Microstructural evolution of Si_3N_4 ceramics from starting powders with different α -to- β ratios

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Microstructural evolution of Si_3N_4 ceramics and thermal/mechanical properties were investigated with respect to the initial α -to- β ratios of the starting powders. The fast growth of elongated β -grains was observed in the α powder, while the growth of relatively equiaxed grains occurred in the β powder. In the cases where α/β mixed raw powder was used, exaggerated bimodal microstructural evolution occurred as a result of the abnormal grain growth. These microstructural variations of the Si_3N_4 had a significant influence on the mechanical and thermal properties, such as strength, fracture toughness and thermal conductivity. The bimodal microstructure, which consisted of large elongated grains surrounded by fine matrix grains, resulted in both high flexural strength and high fracture toughness. Controlling the microstructural evolution, resulted in a high thermal conductivity of 86 W/mK, a high flexural strength of 912 MPa, and a high fracture toughness of 7.88 $\text{MPa}\cdot\text{m}^{1/2}$ from α/β mixed raw powder. The achievement of both high thermal and mechanical properties of Si_3N_4 ceramics was highly essential for thermal management applications.

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1. Introduction

Silicon nitride (Si_3N_4) ceramics have been explored extensively for structural applications. Si_3N_4 exhibit superior properties such as high strength, fracture toughness, good thermal shock, and good oxidation resistance at both room and high temperatures. Recently, due to its potential high thermal conductivity, the application range of Si_3N_4 has expanded to include various applications, such as power electric module and microwave window application.^{1)–6)} However, those properties have not reached their full potential, and a scattering of property data, including strength, fracture toughness and thermal conductivity plus insufficient reproducibility, inhibits the realization of a wide number of applications. Hirao et al. fabricated highly thermal conductive Si_3N_4 ceramics by reducing the oxygen-related defects and using longer annealing processes (60 h). The experiment resulted in a thermal conductivity of 177 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ but, a lower flexural strength of 460 MPa due to the large grain growth and long annealing time.^{7),8)} In actual applications, it is highly essential to simultaneously increase both thermal and mechanical properties.

The properties of Si_3N_4 ceramics are influenced by various factors, and the microstructure is an important factor governing the final properties of Si_3N_4 .^{9)–16)} The microstructural variation of the Si_3N_4 ceramic had a significant influence on its mechanical and thermal properties. The Si_3N_4 ceramic has a relatively complex microstructure, and it is difficult to tailor. Hence, several investigations have been focused on the analysis of the influence of additives on the properties of Si_3N_4 ceramics.^{17)–21)} The microstructural evolution in Si_3N_4 ceramics is important for

optimizing the properties for specific applications. Therefore, tailoring the microstructure is necessary to fulfill the requirement for various applications.

In this study, the Si_3N_4 ceramics were synthesized with MgO–YbF₃ sintering additives. The sintering additive MgO and the non-oxide additive YbF₃ were selected instead of Yb₂O₃ to reduce the excessive oxides that formed at grain boundaries thus generating oxygen-related defects in the microstructure.^{22)–24)} With these sintering additives, we tailored the microstructure of Si_3N_4 ceramics by considering the influence of the Si_3N_4 starting powder, and analyzing the related mechanical and thermal properties. The effects of starting raw Si_3N_4 powders with different α/β ratios on the microstructure and the thermal/mechanical properties of sintered Si_3N_4 were investigated.

2. Experimental procedures

2.1 Powers and sintering of Si_3N_4 ceramics

All samples were prepared from high purity Si_3N_4 raw powders and sintering additives. Three types of Si_3N_4 raw powders were selected as different fraction of β - Si_3N_4 phase. These included A- Si_3N_4 consisting of alpha phase (E10 grade, Ube Industries, Ube, Japan), B- Si_3N_4 consisting of 1:1 mixed of α - β phase (NP-400 grade, Denki Kagaku Kogyo, Tokyo, Japan), and C- Si_3N_4 powder consisting of beta phase (NP-500 grade, Denki Kagaku Kogyo, Tokyo, Japan). The beta-phase fractions of powders B and C were obtained by the direct nitridation of silicon powder. These powders were similar in purity and size, as shown in **Table 1**. The sintering additives including 5 mol % of MgO (Aldrich Chemicals Co., Milwaukee, WI), 2 mol % of YbF₃ (Aldrich Chemicals Co., Milwaukee, WI) and 2 wt % of dispersant (Seruna E503, Chukyoyushi Co.) were mixed with raw Si_3N_4 powder. These mixed powders were ball milled in ethanol

