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Additive effects on electrical properties of $(Bi_{1/2}Na_{1/2})TiO_3$ ferroelectric ceramics

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Abstract

Microstructure, dielectric, ferroelectric and piezoelectric properties of bismuth sodium titanate $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT) were studied for a candidate as lead-free piezoelectric ceramics. In the case of Mn addition, the Curie temperature, T_c, decreases rapidly with increasing amount of doped $MnCO_3$. The resistivity, ρ, is enhanced to 3×10^{14} (Ωcm) (at 40°C) for BNT + $MnCO_3$ 0.2 (wt.%) and electromechanical coupling factor, k_{33}, was obtained the relatively high value under the condition of the low poling field, E_p for the Mn-doped BNT ceramics. It seems that Mn ions exist in the grain, and substitute for the A- or B-site of the perovskite structure, and eject Bi ions to the air.

Keywords: Perovskites; Piezoelectric properties; Lead-free piezoelectric materials; Mn additive

1. Introduction

Bismuth sodium titanate, $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT) [1–5] is considered to be an excellent candidate as a key material of lead-free piezoelectric ceramics. The BNT shows strong ferroelectric properties of a large remanent polarization, $P_r = 38$ μC/cm^2, and has a Curie temperature, $T_c = 320$°C and a phase transition point from ferroelectric to anti-ferroelectric, $T_p = 200$ °C.

Some researchers investigated the effects of small amount of dopants such as Fe_2O_3, MnO_2 and NiO on dielectric and piezoelectric properties for perovskite ceramics.[6–8] Kamiya et al.[9] reported the effects of MnO_2 addition on piezoelectric properties of $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT). They found that Mn-doped PZT possessed properties of 'soft' and 'hard' piezoelectric simultaneously.

In this study, basic dielectric, ferroelectric and piezoelectric properties of the BNT ceramic were studied on $MnCO_3$ additive. Some changes of microstructure, dielectric, ferroelectric and piezoelectric properties were investigated for BNT + $MnCO_3$ x (wt.%).

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2. Experimental

The conventional ceramic fabrication technique was used to prepare BNT ceramics with $MnCO_3$ additives. The high purity of starting metal oxide or carbonate powders were used. These oxide or carbonate powders were mixed in acetone with zirconium balls by ball-milling for 10 h. After calcining, the ground and ball-milled ceramic powders were pressed into discs for samples, and were sintered at 1200°C for 2 h in an air atmosphere. The crystal phase of sintered ceramics was checked using an X-ray diffractometer. Microstructure of these samples were observed with scanning electron microscope (SEM) (Hitachi, S-2400). For preparing SEM samples, ceramics were polished with 3 μm diamond paste, and then were thermally etched at 1100°C for 30 min. An average grain size was obtained using a line intercept method.

Fire-on silver paste was used as the electrode for electrical measurements such as dielectric and piezoelectric measurements. Temperature dependence on dielectric constant, ε_s, and loss tangent, tanδ, was measured for the determination of the Curie temperature, T_c, at 1 MHz by using an automated dielectric measurement system with a multifrequency LCR meter (YHP 4275A). Specimens for piezoelectric measurements were poled in a stirred silicone oil at a room temperature. Piezoelectric properties were measured by means of a resonance–antiresonance

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method on the basis of IEEE standards using an impedance analyzer (YHP 4192A and 4194A). The electromechanical coupling factor, k_{33}, were calculated from the resonance and antiresonance frequencies. Temperature dependence of resistivity, ρ, was measured by using a high resistance meter (YHP 4329A).

3. Results and discussion

Fig. 1 shows X-ray powder diffraction patterns for BNT + $MnCO_3$ x (wt.%) [BNT + Mn] (x = 0, 0.02, 0.1 and 0.3). These patterns show that a single phase of perovskite structure with a rhombohedral symmetry. These ceramics were very easy to sinter the ceramics with a high measured density ratio more than 90% to theoretical density. Lattice parameters, a, of BNT + Mn ceramics are almost constant (a = 3.88 Å). A color of the pure BNT ceramics is white and that of BNT + Mn ceramics becomes black with increasing the amount of $MnCO_3$ content. These results indicate that these ceramics are reduced with increasing the amount of $MnCO_3$ content. The average grain size of BNT + Mn becomes larger than that of pure BNT.

Fig. 2 shows the Curie temperature, T_c, at 1 MHz of BNT + Mn ceramics as a function of $MnCO_3$ content. The T_c becomes lower with increasing the amount of $MnCO_3$. It is supposed that Mn ions mainly exist in the grain and substitute for A- or B-site of the perovskite structure in the range of this study.

