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Effect of B_2O_3 and CuO additives on the sintering temperature and microwave dielectric properties of $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics

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Abstract

The B_2O_3 added $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BBZN) ceramic was sintered at 900 °C. BaB_4O_7, BaB_2O_4, and $BaNb_2O_6$ second phases were found in the BBZN ceramic. Since BaB_4O_7 and BaB_2O_4 second phases have an eutectic temperature around 900 °C, they might exist as the liquid phase during sintering at 900 °C and assist the densification of the BZN ceramics. Microwave dielectric properties of dielectric constant $(\varepsilon_r) = 32$, $Q \times f = 3500$ GHz, and temperature coefficient of resonance frequency $(\tau_f) = 20$ ppm/°C were obtained for the BZN with 5.0 mol% B_2O_3 sintered at 900 °C for 2 h. The BBZN ceramics were not sintered below 900 °C and the microwave dielectric properties of the BBZN ceramics sintered at 900 °C were very low. However, when CuO was added, BBZN ceramic was well sintered even at 875 °C. The liquid phase related to the $BaCu(B_2O_5)$ second phase could be responsible for the decrease of sintering temperature. Good microwave dielectric properties of $\varepsilon_r = 36$, $Q \times f = 19{,}000$ GHz and $\tau_f = 21$ ppm/°C can be obtained for CuO doped BBZN ceramics sintered at 875 °C for 2 h.

Keywords: Microstructure; Dielectric properties; $Ba(Zn_{1/3}Nb_{2/3})O_3$

1. Introduction

For the miniaturization and hybridization of microwave components, the number of investigations on the multi-layer devices has increased. Multi-layer device consists of alternating microwave dielectric ceramics and internal metallic electrode layers.[1] As a metallic electrode, Ag has been widely used because of its high conductivity and low cost. The melting temperature of Ag is low, about 961 °C, but the sintering temperature of the microwave dielectric ceramics is generally high, above 1400 °C. Therefore, for the fabrication of multi-layer devices, it is important to develop microwave dielectric ceramics with a low sintering temperature, which can be co-fired with Ag. Glass with a low melting temperature was used to decrease the sintering temperature of the ceramics. On some occasions, a small amount of oxide was added to form the liquid phase, thus assisting the densification of the ceramics. Chemical processes such as sol–gel and the precipitation method were also used to reduce the sintering temperature of the ceramics.[2–4]

Complex perovskite ceramics were extensively investigated for their application to the dielectric resonators.[5–7] Much research has been conducted on the BZN ceramic as a replacement of the Ta-based complex perovskite ceramics such as $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$ because of the high cost of the Ta_2O_5. BZN ceramic has the disordered cubic structure when it was sintered at high temperatures but the 1:2 ordered hexagonal structure was observed in the BZN ceramic sintered below 1350 °C.[8] Good microwave dielectric properties of $\varepsilon_r = 41$, $Q = 5600$ at 10 GHz, and $\tau_f = 28$ ppm/°C are found in BZN ceramic. Although the microwave dielectric properties of the BZN ceramic are good, no research has been carried out to reduce the sintering temperature of the BZN ceramic because of the high sintering temperature of BZN ceramic. In this work, B_2O_3 and CuO were added to the BZN ceramics to decrease the sintering temperature for the application to the low temperature co-fired ceramics (LTCC). Furthermore, microstructure and microwave dielectric properties of the B_2O_3 and CuO added BZN ceramics were also investigated.

2. Experimental procedure

Oxide compounds of $BaCO_3$ (Aldrich Chemical Co. Milwaukee, WI), ZnO (Junsei Chemical Co., Tokyo, Japan) and Nb_2O_5

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(Junsei Chemical Co., Tokyo, Japan) were mixed for 24 h in a nylon jar with zirconia balls, then dried, and calcined at 1200 °C for 4 h. After remilling with B_2O_3 and CuO (Junsei Chemical Co., Tokyo, Japan), the powder was dried and pressed into discs and sintered at 850–1000 °C for 2 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[9] and Courtney.[10] The temperature coefficients of the resonant frequency was measured at 8 GHz in the temperature range of 20–80 °C.

