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Low temperature sintering of the $Ba_2Ti_9O_{20}$ ceramics using B_2O_3/CuO and $BaCu(B_2O_5)$ additives

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Abstract

The effects of B_2O_3/CuO and $BaCu(B_2O_5)$ additives on the sintering temperature and microwave dielectric properties of $Ba_2Ti_9O_{20}$ ceramics were investigated. The B_2O_3 added $Ba_2Ti_9O_{20}$ ceramics were not able to be sintered below 1000 °C. However, when both CuO and B_2O_3 were added, they were sintered below 900 °C and had the good microwave dielectric properties. It was suggested that a liquid phase with the composition of $BaCu(B_2O_5)$ was formed during the sintering and assisted the densification of the $Ba_2Ti_9O_{20}$ ceramics at low temperature. $BaCu(B_2O_5)$ powders were produced and used to reduce the sintering temperature of the $Ba_2Ti_9O_{20}$ ceramics. Good microwave dielectric properties of Qxf = 16,000 GHz, $\varepsilon_r = 36.0$ and $\tau_f = 9.11$ ppm/°C were obtained for the $Ba_2Ti_9O_{20}$ ceramics containing 10.0 mol% $BaCu(B_2O_5)$ sintered at 875 °C for 2 h.

Keyword: Dielectric properties; A. Sintering; C. Dielectric properties; $Ba_2Ti_9O_{20}$

1. Introduction

Recently, low temperature co-fired ceramic (LTCC) multilayer devices, composed of alternating dielectric ceramics and internal metallic electrode layers, have been extensively investigated for the miniaturization of microwave dielectric components.[1,2] LTCC multilayer devices consist of alternating microwave dielectric ceramics and internal metallic electrode layers.[1] Ag has been widely used as the metallic electrode, because of its high conductivity and low cost. However, the melting temperature of Ag is low, about 961 °C, whereas the sintering temperature of the microwave dielectric ceramics is generally above 1400 °C. Therefore, for the fabrication of multilayer devices, it is necessary to develop microwave dielectric ceramics with a low sintering temperature, which can be co-fired with Ag.

The $BaO–TiO_2$ system has been extensively studied and a number of researchers have reported on this system, which has many compounds and excellent microwave dielectric properties.[3–5] In particular, the $Ba_2Ti_9O_{20}$ microwave dielectric ceramics, which were reported by Jonker and Kwestroo, exhibited good microwave dielectric properties with a high dielectric constant (ε_r) of 39.8, a high Q-factor of 8000 at 4 GHz and near zero temperature coefficient of resonance frequency (τ_f).[5,6] However, since the sintering temperature of these $Ba_2Ti_9O_{20}$ ceramics is high, they can not be used as LTCC and, consequently, many attempts have been made to lower their sintering temperature. $Ba_2Ti_9O_{20}$ ceramics containing 1.0 wt.% $3ZnO–B_2O_3$ were sintered at 940 °C, but their microwave dielectric properties were low.[7] BaBSiO glass was also used to reduce the sintering temperature of $Ba_2Ti_9O_{20}$ ceramics and this enabled their sintering temperature to be reduced to 900 °C, but they exhibited very low microwave dielectric properties of Qxf = 1150 GHz, and $\varepsilon_r = 13.2$.[8] $PbO–B_2O_3–SiO_2$ and $MgO–CaO–SiO_2–Al_2O_3$ glasses were also used to reduce the sintering temperature of $Ba_2Ti_9O_{20}$ ceramics, but the results were not satisfactory.[9,10] In previous studies, the addition of a small amount of B_2O_3 and CuO was found to reduce the sintering temperature of $BaTi_4O_9$ ceramics to below 900 °C and a liquid phase with the composition of $BaCu(B_2O_5)$ was thought to assist in their densification.[11] Moreover, $BaTi_4O_9$ ceramics containing $BaCu(B_2O_5)$ sintered below 900 °C without deteriorating their good microwave dielectric properties.[12] Therefore, it is also possible that these B_2O_3/CuO

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and $BaCu(B_2O_5)$ additives would be effective in decreasing the sintering temperature of the $Ba_2Ti_9O_{20}$ ceramics. In this work, these additives were used to reduce the sintering temperature of $Ba_2Ti_9O_{20}$ ceramics and their effects on the microwave dielectric properties were also investigated.

