

High Thermal Conductivity Non-Oxide Ceramics

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高熱伝導非酸化物セラミックス

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Thermal conductivity is one of significant physical properties of engineering materials. It has been confirmed through the thermal conductivity measurements of natural and synthetic materials, and from theoretical calculations that the theoretical conductivities of diamond, BN, SiC, BeO, BP and AlN are larger than $300 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at room temperature, being classed as high thermal conductivity solids. Non-oxide ceramic polycrystals with conductivities close to those of single crystals have been developed through the advances in ceramic processing. In recent years, the thermal conductivity exceeding $150 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ has been reported for $\beta\text{-Si}_3\text{N}_4$ ceramics, joining a group of high thermal conductivity solids. The non-oxide ceramics have been progressively used as heat-dissipating substrates for highly integrated circuits and optoelectronics, structural components for producing semi-conductors, engine-related material components and so on. Accordingly, the significance of high thermal conductivity non-oxide ceramics has been highly recognized in many industrial fields. In this review, the test results of thermal conductivity of non-oxide ceramics, such as SiC, AlN and Si_3N_4 , are summarized, and then, the effects of processing and microstructural parameters on their thermal conductivities are discussed. Based on the experimental data, the mechanisms of thermal conduction in non-oxide ceramics are examined. The processing strategy leading to high thermal conductivity non-oxide ceramics is also addressed.

[Received August 7, 2000]

Key-words : SiC, AlN, Si_3N_4 , Thermal conductivity

1. Introduction

Many oxide materials are inherently stable. However, the exception of diamond, the majority of non-oxide materials do not exist in the form of minerals. Non-oxide ceramics, which include carbides, nitrides, borides and silicides, were discovered in the 19th century. Researches on their processing and performance have been actively carried out in the eighth and ninth decades of the 20th century, and it has been established that nitride and carbide ceramics demonstrate unique mechanical, electrical, and magnetical performances, compared to oxide ceramics.^{1),2)} Thermal conductivity is an important physical property of ceramics. Practically, it determines the reliability and performance of engineering components in many industrial applications, since the magnitude of thermal conductivity influences strongly the rate of heat dissipation. Development of high thermal conductivity ceramics and enhancement of thermal conductivity are crucial for making reliable components with high performance. In this review, high thermal conductivity carbide (SiC) and nitride (AlN, Si_3N_4) ceramics are discussed, and the studies for their thermal conductivity are summarized.

2. Intrinsic thermal conductivity

Extensive investigation and characterization of high thermal conductivity solids were conducted from 1960 to 1985. These results were systematically summarized by Slack.³⁾ The measurements of thermal conductivity measurements of natural and synthetic diamond, BN, SiC, BeO, BP and AlN confirmed that they are all high thermal conductivity solids with the values at room-temperature of $>300 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$.³⁾ In particular, exciting research on the thermal conductivity of diamond and AlN was carried out. It was found that nitrogen atoms for diamond and oxygen atoms for AlN are impurities which significantly affect the conductivity. It was also predicted, from a relationship between ex-

perimental conductivity and impurity concentration of high purity materials, that intrinsic thermal conductivities at room-temperature of diamond and AlN are 2000 and $320 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively (see Table 1).^{3),4)} On the other hand, intrinsic values for SiC, BeO and BP were estimated from the temperature dependence of the conductivity of single crystals and ceramics, and were reported to be 540, 370 and $360 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively.³⁾

The intrinsic thermal conductivity ($\kappa_{\text{intrinsic}}$) of nonmetallic solids in the temperature range $T \geq \theta_D$, where θ_D is the Debye temperature, can be described by the following equation:

$$\kappa_{\text{intrinsic}} = BM \delta \theta_D^3 / (T\gamma) \quad (1)$$

where B is a constant, M the average mass of atoms in the crystal, δ^3 the average volume occupied by one atom of the crystal, T the absolute temperature and γ Gruneisen's constant.^{5),6)} Slack found a proportional relationship between the intrinsic conductivity calculated from impurity

Table 1. Value of Intrinsic Thermal Conductivity ($\kappa_{\text{intrinsic}}$), Debye Temperature (θ_D), Average Mass (M), Average Volume Occupied by One Atom (δ), Gruneisen's Constant (γ) and $M \delta \theta_D^3$ of Nonmetallic Materials. Data was Obtained from References.^{3),4),9),10),12)}

Crystal	$\kappa_{\text{intrinsic}}$ ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	θ_D (K)	M (g)	δ (10^{-10} m)	γ	$M \delta \theta_D^3$ ($\text{gmK}^3 \times 10^{-4}$)
Diamond	2000	2240	12.0	1.78	1.3	23.8
BN	760	1900	12.4	1.81		15.4
SiC	540	1080	20.1	2.18	0.76	5.5
BeO	370	1280	12.5	1.90		5.0
BP	360	985	20.9	2.27		4.5
AlN	320	950	20.5	2.18	0.77	3.8
Si_3N_4	320	1100	20.0	2.18	0.72	5.8

concentration of high-purity nonmetallic solids and the value of $M \delta \theta_D^3$ at 300 K, and predicted that the intrinsic value of BN is $760 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$.³⁾ The values of $\kappa_{\text{intrinsic}}$, θ_D , M , δ , γ , and $M \delta \theta_D^3$ at 300 K of high thermal conductivity solids are summarized in Table 1. The results suggest that materials with a higher Debye temperature, a lower atomic mass, and a simpler crystalline structure should have higher intrinsic thermal conductivities.³⁾

Recent work has demonstrated that $\beta\text{-Si}_3\text{N}_4$ ceramics with highly oriented grains have thermal conductivities higher than $150 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at room-temperature,^{7,8)} indicating that $\beta\text{-Si}_3\text{N}_4$ is one of the high thermal conductivity nonmetallic solids. Comparison between values of θ_D , M , δ and γ of high thermal conductivity nonmetallic solids and $\beta\text{-Si}_3\text{N}_4$ is of interest. The values for $\beta\text{-Si}_3\text{N}_4$ are $\theta_D = 1100 \text{ K}$,⁹⁾ $M = 20.0 \text{ g}$, $\gamma = 0.218 \text{ nm}$ ¹⁰⁾ and $\gamma = 0.72$,¹⁰⁾ as shown in Table 1. These values are almost equal to those of SiC: $\theta_D = 1080 \text{ K}$, $M = 20.1 \text{ g}$, $\delta = 0.218 \text{ nm}$ and $\gamma = 0.76$,³⁾ and AlN: $\theta_D = 950 \text{ K}$, $M = 20.5 \text{ g}$, $\delta = 0.218 \text{ nm}$ and $\gamma = 0.77$.⁴⁾ The result implies that $\beta\text{-Si}_3\text{N}_4$ satisfies the conditions for high thermal conductivity.

