

High Thermal Conductivity Silicon Nitride Ceramic

Kiyoshi Hirao, Koji Watari, Hiroyuki Hayashi,
and Mikito Kitayama

Introduction

Since the confirmation that nonmetallic single crystals with a diamond-like structure, such as SiC, BP, and AlN, have high intrinsic thermal conductivities of over $300 \text{ W m}^{-1} \text{ K}^{-1}$,^{1,2} a great deal of effort has been focused on the development of nonoxide polycrystalline ceramics with high thermal conductivity. SiC and AlN ceramics with high thermal conductivities of over $200 \text{ W m}^{-1} \text{ K}^{-1}$ have been successfully fabricated, and they are used commercially as high thermal conductivity substrates, heatsinks, and so on. However, widespread use of these materials is still restricted, owing to the low reliability that arises from their poor mechanical properties. In addition, application of SiC ceramics is further limited by their low electric resistance and high dielectric constant. Hence, electrical industries actively search

for alternative materials with both high thermal conductivity and superior mechanical properties in order to manage the ever-increasing heat generated by electric devices.

Silicon nitride (Si_3N_4) ceramic, on the other hand, is well known as a high-temperature structural ceramic having high strength and fracture toughness. The excellent mechanical properties of Si_3N_4 result from its unique microstructure, which is composed of hexagonal, rodlike grains, bonded together and reinforcing each other.^{3–5} Recently, a Si_3N_4 ceramic with thermal conductivities of over $100 \text{ W m}^{-1} \text{ K}^{-1}$ was reported.^{6–9} In addition, considering the similarity of chemical bonding and crystal structure of Si_3N_4 to those of SiC and AlN, Haggerty and Lightfoot¹⁰ pointed out that single-crystal Si_3N_4 has a high intrinsic thermal conduc-

tivity of over $200 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature. These facts, combined with the excellent mechanical properties of Si_3N_4 ceramic, make it a serious candidate for high-performance substrates. This article summarizes recent results on the thermal conductivity of Si_3N_4 and discusses the extrinsic factors governing the thermal conductivity of Si_3N_4 ceramic in terms of microstructural parameters such as lattice defects in single-crystal Si_3N_4 and the morphology of grain-boundary secondary phases, comparing Si_3N_4 with the cases of SiC and AlN ceramics. In addition, high thermal conductivities achieved in textured Si_3N_4 are also introduced.

Processing and Microstructure of Nonoxide Ceramics

In general, because of their low self-diffusion coefficients even at high temperatures, nonoxide ceramics with high covalent bonding, such as Si_3N_4 , AlN, and SiC, are densified with the aid of sintering additives. SiC is generally densified through solid-phase sintering by adding small amounts of additives such as B, C,¹¹ and Be compounds,¹² although liquid-phase sintering of SiC using oxides or carbides has recently attracted attention as a method for developing anisotropic grains that act as reinforcements.¹³ On the other hand, AlN and Si_3N_4 are densified by liquid-phase sintering to lower the sintering temperatures because these nitrides, in particular Si_3N_4 , are not very stable at higher temperatures, as shown in Table I. A wide variety of oxides, such as alkaline-earth oxides and rare-earth oxides, are used as sintering additives for AlN and Si_3N_4 . During sintering, these additives react

Table I: Comparison of Si_3N_4 with AlN and SiC.

