



Structure and Ferroelectric Properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.9}\text{Ba}_{0.07}\text{Sr}_{0.03}\text{TiO}_3$ Ceramics by Mn Doping†

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The effect of a small amount of MnO_2 doping on the structure and ferroelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.9}\text{Ba}_{0.07}\text{Sr}_{0.03}\text{TiO}_3$ (BNBST) ceramics prepared by the conventional mixed oxide method was systematically investigated. X-Ray diffraction shows that all ceramics samples have a pure perovskite structure and a morphotropic phase boundary between tetragonal and rhombohedral phase locates in the range of $0.20 < x < 0.75$. At $x = 0.25$, the MnO_2 -modified BNBST ceramics exhibit excellent ferroelectric properties composed by a higher remanent polarization P_r ($P_r = 25.9 \mu\text{C}/\text{cm}^2$) and lower coercive field E_c ($E_c = 2.54 \text{ kV}/\text{mm}$) at room temperature. Moreover, the two characteristic dielectric peaks can be observed in this ceramics.

Key Words: Ceramics, Microstructure, Ferroelectrics, Manganese-doping.

INTRODUCTION

Bismuth sodium titanate, $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT), firstly discovered by Smolenskii and Aganovskaya in 1960¹, is an greatly attractive A-site complex-perovskite lead-free piezoelectric ceramics due to its relatively large remanent polarization ($P_r = 38 \mu\text{C}/\text{cm}^2$) and high Curie temperature ($T_c = 320^\circ$)²⁻⁴. However, the main shortcoming of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -based ceramics limits their properties and application in devices due to their high coercive field. To solve these problems and improve the electrical properties, various types of compounds were added into $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ to form solid solutions. However, few studies are available on the effect of MnO_2 on electrical properties of the $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.9}\text{Ba}_{0.07}\text{Sr}_{0.03}\text{TiO}_3$ (BNBST) ceramics.

EXPERIMENTAL

The ceramics with the composition $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.9}\text{Ba}_{0.07}\text{Sr}_{0.03}\text{TiO}_3 + x(\text{mol } \%) \text{MnO}_2$ ($x = 0.00, 0.20, 0.25, 0.75, 1.25$) were prepared by the conventional mixed oxide method. Bi_2O_3 (99.5 %), Na_2CO_3 (99.8 %), BaCO_3 (99.9 %), SrCO_3 (99.9 %), TiO_2 (99.9 %), MnO_2 (99.5 %) were used as starting raw materials. They were ball milled for 24 h with agate ball media and alcohol. After calcination at 860°C for 3 h, the calcined powders were milled again and pressed into disks of 1.2 cm diameter and 1 mm thickness under 20 MPa using PVA as a binder. After burning off PVA, the pellets were sintered at 1150°C for 3 h in air. Silver paste was

fired on both sides of the samples at 700°C for 10 min as the electrodes for the electrical measurements. The samples were poled in 80°C silicon oil bath by applying the direct current electric field of $5 \text{ kV}/\text{mm}$ for 0.5 h. The electrical properties of all ceramics were measured more than a day later.

RESULTS AND DISCUSSION

Fig. 1(a) shows all the ceramics have a pure perovskite structure and no second phases are observed, suggesting that Ba^{2+} , Sr^{2+} , Mn^{2+} and Mn^{3+} have completely diffused into the $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ lattice to form a new homogeneous solid solution. With increasing the amount of MnO_2 , the diffraction peaks shift slightly to higher angle, the main reason for the phenomenon may be attributed to the substitution, that is to say Mn^{2+} (0.67 \AA) and Mn^{3+} (0.58 \AA) ions enter the B-site Ti^{4+} (0.68 \AA) ions so as to cause lattice distortion which induces the lattice constant to change and consequently the diffraction peaks appear shift. Fig. 1(b) shows an obscure tetragonal (002)/(200) peak splitting is still distinguishable near $46\text{-}47^\circ$, suggesting that the BNBST-Mn ceramics with $x \leq 0.20$ have a pure perovskite structure with tetragonal structure. However, with increasing x fraction from 0.20-0.75, it is noted that the BNBST-Mn ceramics start to transform to a rhombohedral phase, which is evidenced by the combining of the (002)/(200) diffraction peak to (202) peaks observed in the ceramics with $x \geq 0.75$ near $46\text{-}47^\circ$. These results indicate that the