Calculating the intrinsic conductivity of $\beta\text{-Si}_3\text{N}_4$ is significant. Watari et al. estimated from a proportional relationship between the intrinsic conductivity and the value of $M \delta \theta_D^3$ ³⁾ that the upper limit of the intrinsic conductivity is $400 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at room-temperature.¹¹⁾ On the other hand, Haggerty and Lightfoot stated that SiC and $\beta\text{-Si}_3\text{N}_4$ are almost identical except for the number (n) of atoms in each primitive cell, and reported that a predicted intrinsic value is $\sim 200 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for $n = 14$, and $\sim 320 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for $n = 7$.¹²⁾ Considering the experimental conductivity and the purity of $\beta\text{-Si}_3\text{N}_4$ single crystal grains,¹³⁾ we assume that the intrinsic value is $\sim 320 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$.

3. Experimental thermal conductivity

3.1 Silicon carbide

SiC has polytypisms with over a hundred crystallographic modifications, e.g. cubic 3C, hexagonal 4H, 6H, 8H, rhombohedral 15R, 21R etc..^{14),15)} High-temperature treatments often lead to a change in the crystal structure depending on firing conditions including firing temperature, quality and type of raw powders, and type of sintering aids.¹⁶⁾ Among the SiC polytypes, most work on the conductivity has been focussed on SiC ceramics with a large amount of 6H.

Initial work on SiC ceramics has focussed on densification. It is difficult to obtain dense materials because of the strong covalent bonding. To obtain dense ceramics, applied pressure during sintering and addition of effective additives were key points. Hot-pressing has been always employed for fabricating dense SiC. Addition of useful additives remarkably promotes the densification. Effect of the type of sintering aids on the densification has been investigated since 1956,¹⁷⁾ and it was found that Al,¹⁷⁾ B,¹⁸⁾ BeO¹⁹⁾ and Al_2O_3 ²⁰⁾ are effective sintering aids. One of the most successful methods to obtain dense ceramics at lower firing temperature is liquid-phase sintering by adding Al_2O_3 and Y_2O_3 .^{20),21)} The conductivities of dense SiC are remarkably affected by the type of sintering aids.²²⁾ High thermal conductivity of $270 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ was obtained, when BeO was employed.¹⁹⁾ On the other hand, the conductivity was $170 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for B addition,¹⁹⁾ $60 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for Al addition,¹⁹⁾ $120\text{--}185 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for Al_2O_3 addition²³⁾ and $75\text{--}90 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ addition.²⁴⁾ The difference in conductivities of the samples was explained from the concentration of aid elements dissolved in the grains.¹⁹⁾ The solubility of Be is $\sim 8 \times 10^{18} \text{ cm}^{-3}$, which is much less than those of B and Al, 1×10^{20} and $1 \times 10^{21} \text{ cm}^{-3}$, respectively.²⁵⁾ Therefore, procurement of optimized additives contributed principally to enhancement of the conductivity

of SiC ceramics as shown in Fig. 1.

The effect of phase development of SiC polytypes on the conductivity of ceramics should be noted. Work by Sakai and Aikawa,²⁶⁾ and Liu and Lin²⁴⁾ reported that the conductivity of SiC decreases appreciably with increasing the quantity of 4H SiC. However, a detailed relationship between the conductivity of SiC ceramics and phase content of 4H, 8H, 15R etc., has not yet been clarified.

The polytype 3C SiC, which has a cubic structure, is postulated to have the highest thermal conductivity among the SiC polytypes because of its high symmetry and order in the crystal structure. Yasutomi et al. have fabricated a ceramic consisting of a large amount of 3C by pressureless sintering of B-doped 3C-SiC powders with BeO addition, and reported that this material shows a value of $230 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$.²⁷⁾ Since the relative density of this material was 94%, further enhancement of the conductivity is expected due to full densification.

Thermal conductivity of high-purity 6H SiC single crystals has been studied by many researchers, and is reported to be in the range of $130\text{--}490 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at room-temperature.^{3),28)\text{--}31)} Figure 2 indicates temperature dependence of the conductivity of SiC single crystals and ceramics. Data of intrinsic conductivity of SiC³⁾ is also plotted. Variation of intrinsic conductivities and experimental conductivities of single crystal as a function of temperature is

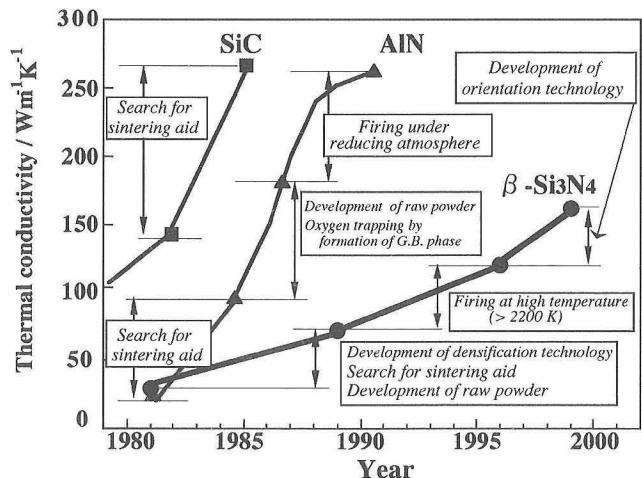


Fig. 1. Enhancement of thermal conductivity of SiC, AlN and $\beta\text{-Si}_3\text{N}_4$ ceramics in the period of 1980–2000.

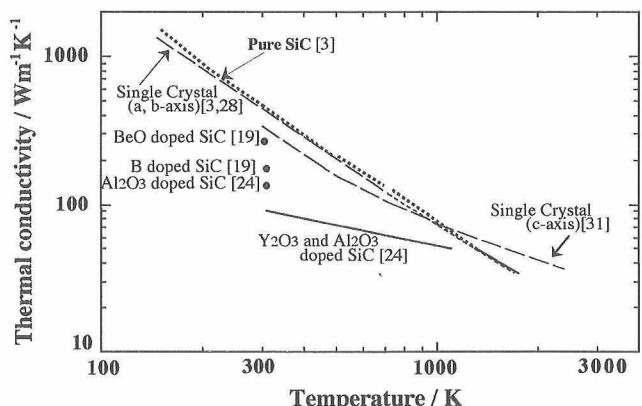


Fig. 2. Thermal conductivity at various temperatures of SiC single crystal and ceramics.

similar, since the single crystal possesses very high-purity. However, thermal conductivities of SiC ceramics with additions of B, Al₂O₃ and Y₂O₃-Al₂O₃ are much lower than intrinsic conductivities and experimental conductivities of single crystals.

