



# Low-Temperature Sintering of Gahnite Ceramic Using Cu-Nb-O Additive and Evaluation of Dielectric and Thermal Properties

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Low-temperature sintering of gahnite ( $\text{ZnAl}_2\text{O}_4$ ) ceramic, which has the potential to exhibit higher thermal conductivity than alumina but sinters densely at a moderate temperature of approximately  $1500^\circ\text{C}$ , has been investigated. When adding only 5 wt.% Cu-Nb-O additive, the sintering temperature was lowered significantly to  $960^\circ\text{C}$ . The sample fired at  $960^\circ\text{C}$  for 2 h exhibited a relative permittivity ( $\epsilon_r$ ) of 9.1, a quality factor multiplied by resonant frequency ( $Q \times f$ ) value of 30,000 GHz (at a measurement frequency of approximately 13 GHz), and a temperature coefficient of resonant frequency ( $\tau_f$ ) of  $-69$  ppm/K, being relatively satisfactory values. However, the thermal conductivity of the sample was  $9.3$  W/m-K, which exceeds that of conventional low-temperature co-fired ceramic (LTCC) materials but is only one-third of that of the pure gahnite sample ( $27$  W/m-K). Our analysis revealed that the main cause was the incorporation of the Cu component into the gahnite lattice. These results enable the proposal of guidelines for the development of new LTCC materials with high thermal conductivity.

**Key words:** Ceramics,  $\text{ZnAl}_2\text{O}_4$ , low-temperature sintering, dielectric property, thermal conductivity

## INTRODUCTION

Low-temperature co-fired ceramics (LTCCs) are dielectric materials that are widely used in small electronic devices such as wiring substrates and integrated circuit packages.<sup>1,2</sup> However, the poor thermal dissipation of LTCC materials has been a problem. Aluminum-based oxide ceramics, e.g., with alumina ( $\text{Al}_2\text{O}_3$ ) as the base material, exhibit relatively high thermal conductivity. However, it is necessary to add a large amount (approximately 50% or more of the total amount) of low-softening-point glass with low thermal conductivity to achieve low-temperature sintering. Consequently, the majority of these conventional LTCC materials exhibit the shortcoming of low thermal conductivity

(of approximately  $2$  W/m-K to  $7$  W/m-K).<sup>3,4</sup> Recently, the heat generation density of semiconductors, such as light-emitting diodes (LEDs) mounted on LTCC multilayer devices, has been increasing, resulting in a demand for LTCC materials with high thermal conductivity.<sup>5</sup> Therefore, in our previous research, utilizing alumina with high thermal conductivity of approximately  $30$  W/m-K as a base material, we developed additives that could enable sintering at low temperature even when using a small amount. As a result, we developed CuO-TiO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub>-Ag<sub>2</sub>O additive that can sinter alumina at a low temperature of  $900^\circ\text{C}$  or less at 5 wt.% addition, enabling the realization of low-temperature co-fired alumina (LTCA) with a high thermal conductivity of  $18$  W/m-K.<sup>6,7</sup>

In this study, we focus on gahnite ( $\text{ZnAl}_2\text{O}_4$ ) as a base material, which is an aluminum-based oxide with greater potential for higher thermal conductivity than alumina.<sup>8-12</sup> According to Surendran

et al., the thermal conductivity of a sample obtained by firing a composition of  $0.83\text{ZnAl}_2\text{O}_4-0.17\text{TiO}_2$  (molar ratio, referred to hereinafter as ZAT) at  $1440^\circ\text{C}$  was  $59\text{ W/m}\cdot\text{K}$ .<sup>8</sup> Therefore, if gahnite can be sintered at a low temperature, its application as a novel highly thermally conductive LTCC substrate may be expected. However, there have been studies on low-temperature sintering by adding glass to gahnite<sup>11</sup> and a few studies on crystalline additives, other than glass. Therefore, we aimed to develop a sintering additive that can sinter gahnite densely, at a low temperature of less than  $1000^\circ\text{C}$ , when adding a small amount. Furthermore, the dielectric properties and thermal conductivity of the developed gahnite sintered bodies were evaluated and analyzed.

### EXPERIMENTAL PROCEDURES

#### Preparation of Gahnite Sintered Bodies

Figure 1a shows the flow process for obtaining the gahnite sintered bodies containing additives. Commercially available  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$  powders (High Purity Chemical Laboratory Co., Ltd., Japan), with

average particle size of  $1\ \mu\text{m}$ , were weighed at molar ratio of 1:1 and mixed in a ball mill for 16 h with water as dispersion medium. The dried powder was calcined at  $1100^\circ\text{C}$  (for 4 h) in air atmosphere to synthesize gahnite. The synthesized gahnite powder was pulverized in a ball mill for 48 h with water as dispersion medium. The dried powder was used as the raw material powder shown in Fig. 1b. The specific surface area measured by the Brunauer–Emmett–Teller (BET) method was  $8.65\text{ m}^2/\text{g}$ . Next, 95 wt.% gahnite powder and 5 wt.% various binary oxide additives were weighed and mixed for 16 h in a ball mill with water as dispersion medium. The dried powder was granulated with a poly(vinyl alcohol) (PVA) binder and formed into disk shape by uniaxial pressing at 75 MPa. The green bodies were fired at  $835^\circ\text{C}$  to  $1485^\circ\text{C}$  in air atmosphere for 2 h. The selection of the binary oxide additives was based on the following criteria: (a) well-studied sintering additive according to literature on LTCC materials, and (b) low melting point. Based on these criteria,  $\text{CuO}$ ,  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{MnCO}_3$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{V}_2\text{O}_5$  were selected as candidate sintering aids,<sup>13–15</sup> and 15 binary additives were created by randomly blending two sintering aids from among the six mentioned above in equal weight ratio (these binary additives are denoted hereinafter according to their constituents, for example,  $\text{CuO-TiO}_2$  additive is referred to as  $\text{Cu-Ti-O}$  additive). As described below, the composition ratio of the  $\text{Cu-Nb-O}$  additive, which resulted in the best sinterability among them, was also examined. Furthermore, for comparison, the same operation was performed with single-component gahnite (without additives) and a ZAT composition.