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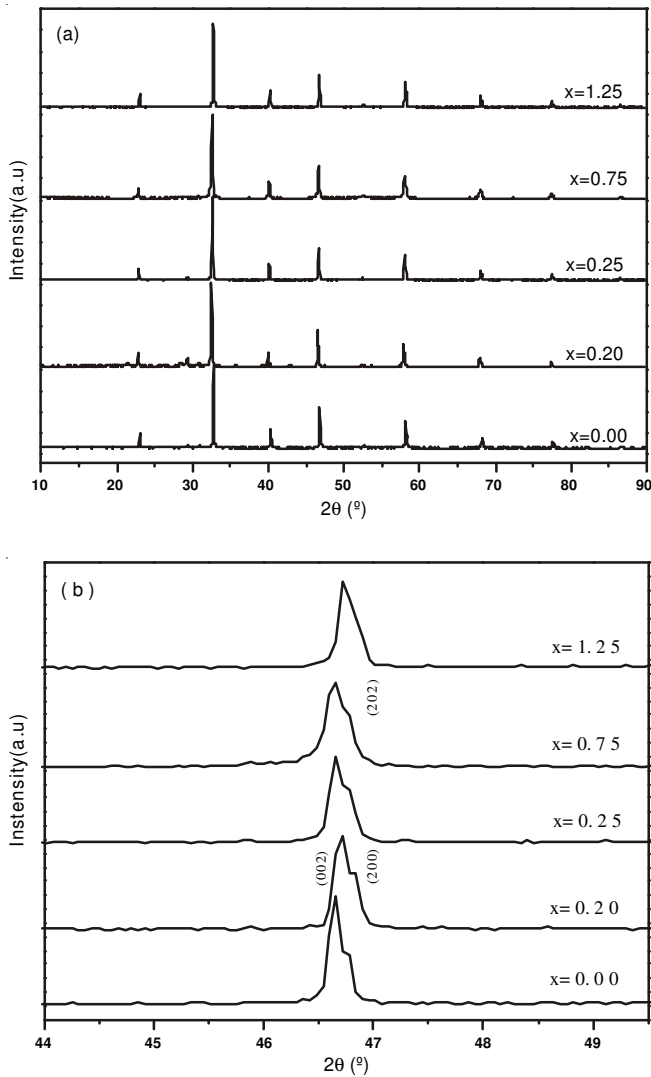


Fig. 1. XRD patterns of the BNBST + x (mol %) MnO_2 ceramics. (a) X-ray diffraction patterns of the BNBST + x (mol %) MnO_2 ceramics as a function of x ; (b) corresponding expanded XRD patterns of the BNBST + x (mol %) MnO_2 ceramics in the ranges of 2θ from 44° to 50°

morphotropic phase boundary (MPB) of tetragonal and rhombohedral phases is formed in the BNBST-Mn ceramics with $0.20 < x < 0.75$. The morphotropic phase boundary phase (MPB) in the BNBST-Mn ceramics will strongly affect the electrical properties of the ceramics, which will be provided below for further discussion.

Fig. 2(a) shows all ceramics exhibit typical and saturated P-E hysteresis loops for ferroelectrics under an electric field of 5 kV/mm at room temperature. As shown in Fig. 2(b), the observed P_r increases with increasing x and then decreases quickly, giving a maximum value of $25.9 \mu\text{C}/\text{cm}^2$ at $x = 0.25$. The observed E_c decreases with increasing x from 0.00-0.25 and then increases with x further increasing to 1.25, so E_c get a minimum value of 2.54 kV/mm at $x = 0.25$. Obviously, the BNBST-Mn ceramics exhibit a much lower E_c as compared to the pure BNT and BNBST ($E_c = 3.5$ kV/mm) ceramic after the introduction of Mn^{2+} and Mn^{3+} into the B-sites of BNBST. The low coercive field facilitates the poling process of the ceramics.