3. Results and discussion

The sintering temperature of BZN is about 1350 °C but it was sintered at 900 °C when B_2O_3 was added. Fig. 1 shows the X-ray diffraction patterns of $BZN + xB_2O_3$ ceramics with $1.0 \leq x \leq 20.0$ mol% sintered at 950 °C for 2 h. For the specimens with $x < 5.0$ mol%, peaks for BZN ceramics without the second phase were found. However, when x exceeded 5.0 mol%, peak for BaB_4O_7 second phase appeared and the amount of the BaB_4O_7 second phase increased with the increase of B_2O_3. BaB_2O_4 and $BaNb_2O_6$ second phases were also observed in the BZN ceramic with 20.0 mol% B_2O_3. According to the phase diagram of the BaO–B_2O_3 solid solution, an eutectic point at 899 °C exists between the BaB_4O_7 and BaB_2O_4 phases.[11] Moreover, the low temperature sintering of both the PbO–B_2O_3 added $BaTiO_3$ ceramics and the B_2O_3 added $Ba_5Nb_4O_{15}$ ceramics was explained by the presence of the BaB_2O_4 and BaB_4O_7 phases.[12,13] Therefore, it is considered that the BaB_4O_7 and BaB_2O_4 phases existed as liquid phase during the sintering above 900 °C and assisted the densification of the BZN ceramic.

Variations of the bulk density and the ε_r of the $BZN + xB_2O_3$ ceramics with $0.0 \leq x \leq 20.0$ mol% with the B_2O_3 and the sintering temperature are illustrated in Fig. 2. Bulk density increased with the addition of the B_2O_3 and the increase of the bulk density could be due to the presence of the BaO-B_2O_3 liquid phase during the sintering which assisted the densification of the BZN ceramics. As the sintering temperature increased, the density of the specimens increased and the amount of the B_2O_3, which is required to obtain the high bulk density decreased. For the BZN sintered at 950 °C, only 2.0 mol% of B_2O_3 was enough to obtain a relatively high bulk density, approximately 93% of the theoretical density of BZN ceramic. The ε_r of the specimens sintered at 900 °C is very low but increased with the increase of the sintering temperature as shown in Fig. 2. For the BZN with 2.0 mol% of B_2O_3 sintered at 950 °C, the ε_r is about 38, which is close to that of BZN ceramic sintered at 1350 °C. Variation of the ε_r is similar to that of bulk density. Therefore, it is considered that the ε_r is closely related to the bulk density.

Fig. 3 illustrates the variation of the Q-value of the $BZN + xB_2O_3$ ceramics with $1.0 \leq x \leq 20.0$ mol% as a function of the B_2O_3. Q-value of the specimens considerably increased with the addition of a small amount of the B_2O_3 and the maximum Q-value was obtained when $x = 2.0$ mol%. The increase

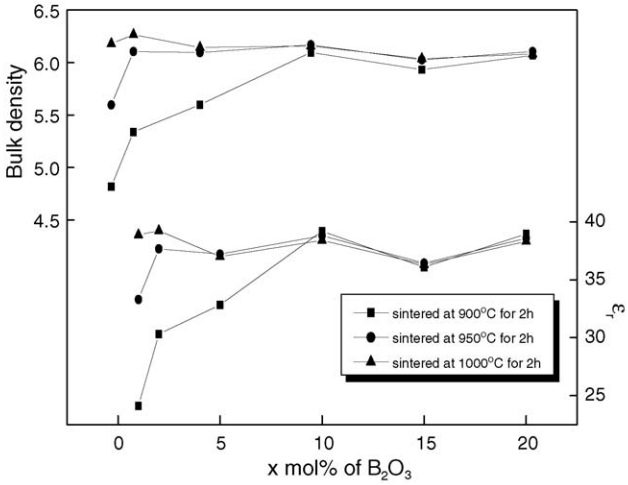

Fig. 2. Variations of the bulk density and the ε_r of the B_2O_3 added BZN ceramics with the B_2O_3 and the sintering temperature.