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for 48 h using silicon nitride balls in a silicon nitride container. After the ethanol in the slurry was removed using a heater, 4 wt.% of paraffin (with a melting point of 46–48°C, Junsei Chemical Co., Japan) and 2 wt.% of DOP (dioctyl phthalate, Wako Pure Chem. Ind., Ltd., Japan) were added as a binder and lubricant, respectively. The mixed powder was sieved using a #60 nylon sieve, and was then molded into 50 × 40 × 5 mm or Ø15 × 3 mm sizes by uniaxial pressing at 50 MPa, followed by CIP (cold isostatic pressuring) at 200 MPa. The green bodies showed approximately 50% of relative density. The organic binder was burned out at 500°C for 3 h at an air flow of 4L/min. After being dewaxed, the green bodies were placed in silicon nitride crucibles and gas-pressured-sintered at 1750°C for 3 h or 1900°C for 6 h at a N₂ pressure of 0.9 MPa (GPS, Himulti 5000, Fujidenpa, Kogyo, Co., Japan)

2.2 Measure the properties

The density of the sintered materials was measured by the Archimedes method, and the phase was identified by X-ray diffractometry (XRD, Rigaku D/MAX-IIIC, Tokyo, Japan). The sintered material was polished with diamond paste and plasma etched in CF₄/O₂ gas for 5 min to examine the microstructure. The microstructure was then characterized by scanning electron microscopy (FE-SEM; Philips XL30 FEG, Eindhoven, Netherlands).

For the measurement of flexural strength, the sintered disks were cut into bars. Rectangular bars of 3.0 mm × 4.0 mm × 35 mm were tested using 20 mm support span and a crosshead speed of 0.5 mm/min. The bars were polished with 6 and 1 µm diamond paste in alcohol-based slurry (Blue Lube, Struers) and the edges were beveled for the three-point bending strength test. The reported flexural strength is an average of five tests.

Fracture toughness, K_{IC} was measured by the Vickers hardness indentation technique. Before the measurement, the surface was

polished with 1 µm diamond paste. Vickers indentations were then placed in the material using a HV-2 (2 kgf) load. The indentation surfaces were observed by SEM and the length of the crack was measured. With these features, fracture toughness was calculated the following equation.²⁵⁾

$$K_{IC} = \alpha \sqrt{\frac{E}{H}} \frac{P}{C^{\frac{3}{2}}}$$

Where α is an empirically determined “calibration” constant, with a value of 0.016 based on a fit to experimental data from B. Lawn.^{3),4),26)} E is the Young’s modulus with a value of 320 GPa, H is the hardness, P is the applied load, and c is the length of the surface trace of the half penny crack measured from the center of the indent.

The thermal conductivities of sintered materials were measured by the laser flash method with a glass-Nd laser and an InSb infrared sensor using a Xenon Flash instrument (LFA 447 Nanoflash, Netzsch Instruments Inc., Burlington, USA). The precision of this apparatus is estimated to be ±3%. Each reported thermal conductivity is an average of three measurements.