#### Characterization

The properties of the obtained sintered bodies were examined by measuring their bulk density, microwave dielectric properties, and thermal conductivity. Three major parameters that describe the dielectric properties, namely the relative permittivity ( $\epsilon_r$ ), the quality factor multiplied by the resonant frequency ( $Q \times f$ ), and the temperature coefficient of resonant frequency ( $\tau_f$ ), were measured using a network analyzer (Agilent Technologies, 8720ES), by the Hakki–Coleman method.<sup>16</sup> The  $\tau_f$  values were calculated using the equation

$$\tau_f = \frac{f_{80} - f_{20}}{f_{20} \times (80 - 20)}, \quad (1)$$

where  $f_{20}$  and  $f_{80}$  are the resonant frequencies at  $20^\circ\text{C}$  and  $80^\circ\text{C}$ , respectively. The thermal conductivity was measured using the xenon flash method (Netzsch, LFA447). In addition, to further discuss the sinterability and thermal conductivity of the developed materials, microstructural observation by scanning electron microscopy (SEM), measurement of the gahnite lattice constant and phase identification by x-ray diffraction (XRD) with a  $\text{Cu K}_\alpha$

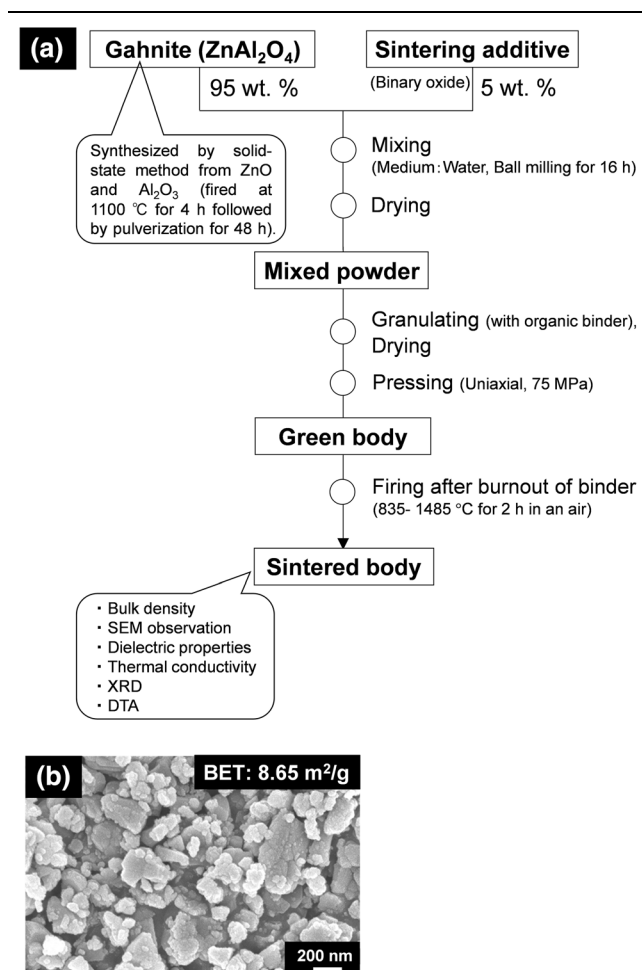


Fig. 1. (a) Experimental flow process for obtaining gahnite ceramics containing sintering additives. (b) SEM image of gahnite raw material powder.

radiation source, and melting temperature measurements of the additive by differential thermal analysis (DTA) were performed.

## RESULTS AND DISCUSSION

### Effect of Type of Binary Oxide Additive on Sinterability of Gahnite

Figure 2 illustrates the density of the sintered bodies of gahnite without additives and with 5 wt.% of the 15 types of binary oxide additives. The theoretical density of gahnite is  $4.61 \text{ g/cm}^3$ . Generally, a sintered body with relative density of 95% or more is highly reliable and without open pores. Here, a dense sintered body was defined as having a bulk density of  $4.38 \text{ g/cm}^3$  or above. The bulk density at  $1085^\circ\text{C}$  of the sample without additives was  $2.59 \text{ g/cm}^3$ . Since the bulk density of the green compact was also  $2.59 \text{ g/cm}^3$ , no densification was observed. On the other hand, the bulk density of the sample with the Cu-Nb-O additive was  $4.52 \text{ g/cm}^3$  (98% relative density), even when using a low temperature of  $985^\circ\text{C}$ , thus clear densification was observed. Densification was also observed in the samples with the other 14 additives; however, even at  $1085^\circ\text{C}$ , they did not reach 95% of the relative density of gahnite. These results indicate that the low-temperature sintering effect of the Cu-Nb-O additive was the strongest within the range of this experiment. In our previous research, low-temperature sintering of alumina was achieved by including  $\text{TiO}_2$  and  $\text{Ag}_2\text{O}$  in the additive.<sup>6</sup> In the future, it is expected that addition of extra components to the system reported herein could achieve densification at even lower temperatures.

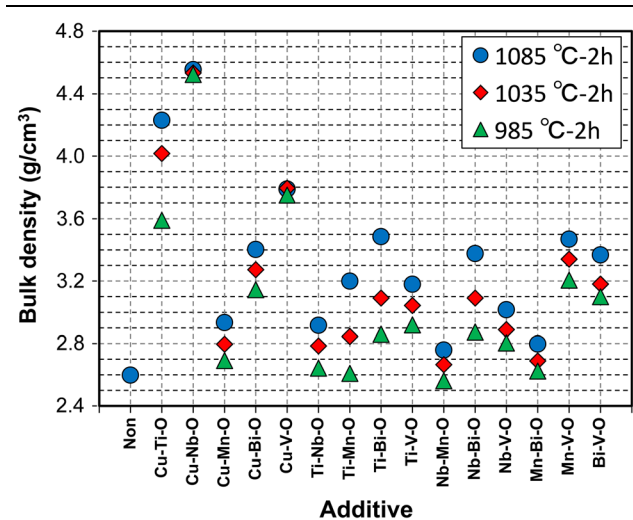


Fig. 2. Bulk density of sintered bodies of gahnite without additives and with 5 wt.% of 15 types of binary oxide additives, fired at temperatures of  $985^\circ\text{C}$ ,  $1035^\circ\text{C}$ , and  $1085^\circ\text{C}$  for 2 h.