	Si_3N_4	AlN	SiC
Single-Crystal Form			
Crystallography	β - Si_3N_4 : hexagonal ($P6_3$)	Hexagonal (wurtzite)	Polypitism (3C, 2H, 4H, 15R, etc.)
Decomposition temperature	1850°C	2200°C (sublimation)	2800°C (sublimation)
Intrinsic thermal conductivity	$200 \text{ W m}^{-1} \text{ K}^{-1}$ or $320 \text{ W m}^{-1} \text{ K}^{-1}$ (Reference 10)	$320 \text{ W m}^{-1} \text{ K}^{-1}$ (Reference 1)	$490 \text{ W m}^{-1} \text{ K}^{-1}$ (Reference 1)
Polycrystalline Form			
General sintering process	Liquid-phase sintering	Liquid-phase sintering	Solid-phase sintering (Liquid-phase sintering)
Secondary phase	Mainly amorphous ($\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$)	Mainly crystalline ($\sim 10 \text{ W m}^{-1} \text{ K}^{-1}$)	—
Morphology of secondary phase	Glass pocket Thin film	Dispersion (Thin film)	—
Highest experimental conductivity	$155 \text{ W m}^{-1} \text{ K}^{-1}$ (Reference 33)	$\sim 260 \text{ W m}^{-1} \text{ K}^{-1}$ (Reference 39)	$270 \text{ W m}^{-1} \text{ K}^{-1}$ (Reference 12)
Bending strength*	600–1500 MPa	300–350 MPa	380–800 MPa
Fracture toughness*	5–7 MPa $\text{m}^{1/2}$	3–4 MPa $\text{m}^{1/2}$	3.5–4.5 MPa $\text{m}^{1/2}$

* Data taken from catalog of commercially supplied materials.

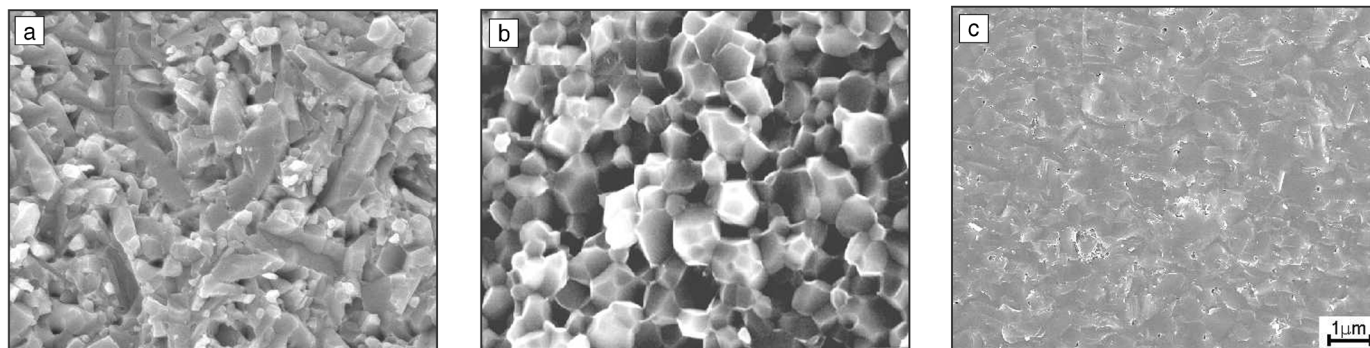


Figure 1. Fractured surfaces of (a) Si_3N_4 , (b) AlN , and (c) SiC ceramics.

with impurity oxides largely present as a surface film on the nitride powder, Al_2O_3 in AlN and SiO_2 in Si_3N_4 , respectively, to form a liquid phase, which enhances densification through the rearrangement of particles and a solution re-precipitation reaction. In silicon nitride, there are two crystalline phases designated as α and β , which are the low- and high-temperature phases, respectively. Since the α -to- β phase transformation during liquid-phase sintering promotes the development of elongated β - Si_3N_4 grains,¹⁴ α - Si_3N_4 powder is generally used as a starting raw powder. After sintering, the liquid phase remains in the corners of or along the matrix grains as a glassy phase or crystalline phases (referred to as secondary phases), the volume fractions of which are typically 5–10%.

Typical fractured surfaces of liquid-phase-sintered Si_3N_4 , as well as of liquid-phase-sintered AlN and solid-phase-sintered SiC , are shown in Figures 1a, 1b, and 1c, respectively. SiC and AlN exhibit homogeneous microstructures composed of equiaxial grains. In addition, SiC shows a transgranular mode of fracture, owing to the strong bonding between grains. Poor fracture toughness of SiC and AlN is ascribed to such homogeneous microstructure. In contrast, Si_3N_4 is composed of rodlike grains, reflecting the preferential growth in the $[001]$ direction in β - Si_3N_4 .¹⁵ These rodlike grains, in turn, act as reinforcements that promote crack-bridging processes and toughen the Si_3N_4 . Figure 2 illustrates the microstructural factors of Si_3N_4 affecting thermal conductivity. Lattice defects in β - Si_3N_4 grains and grain-boundary phases are considered to be extrinsic factors affecting the thermal conductivity of Si_3N_4 . Although the microstructures of AlN and Si_3N_4 are different, the chemistry and processing of them are similar in many ways, as summarized in Table I. The extrinsic factors governing the thermal conductivity of Si_3N_4 , therefore,

can be discussed based on the results obtained for AlN , as described next.