3. Results and discussion

Figure 1 shows the microstructure of raw Si₃N₄ starting powders and their specific properties are shown in Table 1. Three different raw powders appear to have similar features, with respect to size and purity. However, the phase and the morphology are different. Powder A was mainly composed of the round shaped α -phase. Powder C was mainly composed of the round shaped β -phase. On the other hand, Powder B was composed of both α and β phases, with shapes that were rounded and elongated, respectively. While the three powders had similar powder particle sizes, the high BET value of powder B was believed to be due to the influence of the elongated β -Si₃N₄ powder. (Fig. 1 and Table 1)

Figures 2 and 3 show the relative density of sintered materials with different raw Si₃N₄ powders and its polished microstructure, respectively. The relative density of the sintered material with powder A (hereafter called specimen A) was approximately 70 and 80% for sintered specimens at 1750 and 1900°C, respectively. Conversely, materials sintered from powder B (hereafter termed specimen B) and powder C (hereafter termed specimen C) exhibited over 97% of the TD from both sintering temperatures. This result suggested that the existence of β -Si₃N₄ phase in the starting raw powder effectively improves the densification of Si₃N₄ ceramics within the MgO–YbF₃ sintering additive system. Sintering additives, such as MgO, are generally well known

Table 1. Properties of starting raw Si₃N₄ powders

	Powder A	Powder B	Powder C
Vender	Ube E-10	Denka NP400	Denka NP500
α -phase contents/wt. %	95.0–98.0	45.0–50.0	2.0–4.0
Purity			
Oxygen/wt. %	1.27	0.96	0.83
Carbon/wt. %	<0.2	<0.3	<0.5
Aluminum/ppm	<100	<80	<200
BET specific surface area/m ² g ^{−1}	9–13	~15	~9

Fig. 1. Microstructure of starting Si₃N₄ powders. (a) Powder A: Ube-E10, (b) powder B: Denka NP400, and (c) powder C: Denka NP500.

materials, and they accelerate the liquid formation at lower temperatures. The YF₃ additive also formed a liquid phase at lower temperature as it possessed a lower melting temperature of 1157°C. Therefore, the liquid phase formed at the lower temperatures caused the rapid α-to-β phase transformation of Si₃N₄ ceramics at the initial or intermediate sintering stage. It is known that α-Si₃N₄ powder can dissolve into the liquid phase and re-

precipitate as β-Si₃N₄, which has an anisotropic structure. The grain growth of basal plane (001) of β-Si₃N₄ is more favorable than that of prism planes (100). Thus, the densification rate decreased with an increase the content of β-Si₃N₄ grains. That is, the rapid α-to-β phase transformation retarded particle rearrangement.²⁷⁾ As seen in **Table 2** and Fig. 3(a), specimen A had large and elongated β-Si₃N₄ grain. Conversely, specimens B and C sintered at 1750°C had smaller grain sizes, and more equiaxed grains compared with specimen A [Figs. 3(c) and 3(e)]. Specimens B and C had pre-existing β-Si₃N₄ phases in their starting powders, which acted as centers of crystallization. This implies that after the phase transformation was completed, additional β-Si₃N₄ grains surrounded the β-Si₃N₄ grains. Consequently, the anisotropic grain growth was significantly impinged by other β-grains, and then it was minimized by the interruption of densification by anisotropic grain growth. As a result, specimens B and C possessed densities exceeding 97% of the TD. At a temperature of 1900°C, grain growth occurred for all three specimens. Specimen A was composed of large and elongated grains,

Fig. 2. Relative density of sintered specimens at 1750, 1900°C with different raw powders; A, B, and C.

Table 2. Average length, width and aspect-ratio of the three specimens sintered at 1750°C for 3 h

	A specimen	B specimen	C specimen
Length (μm)	1.97	1.18	1.22
Width (μm)	0.80	0.59	0.67
Aspect-ratio	2.95	2.09	1.91

Fig. 3. Microstructure of polished surface of (a), (b) specimens A, (c), (d) specimens B, and (e), (f) specimens C. (a), (c), (e) represent specimens sintered at 1750°C for 3h, and (b), (d), (f) represent specimens sintered at 1900°C for 6h.

Fig. 4. Grain size distribution of Si_3N_4 grains sintered at temperatures of (a), (c), (e) 1750°C, and (b), (d), (f), 1900°C. (a), (b) specimens A, (c), (d) specimens B, and (e), (f) specimens C.

and specimen C had overall homogenous grain growth and B specimen had a bimodal grain structure.