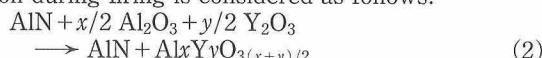
3.2 Aluminum nitride

Thermal conductivity of sintered AlN was enhanced through three developmental stages:³²⁾ (1) search for an effective sintering aid, (2) development of high-purity, fine powders, and oxygen trapping into grains by formation of grain boundary phase, and (3) firing under a reducing N₂ atmosphere as shown in Fig. 1. In the first stage, pioneering work to find effective sintering aids for densification was carried out by Komeya et al.. They found that addition of alkaline-earth oxides and rare-earth oxides is useful to improve densification.^{33),34)} The densification proceeds via liquid-phase sintering, which forms by eutectic reactions between Al₂O₃ normally present as a surface film on AlN particles, AlN and sintering aids. Precise assessment of the eutectic temperature by differential thermal analysis (DTA) was performed by Shinozaki and Mizutani. They showed that the liquidus temperature in the AlN-Al₂O₃-oxide system for AlN sintering is lower (~70 K in maximum) than that in the Al₂O₃-oxide system.³⁵⁾ The additives are not only beneficial for promoting densification, but they also enhance the conductivity. The conductivity of dense AlN produced with raw powders containing oxygen impurity of 3.5 mass% was 75 W·m⁻¹·K⁻¹ for 3 mass% CaCO₃ addition and 72 W·m⁻¹·K⁻¹ for 3 mass% Y₂O₃ addition,³⁶⁾ these values are much higher than that of undoped AlN.

The second stage to improve the conductivity is due to developments in the raw powder. During sintering, oxygen atoms present on the surface of AlN particles incorporate into the AlN lattice by substitutional solution in a nitrogen site, creating an aluminum vacancy and reducing the conductivity.^{4),37)-39)} It is, therefore, important to reduce the oxygen level in the raw AlN powders. On the other hand, a slight amount of oxygen impurity contained in the raw powders helps to promote the densification.^{35),40)} Furthermore, Komeya and Inoue investigated the effect of particle size (0.7–4.4 μm) on densification, and they concluded that finer AlN powders possess favorable densification potential.⁴¹⁾ From these facts, high-purity, fine powders are necessary in order to improve both the sinterability and the conductivity.

Kuramoto et al. have succeeded in synthesizing fine powders with high-purity (>99%) by carbothermal-reduction of Al₂O₃ and nitridation.⁴²⁾ Using this powder, they obtained a translucent ceramic with a value of 130 W·m⁻¹·K⁻¹ by pressureless sintering with Ca(NO₃)₂.⁴³⁾ Thereafter, various methods to synthesize high-purity, fine powders, i.e., direct nitridation of metallic Al with either N₂ or NH₃,⁴⁴⁾ vapor phase reaction, vapor-liquid phase reaction,⁴⁵⁾⁻⁴⁹⁾ have evolved. Through the development of high-purity, fine powders, whole research including effect of powder characteristics on densification,⁵⁰⁾⁻⁵²⁾ phase development,^{36),53),54)} microstructure^{55),56)} and thermal conductivity⁵⁰⁾⁻⁵⁶⁾ have accelerated. Subsequently, thermal conductivity of AlN ceramics increased drastically, and reached to values of 140 to 180 W·m⁻¹·K⁻¹.³⁶⁾

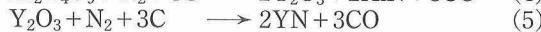
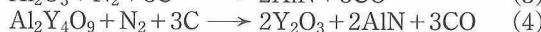
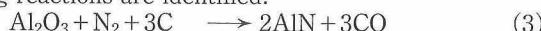
Development of the grain-boundary phase was significantly affected by the oxygen content of raw powders and amount of additive. In the case of Y₂O₃ addition, a possible reaction during firing is considered as follows.³⁹⁾



By Reaction (2), oxygen atoms dissolved into AlN grains diffuse to grain-boundaries, in order to produce stable Al-Y-O compounds as grain-boundary phases. In this case, the grain-boundary phase traps oxygen impurities, and the

concentration of oxygen impurity in the grain is reduced significantly.³⁶⁾ Highest thermal conductivity was obtained when both YAlO₃ and Al₂Y₄O₉ phases were formed.^{39),50)}

In the case of AlN sintering with an oxide additive under a reducing N₂ atmosphere, reactions to decrease oxygen content take place.^{39),56)-59)} This is identified as the third stage of conductivity improvements. For Y₂O₃ addition, the following reactions are identified.^{39),56)-58)}



During the chemical reactions above, migration of the grain-boundary phase is observed under the reducing atmosphere. The grain-boundary phase moves to the surface of AlN specimens, and YN is finally formed on the specimen surface.⁶⁰⁾ Enhancement of the conductivity of AlN ceramics was also found by firing in the reducing atmosphere,^{39),56)-59),61)-63)} and the conductivity of specimen fired at 2250 K for 96 h was 270 W·m⁻¹·K⁻¹,⁶¹⁾ which is 84% of the intrinsic conductivity of AlN.

Thermal conductivity of AlN ceramics at various temperatures is plotted in Figure 3. The intrinsic conductivity of AlN and the conductivity of single crystal are also shown in the same figure. The magnitude of the conductivities of AlN ceramics and single crystal is presented as a function of oxygen impurity amount. Furthermore, samples with lower oxygen content show higher thermal conductivity and strong temperature dependence of the conductivity.

3.3 Silicon nitride

There are two forms of Si₃N₄: α- and β-Si₃N₄.⁶⁴⁾ The crystal structure of the two phases is similar, containing Si₃N₄ tetrahedra forming a corner-shared three-dimensional network with the characteristic (001) plane of a hexagonal structure. However, the stacking of the planes is different in the α and β structures; it is ABCD in α-Si₃N₄ and AB or CD in β-Si₃N₄.⁶⁴⁾ α-Si₃N₄ is unstable relative to β-Si₃N₄, and converts into the latter at high temperature. Furthermore, rod-like β-Si₃N₄ grains are formed with a glassy phase in sintered materials. This gives β-Si₃N₄ a higher fracture toughness.⁶⁵⁾ Hence, β-Si₃N₄ ceramics have been strongly favored compared to α-Si₃N₄ ceramics.