Effect of Impurity Atoms on Thermal Conductivity

The conduction of heat in dielectric ceramics is dominated by phonon transport: at room temperature, a greater influence in phonon scattering is attributed to imperfections in the crystal lattice, for example, impurity atoms, interstitials, and vacancies. Slack et al. have systematically investigated the effect of impurities on thermal conductivities of nonmetallic crystals, and have revealed the strong correlation between the concentration of lattice oxygen and the thermal conductivity of single-crystal AlN .^{1,2} Several additional studies on polycrystalline AlN ceramic were carried out,^{16–18} and it is now well recognized that oxygen as an impurity is a dominant factor lowering the thermal conductivity of AlN ceramic. It is assumed that oxygen dissolved in an AlN lattice creates vacancies

in aluminum sites that scatter phonons and thereby lowers the thermal conductivity.¹ Therefore, in developing high thermal conductivity AlN ceramic, much attention has been paid to researching the sintering additives that are able to remove oxygen from AlN crystals during sintering.^{16,19}

In the case of Si_3N_4 ceramic, it is well recognized that the use of Al_2O_3 , one of the available sintering additives for Si_3N_4 ceramic, considerably lowers the thermal conductivity because Al_2O_3 reacts with Si_3N_4 to form the solid solution of β - Si_3N_4 , which has the chemical formula of $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ (referred to as β -Sialon, $0 < z < 4.2$).^{7,20} β -Sialon is formed by the simultaneous equivalent substitution of Al-O for Si-N in β - Si_3N_4 . However, there have been no reports on whether oxygen alone can be incorporated into the β - Si_3N_4 crystal lattice. Recently, Kitayama et al.²¹ succeeded in measuring the oxygen con-

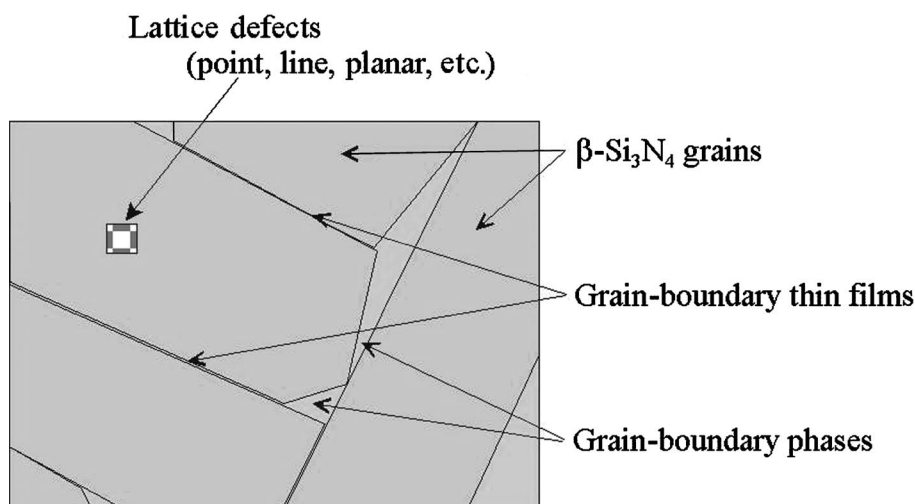


Figure 2. Microstructural factors of Si_3N_4 ceramic affecting thermal conductivity.