### Effect of Cu-to-Nb Ratio on Sinterability, Dielectric Properties, and Thermal Conductivity of Gahnite with Cu-Nb-O Additive

Figure 3a shows the density of the sintered body of gahnite when the Cu:Nb molar ratio in the Cu-Nb-O additive was varied from 100:0 to 0:100 (retention time of 2 h). It was found that a dense sintered body could be obtained when the firing temperature was  $960^\circ\text{C}$  for the compositions with Cu:Nb ratio from 80:20 to 60:40. In other words, low-temperature sintering at less than  $1000^\circ\text{C}$  was successful. Focusing on  $935^\circ\text{C}$ , which is in the process of densification, the difference in sinterability can be better understood, and the composition of

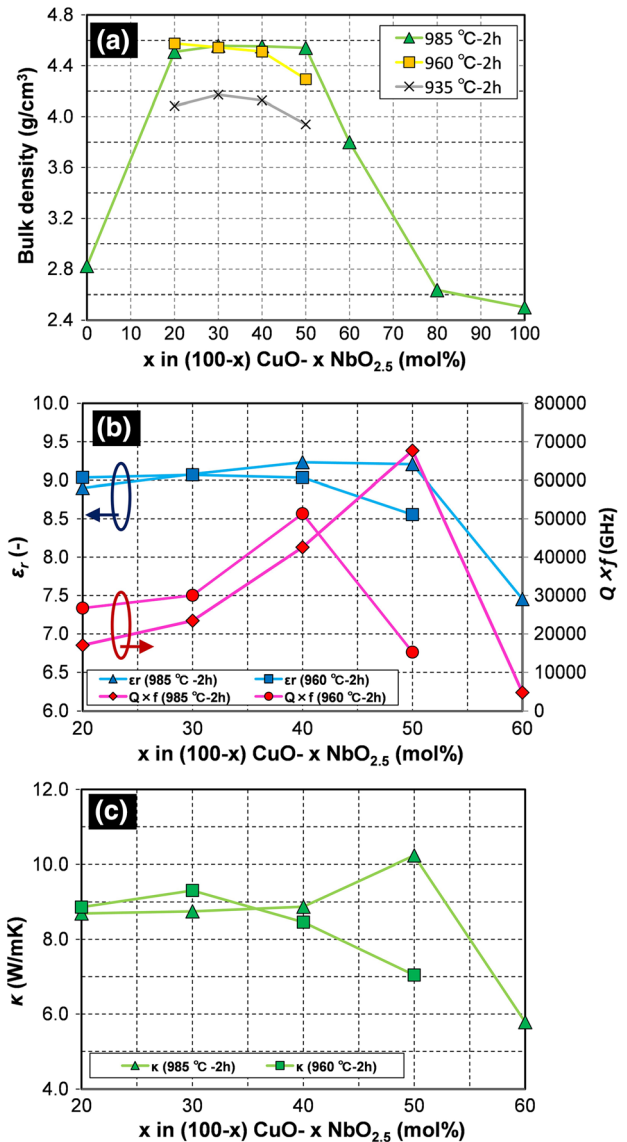


Fig. 3. Bulk density and microwave dielectric properties of gahnite with 5 wt.% Cu-Nb-O additive as function of  $x$  mol.% of  $\text{NbO}_{2.5}$  in  $\text{CuO-NbO}_{2.5}$  additive (at firing temperatures of  $935^\circ\text{C}$ ,  $985^\circ\text{C}$ , and  $1035^\circ\text{C}$  for 2 h): (a) bulk density, (b)  $\epsilon_r$  and  $Q \times f$ , and (c) thermal conductivity.

Cu:Nb = 70:30 has the maximum bulk density, thus being the optimum composition for improving the sinterability.

Figure 3b shows the dielectric properties of gahnite when the Cu:Nb molar ratio in the Cu-Nb-O additive was varied from 80:20 to 40:60 (retention time of 2 h). The samples whose compositions had a Cu:Nb ratio in the range from 80:20 to 60:40 and fired at 960°C and 985°C showed a relative permittivity of approximately 9 and almost no difference. In other words, good sinterability was ensured at 960°C. For the composition with the best sinterability, i.e., that with Cu:Nb = 70:30, the sample fired at 960°C exhibited a relatively good  $Q \times f$  value of 30,000 GHz (at a measurement frequency of approximately 13 GHz). In addition, comparing the dense sintered bodies, it can be seen that the  $Q \times f$  value tended to increase as the ratio of Nb was increased.

Figure 3c shows the thermal conductivity of gahnite when the Cu:Nb molar ratio in the Cu-Nb-O additive was varied from 80:20 to 40:60 (retention time of 2 h). The thermal conductivity of the dense sintered body was approximately 9 W/m-K to 10 W/m-K, regardless of the composition. Compared with the thermal conductivity of 24 W/m-K<sup>17</sup> of alumina with 4 wt.% of Cu-Nb-O with almost the same composition, these values are less than a half.