Experimental values of the conductivity of β-Si₃N₄ have been reported to be in the range 10 to 162 W·m⁻¹·K⁻¹ at room-temperature, and the conductivities were increased through three developmental stages including (1) development of densification technology, search for an effective sintering aid, and development of raw powders, (2) firing at

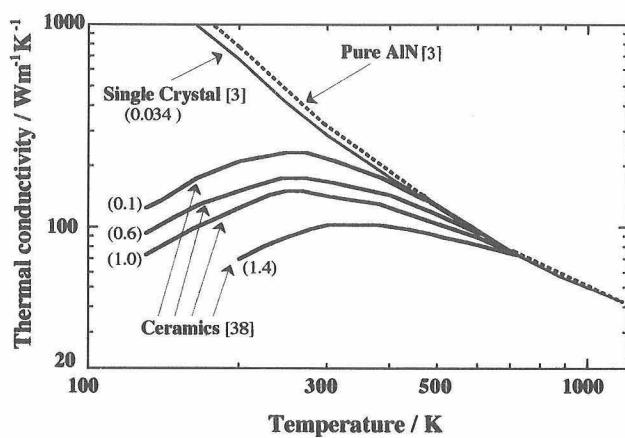


Fig. 3. Thermal conductivity at various temperatures of AlN single crystal and ceramics. Numeral shows oxygen content (mass%) contained in the specimens.

high-temperature (>2200 K), and (3) development of orientation technology, as demonstrated in Fig. 1. In the first stage, development of densification techniques was most important, because it is hard to obtain dense materials due to the strong covalent bonding between Si and N. Sintering techniques such as reaction-bond sintering,⁶⁶⁾ pressureless-sintering,⁶⁷⁾ high-pressure sintering,⁶⁸⁾ capsule-HIPing⁹⁾ and gas-pressure sintering,⁶⁹⁾ have developed, and have been employed to examine the sinterability and thermal conductivity of Si_3N_4 . Besides reaction-bond sintering, production of dense material are possible. Typical values are $17 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for reaction-bond sintering,⁶⁶⁾ $30 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for high-pressure sintering,⁶⁸⁾ $72 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for capsule-HIPing⁶⁾ and $80 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for gas-pressure sintering.⁶⁹⁾

Several powder synthesis methods have developed, and high-purity ($>99\%$), fine powders have been successfully obtained since 1981. Among the synthesis methods, a silicon-imide thermal decomposition method, in particular, provided very high-purity, fine powders.⁷⁰⁾ Utilization of these powders reduced the firing temperature for densification, and increased the conductivity of sintered materials.

Numerous studies have been performed at the first stage to find appropriate sintering aids, and it was found that Al_2O_3 , MgO , Y_2O_3 or rare-earth oxides are useful to sinter Si_3N_4 .^{71),72)} The additives form a liquid phase by the reaction with Si_3N_4 and surface SiO_2 on Si_3N_4 particles to promote densification.^{73),74)} However, the type of aid results in different conductivities, because sintering aids significantly influence the phase transformation from α to β - Si_3N_4 and the formation of crystal defects. The conductivity at room-temperature was $29 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for MgO addition,⁶⁸⁾ $16 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for Al_2O_3 addition, $27 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ addition and $72 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for Y_2O_3 addition,⁹⁾ and $30 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for undopant.⁶⁸⁾ Experimental results indicate that Y_2O_3 is a favorable additive, since this aid accelerates phase transformation of α to β and does not produce Si_3N_4 solid solutions.⁹⁾

Improvement of the conductivity at the second stage is due to high-temperature (>2200 K) firing. For gas-pressure sintering, an increased N_2 pressure suppresses the thermal decomposition of Si_3N_4 powder compacts and allows a higher firing temperature.⁷⁵⁾ In addition, the increased firing temperature results in the formation of large rodlike grains in a fine matrix.⁷⁶⁾ Such sintering produces high thermal conductivity. Hirosaki et al. obtained a β - Si_3N_4 ceramic with a value of $120 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ by gas-pressure sintering at 2273 K.⁷⁷⁾

Orientation of anisotropic β - Si_3N_4 grains results in the enhancement of the conductivity, and is identified as the third

stage for increasing the conductivity. Hirao et al. discovered anisotropic thermal conductivities in oriented β - Si_3N_4 fabricated by tape-casting with β - Si_3N_4 seeds, followed by firing at 2123 K for 66 h, and reported that thermal conductivities along the tape-casting direction and stacking direction were 120 and $60 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively.⁷⁸⁾ Subsequently, strongly anisotropic thermal conductivities were found in textured β - Si_3N_4 ceramics obtained by tape-casting and HIPing at 2773 K,⁷⁾ and by extruding with whiskers and gas-pressure sintering.⁸⁾ The conductivities of the extruded and gas-pressure sintered material were 162 and $85 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ in the directions parallel and perpendicular to the extruding, respectively.⁸⁾

The microstructures of dense β - Si_3N_4 with Y_2O_3 additive fabricated by various methods are shown in Fig. 4. Specimens of Figs. 4(a), (b) and (c) were produced by capsule-HIP sintering,⁹⁾ gas-pressure sintering⁷⁹⁾ and tape-casting and HIPing,⁷⁾ respectively. These materials have distinctive microstructures including grain size, distribution of grain size, aspect ratio and grain orientation. Such microstructural changes affect the conductivity, and reported values were $72 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for the capsule-HIPed material,⁹⁾ $110 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for the gas-pressure sintered material,⁷⁹⁾ and 155 and $65 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ along the tape-casting and stacking directions, respectively, for the tape-casted material.⁷⁾

Thermal conductivity of various Si_3N_4 ceramics as a function of temperature is summarized in Fig. 5. The conductivity at room-temperature and temperature dependence of the conductivity are significantly influenced by processing parameters such as type of sintering aids, forming techniques, and sintering techniques. High conductivity and strong temperature dependence of the conductivity are observed in the oriented ceramic with Y_2O_3 addition.