tent in the β - Si_3N_4 crystal lattice by the hot-gas extraction method, revealing that oxygen can be dissolved into the β - Si_3N_4 lattice up to at least 0.4% by mass. Based on electron spin resonance analysis,²² they also reported that the incorporation of oxygen into the β - Si_3N_4 lattice occurs by the dissolution of SiO_2 in the following plausible reaction:



where O_{N} and V_{Si} denote oxygen in a nitrogen site and a vacant silicon site, respectively. Applying these analytical methods to hot-pressed Si_3N_4 with Y_2O_3 and SiO_2 , they have established that the thermal conductivity of β - Si_3N_4 ceramic increases with decreasing oxygen content in the Si_3N_4 single-crystal lattice. This investigation also indicated that the lattice oxygen content varies with the $\text{Y}_2\text{O}_3/\text{SiO}_2$ ratio. As the grain growth of β - Si_3N_4 after phase transformation occurs such that smaller β - Si_3N_4 grains dissolve into the liquid phase to re-precipitate on larger β - Si_3N_4 grains, the lattice oxygen content might be closely related to the composition of the liquid phase. Kitayama et al. have explained the variation of lattice oxygen with the $\text{Y}_2\text{O}_3/\text{SiO}_2$ ratio, based on the thermodynamic consideration of the grain-boundary phase.²² In addition to the $\text{Y}_2\text{O}_3/\text{SiO}_2$ ratio, a family of rare-earth oxides, Re_2O_3 ($\text{Re} = \text{Sc}, \text{Yb}, \text{Y}, \text{Nd}$, etc.), affects the thermal conductivity of Si_3N_4 ceramic. It was revealed that as the ionic radius of the rare-earth element decreases, grain growth of β - Si_3N_4 is enhanced, lattice oxygen of β - Si_3N_4 grains decreases, and hence thermal conductivity of the specimen increases.²³ The results indicated that Yb_2O_3 and Y_2O_3 are suitable additives for fabricating high thermal conductivity Si_3N_4 , compared with other rare-earth oxides.

Hayashi et al.²⁴ have further investigated the relation between lattice oxygen content and thermal conductivity, using β - Si_3N_4 as a raw powder in order to exclude the influence of phase transformation. In their study, β - Si_3N_4 with concurrent addition of Yb_2O_3 and MgO was sintered at 1900°C under 0.9 MPa nitrogen pressure. Figure 3 shows the effect of sintering time on the lattice oxygen content and the thermal conductivity of sintered Si_3N_4 . The lattice oxygen, which in raw β - Si_3N_4 powders was about 0.4% by mass, decreased with increasing sintering time. As a result, the thermal conductivity of the specimen increased with sintering time, and a high thermal conductivity of about $120 \text{ W m}^{-1} \text{ K}^{-1}$ could be achieved in a specimen sintered for a very long time. Considerable grain growth of β - Si_3N_4

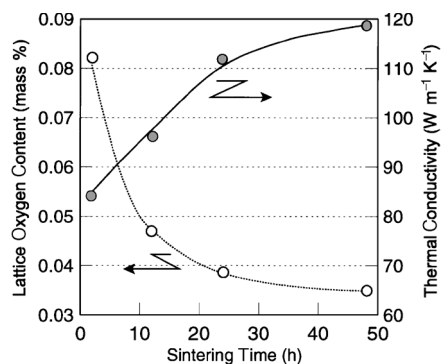


Figure 3. Effect of sintering time on the lattice oxygen content and the thermal conductivity of Si_3N_4 with 2mol% Yb_2O_3 -5mol% MgO sintered at 1900°C under 0.9 MPa N_2 .

with sintering time was observed, as shown in Figure 4. It is therefore evident that a decrease in lattice oxygen content, namely, purification of β - Si_3N_4 grains, is significantly affected by the solution re-precipitation process, which results in grain growth of β - Si_3N_4 . Figure 5 summarizes the relation between the lattice oxygen content in β - Si_3N_4 and the thermal resistivity of these specimens, along with the results obtained by Kitayama et al.²² Although processing method, type of raw Si_3N_4 powder, and additive system used were quite different between these investigations, there is a clear tendency for thermal resistivity to decrease with decreasing lattice oxygen content. The result suggests that lattice oxygen content in β - Si_3N_4 is a dominant extrinsic factor governing the thermal conductivity of Si_3N_4 ceramic, as has been demonstrated in AlN ceramic. Moreover, by extrapolation, it can be said that β - Si_3N_4 free from lattice oxygen should exhibit at least a thermal conductivity of about $180 \text{ W m}^{-1} \text{ K}^{-1}$.