Figure 4 shows the grain size distribution of three Si_3N_4 specimens sintered at 1750 and 1900°C. The grain width and length were measured by processing the picture using a digital image-analyzing program (Image J, NIH Image, Bethesda, Maryland, USA). At a sintering temperature of 1750°C, Specimen A had more grains with large widths compared to specimens B and C. Specimens B and C consisted of small grains, with widths mostly below 1 μm . As explained previously, specimens B and C consisted of β -phase at the beginning of densification and the grain growth was suppressed by other β - Si_3N_4 grains. As the sintering temperature increased to 1900°C, the three specimens exhibited different tendencies of growth. Specimen A was mainly showed growth via the Ostwald ripening process. The frequency of small grains (with widths of less than 1 μm) decreased, whereas the frequency of grains with large widths increased. Specimen B showed bimodal grain size distribution following sintering at 1900°C. This implied that the abnormal grain growth had occurred, consisting of grains with small widths

(less than 1 μm , hereafter termed the matrix grain) and large grains (approximately 3 μm in width or longer). In specimen C, the distribution shifted slightly to the right and became broad, showing a range of 0.6 to 2 μm in width.

Figure 5 shows the aspect-ratio (AR)-width (w) distribution. As shown in the microstructure (Fig. 3), specimen A had several grains with high aspect-ratio and small widths at a sintering temperature of 1750°C due to the strong negative correlation of AR with width. At a sintering temperature of 1900°C, the initial negative correlation of the AR-width distribution decreased. The specimen B showed an almost constant aspect ratio, while the width increased with temperature. The formation of large grains was observed with a constant aspect ratio. However, specimen C had a slight negative correlation of AR-width at both sintering temperatures. It appeared to exhibit overall grain growth.

The α/β ratio in the starting raw powder had significant effects on the microstructural evolution. The microstructural features including the size, distribution, shape, morphology, and aspect ratio, were tailored by controlling the initial β fractions of the starting powder. **Figure 6** shows the schematics of microstruc-

Fig. 5. Evolution of width-aspect-ratio distributions of Si_3N_4 grains sintered at temperatures of (a), (c), (e) 1750°C, and (b), (d), (f), 1900°C. (a), (b) specimens A, (c), (d) specimens B, and (e), (f) specimens C.

tural evolution in three different specimens. As seen in Fig. 1, the three different powders had different α/β ratio. Specimens A and C had rounded shapes of powders whereas specimen B had a mixture of rounded and elongated powder. As sintering proceeded, a liquid phase was formed, and $\alpha\text{-Si}_3\text{N}_4$ powder dissolved into the liquid phase and re-precipitated as $\beta\text{-Si}_3\text{N}_4$ with an anisotropic structure. In the present study, the liquid formation at lower temperatures was promoted and the rapid phase transformation was caused by the sintering additive $\text{MgO}\text{-YbF}_3$ system. Therefore, the α -to- β phase transformation is occurred and formed $\beta\text{-Si}_3\text{N}_4$ grain in the second step of the schematic shown in Fig. 6. Then, the $\beta\text{-Si}_3\text{N}_4$ grain grew in the direction of the length. This was influenced by the initial $\beta\text{-Si}_3\text{N}_4$ particles.

As seen in Fig. 3, the overall grain growth via Ostwald ripening was noted in specimen A, while significant abnormal grain growth was observed in specimen B, and a relatively small amount of grain growth occurred in specimen C.