4. Thermal conductivity of grains

Considering that grains are the major phase of conventional ceramics, measurement of their thermal conductivity is of great interest. Thermoreflectance microscopy is a technique which relies on a local change of reflection coefficient relating to temperature change in a heated sample, and is a powerful tool to measure thermal conductivity of individual grains.⁸⁰⁾ Pelissonnier et al. investigated thermal conductivity of AlN grains without any second phase in a commercial AlN substrate with a value of $167 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$.⁸¹⁾ Li et al.¹³⁾ focussed on β - Si_3N_4 grains of a tape-casted and HIPed ceramic. Figure 6 shows two-dimension phase maps of the thermoreflectance signals on a AlN⁸¹⁾ grain and a β - Si_3N_4 ¹³⁾ grain. The mean diameter of the targeted AlN grain is about $8 \mu\text{m}$, and the mean diameter and length of the targeted β - Si_3N_4 grain are about $17 \mu\text{m}$ and $100 \mu\text{m}$, respectively. It

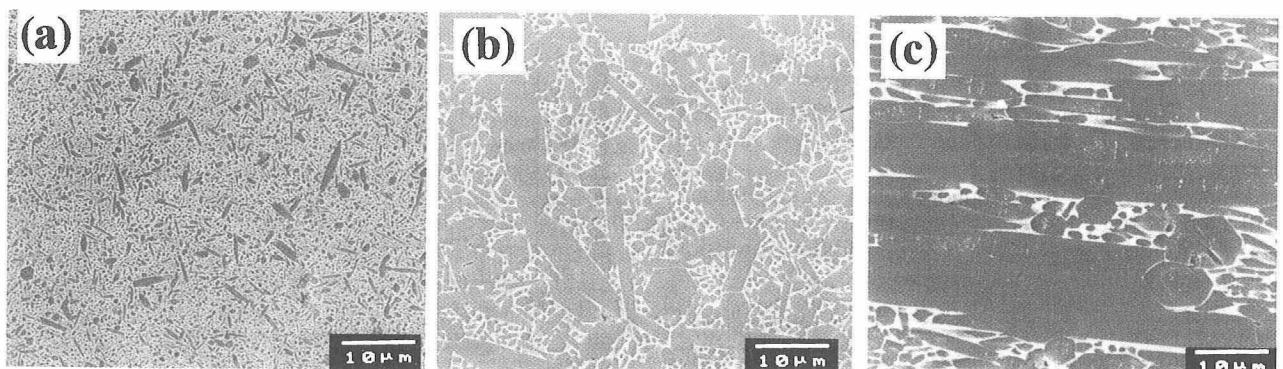


Fig. 4. Microstructure of the polished surface of β - Si_3N_4 ceramics with Y_2O_3 addition obtained by (a) capsule-HIP sintering at 2073 K, (b) gas-pressure sintering at 2273 K, and (c) tape-casting with β - Si_3N_4 single crystal particles as seeds and HIPing at 2773 K.

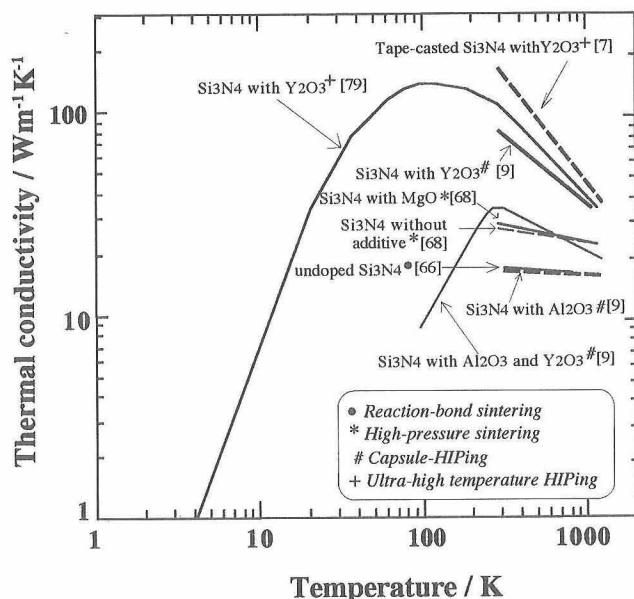


Fig. 5. Temperature dependence of thermal conductivity of various β - Si_3N_4 ceramics.

was found that heat flow was more marked along the *c*-axis, indicating thermal anisotropy in the β - Si_3N_4 grain. The thermal conductivity was calculated from the phase change of the thermoreflectance signals, and was 133–180 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for AlN grains⁸¹⁾ and 180 and 69 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ along the *c*- and *a*-axis, respectively, of a β - Si_3N_4 grain.¹³⁾

5. Thermal conduction mechanism

5.1 Effect of crystal defects

It is important to discuss factors controlling the conductivity at various levels. In the case of SiC, AlN and Si_3N_4 ceramics, heat transfer is dominated by phonon transport. Figure 7 indicates possible thermal conduction models of non-oxide ceramics, when the amount of grain-boundary phase with low thermal conductivity, and defect density of

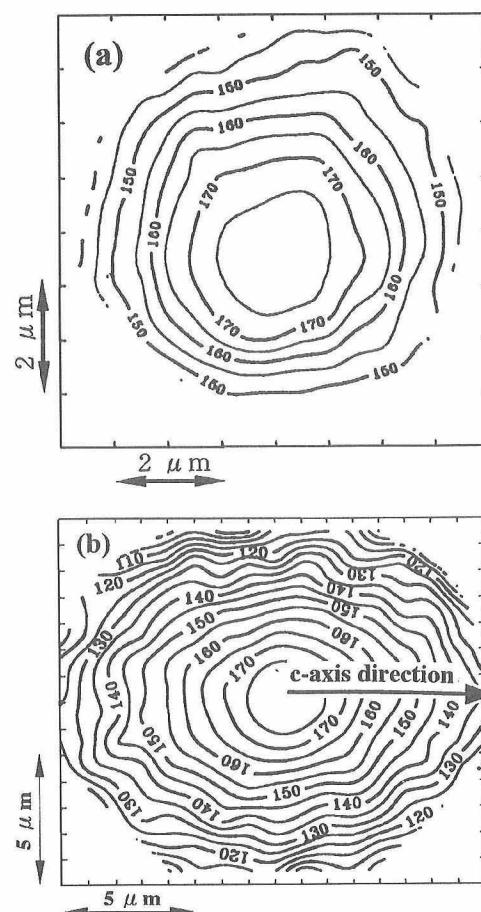


Fig. 6. Contour lines of the phase (in degree) of the thermoreflectance signals obtained on the surface of (a) AlN grain⁸¹⁾ and (b) β - Si_3N_4 grain.¹³⁾ The center of the pattern is the location of the center of the (fixed) probe spot. For a given position [X, Y] (in μm) from the center of the heating spot, the map gives the corresponding phase. The thermal conductivities were calculated using the 'phase method' with Fig. 6, and were 133–180 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for AlN grains,⁸¹⁾ and 180 and 69 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for a β - Si_3N_4 grain along the *c*-axis and *a*-axis, respectively.¹³⁾

Case	I	II	III
Amount of grain boundary	Large	Small	Small
Density of crystal defects in grains	—	Very low	High
Microstructure	Grain boundary phase grain grain	grain Defect grain	grain Defect grain
Controlling factor	Amount of grain boundary phase	Grain size (number of two grain-grain junctions)	Type and number of crystal defects into grains

Fig. 7. Thermal conduction models for non-oxide ceramics.

the grains are changed. With respect to a ceramic including a large amount of grain-boundary phase, the thermal conductivity is determined by the amount of this phase (case I), since the thermal conductivity of the grain-boundary phase in sintered non-oxides is very low ($1\text{--}10 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$).^{82),83)} For a ceramic consisting of a small amount of grain-boundary phase and grains with low density of crystal defects, the conductivity is controlled by grain size (number of two grain-grain junctions). This corresponds to case II. On the other hand, in the case of a ceramic including a small amount of grain-boundary phase, but grains with high density of crystal defects, the conductivity is greatly influenced due to the quantity of crystal defects (case III). The amount of grain-boundary phase of conventional non-oxide ceramics is less than 10 vol %, suggesting case II and III as possible thermal conduction models.

