-3} . The existence of AlPO₄ performing as a binder not only contributes to the low temperature sintering of fully-dense α -Si₃N₄ ceramics, but also reduces the dielectric constant and loss.

Key words: Silicon nitride, Spark plasma sintering (SPS), Phosphate, Dielectric properties.

Introduction

Silicon nitride (Si₃N₄) ceramic has been studied intensively and used in numerous applications as both a structural and functional material because of its superior properties, such as high-temperature strength, good oxidation resistance and low thermal expansion coefficient [1-4]. Si₃N₄ has two forms, α and β phases [5]. Previous studies focused mainly on a complete phase transformation from α -Si₃N₄ to β -Si₃N₄ and achieving perfect mechanical and thermal properties by using different sintering additives, and were aimed at obtaining fully-dense products [6, 7]. However, better dielectric properties [8] of α -Si₃N₄ ceramic whose dielectric constant (ϵ) is 5.6 and dielectric loss (tgδ) is 0.003 at room temperature than β -Si₃N₄ ($\epsilon = 7.9$, tgδ = 0.005) should not be ignored because it can be utilized as an electromagnetic wave penetration material [9].

It is known that spark plasma sintering (SPS) is a newly-developed sintering technique [10] which is similar to the conventional hot-press sintering in configuration, where the precursor powders are loaded in a die and a uniaxial pressure is applied during the sintering process. However, instead of using an external heating source, densification is enhanced by the use of a pulsed direct current passing through the electrically-conducted die and the sample. A high sintering speed and possibly low temperature sintering are characteristics of the SPS technique. It is reported that Si₃N₄ ceramic can be sintered within 15 minute of heating and holding time, but the α to β transformation

is not completed within such a short sintering time [11]. It is assumed that the initial temperature of the α to β transformation is about 1400 °C and the temperature of completion is about 1800 °C. Otherwise, the SPS technique thus provides us with a unique possibility to manipulate the sintering kinetics. The inherent advantages of SPS technique are the reasons why it is selected in this study.

AlPO₄ is chemically inert, thermally stable (melting point of ~2000 °C), electrically neutral, and highly covalent, which makes AlPO₄ an attractive candidate material for high temperature applications [12]. On the other hand, it is also a low temperature binder material which makes it possible for the low temperature sintering of α -Si₃N₄ ceramic. Gitzen *et al.* fabricated AlPO₄-bonded, alumina castables and noted that the castables gave excellent serviceability in temperature ranges to 1870 °C [13].

In this research, we explore an effective method to prepare the α -Si₃N₄ ceramics by using MgO and AlPO₄ as the sintering additives and the SPS technique. The effect of a low sintering temperature and AlPO₄ content on the dielectric properties of the sintered samples is mainly investigated.

Experimental Procedure

Starting materials

The raw materials used in the present study are as follows: α -Si₃N₄ rich powder (produced by UBE industries, Co., Ltd, Japan with an average particle size of ~0.5 μm and $\alpha/(\alpha + \beta) > 93$ wt%), light magnesia (MgO) powder (produced by H.C. Starck, Germany, with an average particle size of ~0.2 μm and a purity of 99.9%) and aluminum phosphate (AlPO₄) powder (produced by H.C. Starck, Germany, with an average particle size of ~0.5 μm and a

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Table 1. Phase and elemental composition of Si_3N_4 raw material, wt.%.

material	α phase	β phase	Si_{free}	N	O	C	Fe
Si_3N_4	> 93	< 5	< 0.3	> 37.0	< 1.5	< 0.1	< 0.3

Table 2. The composition ratio (wt.%) of raw powders of every sample

No.	Si_3N_4	MgO	AlPO_4
A1	94	4	2
A2	92	4	4
A3	86	4	8
A4	80	4	16

purity of 99.9%). Table 1 lists the main compositions of the $\alpha\text{-Si}_3\text{N}_4$ raw powder.