Effect of Secondary Phases on Thermal Conductivity

The morphology of the secondary phases in AlN and Si_3N_4 ceramics, in addition to the lattice oxygen content, negatively affects the thermal conductivity to some extent because these phases have thermal conductivities 1–2 orders of magnitude lower than pure AlN or Si_3N_4 crystals. For example, the thermal conductivities of yttrium aluminate (typical secondary phase in AlN with Y_2O_3 addition) and oxynitride glass (typical secondary phase in Si_3N_4) are about $10 \text{ W m}^{-1} \text{ K}^{-1}$ and $1 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. Considering the effect of distribution of a secondary phase with low thermal conductivity based on the simple dispersed model,²⁵ a continuous distribu-

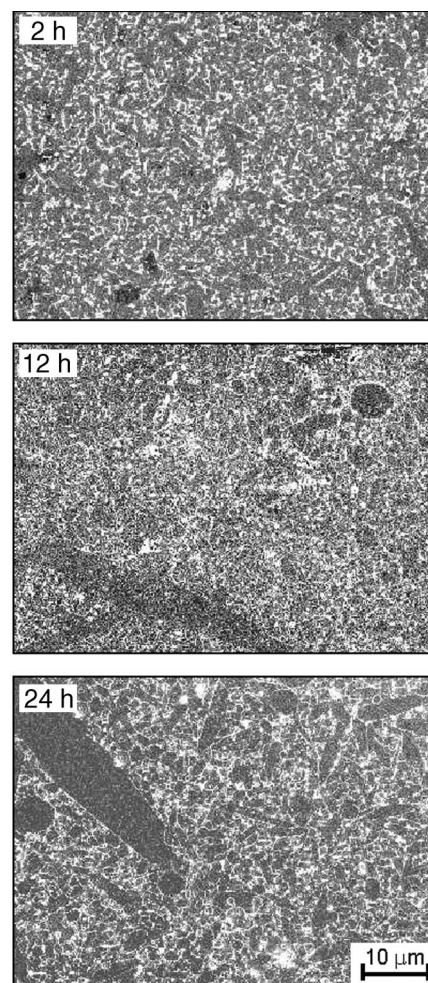


Figure 4. Variation of microstructure of Si_3N_4 with 2mol% Yb_2O_3 -5mol% MgO with sintering time. Specimens were sintered at 1900°C under 0.9 MPa N_2 .

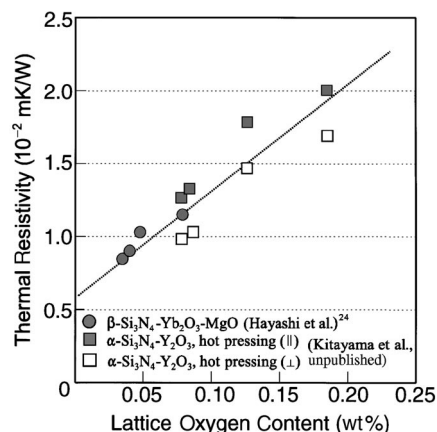


Figure 5. Effect of lattice oxygen content on thermal resistivity of Si_3N_4 fabricated by gas-pressure sintering (●) and hot-pressing (■, □).

tion around the matrix grains extensively lowers the thermal conductivity, while an isolated distribution does not appreciably affect the thermal conductivity. In the case of AlN ceramic, it has been confirmed that the secondary phases have little influence on the thermal conductivity because they are present largely as isolated crystalline phases, and that the amount of secondary phase in AlN ceramic has a major influence on thermal conductivity only if the lattice oxygen content in the AlN is very low and the amount of secondary phase is rather large.^{18,26,27}

Compared with AlN ceramic, the microstructure of Si₃N₄ ceramic is more complicated, owing to the well-faceted grains with a rodlike shape, as illustrated in Figure 2. Most of the secondary phase is generally present as a glassy phase because the liquid phase containing SiO₂ is difficult to crystallize perfectly. It should be noted that the thermal conductivity of glass can be as low as 1 W m⁻¹ K⁻¹, which is about one order of magnitude lower than the thermal conductivity of the crystalline secondary phase in AlN ceramic. In addition, this glassy phase is distributed not only as glass pockets surrounded by β-Si₃N₄ grains, but also in the openings between two grains, as most of rodlike β-Si₃N₄ grains incline toward each other. It is reasonable to think that the negative effect of the secondary phase on thermal conductivity is somewhat more pronounced in Si₃N₄ ceramic than AlN ceramic.