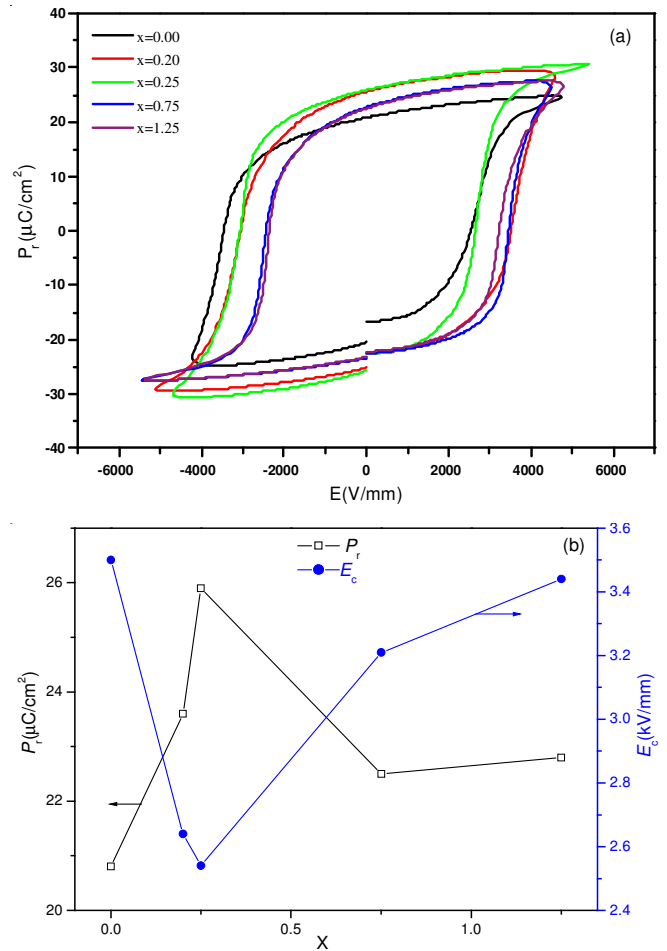


Fig. 2. (a) P-E hysteresis loops of the BNBST-Mn ceramics; (b) Remanent polarization P_r and coercive field E_c of the BNBST-Mn ceramics

Fig. 3 shows that two abnormal dielectric peaks are observed during the heating process. The temperature corresponding to the peak in the low temperature range is denoted as depolarization temperature (T_d), suggesting the stability of the ferroelectric domains^{5,6}. The temperature corresponding to the maximum value of dielectric constant is referred to as the Curie temperature (T_c), showing that the BNBST-Mn ceramics possess relatively higher Curie temperature ($T_c = 392^\circ\text{C}$).

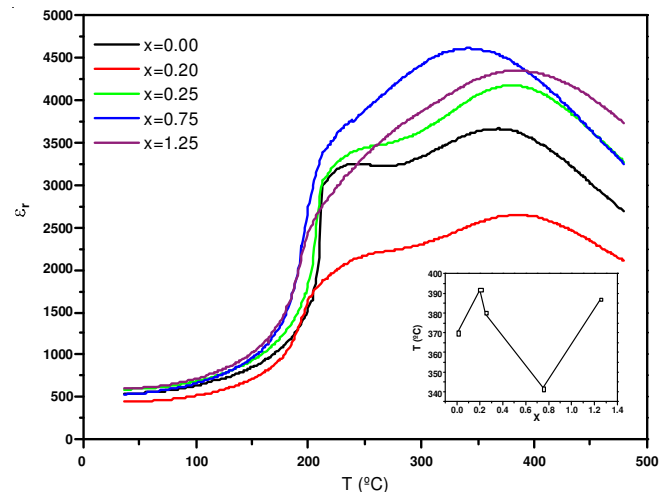


Fig. 3. Temperature dependence of dielectric constant for the BNBST-Mn ceramics at 10 kHz and the Curie temperature as a function of x

Conclusion

A new ceramics $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.9}\text{Ba}_{0.07}\text{Sr}_{0.03}\text{TiO}_3 + x$ (mol %) MnO_2 were prepared by the conventional mixed oxide method. A morphotropic phase boundary (MPB) between tetragonal and rhombohedral phases was confirmed at $0.20 > x > 0.75$. At $x = 0.25$, the BNBST-Mn ceramics exhibit a much lower E_c ($E_c = 2.54$ kV/mm) and a higher remanent polarization P_r ($P_r = 25.9$ $\mu\text{C}/\text{cm}^2$) after the introduction of Mn^{2+} and Mn^{3+} into the BNBST. These results indicate that MnO_2 can enhance the property of lead-free piezoelectric ceramics.

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