Effects of Sintering Atmosphere on Piezoelectric Properties of 0.75BF-0.25BT Ceramic

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ABSTRACT

0.75BF-0.25BT ceramics were prepared by sintering at 980 - 1040°C in air or under atmosphere powder. A sample with 1 mole %-excess Bi_2O_3 was also prepared to compensate for Bi_2O_3-evaporation. Physical and piezoelectric properties of these three samples were compared. When the sintering temperature increased from 980°C to 1040°C, the density of the sample sintered in air decreased continuously due to Bi-evaporation. Due to the suppression of Bi-evaporation, the sample sintered under atmosphere powder had a higher density at sintering temperatures above 1000°C than did the sample sintered in air. The addition of 1 mole %-excess Bi_2O_3 successfully compensated for Bi-evaporation and kept the density at the higher value until 1020°C. Grain size increased continuously when the sintering temperature increased from 980 to 1040°C, irrespective of the sintering atmosphere. When the sintering temperature increased, the piezoelectric constant (d_{33}) and the electromechanical coupling factor (k_p) increased for all samples. The sample with 1 mole % excess-Bi_2O_3 showed the highest density and the best piezoelectric properties at sintering temperature of 1020°C.

Key words : BiFeO$_3$-BaTiO$_3$, Sintering, Excess-Bi$_2$O$_3$, Piezoelectricity

1. Introduction

Pb(Zr,Ti)O$_3$ (PZT)-based piezoelectric ceramics have been applied for many electromechanical devices such as actuators, sensors, and transducers.[1-2] In recent years, due to global environmental regulations, there have been many reports on lead-free piezoelectric materials to replace current PZT-based ceramics.[2-9] Some lead-free piezoelectric ceramics such as (K,Na)NbO$_3$ (KNN) and (Bi,Na)TiO$_3$ (BNT) have showed properties comparable to those of Pb-based ceramics.[2-9] However, because these materials have drawbacks such as unstable temperature characteristics, low depolarization temperature, and poor reproducibility due to the use of humidity-sensitive raw materials, it is not expected that they will replace lead-based piezoelectric ceramics.

In recent years, BiFeO$_3$-BaTiO$_3$ (BF-BT) solid solutions have been reported to show attractive piezoelectric properties and high Curie temperature (above 400°C) around a phase boundary between rhombohedral and pseudo-cubic phases.[10-17] It has been reported that the sintering temperature has a significant influence on the density, grain size, and piezoelectric properties of BF-BT ceramics.[13-14,16] Sintering at high temperature results in a decrease of the density, a deterioration of the piezoelectric properties, and the

formation of impurity phases due to Bi evaporation.[13,14,16] Chen et al. reported that the addition of excess-Bi$_2$O$_3$ to a 0.75BF-0.25BT ceramic improved the piezoelectric properties and the Curie temperature.[11] Suppressing or compensating for Bi evaporation during sintering seems important for the preparation of BF-BT ceramics with good piezoelectric properties. In this work, in order to prevent Bi evaporation, 0.75BF-0.25BT ceramics were sintered in air (Air) and in atmosphere powder (Atmosphere Powder). The 1 mole %-excess-Bi$_2$O$_3$ added sample to compensate for Bi evaporation was also sintered in air (excess Bi$_2$O$_3$). Densification, phase evolution, microstructure development, and piezoelectric properties were examined and the effects of the sintering atmosphere and of excess-Bi$_2$O$_3$ were compared for the 0.75BF-0.25BT ceramics.