Materials preparation

According to Table 2, the powder precursors in various ratios were ball milled in ethanol for 10 h in a nylon jar, using sintered Si_3N_4 grinding balls. After the powder mixtures were dried, they were passed through a 100 mesh sieve to eliminate large agglomerates, then loaded in a graphite die with an inner diameter of 32 mm and pre-pressed to some extent and sintered using a SPS system (model-1050, Sumitomo Coal Mining Co. Ltd., Tokyo). The sintering temperature was 1300–1500 °C, which was measured by an optical pyrometer focused on the surface of the graphite die. An average heating rate of 100 K·min⁻¹ was applied and the holding time for each sample was 5 minute. A uniaxial pressure of 30 MPa and a nitrogen (N_2) atmosphere were applied from the start to the end of the sintering cycle. The samples were cooled naturally within the furnace.

Characterization

After sintering, the bulk density of the sintered products was determined by the Archimedes' immersion method using distilled water. The relative density was calculated directly in this way. The phase compositions were analyzed by X-ray diffraction (XRD) using a Rigaku-D/Max-III A diffractometer. Cu radiation was used and operated at 35 kV and 30 mA. The microstructure of the fractured surfaces was observed by scanning electron microscopy (SEM). The dielectric constant and dielectric loss of bulk samples was tested at a frequency of 10 GHz.

Results and Discussion

Sintering behavior

The porosity of A1-A4 as a function of sintering temperature and the sintering additives content is illustrated in Fig. 1. It can be seen from Fig. 1 that the porosity shows a sharp variation against the sintering temperature from 1300 °C to 1400 °C when the AlPO_4 content is 6 wt.% (A3) and 16 wt.% (A4), while this phenomenon happens from

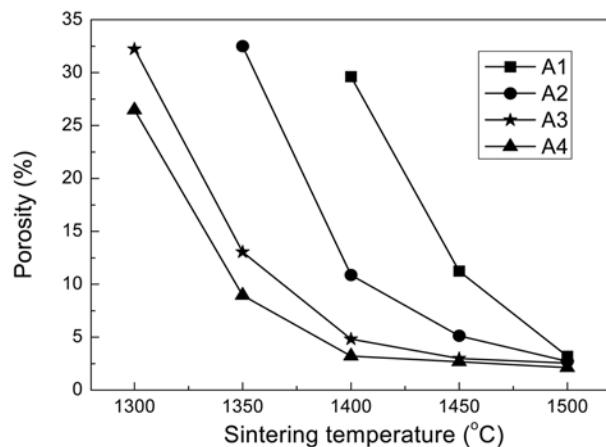


Fig. 1. The porosity of the sintered samples as a function of sintering temperature and the content of sintering additives.

1400 °C to 1500 °C for samples A1 and A2. Samples with the porosity from 2% to 35% are acquired. Thus, we can conclude that when the AlPO_4 content or the sintering temperature reaches certain values, this material can be fully-dense sintered. Moreover, nearly the same porosity of the sintered samples can be obtained by adjusting the AlPO_4 content and sintering temperature. For example, the porosity of A3 sintered at 1400 °C is less than 3%, and the sintering temperature for A1 and A2 with the same porosity is 1500 °C and 1450 °C, respectively. This indicates that Si_3N_4 ceramics can be sintered at a lower temperature with an increase in the AlPO_4 content.

Microstructure and phase analysis

The X-ray diffraction patterns of A4 at different sintering temperatures are shown in Fig. 2. It is obvious that the crystal phases of A4 are $\alpha\text{-Si}_3\text{N}_4$, $\beta\text{-Si}_3\text{N}_4$, MgSiO_3 , AlPO_4 . The existence of $\alpha\text{-Si}_3\text{N}_4$, $\beta\text{-Si}_3\text{N}_4$ is understood because the raw material of the $\alpha\text{-Si}_3\text{N}_4$ powder includes $\alpha\text{-Si}_3\text{N}_4$ and a little of $\beta\text{-Si}_3\text{N}_4$. The product identified as MgSiO_3 illustrates one of the sintering mechanisms that MgO can react with SiO_2 presenting on the surface of the silicon