Specimen A had over 90% $\alpha\text{-Si}_3\text{N}_4$ particle. Hence, a large inter-particle distance between $\beta\text{-Si}_3\text{N}_4$ nuclei resulted in the

grain growth potential, with less impingement by other $\beta\text{-Si}_3\text{N}_4$ grains. An increase in the sintering temperature further led to an increase of $\beta\text{-Si}_3\text{N}_4$ grains in the direction of length [the 3rd step of Fig. 6(a)] and the large elongated grains grew more via the Ostwald ripening process in specimen A. Grains with small sizes dissolved into the large grains, resulting in the large-elongated grain microstructure [the 4th step of Fig. 6(a)]. Conversely, specimens B and C had pre-existing $\beta\text{-Si}_3\text{N}_4$ particles, and hence, the grain growth was suppressed by the impingement of other $\beta\text{-Si}_3\text{N}_4$ grains.

The specimen B had pre-existing rod shaped particles, which acted as a seed and grew. The $\alpha\text{-Si}_3\text{N}_4$ particles also followed the same dissolve-re-precipitate process as in specimen A, but the situation after transformation was different. The formed $\beta\text{-Si}_3\text{N}_4$ could precipitate on either the pre-existing β -seed particle or on the phase transformed $\beta\text{-Si}_3\text{N}_4$ particle. Hence, two types of growth centers existed. With a further increase in the temperature, the initially pre-existing β -seed particle grew faster than the phase transformed $\beta\text{-Si}_3\text{N}_4$ particle resulting in abnormal grain

Fig. 6. Schematic diagram of grain growth process for raw powders with different α/β ratios (a) Powder A (mainly α phase), (b) Powder B (α/β mixed phase), and (c) Powder C (mainly β phase).

growth. The grain size of the phase transformed β - Si_3N_4 particle remained as small as possible, while the pre-existing β -seed particle grew into very large, elongated grains [Fig. 6(b)].

In the extremely β -rich case of specimen C, the initial rounded β - Si_3N_4 particle grew with temperature and time. Although it had a rounded morphology in the initial stage, the β - Si_3N_4 phase had a preferred growth direction, as the calculated equilibrium shape of β - Si_3N_4 was an elongated hexagonal-based prism with pyramidal ends.²⁸⁾ In the 2nd step in Fig. 6(c), the morphology changed into a hexagonal shape, and growth started. However, specimen C had several β -seeds to grow, while growth was already hindered at the beginning of the growth and densification process. This resulted in a monomial distribution and an equiaxed grain structure. [Fig. 6(c)]

With different microstructural evolutions, the properties of Si_3N_4 also varied. These properties are presented in Figs. 7 and 8 and are summarized in Table 3. The length, width, aspect-ratio (matrix grain and large grain, the grain width $< 1\ \mu\text{m}$ and $\geq 1\ \mu\text{m}$), fraction of matrix grain frequency, and flexural strength of the materials sintered at 1900°C were presented. Figure 7 shows the thermal conductivities and flexural strengths of the three specimens sintered at 1900°C . Specimen A had the lowest thermal conductivity and strength value. This was due to insufficient densification with porosity of approximately 20%. The thermal conductivities for specimens B and C showed similar values of 86 and 88 W/mK, respectively. Conversely, the flexural strengths for specimens B and C had different values of 913.6 and 690.5 MPa, respectively.

The enhancement in strength and the fracture toughness are closely related to the microstructure. At a temperature of 1900°C , specimen B has a bimodal microstructure with abnormal grain growth, which includes both small-sized matrix grains and large

Fig. 7. Thermal conductivity and flexural strength of specimens A, B, and C sintered at 1900°C for 6 h.

elongated grains. The large grains were surrounded by fine matrix grains and the amount of matrix grains was approximately 68%. The observed high flexural strength and fracture toughness were due to this bimodal microstructure evolution. The crack interactions increased due to a mix of large grains and fine matrix grains, thereby leading to an enhancement in the flexural strength.

In contrast, specimen C had a broader range of grains with monomial distribution. The size of the large grains was smaller, whereas the size of the matrix grains was larger than that of specimen B. It also had low quantities of matrix grains. Therefore, the crack interactions were reduced as a result of deficient growth of the large, elongated grains and the large-sized matrix grains, thereby resulting in lower flexural strength.