2. Experimental Procedure

Bi$_2$O$_3$ (Sigma Aldrich, 99.9%), Fe$_2$O$_3$ (Sigma Aldrich, 99%), BaCO$_3$ (Sigma Aldrich, 99%), and TiO$_2$ (High Purity Chemicals, 99.9%) powders were weighed and mixed by ball-milling for 24 h in plastic bottles with distilled water and yttria-stabilized zirconia (YSZ) balls. After drying, the mixed powder was calcined by consecutive heat treatments at 750°C for 5 h and at 850°C for 3 h. The calcined powder was pulverized by attrition-milling at 350 rpm for 3 h and then ball-milled for 24 h after adding 1 wt% polyvinyl alcohol (PVA). Disk-type compacts with diameters of 12 mm were formed by uni-axial pressing under 100 MPa and PVA was burned-

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out by annealing compacts at 600°C for 2 h. The samples were sintered in a temperature range of 980 - 1040°C for 3 h in air with a heating rate of 300°C/h and then cooled in a furnace. To suppress evaporation of Bi during sintering, the samples were also sintered in an alumina crucible with atmosphere powders with compositions the same as that of the sample. The samples with 1 mole %-excess Bi_2O_3 were also sintered in air to compensate for Bi-evaporation.

The phases of the samples were identified by X-ray diffraction analysis (XD-D1; Shimadzu, Japan) and the microstructures were observed by scanning electron microscopy (SEC, SNE-4500E). The densities of the sintered samples were measured using Archimedes' principle. For electrical measurements, an Ag paste electrode was printed on the sample and fired at 750°C for 10 minutes. A DC electric field of 3 KV/mm was applied to the samples for 20 minutes in a silicon oil bath maintained at 120°C for dipole alignment, which is the so-called process of poling. An impedance analyzer (Agilent 4294A) was used to measure the capacitance and impedance characteristics. The electromechanical coupling factor (k_p) was measured using the resonance method, and the piezoelectric constant d_{33} was measured with a Berlincourt-type d_{33} meter (YE2730A, APC International Ltd.).

3. Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of the 0.75BF-0.25BT ceramics sintered at 1000°C in air, under atmosphere powder, and with 1 mole %-excess Bi_2O_3. The figure shows that all samples have a single perovskite phase with no impurity and a pseudo-cubic structure. 0.75BF-0.25BT ceramics have been reported to have a rhombohedral crystal structure.[17,18] The pseudo-cubic XRD patterns in Fig. 1 might be the result of very small rhombohedral distortion.[10,11] The peak separations of the $(111)_{cubic}$ planes due to rhombohedral distortion in samples sintered at 980 - 1040°C are shown in Fig. 2. The X-ray diffraction peaks of the $(111)_c$ plane had symmetric shapes in the sam-

ples sintered at 980°C; these shapes became asymmetric or were separated due to rhombohedral distortion when the sintering temperature increased. The peak separation of the $(111)_c$ plane at high sintering temperature was observed in previous studies, which claimed that it was caused by either a more homogeneous chemical reaction or a larger grain size.[13,16] Fig. 2 shows that the peak separations at the sintering temperature of 1040°C are distinct in the order of the sample sintered in air, the sample sintered under atmosphere powder, and the excess Bi_2O_3 sample. This implies that the Bi_2O_3 evaporation also had an effect on the rhombohedral distortion.

Figure 3 illustrates the changes of the densities with the sintering temperature in the 0.75BF-0.25BT ceramics. When the sintering temperature increased from 980°C to 1040°C, the density of the sample sintered in air decreased continuously. The density has been reported to decrease with the formation of large pores at sintering temperatures above 980 °C in 0.75BF-0.25BT ceramics.[16] The decrease of the density in the sample sintered in air supports this previ-
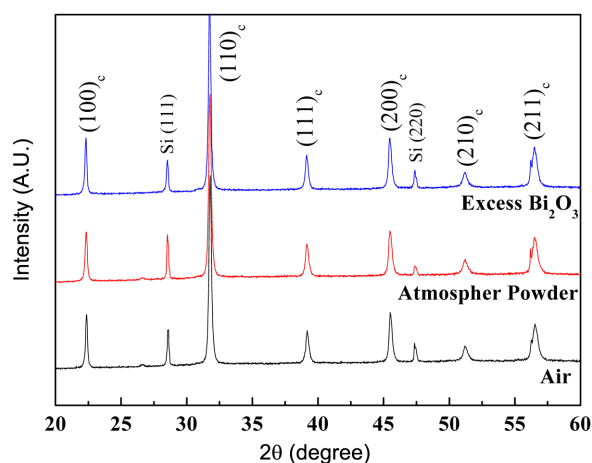