### Properties of Gahnite with Cu-Nb-O Additive and Comparison with Conventional Materials

Figure 4 illustrates the relationship between the firing temperature and sintering density of single-component gahnite, ZAT, and gahnite with 5 wt.% Cu-Nb-O additive with Cu:Nb molar ratio of 70:30. To obtain a dense sintered body, a firing temperature of 1485°C is required for single-component gahnite, whereas 1285°C was required for ZAT. On the other hand, the gahnite with the Cu-Nb-O additive showed a lower sintering temperature of approximately 500°C, compared with the sample without the additive. DTA measurements indicated

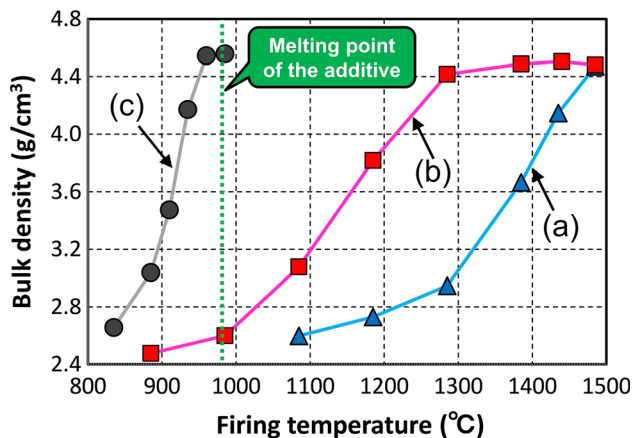


Fig. 4. Relationship between bulk density of sintered bodies and firing temperature of (a) gahnite, (b)  $0.83\text{ZnAl}_2\text{O}_4\text{-}0.17\text{TiO}_2$  (ZAT), and (c) gahnite containing 5 wt.% Cu-Nb-O additive with Cu:Nb molar ratio of 70:30. The holding time at each temperature was 2 h.

that the melting temperature of the Cu-Nb-O additive was 983°C, suggesting that densification was almost complete in the solid state (called solid-state-activated sintering<sup>18</sup>). When studying the low-temperature sintering of alumina, a similar sintering behavior was observed with Cu-Nb-O and Cu-Ti-Nb-O additives.<sup>19,20</sup>

Figure 5 shows SEM images of the sintered bodies, each showing few pores and dense material. The grain size of the single-component gahnite (Fig. 5a) was approximately 1  $\mu\text{m}$  to 2  $\mu\text{m}$ , which is slightly larger than that of the raw powder material (Fig. 1b), while for ZAT (Fig. 5b) it was several microns, with remarkable grain growth being observed. This occurred due to the firing temperature of this sample of 1440°C, exceeding the value of 1285°C (required for densification) by 155°C. The gahnite with Cu-Nb-O additive (Fig. 5c) was fine with a grain size of about 0.5  $\mu\text{m}$ , exhibiting almost no grain growth.

Table I presents the firing temperature, bulk density, and dielectric and thermal properties of the pure gahnite sample, ZAT, gahnite with 5 wt.% Cu-Nb-O additive with Cu:Nb molar ratio of 70:30, and conventional LTCC for substrates.<sup>3,4,9</sup> The dielectric properties of the gahnite with Cu-Nb-O additive are  $\epsilon_r = 9.1$ ,  $Q \times f = 30,000$  GHz (at a measurement frequency of approximately 13 GHz), and  $\tau_f = -69$  ppm/K, being relatively more desirable than those of the single-component gahnite. The thermal conductivity was 9.3 W/m-K, higher than that of the conventional LTCC material. However, this value is only approximately one-third of that of the single-component gahnite (27 W/m-K). For ZAT, the thermal conductivity was 59 W/m-K and  $\tau_f$  was  $\pm 0$  ppm/K in the report of Surendran et al.,<sup>8</sup> however, the thermal conductivity of our ZAT sample was 19 W/m-K, while  $\tau_f$  was  $-32$  ppm/K but could not be reproduced. A detailed examination is expected in the future.

### Discussion of Cause of Low Thermal Conductivity of Gahnite with Cu-Nb-O Additive

As mentioned above, the cause of the low thermal conductivity of the gahnite with Cu-Nb-O additive is now considered. Specifically, three reasons are proposed for this analysis:

1. Precipitation of the additive component with low thermal conductivity
2. The dependence of the thermal conductivity on the grain size
3. The effect of the solid solution of the Cu component on the thermal conductivity

An experiment was performed to verify each of these.

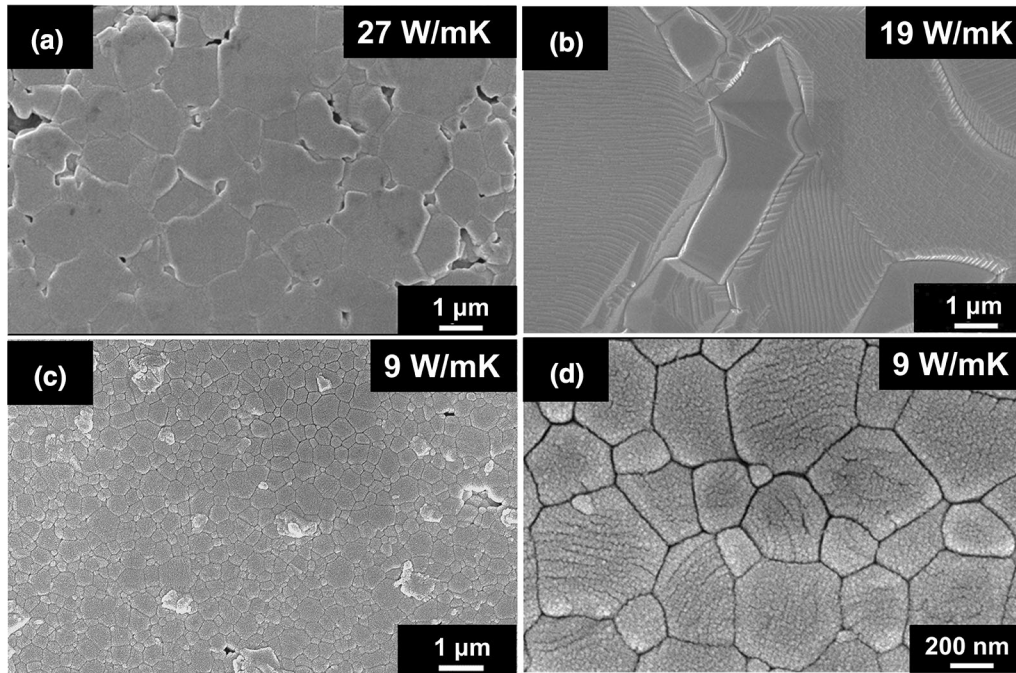


Fig. 5. SEM images of (a) gahnite fired at 1485°C for 2 h, (b) 0.83ZnAl<sub>2</sub>O<sub>4</sub>-0.17TiO<sub>2</sub> (ZAT) fired at 1440°C for 4 h, (c) the sintered sample in this study (gahnite + 5 wt.% Cu-Nb-O additive with Cu:Nb molar ratio of 70:30) fired at 960°C for 2 h, and (d) an enlargement of (c).