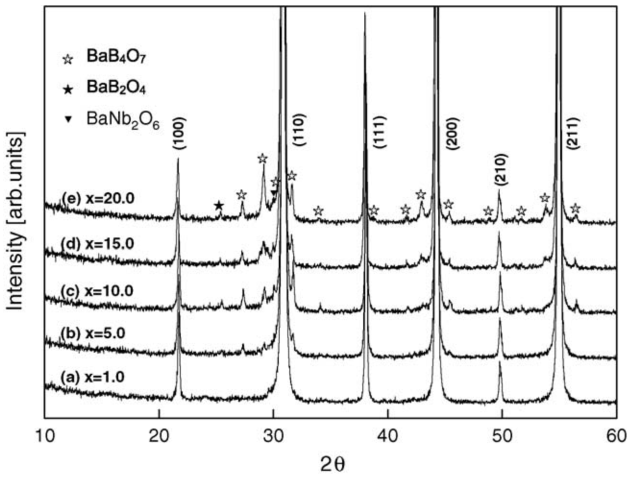

Fig. 1. X-ray diffraction patterns of $BZN + xB_2O_3$ ceramics with $1.0 \leq x \leq 20.0$ mol% sintered at 950 °C for 2 h.

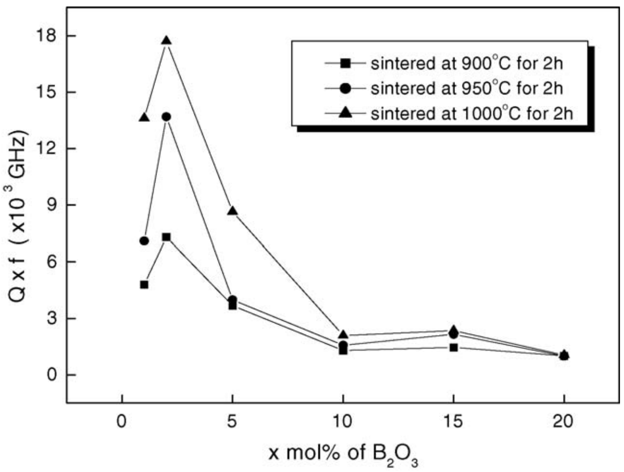

Fig. 3. Variation of the $Q \times f$ value of the B_2O_3 added BZN ceramics as a function of sintering temperature and the amount of the B_2O_3.

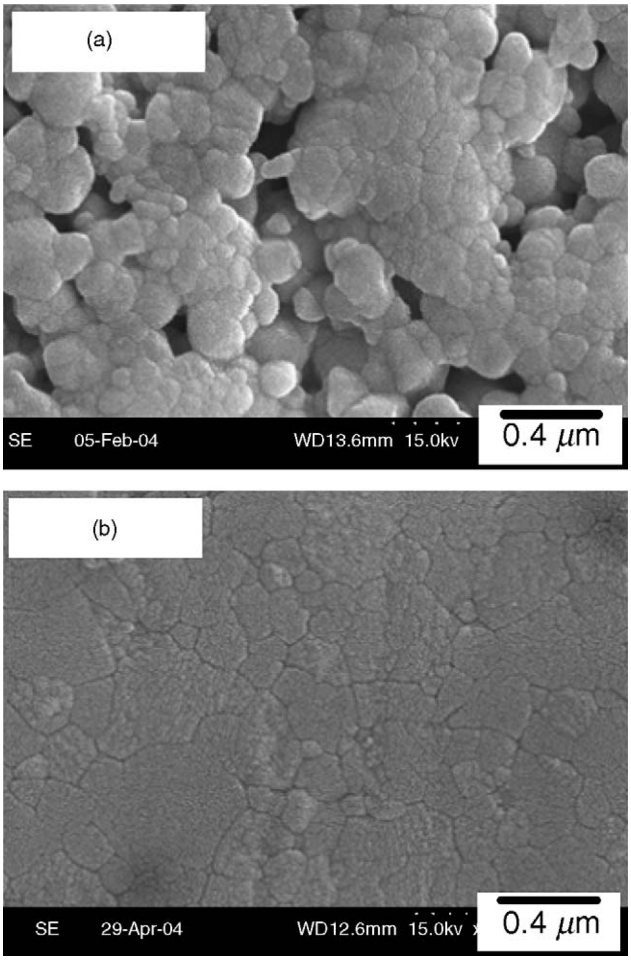

Fig. 4. SEM images of the thermal etched surface of the 1.0 mol% B_2O_3 added BZN + xCuO ceramics sintered at 875 °C for 2 h: (a) x = 0.0 mol% and (b) x = 5.0 mol%.