Fig. 1. X-ray diffraction patterns of 0.75BF-0.25BT ceramics sintered at 1000°C.
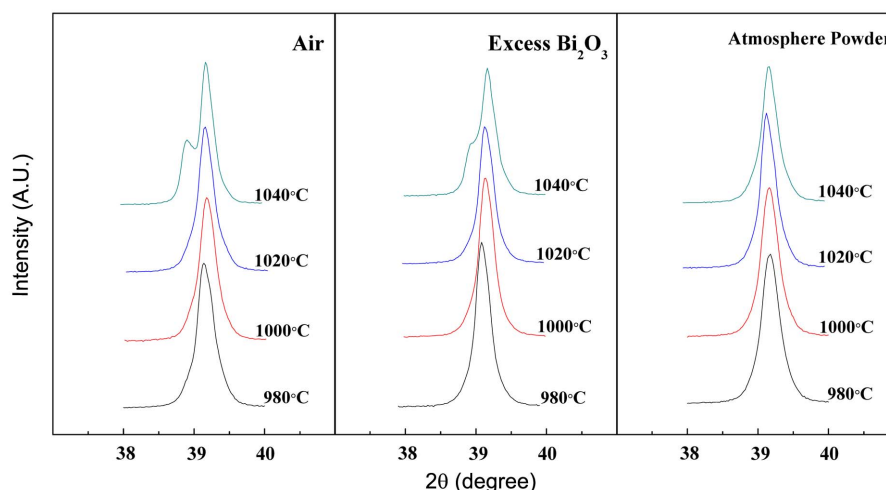

Fig. 2. X-ray diffraction patterns showing the peak separations of the $(111)_{cubic}$ planes due to rhombohedral distortion.
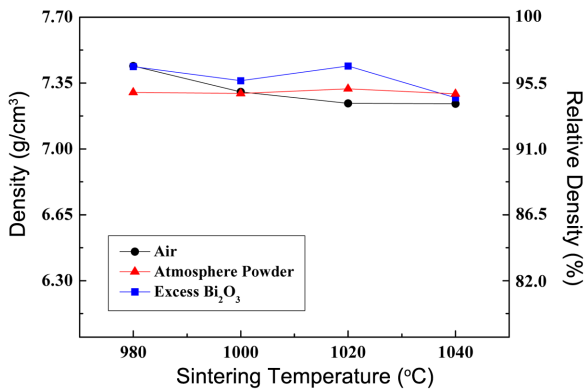
Fig. 3. Density as a function of sintering temperature in 0.75BF-0.25BT ceramics.

ous report. However, the density changes little until 1020°C and then decreases slightly when the sintering temperature increases in 0.75BF-0.25BT ceramics with 1 mole % excess-Bi_2O_3, as can be seen in Fig. 3. The sample with excess-Bi_2O_3 has higher density at sintering temperatures above 980°C. This indicates that Bi-evaporation was successfully compensated for by the addition of 1 mole % excess-Bi_2O_3 until 1020°C. The density of the sample sintered under atmosphere powder had a smaller than the sample sintered in air at the sintering temperature of 980°C, but did not change with the increase of the sintering temperature and showed a higher value above 1000°C than that of the sample sintered in air. Sintering under atmosphere powder seems to be effective in suppressing Bi-evaporation until 1040°C.

Figure 4 illustrates the change in microstructure when the sintering temperature is increased from 980 to 1040°C in the 0.75BF-0.25BT ceramics. All samples show well-developed polyhedron-shape grains. Fig. 4 shows that the grain sizes were 2 - 3 μm at the sintering temperature of 980°C, and that these grain sizes increased continuously when the sintering temperature increased from 980 to 1040°C, irrespective of the sintering atmosphere.