Fig. 3 shows the SEM micrograph of BNT + $MnCO_3$ 0 wt.% (BNT) and 0.4 wt.% on the inside and outside of the bulk sample. The shape of grains on the BNT + $MnCO_3$ 0.4 wt.% ceramic was difference between inside and outside of sample, and that on the outside of sample displays like a needle shape. However, that of the non-doped BNT ceramic was not like the needle shape in

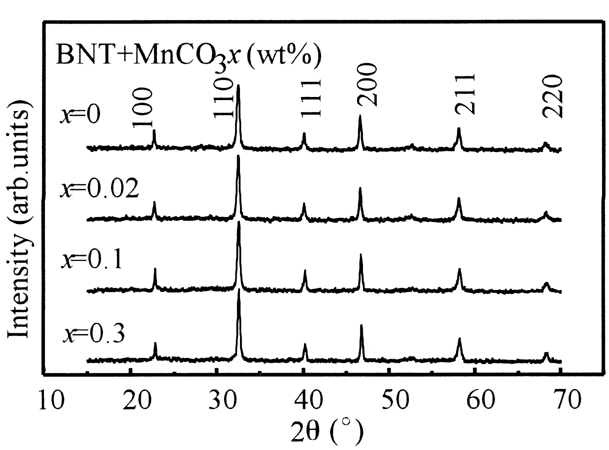

Fig. 1. X-ray powder diffraction patterns for BNT + $MnCO_3$ x (wt.%) (BNT + Mn).

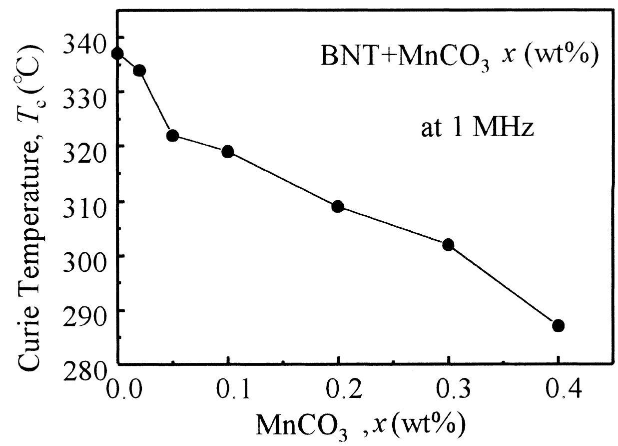

Fig. 2. Curie temperature, T_c at 1 MHz of BNT + Mn ceramics as a function of $MnCO_3$ content.

both inside and outside of the sample. Therefore, the shape of grains was changed by adding Mn ions in the outside of Mn-doped BNT ceramics.

Fig. 4 shows the X-ray diffraction patterns of the TiO_2 powder and on the surface of inside and outside for BNT + $MnCO_3$ 0 wt.% (BNT), and 0.2 wt.% ceramics. TiO_2 and unknown peaks exist on the outside of the BNT + $MnCO_3$ 0.2 wt.% ceramic. Table 1 shows the EDX analysis of BNT + 0 wt.% (BNT), and + 0.4 wt.% ceramics. The ratio of Bi/Ti ions on the stoichiometric BNT ceramic is about 0.49–0.50. However, that on the BNT + 0.4 wt.% ceramic was 0.439 and 0.213 in the inside and outside of the sample, respectively. It seems that Bi ions were ejected by Mn ions to the air, so that TiO_2 peak was appeared on the X-ray diffraction pattern of Mn-doped BNT ceramics.

Fig. 5 shows the resistivity, ρ, as a function of $MnCO_3$ content for BNT + Mn. A maximum value of the ρ is 8×10^{14} Ωcm for the BNT + $MnCO_3$ 0.2 (wt.%) at 40°C. Mn ions of BNT + $MnCO_3$ 0.2 (wt.%) ceramic compensate an electrical neutrality. It is considered that Mn^{4+} ions substitute for Ti^{3+} and Ti^{4+} ions.

Table 1
EDX analysis of BNT + $MnCO_3$ 0 wt.% (BNT) and + 0.4 wt.% ceramics

	BNT		BNT + Mn 0.4 (wt.%)	
	Inside (at %)	Outside (at %)	Inside (at %)	Outside (at %)
Bi	9.01	9.10	8.43	5.22
Ti	18.4	18.2	19.2	24.5
Na	14.8	15.0	13.7	7.80
Mn	0	0	0.32	0.54
O	17.7	57.8	58.4	61.5
	↓	↓	↓	↓
Bi/Ti	0.489	0.498	0.439	0.213

