Improving the sintering performance and dielectric properties of thermally conductive low-temperature co-fired alumina by controlling the firing atmosphere

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ABSTRACT
Here, we focused on the firing atmosphere to promote low-temperature sintering and enhance the dielectric properties of low-temperature co-fired alumina (LTCA) containing 5 wt.% of CuO–TiO\(_2\)–Nb\(_2\)O\(_5\)–Ag\(_2\)O as the sintering aid. Controlling the oxygen partial pressure (pO\(_2\)) to form Ag–Cu–Ti–Nb–O-based complex oxides and lowering the melting temperature of the sintering aid are necessary to improve the sinterability. Moreover, controlling the pO\(_2\) such that Ag\(_2\)O and Nb\(_2\)O\(_5\) disappear is important to improve the dielectric properties of LTCA. A dense sintered body with approximately 95% relative density was obtained by firing an LTCA sample for 2 h at a firing temperature of 900°C and pO\(_2\) of 0.02 atm, and its dielectric properties were measurable. The thermal conductivity of 17 W/mK was better than that of conventional low-temperature co-fired ceramics (2–7 W/mK). These results provide important guidelines for low-temperature sintering and producing LTCA with enhanced dielectric properties.

1. Introduction
Alumina (Al\(_2\)O\(_3\)) has a high thermal conductivity, high physical strength, and excellent dielectric properties [1–5], and it is therefore widely used to fabricate electronic components, such as wiring substrates and integrated circuits (IC) packages. However, in general, the sintering temperature of pure alumina, even in fine powder form, is approximately 1400°C or higher, which is not preferable for energy saving and realizing a carbon-neutral society. Furthermore, co-fired conductor materials must have a high melting point, such as that of W or Mo, resulting in high electrical resistance. The ceramics that can be fired together with low-resistance conductor materials, such as Ag (melting point of 961°C) or Cu (melting point of 1084°C), are called low-temperature co-fired ceramic (LTCC) materials [6–10]. Because LTCC materials allow the fabrication of several electrical components, including built-in capacitors, inductors, and low-loss transmission lines, they are widely used for producing high-frequency modules. However, LTCC materials must contain large amounts of glass in alumina (approximately 50–60% of the total weight) to achieve low-temperature sintering; hence, the majority of these materials exhibit several limitations, such as low thermal conductivities.

As a first step toward the production of LTCC modules with high thermal conductivities and physical strengths (such as those of alumina), several researchers have developed sintering aids that allow low-temperature sintering when mixed in small quantities. Although researchers [11–16] have previously examined sintering aids based on MnO–TiO\(_2\) [11,13], CuO–TiO\(_2\) [11,12,14,15], and CuO–TiO\(_2\)–MgO [16], none of the compositions delivered adequate sintering performance at 1000°C. In contrast, we obtained dense alumina at sintering temperatures of 935–1000°C by adding 4–10 wt.% of CuO–Nb\(_2\)O\(_5\) (binary type) and CuO–TiO\(_2\)–Nb\(_2\)O\(_5\) (ternary type) sintering aids to alumina [17–20]. Furthermore, the sintering temperature could be decreased to 900°C (or below) using 5 wt.% of quaternary sintering aids. In this case, Ag\(_2\)O was added to a CuO–TiO\(_2\)–Nb\(_2\)O\(_5\) ternary sintering aid [21–23]. We confirmed that the melting temperature of CuO–TiO\(_2\)–Nb\(_2\)O\(_5\) was lowered by the addition of Ag\(_2\)O [21,23]. The production of Co-firing alumina, containing 5 wt.% of the aforementioned quaternary sintering aids, with Ag electrodes at 900°C or below was also possible by increasing the Ag\(_2\)O content in the sintering aid [22]. One of the obtained sintered materials exhibited a thermal conductivity of 18 W/mK [21,22], which was significantly higher than that of conventional LTCC materials (approximately 2–7 W/mK [8,9]). The microwave relative dielectric constant (\(\varepsilon_r\)) (measured at approximately 12 GHz) after firing at 860°C for 24 h was 11.2, and the product of the quality factor and resonant frequency (\(Q \times f\)) was 4600 GHz [22]. These values are sufficient for the LTCC materials used in the
microwave region spanning from 300 MHz to 30 GHz. This suggests that the obtained novel materials, named as “low-temperature co-fired alumina” (LTCA) materials, can be used as LTCC modules owing to their high thermal conductivities [23].