Table 3. Average lengths, and aspect-ratios of matrix grains and large grains, fraction of matrix grains, and flexural strengths of the three specimens sintered at 1900°C for 6 h (matrix grain: grain size < 1 μ m, large grain: grain size $\geq$ 1 μ m)

	A specimen		B specimen		C specimen	
	matrix	large	matrix	large	matrix	large
Length (μ m)	2.51	3.65	1.22	5.21	1.80	3.77
Aspect-ratio	3.12	2.47	2.56	2.48	2.49	2.45
Fraction of matrix grains (%)	27.3		68.5		52.2	
Flexural strength (MPa)	597.9		913.6		690.5

Fig. 8. Fracture toughness measured by Vickers hardness toughness technique for specimens B and C sintered at 1750 and 1900°C, respectively.

The starting raw powders also influenced the fracture toughness of the specimens. When α/β mixed raw powder was used, the fracture toughness increased and showed higher values than that of the specimens from β -rich raw powder, i.e., specimen C (Fig. 8). Although the fracture toughness increased with the sintering temperature for both specimens B and C, the significant increase with temperature was observed only in specimen B: resulting in value of 6.36 MPa.m^{1/2} at 1750°C, 7.81 MPa.m^{1/2} at 1900°C in specimen B and 6.13 MPa.m^{1/2} at 1750°C, 6.64 MPa.m^{1/2} at 1900°C in specimen C. **Figure 9** presents the crack propagation of specimen B and C sintered at 1750 and 1900°C. The crack propagations of both specimen B and C sintered at 1750°C were practically straight showing small amount of crack deflections due to the microstructure composed of small and more equiaxed grains [Figs. 9(a) and 9(c)]. The crack path in specimen B and C sintered at 1900°C showed that the crack tortuously propagated with the self-reinforced microstructure. Especially, the specimen B had large elongate grains embedded in a fine matrix grains resulting the toughening mechanism by crack deflection and bridging. On the other hand, specimen C had low quantities of fine matrix grains embedding the large elongated grains which indicated the monomial distribution of grains. As seen in Fig. 9(d), the crack deflection and bridging were occurred but the crack was more like a straight where large grains adjacent each other. Therefore, the significant toughening mechanism was observed only in specimen B.

4. Conclusion

The microstructural evolution of Si₃N₄ ceramics and their properties were analyzed, with respect to the initial α/β ratios of starting raw powders. The microstructure was tailored by varying

Fig. 9. The crack propagation of (a) specimen B, (c) specimen C sintered at 1750°C and (b) specimen B, (d) specimen C sintered at 1900°C. The crack propagated from left to right direction.

the with α/β ratio of the starting Si₃N₄ powders. The sintering of α/β mixed raw powder resulted in the evolution of a bimodal microstructure, where large elongated grains from pre-existing β -seeds were surrounded by finer matrix grains from phase transformed β -Si₃N₄ particles. Further, it was shown that the properties were related to their microstructures. Both high flexural strength and fracture toughness were observed for the Si₃N₄ ceramic sintered from α/β mixed raw powder. A relatively high thermal conductivity of 86 W/mK, a high flexural strength of 912 MPa, and a high fracture toughness of 7.88 MPa.m^{1/2} were obtained by controlling the microstructural evolution. In conclusion, it should be noted that the microstructure and the related properties of Si₃N₄ ceramics could be optimized for specific applications.

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Reference

- 1) F. L. Riley, *J. Am. Ceram. Soc.*, **83**, 245–265 (2000).
- 2) G. A. Schneider, *Ceram. Int.*, **17**, 325–333 (1991).
- 3) G. R. Anstis, P. Chantikul, B. R. Lawn and D. B. Marshall, *J. Am. Ceram. Soc.*, **64**, 533–538 (1981).
- 4) P. Chantikul, G. R. Anstis, B. R. Lawn and D. B. Marshall, *J. Am. Ceram. Soc.*, **64**, 539–543 (1981).