From results of the conductivity of individual grains, it is possible to discuss their defect density. According to the measurement by thermoreflectance microscopy, the conductivity of AlN grains in usual AlN ceramics was 133 to $180 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$,⁸¹⁾ which is 41 to 56% of the intrinsic conductivity. The conductivity of a $\beta\text{-Si}_3\text{N}_4$ grain was 180 and $69 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ along the c - and a -axis, respectively,¹³⁾ and is 56 and 22%, respectively, of the intrinsic value. These results indicate that there exists a large amount of crystal defects in the grains of conventional non-oxide ceramics with values of $150\text{--}170 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. It is also assumed that the conductivity of each SiC grain is much less than the intrinsic conductivity, because experimental conductivities of SiC ceramics are so low. Consequently, the thermal conduction mechanism of non-oxide ceramics involving recently developed materials is close to the model of case III, and is considered to be strongly affected by the type and amount of crystal defects. The reason why thermal conductivity of non-oxide ceramics is controlled by the type and amount of crystal defects, is also explained from calculations of the phonon mean free path^{37),38),84)} and a relationship between the conductivity of ceramics and grain size.^{37),84)}

Point defects, line defects and plane defects are considered as crystal defects in grains. Table 2 summarizes the type of crystal defects observed in grains of high thermal conductivity non-oxide ceramics. As point defects, dissolved N,³⁾ Al,^{19),25)} B^{19),25)} and BeO^{19),25)} have been observed in SiC. On the other hand, reports concerning dislocations and stacking faults have not been published for high thermal conductivity SiC ceramics, however these crystal defects

may influence strongly the conductivity, because they are frequently observed in conventionally sintered SiC.^{16),85)}

In the case of AlN, oxygen is the most deleterious impurity for the conductivity. The type of oxygen-related defects is dependent on the level of impurity. Harris et al. proposed an oxygen-related defect evolution mechanism as a function of oxygen content. At low oxygen concentrations, isolated oxygen impurities exist uniformly in the AlN lattice. The oxygen impurity and an aluminum vacancy form a collective defect, attracted together via a Coulombic interaction. This corresponds to point defects. Higher oxygen concentrations result in octahedrally coordinated aluminum sites, and these octahedra are organized to form extended defects such as inversion domain boundaries (IDBs) as line defects and oxygen-containing stacking faults as plane defects.^{86),87)}

With respect to $\beta\text{-Si}_3\text{N}_4$, several crystal defects in the grains have been identified. Very recently, Kitayama et al. have succeeded in measuring the oxygen content in $\beta\text{-Si}_3\text{N}_4$ crystal lattices by the hot-gas extraction method, and found that $\beta\text{-Si}_3\text{N}_4$ grains contain oxygen contents of 0.158–0.258 % depending on additive compositions.⁸⁸⁾ Furthermore, they applied electron spin resonance (ESR) to measure the concentration of vacancies in the $\beta\text{-Si}_3\text{N}_4$ grains, and detected nitrogen vacancies, which associate with dissolved oxygen atoms.⁸⁹⁾ Yokota and Iburiyama carried out precise chemical analysis of $\beta\text{-Si}_3\text{N}_4$ grains in a sintered specimen with a conductivity value of $100 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and observed that around 200 ppm by weight of Al always remains in the grains. The Al impurity is considered to originate from the raw powders.⁹⁰⁾ Therefore, dissolved oxygen and aluminum are one kind of point defect.

Dislocations in $\beta\text{-Si}_3\text{N}_4$ grains have been reported.^{91)–95)} Brito et al. observed the internal structure of $\beta\text{-Si}_3\text{N}_4$ grains in a ceramic with a room temperature conductivity of $120 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and found dislocations and strong strain contrast inside the grains. In particular, there existed a large amount of dislocations in smaller matrix grains.^{93),94)}

For plane defects, solid solutions may also affect the conductivity. Hirosaki et al. observed the internal structure of $\beta\text{-Si}_3\text{N}_4$ grains in a ceramic with $\text{Y}_2\text{O}_3\text{-Nd}_2\text{O}_3$ additives, and found amorphous particles, $\sim 5 \text{ nm}$ in size, and crystalline particles, $10\text{--}30 \text{ nm}$ in diameter, of Y-Nd-apatite ((Y, Nd)₁₀ $\text{Si}_6\text{O}_{24}\text{N}_2$) in the Si_3N_4 grains, which are presumably formed during cooling by the precipitation of Y-Nd-Si-O-N.⁹⁶⁾ A change of crystal structure was also observed for the $\beta\text{-Si}_3\text{N}_4$ grains, although the specimens were fired at ultra-

Table 2. Type of Crystal Defects Observed into High Thermal Conductivity Non-oxide Ceramics

Type of defect	SiC	AlN	Si_3N_4
Point defects	Dissolved N [3], Al [19, 25], B [19, 25], BeO[19, 25]	Dissolved O [3, 4, 86, 87]	Dissolved O [88, 89], Al [90]
Line defects	*	Inversion domain boundary [86, 87]	Dislocation [93-95]
Plane defects	**	Stacking fault [86, 87]	Si_3N_4 solid solution (Y,Nd) ₁₀ $\text{Si}_6\text{O}_{24}\text{N}_2$ [96] $\alpha\text{-Si}_3\text{N}_4$ [95]

* Reports concerning line defects such as dislocations on high thermal conductivity SiC have not been published, but their existence is considered.

** Reports concerning plane defects such as stacking fault on high thermal conductivity SiC have not been published, but their existence is considered.

high temperature. Munakata et al. annealed β - Si_3N_4 grains under a firing condition of 2473 K and 30 MPa in N_2 , and observed the existence of the α -type structure in β - Si_3N_4 grains by transmission electron microscopy.⁹⁵⁾

The type and amount of crystal defects in the grains significantly affect the conductivity of ceramics. Materials with higher conductivity have lower crystal defects. The author has been focussing on the effect of point defects as the most important factor on the thermal conduction mechanism, because the number of point defects inside the grains is much larger than the number of line defects. It is, therefore, essential to remove the point defects in the grains, in order to improve the conductivity at present level of non-oxide ceramics.