2. Experimental procedure

To prepare the $Ba_2Ti_9O_{20}$ ceramics, $BaCO_3$ (High Purity Chemicals, >99%, Japan) and TiO_2 (High Purity Chemicals, >99%, Japan) were mixed in a nylon jar with zirconia balls for 24 h, and then dried and calcined at 1180 °C for 6 h. After remilling with the B_2O_3 (High Purity Chemicals, >99%, Japan) and CuO (High Purity Chemicals, >99%, Japan) and $BaCu(B_2O_5)$ additives, the powder was dried, pressed into discs and sintered at 875–1000 °C for 2 h. For the $BaCu(B_2O_5)$, oxide compounds of BaO (High Purity Chemicals, >99%, Japan), CuO (High Purity Chemicals, >99%, Japan) and B_2O_3 (High Purity Chemicals, >99%, Japan) were mixed in a nylon jar with zirconia balls for 24 h, and then dried and calcined at 700 °C for 3 h. The microstructure of the specimens was studied using X-ray diffraction (Rigaku D/max-RC, Japan), and scanning electron microscopy (SEM: Hitach S-4300, Japan). The densities of the sintered specimens were measured by a water-immersion technique. The dielectric properties in the microwave frequency range were measured by a dielectric post resonator technique suggested by Hakki and Coleman and Courtney.[13,14] The temperature coefficients of the resonant frequency was measured at 6.5 GHz in the temperature range of 25–90 °C.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of the $Ba_2Ti_9O_{20}$ powders calcined at 1180 °C for 6 h. Most of the peaks were indexed as those of the $Ba_2Ti_9O_{20}$. Peaks for the $BaTi_4O_9$ and $Ba_4Ti_{13}O_{30}$ second phases were also observed in this specimen. Fig. 1(b)–(e) show the XRD patterns of the $Ba_2Ti_9O_{20}$ ceramics containing x mol% of B_2O_3 with $2.0 \le x \le 20.0$ sintered at 1000 °C for 2 h. When B_2O_3 was added to the $Ba_2Ti_9O_{20}$ ceramics, their

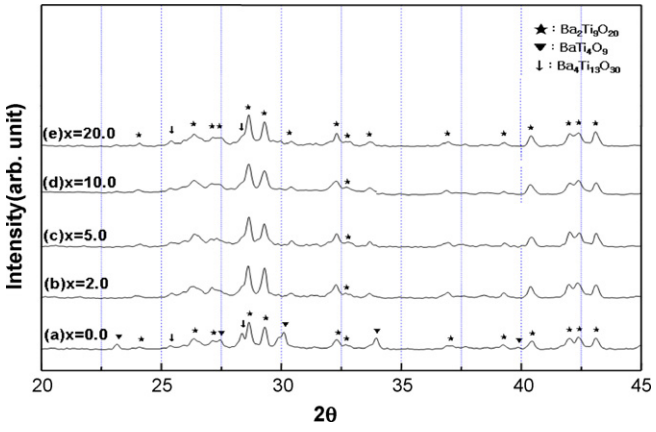

Fig. 1. (a) XRD pattern of the $Ba_2Ti_9O_{20}$ powders calcined at 1180 °C and XRD patterns of the $Ba_2Ti_9O_{20}$ ceramics containing x mol% of B_2O_3 with (b) $x = 2.0$; (c) $x = 5.0$; (c) $x = 10.0$; $x = 20.0$ sintered at 1000 °C for 2 h.