In addition, grain-boundary thin films with an equilibrium thickness (typically 1–2 nm) are generally present between two-grain junctions in liquid-phase-sintered Si₃N₄ ceramic.²⁸ A calculation based on a simple modified Wiener's model²⁹ for the thermal conductivity of a composite material predicts that the thermal conductivity of β-Si₃N₄ ceramic having grain-boundary films of a few nanometers' thickness de-

creases quickly as the size of the β-Si₃N₄ grains decreases to less than 1 μm.³⁰ From this viewpoint, in addition to the role of purifying the β-Si₃N₄ lattice, grain growth is necessary in order to improve the thermal conductivity of Si₃N₄ ceramic. However, it should be noted that grain-boundary thin films have little effect on the thermal conductivity of Si₃N₄ when the grain size exceeds certain critical values (about 1 μm).

High Thermal Conductivity in Anisotropic Microstructures

Another approach for achieving high thermal conductivity in Si₃N₄ ceramic is to develop a textured microstructure in which elongated β-Si₃N₄ grains are oriented almost unidirectionally. High thermal conductivity along the grain orientation is expected, compared with material with a random distribution of β-Si₃N₄ grains, for the following reasons: the alignment of elongated β-Si₃N₄ grains, in turn, causes the glassy phase to be distributed parallel to the grain orientation, which minimizes the negative effect of the glassy phase with low thermal conductivity; in addition, high-resolution thermoreflectance microscopy measurements of the extra large β-Si₃N₄ grains reveal that the thermal diffusivity and conductivity of β-Si₃N₄ crystals along the *c* axis, namely, along the length of the rodlike grains, are higher than those along the *a* axis.³¹ Detailed microthermal characterization of grains in ceramic materials is mentioned in the article by Fournier in this issue.

Such anisotropic microstructures can be fabricated by the combination of the seeding of rodlike β-Si₃N₄ nuclei and a forming process generating shear stress, such as tape casting and extrusion.^{6,32–35} This process is based on the grain-growth behavior of silicon nitride: during α-to-β phase transformation, the preferential nucleation site of the newly formed β-Si₃N₄

phase is pre-existing β particles,^{36,37} and after transformation, only some large β grains selectively grow, particularly along the *c* axis direction, by a solution reprecipitation reaction.³⁸ Figure 6 shows the typical microstructure of seeded and extruded Si₃N₄. The material exhibits high anisotropy where large elongated grains, grown from seeds, are almost unidirectionally oriented parallel to the extruding direction.³⁵ Table II summarizes the thermal conductivities, measured in three different directions, for textured Si₃N₄ fabricated by this method with different sintering additives. As expected, for all of the specimens, thermal conductivity is highest along the grain alignment. In particular, highly anisotropic Si₃N₄ with very long grains, fabricated under extreme conditions, exhibits a high thermal conductivity of about 150 W m⁻¹ K⁻¹ in the direction parallel to the grain alignment.³³

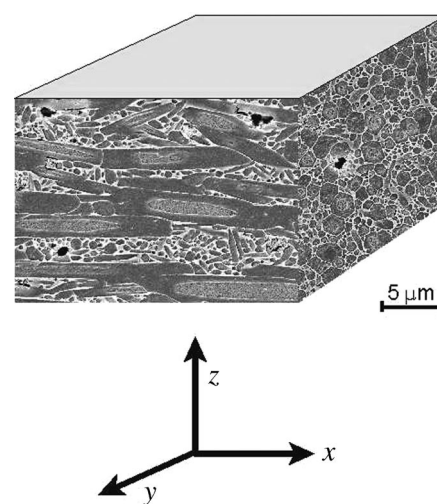


Figure 6. Microstructure of textured Si₃N₄ ceramic.