5.2 Effect of thermal anisotropy

Strong thermal anisotropy has been observed in textured β - Si_3N_4 ceramics. However, strong anisotropic conductivity in 6H SiC and AlN ceramics has not yet been identified. These materials have crystallographical anisotropy, so the possible effect on the conductivity should be mentioned. Experimental conductivity dependence on crystal axis was found for single crystals,^{3),13),28)-31)} and is summarized in Table 3. For 6H SiC, maximum conductivity was 490 $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ along the *a*- and *b*-axes,²⁸⁾ while the conductivity was 330 $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ along the *c*-axis.³¹⁾ In this case, the ratio of thermal anisotropy (*a*, *b*/*c*) was about 1.5, indicating weak thermal anisotropy. Thus, it is assumed that textured SiC does not possess strong thermal anisotropy. As for β - Si_3N_4 , the conductivity was 69 and 180 $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ along the *a*- and *c*-axis, respectively, and the ratio of thermal anisotropy (*c/a*) was 2.6. It is, therefore, considered that the alignment of β - Si_3N_4 grains results in highly anisotropic conductivity in textured β - Si_3N_4 ceramics.^{7),8),78)} Consequently, in addition to the removal of crystal defects, it is important to have grains with a high degree of orientation in sintered materials, in order to develop high thermal conductivity ceramics.

6. Processing strategy to increase the conductivity

As previously noted, Be for SiC ceramics, Y_2O_3 , Alkali-earth oxides and rare-earth oxides for AlN ceramics, and Y_2O_3 for Si_3N_4 ceramics are useful sintering additives. The reason why Y_2O_3 , alkali-earth oxides and rare-earth oxides are effective aids for AlN ceramics, is clearly explained through thermodynamic considerations. One of the necessary conditions is that effective sintering aids do not induce decomposition and oxidation of AlN during firing. The pos-

sibility of the reaction between AlN and various metal-oxides has been investigated by assessing the change in standard Gibbs free energy of an oxidation reaction of AlN with the formation of metal or metal-nitride.⁹⁷⁾ Useful additives, which do not cause oxidation of AlN during firing, are summarized in Fig. 8, and are presented in the shaded area of a horizontal plane. Y_2O_3 , alkali-earth oxides, rare-earth oxides and HfO_2 satisfy this necessary condition.

Formation of crystal defects is mainly due to the incorporation of foreign atoms into the grains. In this case, the processing strategy must minimize soluble impurities. If oxygen impurities in raw AlN powders react with the sintering aid to form stable Al_2O_3 compounds in grain boundaries, oxygen impurities do not diffuse into AlN lattices and crystal defects in AlN lattices do not form. This is a sufficient condition to increase the conductivity of AlN ceramics, and it has been evaluated by formation of a stable Al_2O_3 -compound as a grain-boundary phase in sintered AlN.^{54),98)} In the vertical plane of Fig. 8, formation of the Al_2O_3 -compound is discussed. Lower ΔG_f° means that oxygen content in AlN lattices decreases through formation of the stable Al_2O_3 -compound. Y_2O_3 , alkali-earth oxides and rare-earth oxides are good additives for forming stable Al_2O_3 -compounds in the grain-boundaries. From the thermodynamic evaluations, it is seen that Y_2O_3 , alkali-earth oxides and rare-earth oxides are significant additives. The thermodynamic consideration is consistent with experimental results of the conductivity of AlN ceramics. As such the selection of sintering aids to suppress the oxidation of AlN and to minimize soluble impurities by formation of stable compounds in grain-boundaries is also considered to be applicable for improving thermal conductivity of SiC and β - Si_3N_4 . In particular, the thermal conductivity of SiC ceramics is much lower than their intrinsic conductivity, suggesting that enhancements in conductivity may be achieved with effective sintering aids.

7. Concluding remarks

Active research concerning development of high thermal conductivity non-oxide ceramics has been carried out. For AlN ceramics, high thermal conductivity, which is close to its intrinsic thermal conductivity, is obtained, while thermal conductivities of SiC and Si_3N_4 are much lower, compared to their intrinsic conductivities. Thus, technological innovation such as enhancement of material purity, the search for effective additives and microstructural control is required for improving the conductivity of SiC and Si_3N_4 ceramics.

Table 3. Thermal Anisotropy of Non-Oxide Single Crystals

Sample	Crystal Structure	Crystal direction	Thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)	Remarks
SiC	6H	a, b	490	Slack [3, 28]
	6H	a, b	430	Slack [28]
	6H	a, b	430	Morelli et al. [30]
	6H	a, b	387	Burgemeister et al. [29]
	6H	a, b	300	Morelli et al. [30]
	6H	a, b	295	Burgemeister et al. [29]
	6H	a, b	142	Burgemeister et al. [29]
	6H+15R	a, b	130	Slack [28]
β - Si_3N_4	6H	c	330	Nilsson et al. [31]
	6H	a c	69 180	Li et al. [13] Li et al. [13]