Figure 5 shows the dielectric constants as a function of the sintering temperature. The dielectric constant decreases continuously with the sintering temperature in the 0.75BF-0.25BT ceramic sintered in air. This change is thought to result from the decrease in the density with the sintering temperature, as can be seen in Fig. 3. The dielectric constant changed little in the sample with excess-Bi_2O_3 and increased slightly in the samples sintered under atmosphere powder with increasing sintering temperature. The increase in the grain size at sintering temperatures above 1000°C contributes to the increase in the dielectric constant and this results in only little change or a slight increase of the dielectric constant, in spite of the decrease of the density in this temperature range. These results suggest that the grain size as well as the density influences the dielectric constant.

Figure 6 illustrates the changes of the piezoelectric constant (d_{33}) and electromechanical coupling factor (k_p) with increasing sintering temperature. When the sintering temperature increased, the piezoelectric constant and the electromechanical coupling factor increased continuously for all samples, even though the densities decreased. The increase in the grain size with the sintering temperature seems to influence more strongly on the piezoelectric properties than the decrease in the density. It has been reported that strong coupling between grain boundaries and domain walls in $Pb(Zr,Ti)O_3$ ceramics hinders domain reorientation and severely restricts domain wall motion when the grain size is reduced below a critical value.[19] Fig. 6 strongly suggests that BF-BT ceramics with small grain sizes have low piezoelectric constants and electromechanical coupling factors because of constrained domain wall motion. The easier domain wall motion in larger grains facilitates the alignment of the dipoles to the applied electric field during poling and increases the contribution of the domain wall vibration to the piezoelectric properties. This explains the enhancement of the piezoelectric properties in the BF-BT ceramics with large grain size as in the case for $Pb(Zr,Ti)O_3$ ceramics.
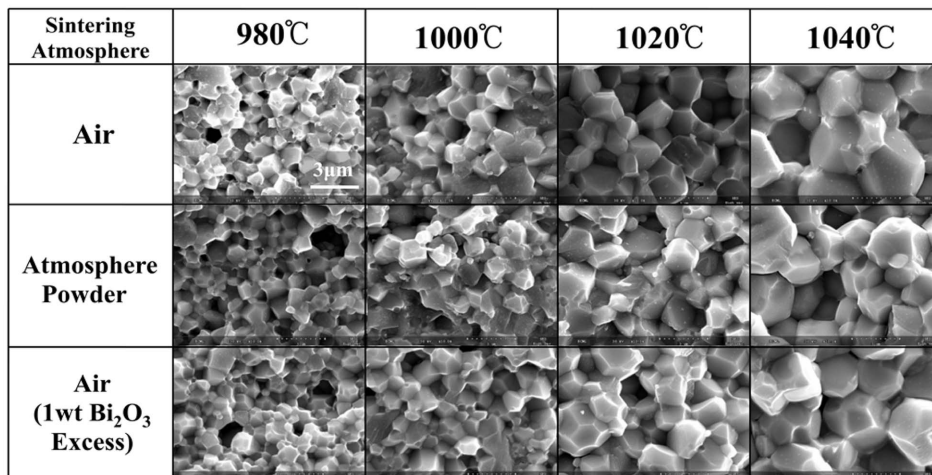