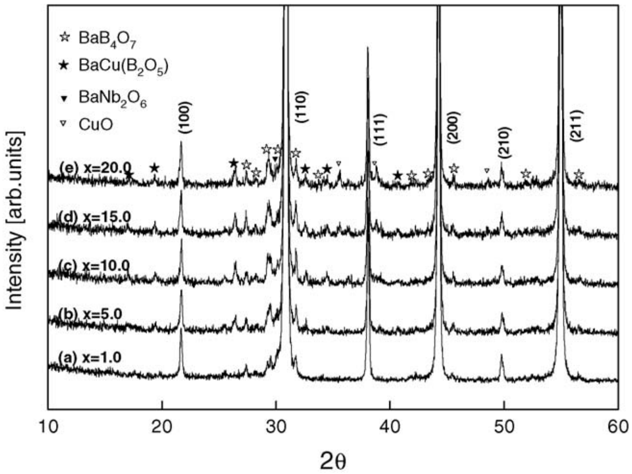

Fig. 5. X-ray diffraction patterns of the 10.0 mol% B_2O_3 added BZN + xCuO with $1.0 \leq x \leq 20.0$ mol% sintered at 900 °C for 2 h.

of Q-value could be attributed to the increase of bulk density. However, as x exceeded 2.0 mol%, Q-value significantly decreased although bulk density increased. According to the X-ray diffraction patterns, BaB_2O_4 and $BaNb_2O_6$ second phases formed when a large amount of B_2O_3 was added. Therefore, the decrease of the Q-value with the increase of the B_2O_3 could be due to the presence of the second phases. The τ_f of the BBZN ceramics was also measured and it slightly decreased when B_2O_3 was added. The microwave dielectric properties of $\varepsilon_r = 32$, $Q \times f = 3500$ GHz, and $\tau_f = 20$ ppm/°C were obtained for the BZN with 5.0 mol% B_2O_3 sintered at 900 °C for 2 h.

The sintering temperature of the BZN ceramics decreased to 900 °C when B_2O_3 was added. However, BBZN ceramic was not sintered below 900 °C and the microwave dielectric properties of the BBZN ceramics sintered at 900 °C are not satisfactory. We added the CuO to the BBZN ceramics to decrease the sintering temperature below 900 °C and improve the microwave dielectric properties. Fig. 4a and b show the SEM images of the thermal etched surface of the 1.0 mol% B_2O_3 added BZN + xCuO ceramics with $0.0 \leq x \leq 5.0$ mol% sintered at 875 °C for 2 h. For the BZN with 1.0 mol% of B_2O_3, a porous microstructure with many pores was developed as shown in Fig. 4a. When CuO was added, the dense microstructure was formed and the numbers of pores decreased. The BBZN ceramics with 5.0 mol% CuO shows a homogeneous and dense microstructure with the average grain size of 300 nm.

Fig. 5 shows the X-ray diffraction patterns of the 10.0 mol% B_2O_3 added BZN + xCuO with $1.0 \leq x \leq 20.0$ mol% sintered at 900 °C for 2 h. The BaB_4O_7 second phase was found in the all the specimens. When a small amount of CuO was added, the $BaCu(B_2O_5)$ second phase appeared. Furthermore, when CuO exceeded 10.0 mol%, peaks for the CuO were observed. Therefore, it can be suggested that when CuO and B_2O_3 were added to the BZN ceramics, CuO, B_2O_3 and BaO ions reacted together forming both the BaB_4O_7 and $BaCu(B_2O_5)$ second phases. However, the amount of CuO which contributes to form the $BaCu(B_2O_5)$ second phase is limited because the CuO second phase precipitated when CuO exceeded 10.0 mol%. BaB_4O_7 exists in the BBZN ceramics and assists the sintering at 900 °C. However, BBZN ceramics were not sintered below 900 °C. The addition of CuO cannot decrease the sintering temperature of BZN below 900 °C. Therefore, it is considered that the $BaCu(B_2O_5)$ second phase might help the sintering of the CuO and B_2O_3 added BZN ceramics at low temperature. Since the melting temperature of the $BaCu(B_2O_5)$ phase was not found in the literature, we produced the $BaCu(B_2O_5)$ phase and found that the $BaCu(B_2O_5)$ phase melts at 875 °C. Therefore, it is considered that the $BaCu(B_2O_5)$ second phase existed as the liquid phase during the sintering and assisted the densification of the CuO and B_2O_3 added BZN ceramics sintered below 900 °C.