Table II: Thermal Conductivity in Three Directions for Textured Si₃N₄ fabricated by Combined Seeding and Tape Casting.

Sample No.	Sintering Additives	Annealing Conditions (temperature, time, pressure)	Thermal Conductivity	References
			(W m ⁻¹ K ⁻¹) (x direction, y direction, z direction)	
1	5 mass% Y ₂ O ₃	2123 K 66 h 0.9 MPa N ₂	121, 75, 60	Hirao et al. ⁶
2	5 mass% Y ₂ O ₃	2773 K 2 h 200 MPa N ₂	155, 67, 52	Watari et al. ³³
3	0.5 mol% Y ₂ O ₃ 0.5 mol% Nd ₂ O ₃	2423 K 4 h 30 MPa N ₂	137, 97, 72	Hirosaki et al. ³⁴

Summary

The thermal conductivity of Si_3N_4 ceramic at room temperature is basically governed by the lattice oxygen content in the $\beta\text{-Si}_3\text{N}_4$ crystal. Therefore, in order to improve thermal conductivity, it is important to purify the grains, as has been demonstrated in AlN ceramic. The purification of $\beta\text{-Si}_3\text{N}_4$ grains can be achieved through a solution re-precipitation reaction during sintering using sintering additives that have a great affinity for SiO_2 , such as Y_2O_3 and Yb_2O_3 . As far as the authors know, Si_3N_4 ceramic with a high thermal conductivity of over $100 \text{ W m}^{-1} \text{ K}^{-1}$ has been fabricated only by gas-pressure sintering. From a commercial point of view, it is very important to fabricate high thermal conductivity Si_3N_4 ceramic by a conventional sintering technique such as pressureless sintering. Seeding, combined with careful control of grain-boundary composition, may be one of the processing strategies for this purpose. In addition, microstructure design for harmonizing high thermal conductivity with good mechanical and electrical properties (such as low dielectric constant) is also very important for the widespread use of Si_3N_4 ceramic as a high thermal conductivity material.