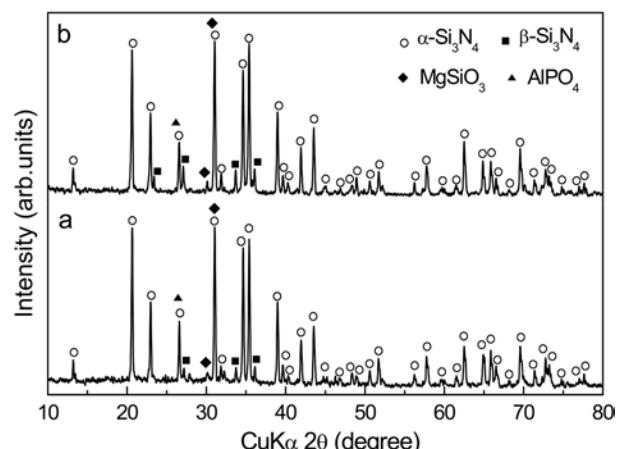


Fig. 2. The XRD patterns of A4 at different sintering temperatures: (a) 1350 °C; (b) 1500 °C.

nitride particles [13] and the reaction promotes the mixed powders initial adherence [14-15] which to some extent assures certain mechanical properties of the sintered samples. AlPO₄ is chemically inert, thermally stable (melting point ~2000 °C) and highly covalent, which exists stably during the sintering process [16]. Kim and Kriven fabricated AlPO₄ composites and found no volatilization of P₂O₅ from AlPO₄ [17]. Due to the solid state sintering of AlPO₄ around the Si₃N₄ grains, the sintering of the whole composite is finished at 1300 °C to 1500 °C according to the different contents of AlPO₄, which was the other sintering mechanism.

The SEM images of the sintered samples at different sintering temperatures are shown in Fig. 3. From the SEM images of the fracture surfaces of A4 sintered at 1400 °C and 1500 °C, it is worth noting that nearly no β-Si₃N₄ is observed and the grain size is about 0.5 μm which maintains the character of the raw Si₃N₄ materials, indicating there is no obvious grain growth in the SPS process. Porosity in this situation is mainly caused by partially-sintered Si₃N₄ particles and a non compact structure is observed. On the other hand, it is seen that the AlPO₄ binder phase performs a well binding property with Si₃N₄ grains, indicating a good adhesion between the grains and, thus, overall good sintering behavior and promising mechanical properties.

Dielectric properties

The dielectric constant and dielectric loss of the sintered samples as a function of porosity and sintering temperature are listed in Table 3. It is clearly observed that the highest dielectric constant is 7.4 and the lowest is below 5.0 when the porosity varies from 2% to 30%. Obviously, the dielectric constant is almost decreased with an increase of the porosity, which is in good agreement with the following formula:

$$\log \epsilon_p = (1-p) \log \epsilon_0 \quad (1)$$

where p is the porosity of the sample, ϵ_p is the dielectric constant when the porosity is p and ϵ_0 is the dielectric constant when the porosity rate is 0.

On the other hand, it can be seen that the dielectric loss is less than 10×10^{-3} for each sample regardless of the porosity and sintering temperature, and it increases with a decrease of the porosity as shown in Table 3.

The effect of AlPO₄ content on both the dielectric constant and dielectric loss is compared. We can conclude

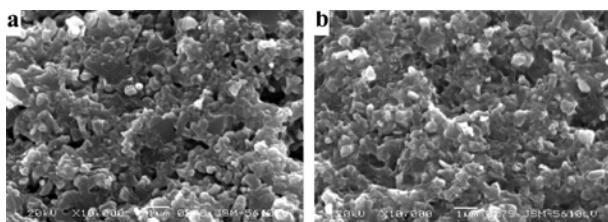


Fig. 3. SEM images of A4 at different sintering temperatures: (a) 1400 °C; (b) 1500 °C.

Table 3. Dielectric properties of the sintered samples as a function of the porosity and sintering temperature

Sample	Sintering temperature (°C)	Porosity (%)	Dielectric constant	Dielectric loss ($\times 10^{-3}$)
A1	1400	29.6 ± 0.2	4.5 ± 0.1	4.5 ± 1.0
	1450	11.2 ± 0.1	5.4 ± 0.1	3.5 ± 0.5
	1500	3.2 ± 0.3	7.4 ± 0.2	7.5 ± 0.5
A2	1400	10.9 ± 0.1	6.7 ± 0.1	2.4 ± 0.8
	1450	5.1 ± 0.3	7.0 ± 0.1	6.2 ± 0.7
	1500	2.7 ± 0.2	7.1 ± 0.2	8.6 ± 1.1
A3	1400	4.8 ± 0.2	6.4 ± 0.2	3.6 ± 1.5
	1450	3.0 ± 0.2	7.0 ± 0.3	7.2 ± 0.3
	1500	2.6 ± 0.2	7.1 ± 0.1	6.5 ± 0.5
A4	1400	3.2 ± 0.4	7.1 ± 0.1	5.5 ± 0.9
	1450	2.7 ± 0.3	7.0 ± 0.1	5.3 ± 0.8
	1500	2.1 ± 0.1	7.0 ± 0.1	6.2 ± 0.5