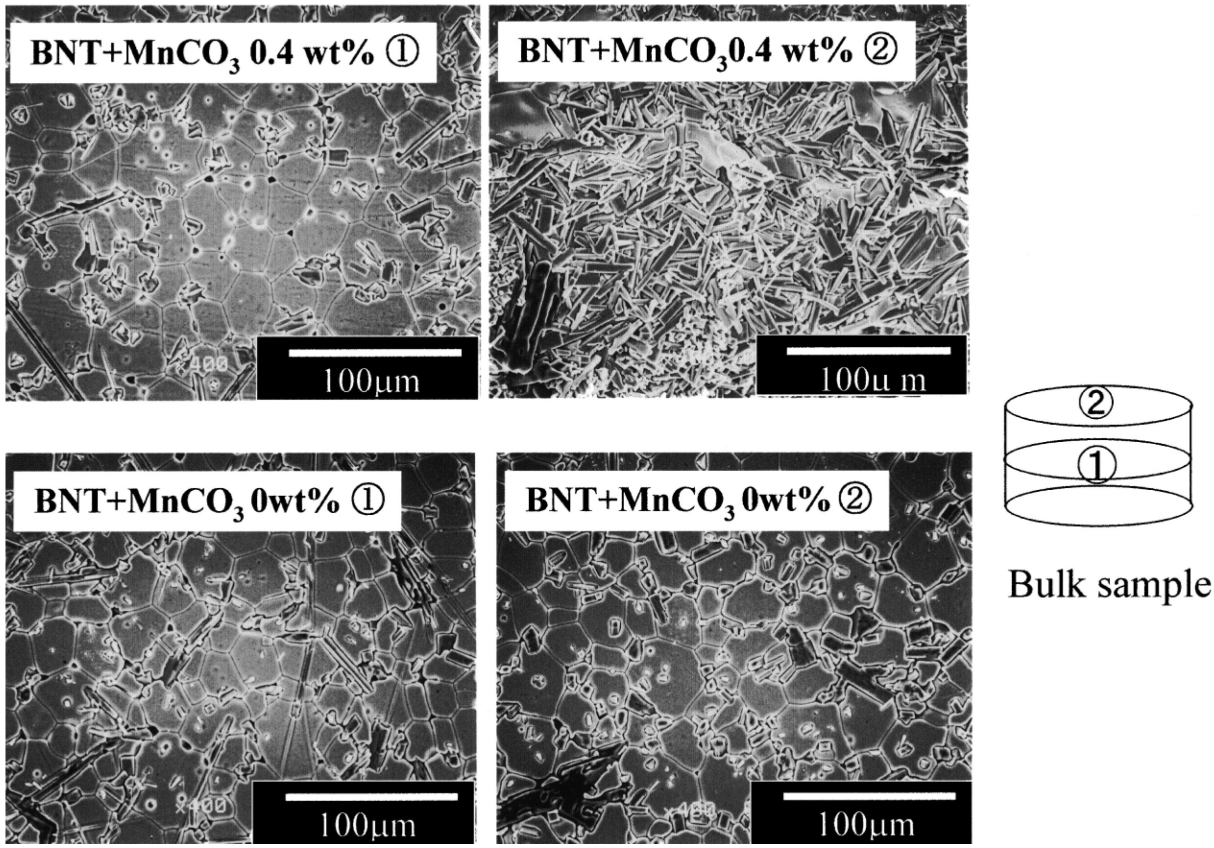

Fig. 3. SEM micrograph of BNT + $MnCO_3$ 0 wt.% (BNT) and 0.4 wt.% on the inside and outside of the bulk sample.