**Table I. Firing temperature, bulk density, and dielectric and thermal properties of pure gahnite sample, 0.83ZnAl<sub>2</sub>O<sub>4</sub>-0.17TiO<sub>2</sub> (ZAT), the sintered sample in this study (gahnite + 5 wt.% Cu-Nb-O additive with Cu:Nb molar ratio of 70:30), and conventional LTCC materials (alumina + glass) for substrates**

Name	Firing temp. °C	Bulk density g/cm <sup>3</sup>	$\epsilon_r$ -	$Q \times f$ GHz	$\tau_f$ ppm/K	$\kappa$ W/m-K
Gahnite only	1485	4.47	9.0	16000	- 73	27.3
ZAT	1440	4.48	11.3	46000	- 32	19.2
Gahnite + 5 wt.% Cu-Nb-O (Cu:Nb = 70:30)	960	4.54	9.1	30000	- 69	9.3
Examples of conventional LTCC for substrates <sup>3,4,9</sup>	900-1100	-	< 15	> 1000	$ \tau_f  < 100$	2-7

#### Precipitation of Additive Component with Low Thermal Conductivity

First, the difference between the compounds was analyzed by XRD. Figure 6 shows the XRD patterns of the three types of gahnite sintered bodies. For the single-component gahnite and the gahnite with Cu-Nb-O additive, almost only a clear peak of ZnAl<sub>2</sub>O<sub>4</sub> was detected. Cu-Nb-O-based compounds also probably precipitated, but it is assumed that they could not be detected due to their low content. On the other hand, for ZAT, TiO<sub>2</sub> was detected in addition to ZnAl<sub>2</sub>O<sub>4</sub>, but there was no other difference.

According to the CuO-Nb<sub>2</sub>O<sub>5</sub> phase diagram,<sup>21</sup> Cu<sub>3</sub>Nb<sub>2</sub>O<sub>8</sub><sup>22</sup> exists as a compound formed in a composition range with good sinterability. However, no thermal conductivity data are available.

Therefore, Cu<sub>3</sub>Nb<sub>2</sub>O<sub>8</sub> was synthesized by the usual solid-phase method, which after pulverization for 48 h and firing at 885°C for 2 h, produced a dense sintered body. The thermal conductivity was measured to be 6.1 W/m-K, which is not low. It is also known that the thermal conductivity of TiO<sub>2</sub> is approximately 7 W/m-K.<sup>23</sup> Therefore, it was assumed that the gahnite sintered body with 5 wt.% Cu-Nb-O (Cu:Nb = 70:30) additive developed in this study and ZAT were formed of a composite of gahnite and additive. The thermal conductivity of the binary mixture was calculated using the following equation<sup>24</sup> proposed by Eucken:

$$K = K_f \left( \frac{1 + 2\phi A}{1 - \phi A} \right) \quad (2)$$

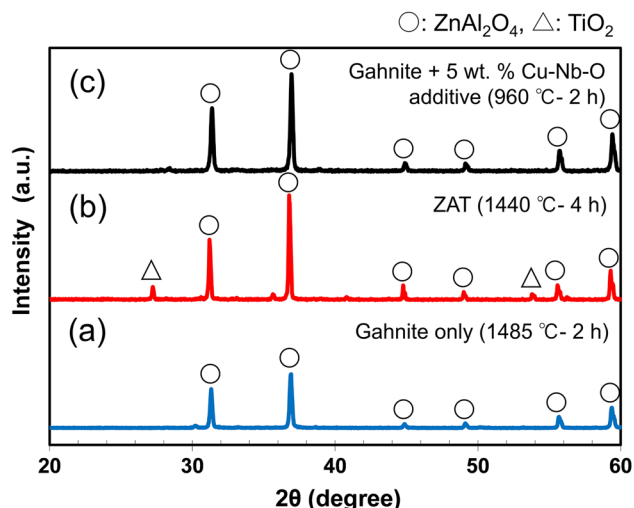


Fig. 6. X-ray diffraction patterns of (a) gahnite fired at 1485°C for 2 h, (b)  $0.83\text{ZnAl}_2\text{O}_4\text{-}0.17\text{TiO}_2$  (ZAT) fired at 1440°C for 4 h, and (c) the sintered sample in this study (gahnite + 5 wt.% Cu-Nb-O additive with Cu:Nb molar ratio of 70:30) fired at 960°C for 2 h.

$$A = \frac{\left(1 - \frac{K_f}{K_s}\right)}{\left(2\frac{K_f}{K_s} + 1\right)}, \quad (3)$$

where  $K$  is the thermal conductivity of the binary mixture,  $K_s$  is the thermal conductivity of gahnite,  $\varphi$  is the gahnite volume fraction, and  $K_f$  is the thermal conductivity of the Cu-Nb-O additive or  $\text{TiO}_2$ .

The thermal conductivity  $K_s$  of gahnite has an experimental value of 27 W/m-K, and the volume fraction  $\varphi$  of gahnite was 0.954 (in the case of gahnite with Cu-Nb-O additive) or 0.912 (in the case of ZAT). The thermal conductivity  $K_f$  of the Cu-Nb-O additive or  $\text{TiO}_2$  was uniformly set to 6.1 W/m-K, which is the thermal conductivity of  $\text{Cu}_3\text{Nb}_2\text{O}_8$ .

Figure 7 shows the calculated and experimental values of the thermal conductivity of the binary mixture. ZAT showed a relatively small difference between the calculated and experimental values. On the other hand, the experimental value for gahnite with the Cu-Nb-O additive was much lower than the calculated value. The thermal conductivity was approximately half that of ZAT, even though the volume fraction of gahnite was larger than in ZAT. Indeed, when the value of  $K_f$  was back-calculated to match the experimental value, it was 0.2 W/m-K, which is unrealistic. Therefore, the hypothesis that the thermal conductivity of the additive was low can be rejected.