However, the retention time of LTCA at the firing temperature is 24 h, and further enhancement in sinterability (that is, shortening of the retention time) is essential for its practical use. In addition, the dielectric properties of LTCA are significantly inferior to those of the alumina single component [21–23]. At present, efforts are being made to use millimeter waves (region: 30 GHz or higher) for high-speed data transfer [24]; hence, a significant improvement in the $Q \times f$ value of LTCA fired for a relatively shorter retention time is required. However, in reality, the sinterability of the LTCA sample with a retention time of 2 h at 900°C in an air atmosphere is worse than that of the sample with a retention time of 24 h at the same temperature [23]; hence, we were unable to measure the dielectric properties. Therefore, in this study, we focused on the firing atmosphere. Although certain studies on the effect of firing atmosphere on the sinterability of alumina have been conducted [18,25], none of them were centered on LTCA. Here, we investigated the enhancement in both the sinterability and dielectric property of LTCA, specifically by controlling the oxygen partial pressure ($pO_2$).

2. Materials and methods

2.1. Fabrication of LTCA

Figure 1 shows the process flow for obtaining alumina ceramics containing the CuO–TiO$_2$–Nb$_2$O$_5$–Ag$_2$O sintering aid used in this study. Alumina powder (95 wt.%; TM-5D; Taimei Chemical Co., Ltd.; average particle diameter of 0.2 µm) was mixed with 5 wt.% of a sintering aid composed of CuO, TiO$_2$, Nb$_2$O$_5$, and Ag$_2$O (commercially available chemicals). The molar ratio of CuO:TiO$_2$:Nb$_2$O$_5$:Ag$_2$O was fixed at 4:1:2:3.2, which was previously determined as the best co-firing ratio for quaternary oxides [22]. The powder was mixed in a ball mill for 16 h using water as the dispersion medium. The mixture was then dried, granulated in polyvinyl alcohol binder, and finally molded into discs by applying a uniaxial pressure of 75 MPa. After burning the binder, the green bodies (unfired discs) were fired at temperatures ranging from 750 to 1000°C for 2 h (heating and cooling rates: 10°C/min); nitrogen ($N_2$) gas, air, and oxygen ($O_2$) gas, were used in the firing atmosphere. The $pO_2$ was controlled by changing the flow ratio of the $O_2$ and $N_2$ gases, as required. For comparison, samples fired in the same atmosphere for 24 h were also prepared and evaluated.

Figure 1. Experimental procedure to obtain alumina ceramics containing the CuO–TiO$_2$–Nb$_2$O$_5$–Ag$_2$O sintering aid.
2.2. Characterizations

The properties of the sintered samples, such as the bulk density ($\rho$), microwave dielectric property, and thermal conductivity ($\kappa$), were measured. The theoretical densities of the samples were calculated from those of alumina (3.99 g/cm$^3$), CuO (6.31 g/cm$^3$), TiO$_2$ (4.25 g/cm$^3$), Nb$_2$O$_5$ (4.47 g/cm$^3$), and Ag$_2$O (7.14 g/cm$^3$), assuming the properties to be additive; the theoretical density of alumina containing 5 wt.% of the sintering aid used in this study was 4.05 g/cm$^3$. The relative density was calculated as the ratio of measured bulk density to theoretical density. The following three major dielectric properties were analyzed using a network analyzer (Agilent Technologies, 8720ES) using the Hakki-Coleman method [26]:

1. Relative dielectric constant ($\varepsilon_r$)
2. Product of the quality factor and resonant frequency ($Q \times f$)
3. Temperature coefficient of the resonant frequency ($\tau$)

The $\tau$ values were calculated using the following equation:

$$\tau = \frac{1}{f(\tau)} \times \frac{f(T) - f(T_0)}{T - T_0}$$

where $f(T_0)$ and $f(T)$ are the resonant frequencies at 20 and 80°C, respectively. The thermal conductivities were measured using the xenon flash method (Netzsch, LFA447).

Further measurements for analyzing the sintering performance and dielectric properties of the LTCA were conducted using scanning electron microscopy (SEM; JEOL, JSM-7600 F) and X-ray diffraction (XRD; Rigaku, Ultima IV) with a Cu Ka radiation source, along with a differential thermal analyzer (DTA; Seiko Instruments, TG/DTA32).