- 5) J. S. Haggerty, A. Lightfoot, J. E. Ritter, P. A. Gennari and S. V. Nair, *J. Am. Ceram. Soc.*, **72**, 1675–1679 (1989).
- 6) J. Szepvolgyi, I. Mohaitoth, I. Bertoti, E. Gilbart and F. L. Riley, *Key Engineering Materials*, **89–91**, 35–40 (1994).
- 7) K. Hirao, Y. Zhou, H. Hyuga, T. Ohji and D. Kusano, *J. Korean Ceram. Soc.*, **49**, 380–384 (2012).
- 8) Y. Zhou, H. Hyuga, D. Kusano, Y. Yoshizawa and K. Hirao, *Adv. Mater.*, **23**, 4563–4567 (2011).
- 9) P. F. Becher, G. S. Painter, N. Shibata, R. L. Satet, M. J. Hoffmann and S. J. Pennycook, *Materials Science and Engineering A*, **422**, 85–91 (2006).
- 10) M. J. Hoffmann, *Pure Appl. Chem.*, **67**, 939–946 (1995).
- 11) P. Sajgalik, J. Dusza and M. J. Hoffmann, *J. Am. Ceram. Soc.*, **78**, 2619–2624 (1995).
- 12) M. K. Park, H. N. Kim, K. S. Lee, S. S. Baek, E. S. Kang, Y. K. Baek and D. K. Kim, *Key Engineering Materials*, **287**, 247–252 (2005).
- 13) S. K. Lee, K. S. Lee, B. R. Lawn and D. K. Kim, *J. Am. Ceram. Soc.*, **81**, 2061–2070 (1998).
- 14) Y. G. Kim, J. Tatami, K. Komeya and D. K. Kim, *Thin Solid Films*, **510**, 222–228 (2006).
- 15) D. X. Yao, Y. F. Xia, Y. P. Zeng, K. H. Zuo and D. L. Jiang, *Mater. Lett.*, **68**, 75–77 (2012).
- 16) D. X. Yao, Y. F. Xia, K. H. Zuo, D. L. Jiang, J. Giinster, Y. P. Zeng and J. G. Heinrich, *J. Eur. Ceram. Soc.*, **34**, 3461–3467 (2014).
- 17) J. R. Zeng, I. Tanaka, Y. Miyamoto, O. Yamada and K. Niihara, *J. Am. Ceram. Soc.*, **75**, 148–152 (1992).
- 18) G. Woetting and E. Gugel, *Ceramic Forum International*, **74**, 239–244 (1997).
- 19) R. Klein, V. Medri, M. Desmaison-Brut, A. Bellosi and J. Desmaison, *J. Eur. Ceram. Soc.*, **23**, 603–611 (2003).
- 20) X. Lu, X. S. Ning, W. Xu, K. X. Chen and F. P. Zhou, *Rare Metal Mat Eng*, **32**, 129–132 (2003).
- 21) J. Q. Li, F. Luo, D. M. Zhu and W. C. Zhou, *J. Am. Ceram. Soc.*, **90**, 1950–1952 (2007).
- 22) S. Kuang, M. J. Hofmann, H. L. Lukas and G. Petzow, *Key Engineering Materials*, **89–91**, 399–404 (1994).
- 23) G. Ling and H. T. Yang, *Mater. Chem. Phys.*, **90**, 31–34 (2005).
- 24) N. Zhong, X. S. Ning, B. Bai and L. Du, *Rare Metal Mat Eng*, **40**, 506–509 (2011).
- 25) J. J. Kruzic, D. K. Kim, K. J. Koester and R. O. Ritchie, *J Mech Behav Biomed*, **2**, 384–395 (2009).
- 26) B. R. Lawn, D. B. Marshall, P. Chantikul and G. R. Anstis, *J Aust Ceram Soc*, **16**, 4–9 (1980).
- 27) M. Prokesova and Z. Panek, *Ceramics International*, **15**, 369–374 (1989).
- 28) M. Kramer, D. Wittmuss, H. Kuppers, M. J. Hoffmann and G. Petzow, *J. Cryst. Growth*, **140**, 157–166 (1994).