#### Fine Grain Size of Sintered Bodies

As shown in Fig. 5, the sintered grain size of ZAT was approximately 10 times larger than that of the gahnite with Cu-Nb-O additive, and the particle size may affect the thermal conductivity. Therefore, the firing temperature of gahnite with the Cu-Nb-O

additive was intentionally increased from 960°C to 985°C, 1035°C, and 1085°C, and the relationship between the grain size of the sintered body and the thermal conductivity was examined (retention time of 2 h). Figure 8 shows SEM images of gahnite with the Cu-Nb-O additive. The grain size became larger by approximately 10 times when firing at 1035°C and 1085°C than at 960°C. However, as illustrated in Fig. 9, no difference in the thermal conductivity with such an increase in the grain size was detected. Thus, it was found that, at least in the present system, when the grain size of the sintered body was in the range of 0.5  $\mu\text{m}$  to 5  $\mu\text{m}$ , there was almost no dependence of the thermal conductivity on the grain size.

#### Incorporation of Cu Component in Gahnite

Gahnite is known to have a positive spinel structure represented by the chemical formula  $\text{AB}_2\text{X}_4$ . The A-site contains four-coordinated  $\text{Zn}^{2+}$ , the B-site contains six-coordinated  $\text{Al}^{3+}$ , and the X-site contains  $\text{O}^{2-}$ . However, it was considered that  $\text{Cu}^{2+}$  might have been dissolved and substituted part of the  $\text{Zn}^{2+}$  at the A site during firing. According to Shannon et al., the ionic radii of four-coordinated  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  are 60 pm and 57 pm, respectively. Although these values are similar,  $\text{Cu}^{2+}$  is slightly smaller<sup>25</sup> but has the same valence, which satisfies the condition for easy substitution and solid solution. Therefore,  $(\text{Zn}_{1-y}\text{Cu}_y)\text{Al}_2\text{O}_4$  ( $y = 0.02, 0.05, 0.10, 0.20$ ), in which Cu was substituted up to a maximum of 20% at the Zn site of gahnite, was synthesized by the solid-phase method under the same conditions as for single-component gahnite ( $y = 0.00$ ). Then, the gahnite in which Cu was dissolved as a solid solution was pulverized for 48 h, dried, molded, then fired at 1435°C (for 2 h). All the samples had a density of 4.4 g/cm<sup>3</sup> or greater and were sufficiently densified.

Figure 10 shows the XRD patterns of the powders obtained by substituting Cu for a solid solution at the Zn site of gahnite. Even when Cu was replaced, a peak appeared at a position almost equivalent to that observed for single-component gahnite. Although a partly unknown peak was observed for the compositions with 10% or 20% substitution, a remarkable second phase was hardly observed, suggesting a solid solution of Cu. Figure 11 illustrates the lattice constant (lattice parameter  $a$ ) of the  $(\text{Zn}_{1-y}\text{Cu}_y)\text{Al}_2\text{O}_4$  ( $y = 0.00, 0.02, 0.05, 0.10, 0.20$ ) powders (spinel structure in space group  $Fd\bar{3}m$ ) as determined by XRD measurements (with Si as internal standard sample), and by using the thermal conductivity of sintered bodies as a function of the substitution amount of Cu ( $y$ ). As the substitution amount  $y$  of Cu was increased, the lattice constant tended to decrease. Correspondingly, the thermal conductivity dropped dramatically. Specifically, the thermal conductivity was 11 W/m-K and 9.0 W/m-K even when the substitution amount  $y$  of

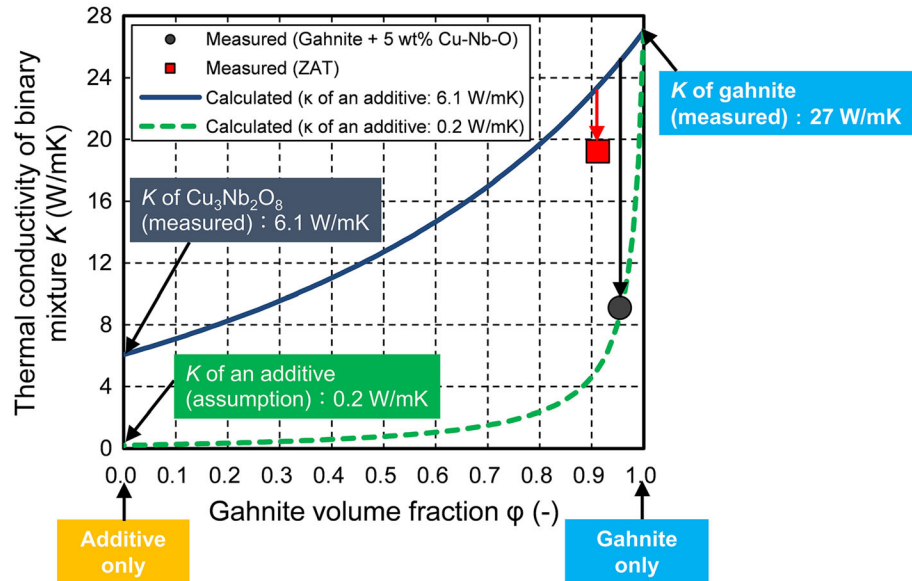


Fig. 7. Calculated<sup>22</sup> and experimental values of thermal conductivity of binary mixture (gahnite + additive) as functions of gahnite volume fraction.