3. Results and discussion

3.1. Effect of three firing atmospheres (air, $O_2$, and $N_2$) on the sintering performance of the LTCA

Figure 2 shows the relationship between the ceramic density and firing temperature of the alumina containing 5 wt.% of the CuO–TiO$_2$–Nb$_2$O$_5$–Ag$_2$O sintering aid. It can be seen that the sintering performance changes according to the firing atmosphere. No significant dependence of the sintered density on the firing atmosphere was observed at a firing temperature of 750°C. The densities of the samples were approximately the same as those of the green compacts, indicating that densification of alumina was not initiated at this temperature. At a firing temperature of 800°C, densification was observed in all the samples, and the sintered density of the samples was higher in the $N_2$ (Figure 2a) atmosphere than that in air (Figure 2b) or the $O_2$ (Figure 2c) atmosphere. The obtained sintered densities of the samples in the three firing atmospheres were in the following order: $N_2$ = air $> O_2$. At firing temperatures in the range of 800–900°C, the increase in the sintered density of the samples under air and $O_2$ atmospheres was larger than that in the $N_2$ atmosphere.
atmosphere. Furthermore, the sintered density was in the following order: air > O$_2$ > N$_2$. At the firing temperature of 900°C, the sintered density of the sample fired in air reached approximately 3.79 g/cm$^3$, which is approximately 94% of the theoretical density of the material (4.05 g/cm$^3$). At the firing temperature of 1000°C, the sintered densities of the samples under all the three firing atmospheres were more than 94% of their theoretical densities.

Figure 3 presents the SEM images of the fractured surfaces of the sintered samples under various firing conditions. At a firing temperature of 800°C in air, a slight necking was observed (Figure 3a). Necking and grains with angular shapes were observed clearly at a firing temperature of 900°C (Figure 3b). At a firing temperature of 950°C, grain growth and near disappearance of voids were observed (Figure 3c). For the samples fired at 900°C in N$_2$ and O$_2$ atmospheres (Figures 3d and e), the grain morphologies were similar to that of the sample fired at the same temperature in air (Figure 3b); however, the porosities were slightly higher.

The above results clarify the dependence of the sintering behavior of alumina on the firing atmosphere, despite containing the same sintering aid. Figure 4 shows the DTA curves of the heat-treated sintering aids in different atmospheres (heating rate was 10°C/min). The melting temperature of the sintering aid determined from the endothermic peak in air was approximately 866°C (Figure 4a), which was lower than that in the O$_2$ atmosphere (approximately 875°C) (Figure 4b). It can also be seen that the melting temperatures of the sintering aid in the N$_2$ atmosphere was approximately 831°C (Figure 4c), which was more than 30°C lower than the melting temperatures in the other atmospheres. However, at temperatures between 800 and 850°C (see Figure 2), the densification of the samples fired in air and the O$_2$ atmosphere was faster.

**Figure 3.** SEM images of the fractured surfaces of the sintered samples fired at (a) 800°C in air, (b) 900°C in air, (c) 950°C in air, (d) 900°C in an N$_2$ atmosphere, (e) 900°C in an O$_2$ atmosphere, and (f) 900°C in an N$_2$–O$_2$ atmosphere (pO$_2$ = 0.02 atm). The retention time at each temperature was 2 h.

**Figure 4.** DTA curves of the CuO–TiO$_2$–Nb$_2$O$_5$–Ag$_2$O sintering aids obtained in (a) air, (b) O$_2$ atmosphere, (c) N$_2$ atmosphere, and (d) N$_2$–O$_2$ (pO$_2$ = 0.02 atm) atmosphere.
Figure 5 presents the XRD patterns of the sintering aids after heat treatment at 750, 800, and 850°C in air. According to the DTA results (Figure 4a), the sintering aids fired in air did not yield the liquid phase until the firing temperatures reached 866°C. Instead, a novel Ag–Cu–Ti–Nb–O-type complex oxide (represented by the symbol ⌨) was produced in the temperature range of 750–800°C. This compound was presumed to have the same crystal structure as that of the quadruplerorphoskite-type Cu$_{3.21}$Ti$_{1.18}$Nb$_{2.69}$O$_{12}$ (ICDD-PDF 01-080-7641; space group: Im 3; lattice parameter a: 0.747946 (4) nm) [27], and Ag was incorporated into the structure. This complex oxide was considered to significantly promote solid-state sintering [23] in the temperature range of 750–850°C, as shown in Figure 2a. Currently, we are also conducting a detailed study to determine the accurate composition and structure of the novel Ag–Cu–Ti–Nb–O-type complex oxide, which will be beneficial for future studies in this field.