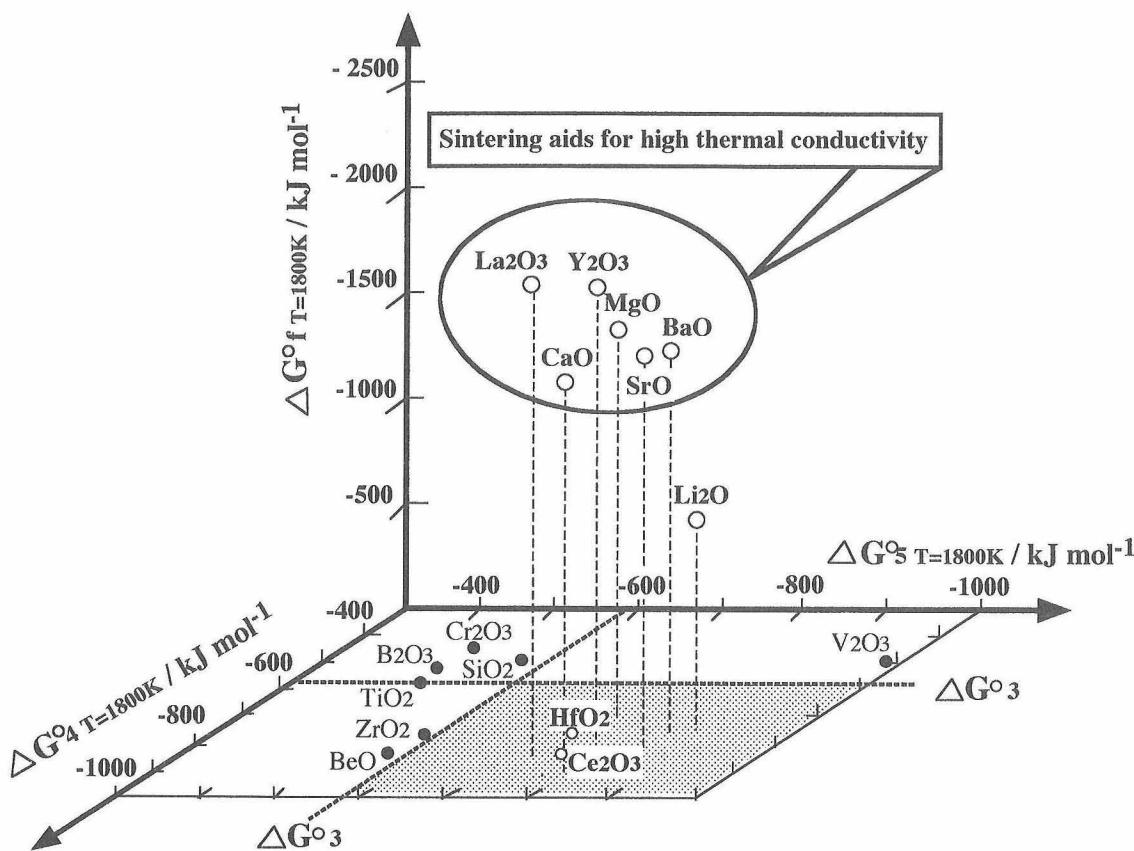


Fig. 8. Phase diagram for evaluating the sintering aids for AlN ceramics with high thermal conductivity. In the horizontal plane, possibility of the reaction between AlN and various metal-oxides is discussed. The oxidation reactions of AlN ceramics with oxide additives are described by the following equations:⁹⁷⁾ $4/3\text{AlN}(s) + b\text{MxOy}(s, l) \rightarrow 2/3\text{Al}_2\text{O}_3(s) + 2/3\text{N}_2(g) + a\text{M}(s, l)$ (1), $4/3\text{AlN} + d\text{Mx}'\text{Ny}'(s, l) \rightarrow 2/3\text{Al}_2\text{O}_3(s) + c\text{M}'\text{xN}_y'(s, l) + f\text{N}_2(g)$ (2). Here, MxOy and $\text{Mx}'\text{Ny}'$ are metal oxides, M the metal, and $\text{M}'\text{N}'$ the metal nitride. Reactions (1) and (2) are conducted by subtracting Reactions (4) and (5) from Reaction (3), respectively. $4/3\text{AlN}(s) + \text{O}_2(g) \rightarrow 2/3\text{Al}_2\text{O}_3(s) + 2/3\text{N}_2(g)$ (3), $a\text{M}(s, l) + \text{O}_2(g) \rightarrow b\text{MxOy}(s, l)$ (4), $c\text{Mx}'\text{Ny}'(s, l) + \text{O}_2(g) \rightarrow d\text{Mx}'\text{Ny}'(s, l) + \text{N}_2(g)$ (5). The possibility of reaction between AlN and various metal oxide is characterized by the change in standard Gibbs free energies, ΔG_3° , ΔG_4° , and ΔG_5° of Reactions (3), (4), and (5). The conditions to suppress oxidation of AlN are indicated in the expressions $\Delta G_3^\circ > \Delta G_4^\circ$ and $\Delta G_3^\circ > \Delta G_5^\circ$, and the area which satisfies this condition is shaded in this figure.

The thermodynamic process for removing oxygen in AlN lattices is examined by assessing the change in the standard Gibbs free energy of the formation, ΔG_f° , for the respective Al_2O_3 -compounds,^{54),98)} and the assessment is plotted in a vertical plane. If oxygen impurities in raw powders react with the sintering aid to form stable Al_2O_3 -compounds in grain-boundaries, oxygen impurities do not diffuse into AlN lattices and crystal defects in the lattices are not produced. Lower ΔG_f° indicates that oxygen content in the lattices decreases through formation of stable Al_2O_3 -compounds. The thermodynamic data was obtained from a reference.⁹⁸⁾ This figure suggests that Y_2O_3 and CaO are useful aids for AlN, because addition of these aids does not cause decomposition of AlN, and produces stable Al_2O_3 -compounds to decrease the oxygen content in the lattices during firing.

Regarding the applications, although commercial production of high thermal conductivity non-oxide ceramics has shown a sharp increase during the last decade, it is still very small scale. One reason for this is undoubtedly the higher cost of the non-oxide ceramics. Recently, low-temperature manufacturing processes for high thermal conductivity ceramics have been suggested.⁹⁷⁾⁻¹⁰⁰⁾ Furthermore, low-cost, high-purity powders have been supplied. Development of low-cost and high thermal conductivity non-oxide ceramics will be achieved in the near future. On the other hand, high thermal conductivity composites have been obtained in recent years. Porous SiC and AlN ceramics have been produced,*¹⁰¹⁾ and metal and plastic sources have been infiltrated to them.* The obtained ceramic/metal and ceramic/plastic composites show much higher conductivity compared to conventional metals and plastics. It is also pos-

sible to improve the mechanical properties and to control the electrical properties such as dielectric constant. As such these materials open up new industrial fields. The author expects a significant increase in the market relating to high thermal conductivity non-oxide ceramics in the 21st century.

Acknowledgements I wish to express my deep appreciation to Dr. Shuzo Kanzaki and Dr. Motohiro Toriyama of NIRIN, Prof. Dr. Kozo Ishizaki of Nagaoka University of Technology, and Mr. Mitsuo Kasori of Toshiba Co., for useful suggestions and continuous encouragement. The author would like to thank Drs. Kiyoshi Hirao, Manuel E. Brito and You Zhou of NIRIN, Prof. Dr. Mikito Kitayama of Fukuoka Institute of Technology, Kunihiro Maeda and Takao Kanai of Synergy Ceramics Laboratory, Fine Ceramics Research Association, for valuable comments and discussion on this work. Thanks are also extended to Drs. L. Pottier, B-C. Li and J. P. Roger, and Prof. Dr. D. Fournier of Laboratoire d'Instrumentation de l'Université Pierre et Marie Curie for very useful measurements of local thermal conductivity of ceramic grains and its valuable com-

* NGK Insulators Catalogue, "New SiC, Si-SiC of NGK Insulators."

ments. Finally, I am grateful to Dr. M. Jones of NIRIN for critical review.

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