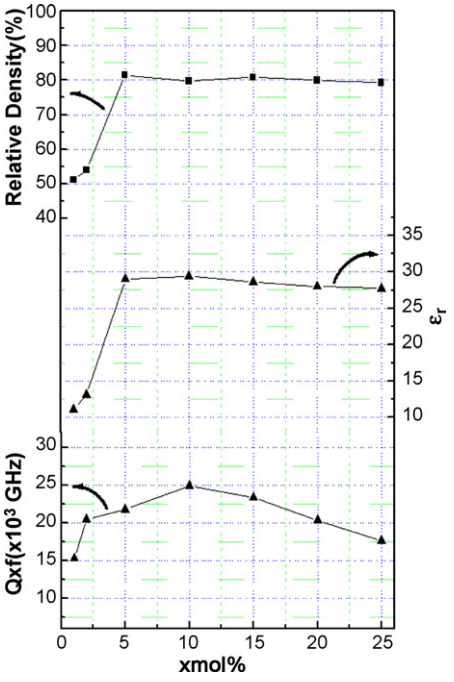

Fig. 2. Variations of the relative density, ε_r and Qxf value of the $Ba_2Ti_9O_{20}$ ceramics containing x mol% of B_2O_3 with $1.0 \le x \le 25.0$ sintered at 1000 °C for 2 h.

sintering temperature was reduced to 1000 °C and the amount of $BaTi_4O_9$ and $Ba_4Ti_{13}O_{30}$ second phases decreased. Previously, it was suggested that the sintering of the 5.0 wt.% B_2O_3 added $Ba_2Ti_9O_{20}$ ceramics was assisted by the presence of a liquid.[15] Furthermore, for the B_2O_3 added $BaTi_4O_9$ ceramics, a liquid phase containing BaO and B_2O_3 was formed during the sintering and assisted in the densification of the $BaTi_4O_9$ ceramics at 875 °C.[11] For the B_2O_3 added $Ba_2Ti_9O_{20}$ ceramics, peaks for the BaO–B_2O_3 second phase were not found. However, since the amounts of the $BaTi_4O_9$ and $Ba_4Ti_{13}O_{30}$ second phases decreased with the addition of B_2O_3, it is considered that some of the BaO in these second phases reacted with B_2O_3, resulting in the formation of BaO–B_2O_3 liquid phase, which assisted the densification of the $Ba_2Ti_9O_{20}$ at 1000 °C. Furthermore, these second phases changed into the Ti-rich phase, i.e. $Ba_2Ti_9O_{20}$ phase, after reacting with B_2O_3.

Fig. 2 shows the variations of the relative density, ε_r and Qxf value of the $Ba_2Ti_9O_{20}$ ceramics containing x mol% of B_2O_3 with $1.0 \le x \le 25.0$ sintered at 1000 °C for 2 h. The relative density of the specimen with 2.0 mol% of B_2O_3 was very low, being approximately 55% of the theoretical density, and increased with increasing B_2O_3 content to reach a saturated value when 5.0 mol% of B_2O_3 was added. The variation of ε_r is similar to that of the relative density. The Q-value increased with the addition of B_2O_3 due to the increase in the density and reached a maximum value of 25000 GHz for the specimen containing 10.0 mol% of B_2O_3. However, it decreased when the B_2O_3 content was further increased and this decrease was attributed to the increase in the amount of the liquid phase. The B_2O_3 added $Ba_2Ti_9O_{20}$ ceramics were not able to be sintered below 1000 °C and, thus, it would be difficult to use Ag as the

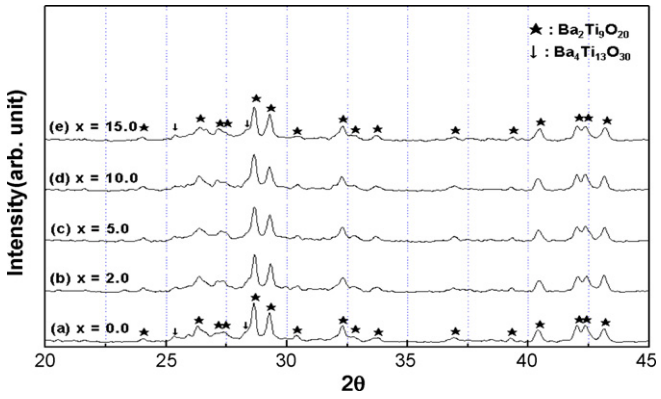

Fig. 3. XRD patterns of the $Ba_2Ti_9O_{20}$ ceramics containing 10.0 mol% of B_2O_3 and x mol% of CuO with (a) $x = 0.0$; (b) $x = 2.0$; (c) $x = 5.0$; (d) $x = 10.0$; (e) $x = 20.0$ sintered at 900 °C for 2 h.

electrode for them. Therefore, both CuO and B_2O_3 were added to the $Ba_2Ti_9O_{20}$ ceramics in an attempt to reduce the sintering temperature below 950 °C.