that increasing the AlPO₄ content greatly reduces both the dielectric constant and dielectric loss due to the low dielectric constant ($\epsilon_0 = 6.0$) and dielectric loss (The existence of a high AlPO₄ content not only affects the sintering behavior of α-Si₃N₄ at a lower temperature but also greatly restrains the transmission of ion and ionic polarization because of the fact that AlPO₄ itself embodies excellent adhesive action at elevated temperature) of AlPO₄.

Conclusions

The effect of sintering additives based on MgO and AlPO₄ on the sintering and dielectric properties of α-Si₃N₄ matrix ceramics has been examined using the spark plasma sintering (SPS) technique. The results obtained are as follows:

- 1) The main crystal phase of all samples is α-Si₃N₄, realized by controlling the sintering temperature and the sintering additive content.
- 2) The sintering mechanism of α-Si₃N₄ matrix ceramics by adding MgO and AlPO₄ could be attributed to both a reaction between MgO and SiO₂ present on the powders which promotes the mixed powders adherence and the solid state sintering of AlPO₄.
- 3) The dielectric constant is in the range of 4.5-7.4, the dielectric loss is less than 10×10^{-3} , and decreases with an increase of the porosity. The existence of a high content of AlPO₄ greatly restrains the transmission of ion and ionic polarization because of the fact that AlPO₄ itself embodies excellent adhesive action at high temperature.

References

1. P. Popov and S.N. Riddlesden, Trans. Br. Ceram. Soc., 60 (1961) 603-626.
2. G. Ziegler, J. Heinrich and G. Wotting, J. Mater. Sci., 22[9]

- (1987) 3041-3086.
3. A.J. Pyzik and D.R. Beaman, *J. Am. Ceram. Soc.*, 76[11] (1993) 2737.
 4. C.J. Lee and D.J. Kim, *J. Am. Ceram. Soc.*, 82[3] (1999) 753-756.
 5. C.M. Wang, X.Q. Pan, M. Ruhel, F.L. Riley and M. Mitomo, *J. Mater. Sci.*, 31 (1996) 5281-5298.
 6. F.L. Riley, *J. Am. Ceram. Soc.*, 83[2] (2000) 245-265.
 7. Z.J. Shen, Z. Zhao, H. Peng and M. Nygren, *Nature*, 417[16] (2002) 267-269.
 8. F.H. Simpson and J. Verzemnieks, In: Proceedings of the 16th symposium on electromagnetic windows. (1982) 81.
 9. C.L. Chen, F. Chen, Q. Shen, L.M. Zhang and F.Q. Yan, *J. Wuhan. Univ. Technol.*, 21[2] (2006) 98-100.
 10. M. Tokita, *J. Soc. Powder. Tech.*, 30 (1993) 790.
 11. T. Nishimura, H. Mitomo and M. Kawahara, *J. Mater. Sci. Lett.*, 14 (1995) 1046.
 12. J.V. Bothe Jr. and P.W. Brown. Low-Temperature Formation of Aluminum Orthophosphate, *J. Am. Ceram. Soc.*, 76[2] 362-68 (1993).
 13. W.H. Gitzen, L.D. Hart and G. Maczura, Phosphate-Bonded Alumina Castables: Some Properties and Applications. *Am. Ceram. Soc. BuL*, 35[6] 217-223 (1956).
 14. J. Wan, R.G. Duan and A.K. Mukherjee, *Scripta. Mater.*, 53 (2005) 663.
 15. D.E. Harrison, H.A. McKinstry and F.A. Hummel, *J. Am. Ceram. Soc.*, 37[6] (1954) 277.
 16. L.K.L. Falk, *J. Mater. Sci.*, 39 (2004) 6655-6673.
 17. D.K. Kim and W.M. Kriven, *J. Am. Ceram. Soc.*, 86 (11) (2003) 1962-1964.