Bulk density, ε_r and $Q \times f$ value of the 1.0 mol% B_2O_3 added BZN + xCuO ceramics with $1.0 \leq x \leq 15.0$ mol% are illustrated in Fig. 6. Bulk density increased with the addition of the CuO and saturated when 5.0 mol% of CuO was added. Since a dense microstructure formed when 5.0 mol% of CuO was added to the BBZN ceramics, the increase of the bulk density is closely related to improvement of the microstructure. The ε_r and the $Q \times f$ value of the specimens increased with the addition of the CuO. Since the variations of the ε_r and the $Q \times f$ value are similar

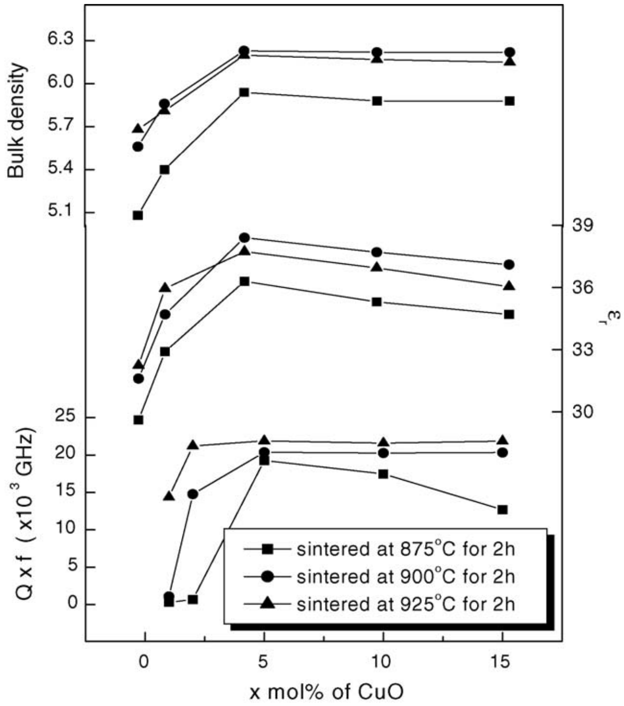

Fig. 6. Bulk density, ε_r and $Q \times f$ value of the 1.0 mol% B_2O_3 added BZN + xCuO ceramics with $1.0 \leq x \leq 15.0$ mol%.

to that of the bulk density, the increases of the ε_r and $Q \times f$ value with the addition of the CuO can be explained by the increase of the bulk density. Good microwave dielectric properties of $\varepsilon_r = 36$, $Q \times f = 19{,}000$ GHz and $\tau_f = 21$ ppm/°C can be obtained for BZN + 1.0 mol% B_2O_3 + 5.0 mol% CuO ceramic sintered at 875 °C for 2 h. Therefore, the CuO and B_2O_3 added BZN ceramic is a good candidate material for the LTCC application.

4. Conclusions

The effects of B_2O_3 and CuO additives on the sintering temperature and microwave dielectric properties of $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics have been investigated. When B_2O_3 was added, BZN ceramics were sintered at 900 °C. BaB_4O_7 and BaB_2O_4 second phases were observed in the B_2O_3 added BZN and they existed as the liquid phase during the sintering and assisted the sintering of the BZN ceramics. However, the B_2O_3 added BZN ceramics were not sintered below 900 °Cand the microwave dielectric properties of the BBZN ceramics sintered were very low. When CuO and B_2O_3 were added, BZN was well sintered even at 875 °C. $BaCu(B_2O_5)$ second phase, which melts below at 900 °C was observed in the CuO and B_2O_3 added BZN ceramics and it could be responsible for the decrease of sintering temperature. Good microwave dielectric properties of $\varepsilon_r = 36$, $Q \times f = 19{,}000$ GHz and $\tau_f = 21$ ppm/°C can be obtained for 5.0 mol% CuO and 1.0 mol% B_2O_3 doped BZN ceramics sintered at 875 °C for 2 h.

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