When CuO was added to the $Ba_2Ti_9O_{20}$ ceramics containing 10.0 mol% B_2O_3, they were able to be sintered at temperatures as low as 875 °C. Fig. 3 shows the X-ray diffraction patterns of the $Ba_2Ti_9O_{20}$ ceramics containing 10.0 mol% of B_2O_3 and x mol% of CuO with $0.0 \leq x \leq 15.0$ sintered at 900 °C for 2 h. Most of the peaks were indexed as those of the $Ba_2Ti_9O_{20}$ phase and peaks for the $Ba_4Ti_{13}O_{30}$ second phase indicated by an arrow were also observed. No variation of the XRD pattern was observed with the addition of CuO. The CuO additive itself cannot be responsible for reducing the sintering temperature of the $Ba_2Ti_9O_{20}$ ceramics below 900 °C, because the CuO added $Ba_2Ti_9O_{20}$ ceramics were not sintered below 1060 °C. According to a previous work, $BaCu(B_2O_5)$ second phase was observed in the CuO and B_2O_3 added $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics and assisted in the densification of the specimens at low temperature.[16] In the case of the $Ba_2Ti_9O_{20}$ ceramics, however, it was difficult to identify the presence of the $BaCu(B_2O_5)$ second phase using XRD pattern. A similar result was also observed for the CuO and B_2O_3 added $BaTi_4O_9$ ceramics.[11] On the other hand, the $Ba_2Ti_9O_{20}$ ceramics were well sintered even at 875 °C when a small amount of $BaCu(B_2O_5)$ was added, as will be discussed later. Therefore, it is considered that the liquid phase with the composition of $BaCu(B_2O_5)$ might be responsible for the densification of the CuO and B_2O_3 added $Ba_2Ti_9O_{20}$ ceramics at low temperature. Furthermore, it is thought that $BaCu(B_2O_5)$ second phase existed as an amorphous phase in $Ba_2Ti_9O_{20}$ ceramics after cooling.

Fig. 4(a)–(c) show the SEM images of the thermally etched surfaces of the $Ba_2Ti_9O_{20}$ ceramics containing 10.0 mol% of B_2O_3 and x mol% of CuO with $2.0 \leq x \leq 15.0$ sintered at 900 °C for 2 h. For the specimen containing 2.0 mol% of CuO, a porous microstructure was formed. However, when 10.0 mol% CuO was added, a dense microstructure developed. Therefore, densification occurred when x exceeded 10.0 mol%.

Fig. 5 shows the variations in the relative density and ε_r value of the $Ba_2Ti_9O_{20}$ ceramics containing 10.0 mol% of B_2O_3 and x mol% of CuO with $2.0 \leq x \leq 15.0$ sintered at 900 °C. The relative density of the specimens was low when a small amount of CuO was added, but it considerably increased when x exceeded 5.0 mol%. The variation in the relative density is closely related to the microstructure, as shown in Fig. 4(a)–(c). A similar result was also obtained for the specimens sintered at 875 °C, although the relative density of all these specimens is low. The variation in ε_r is similar to that of the density and a saturated ε_r value of 33.6 was obtained for the specimens with 10.0 mol% of CuO. Thus, it can be inferred that the density is the important factor contributing to the improvement of the ε_r value of the specimen. The Q-value of the specimens increased with the addition of CuO and