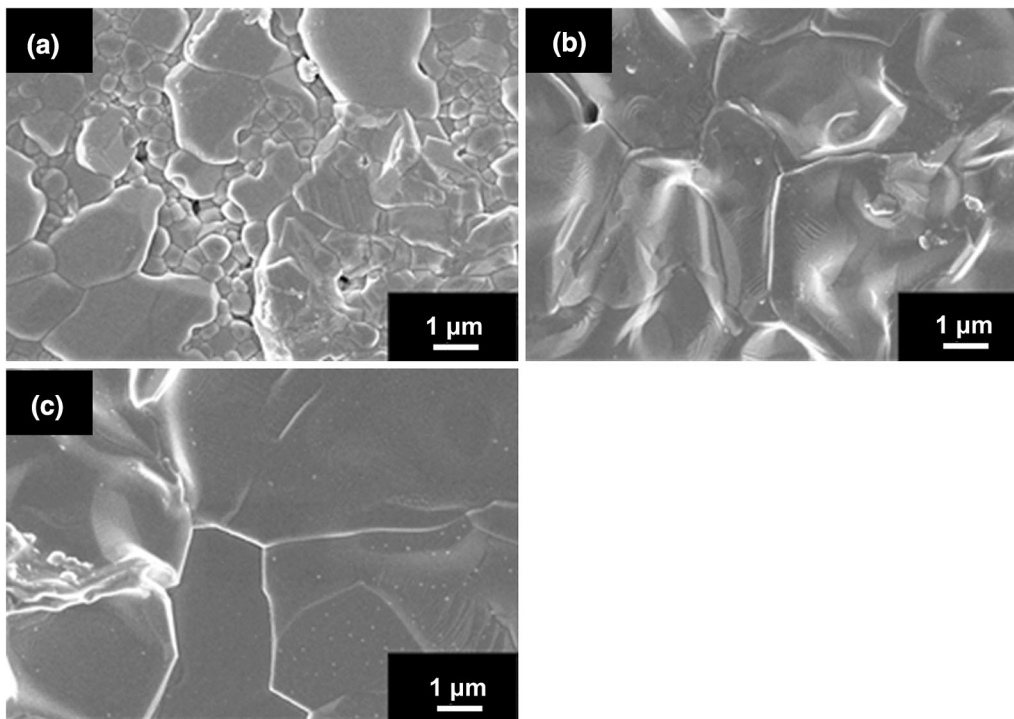


Fig. 8. SEM images of gahnite with 5 wt.% Cu-Nb-O additive with Cu:Nb molar ratio of 70:30 fired at various temperatures for 2 h: (a) 985°C, (b) 1035°C, and (c) 1085°C.

Cu was as low as 0.02 and 0.05, respectively. This revealed that the thermal conductivity decreased due to the solid solution of Cu. On the other hand, it is presumed that the reason for the relatively high thermal conductivity of ZAT is that Ti was not incorporated at Zn or Al sites of the gahnite lattice;

therefore, it did not significantly affect the thermal conductivity.

Based on the results described above, guidelines can be proposed for developing gahnite that does not form a solid solution at the  $\text{Zn}^{2+}$  site, that is, which develops additives composed of elements with

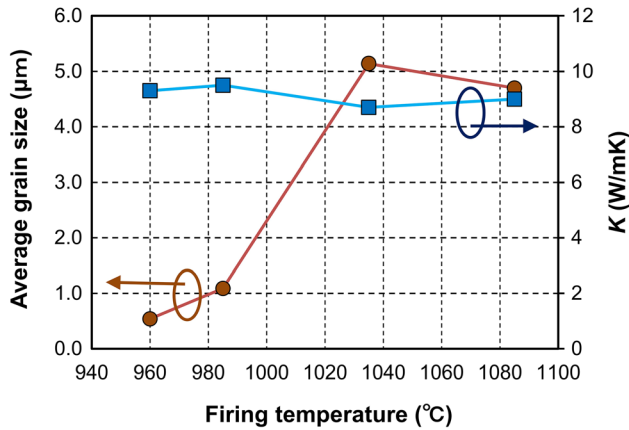


Fig. 9. Average grain size and thermal conductivity of gahnite with 5 wt.% Cu-Nb-O additive with Cu:Nb molar ratio of 70:30 as a function of firing temperature. The holding time at each temperature was 2 h.

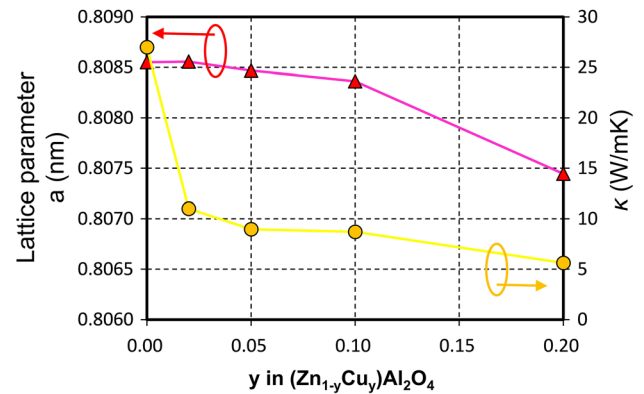


Fig. 11. Lattice parameter  $a$  of  $(Zn_{1-y}Cu_y)Al_2O_4$  ( $y = 0.00, 0.02, 0.05, 0.10, 0.20$ ) powders (spinel structure in space group  $Fd3m$ ) and thermal conductivity of the sintered bodies as function of the substitution amount of Cu ( $y$ ). In the case of  $y$  ranging from 0.02 to 0.20, the samples were fired at 1435°C, while in the case of  $y = 0.00$ , the sample fired at 1485°C was used. The holding time at each temperature was 2 h.

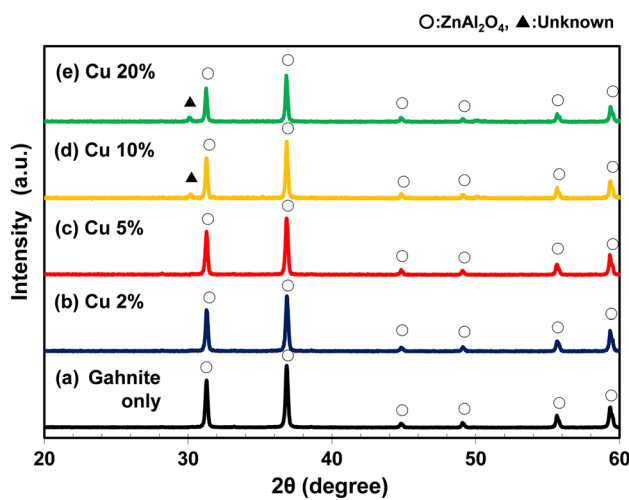


Fig. 10. X-ray diffraction patterns of powders obtained by substituting Cu for a solid solution at Zn site of gahnite  $(Zn_{1-y}Cu_y)Al_2O_4$  ( $y = 0.00, 0.02, 0.05, 0.10, 0.20$ ): (a)  $y = 0.00$ , fired at 1485°C; (b)  $y = 0.02$ , fired at 1435°C; (c)  $y = 0.05$ , fired at 1435°C; (d)  $y = 0.10$ , fired at 1435°C; and (e)  $y = 0.20$ , fired at 1435°C. The holding time at each temperature was 2 h.

different valences and ionic radii from  $Zn^{2+}$  to increase the thermal conductivity of gahnite.