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References

- G.A. Slack, *J. Phys. Chem. Solids* **34** (1973) p. 321.
- G.A. Slack, R.A. Tanzilli, R.O. Pohl, and J.W. Vandersande, *J. Phys. Chem. Solids* **48** (1987) p. 641.
- E. Tani, S. Umebayashi, K. Kishi, K. Kobayashi, and M. Nishijima, *Am. Ceram. Soc. Bull.* **65** (1986) p. 1311.
- C.W. Li and J. Yamanis, *Ceram. Eng. Sci. Proc.* **10** (1989) p. 632.
- P.F. Becher, *J. Am. Ceram. Soc.* **74** (1991) p. 255.
- K. Hirao, K. Watari, M.E. Brito, M. Toriyama, and S. Kanzaki, *J. Am. Ceram. Soc.* **79** (1996) p. 2485.
- N. Hirotsaki, Y. Okamoto, M. Ando, F. Munakata, and Y. Akimune, *J. Am. Ceram. Soc.* **79** (1996) p. 2878.
- K. Watari, K. Hirao, M. Toriyama, and K. Ishizaki, *J. Am. Ceram. Soc.* **82** (1999) p. 777.
- N. Hirotsaki, Y. Okamoto, F. Munakata, and Y. Akimune, *J. Eur. Ceram. Soc.* **19** (1999) p. 2183.
- J.S. Haggerty and A. Lightfoot, *Ceram. Eng. Sci. Proc.* **16** (1995) p. 475.
- S. Prochazka and R.J. Charles, *Am. Ceram. Soc. Bull.* **52** (1973) p. 885.
- Y. Takeda, K. Usami, K. Nakamura, S. Ogihara, K. Maeda, T. Miyoshi, S. Shinozaki, and M. Ura, *Advances in Ceramics*, Vol. 7, edited by M.F. Yan and A.H. Heuer (American Ceramic Society, Columbus, OH, 1984) p. 253.
- N.P. Padture, *J. Am. Ceram. Soc.* **77** (1994) p. 519.
- F.F. Lange, *J. Am. Ceram. Soc.* **62** (1979) p. 428.
- C.M. Hwang, T.Y. Tien, and I.-W. Chen, in *Proc. Sintering '87*, edited by S. Somiya, M. Shimada, M. Yoshimura, and R. Watanabe (Elsevier Applied Science Publishers, Essex, 1988) p. 1034.
- A.V. Virkar, T.B. Jackson, and R.A. Cutler, *J. Am. Ceram. Soc.* **72** (1989) p. 2031.
- R.R. Lee, *J. Am. Ceram. Soc.* **74** (1991) p. 2242.
- T.B. Jackson, A.V. Virk, K.L. More, R.B. Dinwiddie Jr., and R.A. Cutler, *J. Am. Ceram. Soc.* **80** (1997) p. 1421.
- K. Watari, H.J. Hwang, M. Toriyama, and S. Kanzaki, *J. Mater. Res.* **14** (1999) p. 1409.
- K. Watari, Y. Seki, and K. Ishizaki, *J. Ceram. Soc. Jpn.* **97** (1989) p. 56.
- M. Kitayama, K. Hirao, A. Tsuge, M. Toriyama, and S. Kanzaki, *J. Am. Ceram. Soc.* **82** (1999) p. 3263.
- M. Kitayama, K. Hirao, A. Tsuge, K. Watari, M. Toriyama, and S. Kanzaki, *J. Am. Ceram. Soc.* **83** (2000) p. 1985.
- M. Kitayama, K. Hirao, K. Watari, M. Toriyama, and S. Kanzaki, *J. Am. Ceram. Soc.* **84** (2001) p. 353.
- H. Hayashi, M. Kitayama, K. Hirao, Y. Yamauchi, and S. Kanzaki, submitted to *J. Am. Ceram. Soc.*
- W.D. Kingery, *J. Am. Ceram. Soc.* **42** (1959) p. 617.
- H. Buhr and G. Müller, *J. Eur. Ceram. Soc.* **12** (1993) p. 271.
- W.-J. Kim, D.K. Kim, and C.H. Kim, *J. Am. Ceram. Soc.* **79** (1996) p. 1066.
- H.-J. Kleebe, M.K. Cinibulk, R.M. Cannon, and M. Rühle, *J. Am. Ceram. Soc.* **76** (1993) p. 1969.
- O. Wiener, *Phys. Z.* **5** (1904) p. 332.
- M. Kitayama, K. Hirao, K. Watari, M. Toriyama, and S. Kanzaki, *J. Am. Ceram. Soc.* **82** (1999) p. 3105.
- B. Li, L. Pottier, J.P. Roger, D. Fournier, K. Watari, and K. Hirao, *J. Eur. Ceram. Soc.* **19** (1999) p. 1631.
- K. Hirao, M. Ohashi, M.E. Brito, and S. Kanzaki, *J. Am. Ceram. Soc.* **78** (1995) p. 1687.
- K. Watari, K. Hirao, M.E. Brito, M. Toriyama, and S. Kanzaki, *J. Mater. Res.* **14** (1999) p. 1538.
- N. Hirotsaki, M. Ando, Y. Okamoto, F. Munakata, Y. Akimune, K. Hirao, K. Watari, M.E. Brito, M. Toriyama, and S. Kanzaki, *J. Ceram. Soc. Jpn.* **104** (1996) p. 1171.
- H. Teshima, K. Hirao, M. Toriyama, and S. Kanzaki, *J. Ceram. Soc. Jpn.* **107** (1999) p. 1216.
- G. Petzow and M.J. Hoffmann, *Mater. Sci. Forum* **113–115** (1993) p. 91.
- W. Dressler, H.-J. Kleebe, M.J. Hoffmann, M. Rühle, and G. Petzow, *J. Eur. Ceram. Soc.* **16** (1996) p. 3.
- H. Emoto and M. Mitomo, *J. Eur. Ceram. Soc.* **17** (1997) p. 797.
- H. Buhr, G. Müller, H. Wiggers, F. Aldinger, P. Foley, and A. Roosen, *J. Am. Ceram. Soc.* **74** (1991) p. 718. □

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