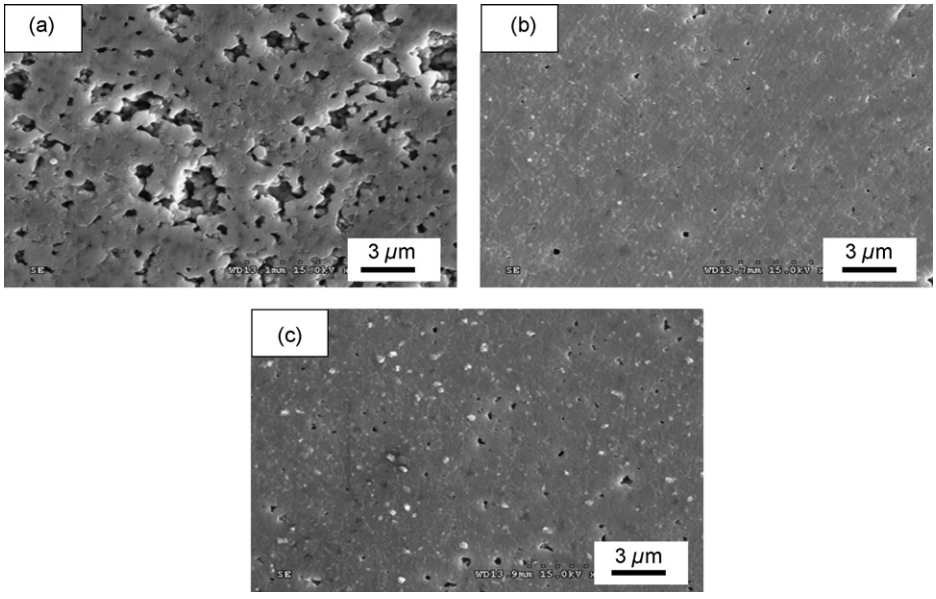

Fig. 4. SEM images of the thermally etched surfaces of the $Ba_2Ti_9O_{20}$ ceramics containing 10.0 mol% of B_2O_3 and x mol% of CuO with (a) $x = 2.0$; (b) $x = 10.0$; (c) $x = 15.0$ sintered at 900 °C for 2 h.

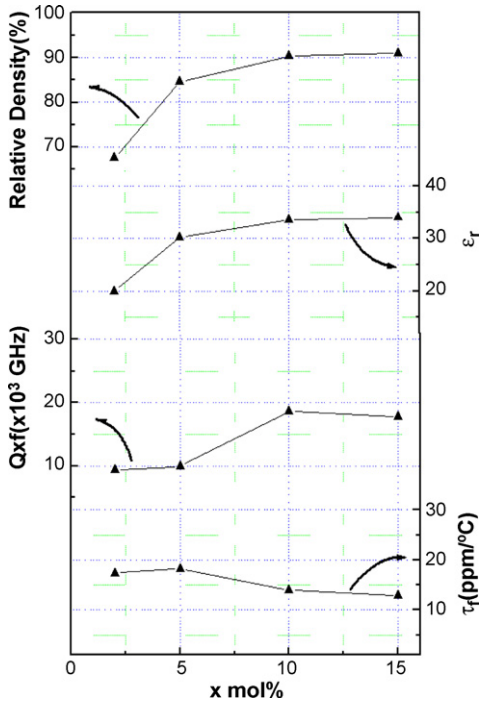

Fig. 5. Variations in the relative density, ε_r, Qxf value and τ_f of the $Ba_2Ti_9O_{20}$ ceramics containing 10.0 mol% of B_2O_3 and x mol% of CuO with $2.0 \le x \le 15.0$ sintered at 900 °C for 2 h.

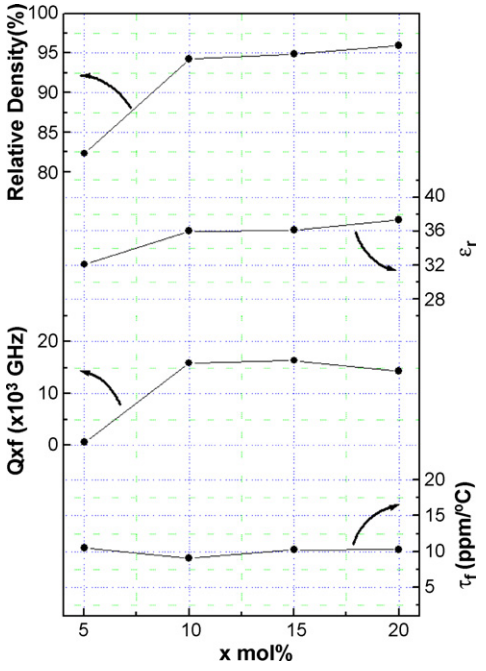

Fig. 6. Variations of the relative density, ε_r, Qxf value and τ_f of the $Ba_2Ti_9O_{20} + xBaCu(B_2O_5)$ ceramics with $5.0 \le x \le 20.0$ mol% sintered at 875 °C for 2 h.