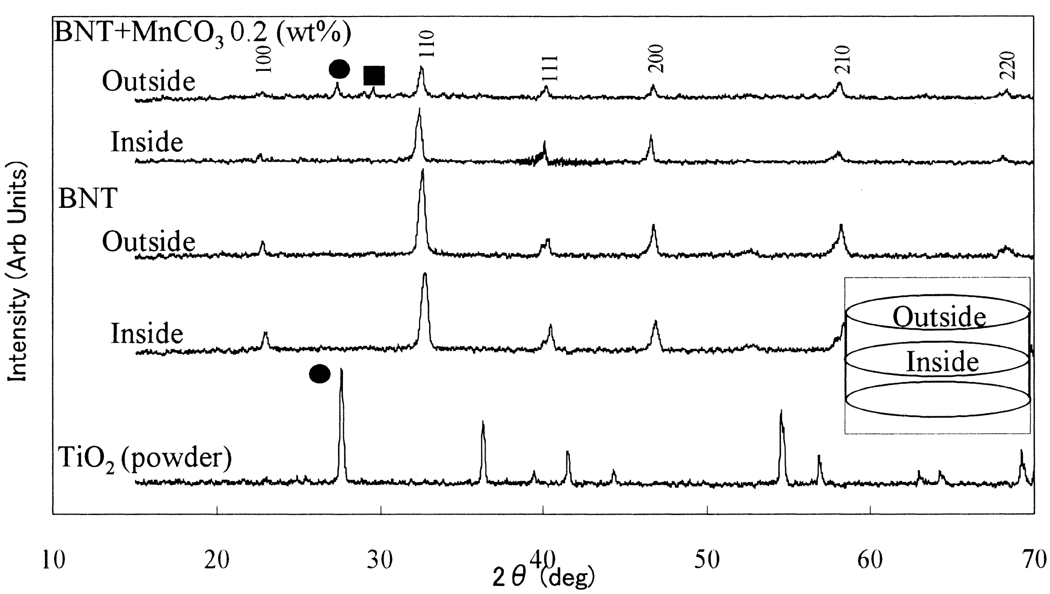

Fig. 4. X-ray diffraction patterns of the TiO_2 powder and on the surface of inside and outside for BNT $MnCO_3$ + 0 wt.% (BNT) and + 0.2 wt.% ceramics.

Fig. 6 shows the poling field dependence on the coupling factor, k_{33}, of BNT + Mn ceramics. The k_{33} is almost the same under the condition of the high poling field, $E_p = 10$ kV/mm. On the other hand, the k_{33} of the BNT and BNT + $MnCO_3$ 0.02 (wt.%) ceramics display 0.28 and 0.41 under the low poling field, $E_p = 5$ kV/mm,

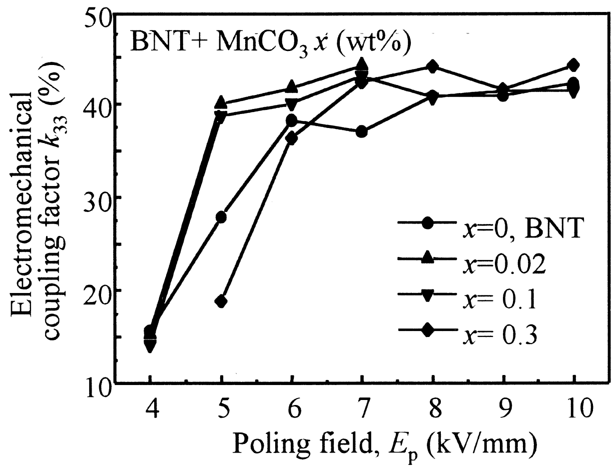

Fig. 5. Resistivity, ρ, of BNT + Mn ceramics as a function of $MnCO_3$ content.

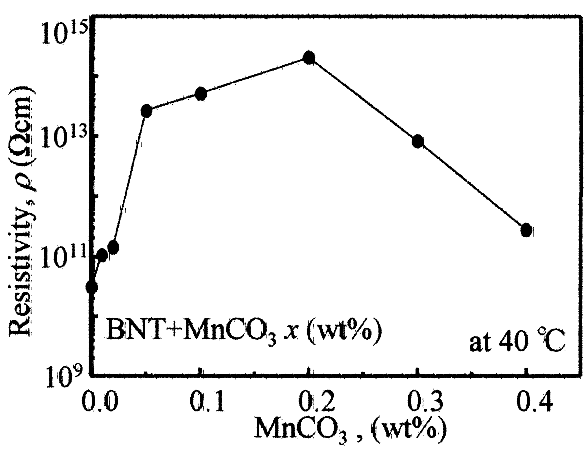

Fig. 6. Poling field dependence on the electromechanical coupling factor, k_{33}, of BNT + Mn ceramics.

respectively. The k_{33} of Mn-doped BNT ceramics could be obtained the relatively high under the condition of the low poling field, E_p.

4. Conclusions

Microstructure, dielectric, ferroelectric and piezoelectric properties of bismuth sodium titanate, $(Bi_{1/2}Na_{1/2})$ TiO_3 (BNT) were studied on $MnCO_3$ additive for a candidate as lead-free piezoelectric ceramics. The Curie temperature, T_c, decreases rapidly with increasing amount of doped $MnCO_3$. It is supposed that Mn ions mainly exist in the grain and substitute for A- or B-site of the perovskite structure in the range of this study. Furthermore, it seems that Mn ions eject Bi ions to the air as results from SEM, EDX and X-ray diffraction data. The resistivity, ρ, is enhanced to 3×10^{14} (Ωcm) (at 40°C) for BNT + $MnCO_3$ 0.2 (wt.%) and electromechanical coupling factors, k_{33}, are obtained the relatively high k_{33} under the low poling field, E_p for the Mn-doped BNT ceramics.

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