Figure 6 shows the XRD patterns of the sintering aid after heat treatment at 850°C in different firing atmospheres. The sintering aid samples fired in the O$_2$ atmosphere did not yield the liquid phase until the firing temperature reached 875°C; however, the Ag–Cu–Ti–Nb–O-type complex oxide was also detected at 850°C (Figure 6a), as in the case of heat treatment in air (Figure 6b). Therefore, we assumed that the difference in the sinterability of the samples fired in air and the O$_2$ atmosphere was due to the difference in their solid-phase diffusivity, which depends on the melting temperature of each sintering aid. In contrast, the sinterability of the sample fired in the N$_2$ atmosphere at 800°C was better than those of the samples fired in other atmospheres, because the melting temperature of the former sample was the lowest among those observed in the three atmospheres, as shown in Figure 4. However, the Ag–Cu–Ti–Nb–O-type complex oxide was not produced, even at the elevated firing temperature of 850°C (Figure 6c). Therefore, we concluded that the degree of sintering was lower in the N$_2$ atmosphere than in air and the O$_2$ atmosphere at 850–900°C.

For reference, the trends of the melting temperature and the XRD patterns shown in Figures 4, 5, and 6 were qualitatively consistent with the results of the experiments performed using the CuO–TiO$_2$–Nb$_2$O$_5$ sintering aid [18].

### 3.2. Improvement in the sinterability of LTCA by controlling pO$_2$ during firing

From the above results, two factors that enhance the sinterability of LTCA were suggested, as reported in a previous study on alumina with ternary sintering aids [18]:

1. Formation of Ag–Cu–Ti–Nb–O complex oxide from the sintering aid.
2. Low melting temperature of the sintering aid.

To verify these aforementioned factors, the pO$_2$ in our study was controlled by changing the flow rate ratio of N$_2$ and O$_2$, and the effect of the pO$_2$ on the density of the sintered body was investigated in detail.
Figures 7 a and b show the pO$_2$ dependence of the sintered densities of alumina containing 5 wt.% of the CuO–TiO$_2$–Nb$_2$O$_5$–Ag$_2$O quaternary sintering aid obtained by firing at 920 and 850°C for 2 h, respectively. Furthermore, previous results for alumina containing 5 wt.% of the CuO–TiO$_2$–Nb$_2$O$_5$ ternary sintering aid (the molar ratio CuO: TiO$_2$: Nb$_2$O$_5$ was 4: 1: 2) are also shown [18]. In these figures, the curve exhibits a convex shape, indicating the pO$_2$ dependence of the density of the sintered body. Although the pO$_2$ dependence of the density of the sintered sample with the quaternary sintering aid was smaller than that of the sintered alumina with the abovementioned ternary sintering aid, a similar pO$_2$ dependence was observed. Moreover, the density of the sintered body reached the maximum value at a pO$_2$ of 0.02 atm, which is lower than that in air. In addition, the densities of the sintered bodies fired at 0.002 atm ≤ pO$_2$ < 0.21 atm exceeded those of the samples fired in air.

In this study, the pO$_2$ during firing was found to play a crucial role in determining the density of the sintered body. Figure 2d shows the relationship between the firing temperature and the sintered densities of the samples fired in an atmosphere with a pO$_2$ of 0.02 atm. At all the firing temperatures, the sintered density in the atmosphere with a pO$_2$ of 0.02 atm was higher than those of the samples fired in the other three atmospheres. In addition, as shown in Figure 3f, the fractured surface of the sample fired at 900°C was angular, and grain boundary fracture as well as traces of intragranular fracture were observed.

To understand the reason for these results, the following qualitative analysis was performed. Figure 7 presents the pO$_2$ dependence of the XRD patterns of the sintering aids after heat treatment at 850°C for 2 h using N$_2$–O$_2$ mixed gas. Interesting results were obtained that differed from those obtained using the ternary sintering aid. At a pO$_2$ of 0.5 atm, AgNbO$_3$ was obtained as the main phase, although the Ag–Cu–Ti–Nb–O complex oxide was also present. The intensity of the peak corresponding to AgNbO$_3$ decreased with decreasing pO$_2$, and nearly disappeared at pO$_2$ ≤ 0.02 atm (Figure 6d). In contrast, the Ag–Cu–Ti–Nb–O complex oxide remained when the pO$_2$ was equal to or more than 0.005 atm. When the pO$_2$ was 0.002 atm, the intensity of the peak of the complex oxide significantly decreased. Furthermore, as described in Figure 6c, formation of the complex oxide was not confirmed in the case of firing in the N$_2$ atmosphere.