Fig. 4. Changes in microstructures with increasing sintering temperature in 0.75BF-0.25BT ceramics.
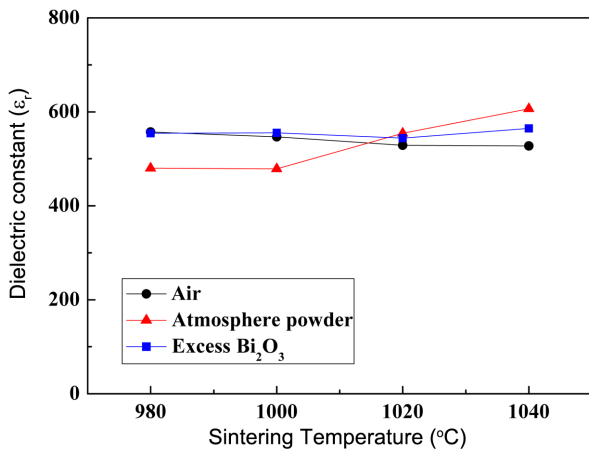
Fig. 5. Dielectric constant as a function of sintering temperature in 0.75BF-0.25BT ceramics.
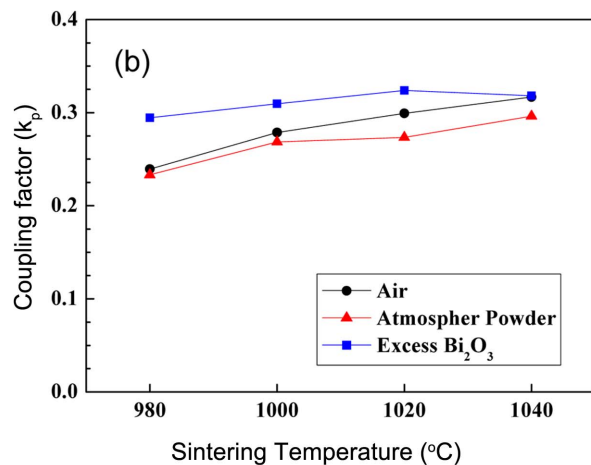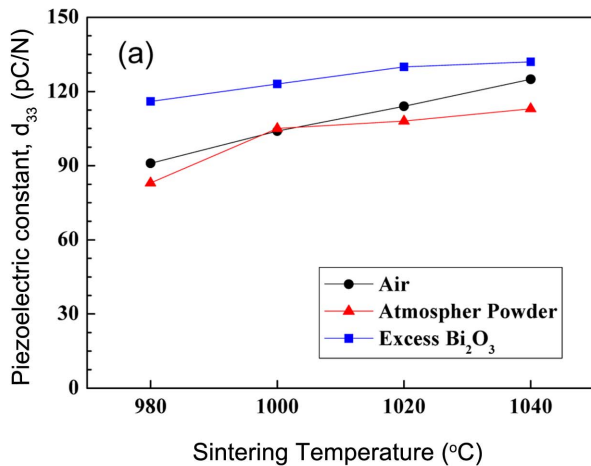

Fig. 6. (a) Piezoelectric constant (d_{33}) and (b) electromechanical coupling factor (k_p) as a function of sintering temperature in 0.75BF-0.25BT ceramics.

The sample with 1 mole % excess-Bi_2O_3 has better piezoelectric properties than those of the samples sintered in air and atmosphere powder because the grain size was similar but the density was higher at the same temperature.

4. Conclusions

Sintering under atmosphere powder and with the addition of 1 mole %-excess Bi_2O_3 were performed to suppress and compensate for Bi_2O_3-evaporation in 0.75BF-0.25BT ceramics. A pseudo-cubic structure was found in all samples when they were sintered at temperatures below 1040°C; peak separations of the $(111)_{cubic}$ planes due to rhombohedral distortion were observed in samples sintered at 1040°C. When the sintering temperature increased from 980°C to 1040°C, the density of the sample sintered in air decreased continuously due to Bi-evaporation. By compensating for Bi-evaporation, the addition of 1 mole %-excess Bi_2O_3 kept the density at a higher value until 1020°C. Due to the suppression of Bi-evaporation, the sample sintered under atmosphere powder had higher density at sintering temperatures above 1000°C than did the sample sintered in air. Grain size increased continuously when the sintering temperature increased from 980 to 1040°C, irrespective of the sintering atmosphere. The dielectric constant of the 0.75BF-0.25BT ceramic was influenced by the grain size as well as by the density. When the sintering temperature increased, the piezoelectric constant (d_{33}) and the electromechanical coupling factor (k_p) increased continuously in all samples. The grain size has a stronger effect on the piezoelectric properties in 0.75BF-0.25BT ceramics than does the density. The sample with 1 mole % excess-Bi_2O_3 had the highest density (7.44 g/cm³) and the best piezoelectric properties (d_{33} = 130 pC/N , k_p = 0.324) when sintered at 1020°C.

Acknowledgments

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