showed a maximum value of 18,600 GHz when $x = 10.0$ mol%, as shown in Fig. 5. The increase in the Q-value is attributed to the increase in the density. The τ_f of specimens ranged between 12.9 and 18.3 ppm/°C and did not change with the addition of CuO. Therefore, the $Ba_2Ti_9O_{20}$ ceramics containing 10.0 mol% B_2O_3 and 10.0 mol% CuO sintered at 900 °C exhibited good microwave dielectric properties of $\varepsilon_r = 33.6$, Qxf = 18,600 GHz and $\tau_f = 14.0$ ppm/°C.

To clarify the effect of the $BaCu(B_2O_5)$ phase on the sintering temperature and microwave dielectric properties of the $Ba_2Ti_9O_{20}$ ceramics, $BaCu(B_2O_5)$ powders were synthesized and added to the $Ba_2Ti_9O_{20}$ ceramics. Fig. 6 shows the variations of the relative density, ε_r, Qxf value and τ_f of the $Ba_2Ti_9O_{20} + xBaCu(B_2O_5)$ ceramics with $5.0 \le x \le 20.0$ mol% sintered at 875 °C for 2 h. The relative density was low for the specimen containing 5.0 mol% of $BaCu(B_2O_5)$ and increased with increasing $BaCu(B_2O_5)$ content. The variation of ε_r is similar to that of the relative density and a saturated ε_r value of 36.0 was obtained for the specimen with $x = 10.0$ mol%. The Qxf value also increased with the addition of $BaCu(B_2O_5)$, because of the increased density. However, it slightly decreased when x exceeded 15.0 mol% and this decrease can be explained by the formation of a large amount of liquid phase. A maximum Qxf value of 16,000 GHz was obtained when $x = 10.0$ mol%. The variation of τ_f with the addition of $BaCu(B_2O_5)$ was not significant, with its value ranging between 9.11 and 10.30 ppm/°C, as shown in Fig. 6. Good microwave dielectric properties of Qxf = 16,000 GHz, $\varepsilon_r = 36.0$ and $\tau_f = 9.11$ ppm/°C were obtained for the $Ba_2Ti_9O_{20} + 10.0$ mol% $BaCu(B_2O_5)$ ceramics sintered at 875 °C for 2 h. These results are similar to those of B_2O_3 and CuO added $Ba_2Ti_9O_{20}$ ceramics. Therefore, it can be inferred that $BaCu(B_2O_5)$ second phase was formed in the B_2O_3 and CuO added $Ba_2Ti_9O_{20}$ ceramics and helped in their densification at low temperature. Moreover, it can be concluded that the $BaCu(B_2O_5)$ phase constitutes a good additive for decreasing the sintering temperature of $Ba_2Ti_9O_{20}$ ceramics.

4. Conclusions

The sintering temperature of $Ba_2Ti_9O_{20}$ ceramics is near 1300 °C but it was reduced to 1000 °C when B_2O_3 was added. $BaTi_4O_9$ and $Ba_4Ti_{13}O_{30}$ second phases reacted with the B_2O_3 forming a liquid phase containing BaO and B_2O_3 which assisted in the densification of the $Ba_2Ti_9O_{20}$ ceramics at low temperature. The B_2O_3 added $Ba_2Ti_9O_{20}$ ceramics were not able to be sintered below 1000 °C, but the $Ba_2Ti_9O_{20}$ ceramics containing both CuO and B_2O_3 were sintered at 900 °C. It was suggested that $BaCu(B_2O_5)$ liquid phase was responsible for the densification of the CuO and B_2O_3 added $Ba_2Ti_9O_{20}$ ceramics at low temperature. $BaCu(B_2O_5)$ was also added $Ba_2Ti_9O_{20}$ in order to reduce its sintering temperature. Good microwave dielectric properties of Qxf = 16,000 GHz, $\varepsilon_r = 36.0$ and $\tau_f = 9.11$ ppm/°C were obtained for the $Ba_2Ti_9O_{20}$ ceramics containing10.0 mol% $BaCu(B_2O_5)$ sintered at 875 °C for 2 h.

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