The presence or absence of the Ag–Cu–Ti–Nb–O complex oxides (Figure 8) and the pO$_2$ dependence of the sintered densities (Figure 8) are qualitatively consistent. In addition, as shown in Figures 4 a and d, among the firing conditions for forming the Ag–Cu–Ti–Nb–O complex oxide, the melting point of the sintering aid at the pO$_2$ of 0.02 atm was 840°C, which was lower than that in air (866°C). Thus, the melting point of the sintering aid (Figure 4) was in qualitative agreement with the pO$_2$ dependence of the sintered densities (Figure 7). As shown in Figure 4, the factor leading to the decrease in the melting temperature of the sintering aid due to the decrease in pO$_2$ during heat treatment is unclear at this time. We presume that the ratio of Cu$^+$ to Cu$^{2+}$ in the sintering aid increases with
decreasing $pO_2$, which may be the cause of the decrease in the melting temperature; further research on this topic will be presented in our future studies. Figure 9 summarizes the relationship between the melting temperatures of the quaternary sintering aids used in this study and those of the ternary sintering aids reported in a previous study [18], as well as the sintered densities of the alumina containing the above sintering aids after firing at 850°C for 2 h. In this figure, the plots are divided into the cases where the (Ag–) Cu–Ti–Nb–O complex oxides are formed and those where they are absent. From the above figure, it is clear that increasing the density of the sintered body of alumina is effective as the sintering aid forms the abovementioned complex oxide and has a low melting point. This clarifies the factors essential for enhancing the sinterability of alumina in this system.

3.3. Effect of firing atmosphere on the dielectric properties of LTCA

Notably, the $pO_2$ during firing also affects the dielectric properties of the LTCA. Table 1 shows the sintered densities, dielectric properties, and thermal conductivities of the samples prepared under different firing atmospheres, firing temperatures, and retention times. The dielectric properties of the samples fired for 2 h at 900°C in the $O_2$
Figure 8. XRD patterns of the sintering aid after heat treatment at 850°C and different pO$_2$ adjusted by the N$_2$–O$_2$ mixture atmosphere. The retention time at each temperature was 2 h.

Figure 9. Relationship between the sintering densities of the alumina containing 5 wt.% of the CuO–TiO$_2$–Nb$_2$O$_5$ (ternary) or CuO–TiO$_2$–Nb$_2$O$_5$–Ag$_2$O (quaternary) sintering aids, and the melting temperatures of these sintering aids under different firing atmospheres after firing at 850°C for 2 h. Compound ● denotes that the quadruple-perovskite-type Cu–Ti–Nb–O-based or Ag–Cu–Ti–Nb–O-based complex oxides were produced during the heat treatment; No-compound ● denotes that these compounds were not produced.
Table 1. Firing conditions, sintered densities, dielectric properties ($\varepsilon_r, Q \times f$, and $\tau_f$), and thermal conductivities of alumina containing 5 wt.% of the CuO–TiO$_2$–Nb$_2$O$_5$–Ag$_2$O sintering aid. The cross marks (×) denote that the dielectric measurements of the samples could not be performed owing to the significantly low values of the properties.

| Sample | Firing temp. (°C) | Retention time (h) | Atmosphere [pO$_2$] | Sintered density (g/cm$^3$) | $\varepsilon_r$ (–) | $Q \times f$ (GHz) | $\tau_f$ (ppm/K) | $\kappa$ (W/mK) |
|--------|------------------|-------------------|---------------------|--------------------------|-----------------|-----------------|----------------|--------------|
| K01    | 900              | 2                 | O$_2$ (1 atm)       | 3.67                     | ×               | ×               | ×              | 15           |
| K02    | 900              | 2                 | Air (0.21 atm)      | 3.78                     | ×               | ×               | ×              | 17           |
| K03    | 900              | 2                 | N$_2$–O$_2$ (0.02 atm) | 3.82                     | 10.8            | 3830            | –52            | 17           |
| K04    | 900              | 2                 | N$_2$ (10$^{-4}$ atm) | 3.65                     | ×               | ×               | ×              | 15           |
| K05    | 900              | 24                | O$_2$ (1 atm)       | 3.88                     | ×               | ×               | ×              | 20           |
| K06    | 850              | 24                | Air (0.21 atm)      | 3.80                     | 10.4            | 3510            | –64            | 19           |
| K07    | 850              | 2                 | N$_2$–O$_2$ (0.02 atm) | 3.83                     | 10.7            | 4150            | –49            | 19           |
| K08    | 900              | 24                | N$_2$ (10$^{-4}$ atm) | 3.75                     | 9.8             | 6330            | –47            | 19           |