### CONCLUSIONS

We focused on gahnite ( $ZnAl_2O_4$ ), an aluminum-based oxide that is expected to exhibit high thermal conductivity, and developed a sintering additive that, even at small amounts, can enable gahnite to sinter at low temperature below 1000°C. Furthermore, the dielectric and thermal properties were evaluated. The results can be summarized as follows:

1. For single-component gahnite, a dense sintered body was obtained at a high temperature of 1485°C. The Cu-Nb-O additive was effective for

low-temperature sintering of gahnite, with the composition having a Cu:Nb molar ratio of 70:30 resulting in the best sinterability. Gahnite with 5 wt.% of this additive formed a dense sintered body at 960°C.

2. The dielectric properties of the gahnite sintered body with the Cu-Nb-O additive were  $\epsilon_r = 9.1$ ,  $Q \times f = 30,000$  GHz (at measurement frequency of approximately 13 GHz), and  $\tau_f = -69$  ppm/K, being superior to those of single-component gahnite. The thermal conductivity was 9.3 W/m-K, exceeding values for conventional LTCC materials. However, this value is still approximately one-third of that of single-component gahnite (27 W/m-K).
3. We investigated the reasons behind the low thermal conductivity and found that the lattice constant of gahnite decreased when the substitution amount of Cu was increased. The thermal conductivity decreased correspondingly, indicating that the thermal conductivity decreases due to the solid solution of Cu in gahnite. These results indicate that it is necessary to develop low-melting sintering additives that do not enter the  $Zn^{2+}$  site of gahnite as solid solution, in order to achieve low-temperature sintering without losing the high thermal conductivity of gahnite.

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### CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

### REFERENCES

1. M.T. Sebastian, *Dielectric Materials for Wireless Communication* (New York: Elsevier, 2008), pp. 445–512.
2. Y. Imanaka, *Multilayered Low Temperature Cofired Ceramics (LTCC) Technology* (New York: Springer, 2005), pp. 1–18.
3. M.T. Sebastian and H. Jantunen, *Int. Mater. Rev.* 53, 58 (2008).
4. I.J. Induja, P. Abhilash, S. Arun, K.P. Surendran, and M.T. Sebastian, *Ceram. Int.* 41, 13572 (2015).
5. M. Shimizu, S. Tomioka, N. Yoshida, I. Kameyama, and K. Okuda, Japanese Patent Publication No. 2015-156406 (2015).
6. K. Shigeno, H. Katsumura, H. Kagata, H. Asano, and O. Inoue, *Ferroelectrics* 356, 189 (2007).
7. K. Shigeno, T. Asakawa, Y. Kuraoka, and H. Fujimori, *Trans. Mater. Res. Soc. Jpn.* 41, 121 (2016).
8. K.P. Surendran and M.T. Sebastian, *J. Appl. Phys.* 98, 044101 (2005).
9. S.B. Roshni, M.T. Sebastian, and K.P. Surendran, *Sci. Rep.* 7, 40839 (2017).
10. P. Fu, Z.Y. Wang, Z.D. Lin, Y.Q. Liu, and V.A.L. Roy, *J. Mater. Sci. Mater. Electron.* 28, 9589 (2017).
11. S. Thomas and M.T. Sebastian, *Mater. Res. Bull.* 43, 843 (2008).
12. S. Takahashi, A. Kan, and H. Ogawa, *J. Eur. Ceram. Soc.* 37, 3059 (2017).
13. H. Kagata, T. Inoue, J. Kato, and I. Kameyama, *Jpn. J. Appl. Phys.* 31, 3152 (1992).
14. K. Shigeno, H. Katsumura, H. Kagata, H. Asano, and O. Inoue, *Key Eng. Mater.* 320, 181 (2006).
15. M. Shimizu, Japanese Patent Publication No. 2013-115107 (2013).
16. B.W. Hakki and P.D. Coleman, *IRE Trans. Microw. Theory Tech.* 8, 402 (1960).
17. K. Shigeno, S. Kaneko, T. Yamane, J. Shimokawa, and H. Fujimori, *J. Jpn. Soc. Powder Metall.* 65, 347 (2018).
18. R.M. German, S. Farooq, and C.M. Kippbut, *Mater. Sci. Eng. A* 105/106, 215 (1988).
19. K. Shigeno, T. Asakawa, Y. Kuraoka, S. Kaneko, and H. Fujimori, *Trans. Mater. Res. Soc. Jpn.* 44, 203 (2019).
20. H.H. Liu and J.H. Jean, *Int. J. Ceram. Eng. Sci.* 2, 38 (2020).
21. E. Wahlstrom and B.O. Marinder, *Inorg. Nucl. Chem. Lett.* 13, 559 (1977).
22. D.W. Kim, I.T. Kim, B. Park, and K.S. Hong, *J. Mater. Res.* 16, 1465 (2001).
23. T. Yamamoto, Y. Ohishi, K. Kurosaki, H. Muta, and S. Yamana, *J. Jpn. Soc. Powder Powder Metall.* 59, 196 (2012).
24. A. Eucken, *Fortchg. Gebiete Ingenieurw. B3 Forschungsheft* 16, 353 (1932).
25. R.D. Shannon, *Acta Crystallogr. A* 32, 751 (1976).

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