Atmosphere (pO$_2$ = 1.0 atm, K01) and air (pO$_2$ = 0.21 atm, K02) were extremely poor, and the dielectric measurements were impossible, although the relative density of the sample was approximately equal to or more than 90%. For reference, the dielectric properties of the sample that was fired for 24 h at 850°C in air (K06) were as follows: $\varepsilon_r = 10.4$, $Q \times f = 3510$ GHz (measurement frequency of approximately 12 GHz), and $\tau_f = –64$ ppm/K. In addition, according to our previous study [28], it has been reported that the dielectric property of the sample fired for 24 h at 900°C in an air atmosphere using the same kind of raw material powder and composition as in this study was low and could not be measured. In contrast, the dielectric properties of the sample fired for 2 h at 900°C and a PO$_2$ controlled to 0.02 atm (K03) were measurable, yielding $\varepsilon_r = 10.8$, $Q \times f = 3830$ GHz, and $\tau_f = –52$ ppm/K, which were also equal to or higher than those of K06 described above. The thermal conductivity of the sample was 17 W/mK, which is higher than those of conventional LTCC materials.

The dielectric properties of the sample fired at 850°C for 24 h in the N$_2$–O$_2$ atmosphere (pO$_2$ = 0.02 atm, K07) were $\varepsilon_r = 10.7$, $Q \times f = 4150$ GHz, and $\tau_f = –64$ ppm/K. Furthermore, the dielectric properties of the sample (K04) fired for 2 h at 900°C in the N$_2$ atmosphere were extremely poor and unmeasurable. Because the dielectric properties of the sample (K08) fired at 900°C for 24 h in the same N$_2$ atmosphere can be measured, it was considered that the difference between these two samples lies in the sinterability. Therefore, lowering the pO$_2$ within the range in which sinterability can be ensured, can yield higher Q X f and $\tau_f$ values; in particular, the value of $\tau_f$ can be remarkably enhanced.

From the XRD patterns of the sintered bodies (Figure 10), the dielectric properties are considered to be related to the disappearance of the AgNbO$_3$ phase owing to the decrease in the pO$_2$. This is because AgNbO$_3$ has a Q value (measured at 1 MHz) less than 1000, and a temperature coefficient of dielectric constant ($\tau_f$) of approximately

![Figure 10. XRD patterns of the alumina containing 5 wt.% of the CuO–TiO$_2$–Nb$_2$O$_5$–Ag$_2$O sintering aids fired at 900°C for 2 h under different firing atmospheres.](image-url)
5000 ppm/K (or $\tau_f \sim -2500$ ppm/K) [29,30]. A similar relationship between the disappearance of AgNbO$_3$ and $\tau_f$ has been confirmed in the low-temperature sintered Al$_2$O$_3$–TiO$_2$ [28]. However, Ag is also precipitated when the po$_2$ decreases, as shown in Figure 10, and the verification of insulation reliability will be necessary for future studies.

Thus, it was observed that by controlling the po$_2$, even with the same composition of LTCA, both the sinterability and precipitation phase can be modified to enhance the dielectric properties of LTCA; this results in the shortening of the firing time.

4. Conclusions

In this study, we focused on the firing atmosphere to promote low-temperature sintering and enhance the dielectric properties of LTCA containing 5 wt.% of the CuO–TiO$_2$–Nb$_2$O$_5$–Ag$_2$O sintering aid. From the results, we conclude the following:

(1) The sintered body density is maximized at po$_2 < 0.21$ atm, which is the po$_2$ of atmospheric air. Thus, the sinterability is enhanced by shortening the firing time.

(2) To improve sinterability, the formation of the Ag–Cu–Ti–Nb–O-based complex oxide and lowering of the melting temperature of the sintering aid is necessary.

(3) A dense sintered body was obtained with a relative density of approximately 95% for the sample fired for 2 h at a po$_2$ of 0.02 atm and a firing temperature of 900°C. The dielectric and thermal properties of the LTCA significantly improved and were observed to be better than those of conventional LTCC materials.

(4) By controlling the po$_2$ such that the Ag–Cu–Ti–Nb–O-based complex oxide remains and AgNbO$_3$ disappears, the dielectric properties, particularly $Q \times f$ and $\tau_f$, can be enhanced.

For practical use, $\tau_f$ must be reduced to zero while ensuring sinterability. Further improvements in the $Q \times f$ value is also desirable for applications in the millimeter-wave region.

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