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Piezoelectric and Ferroelectric Properties of $(Bi_{0.5}Na_{0.5})_{0.9}Ba_{0.07}Sr_{0.03}TiO_3$ Lead-Free Ceramics with MnO_2 Doping†

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The effect of a small amount MnO_2 doping on the piezoelectric and ferroelectric properties of $(Bi_{0.5}Na_{0.5})_{0.9}Ba_{0.07}Sr_{0.03}TiO_3$ (BNBST) lead-free ceramics prepared by the conventional mixed oxide method was systematically investigated. At x = 0.25, the MnO_2-modified BNBST ceramics exhibit optimal piezoelectric and dielectric properties (d_{33} = 157pC/N, k_p = 33 %, Q_m = 364, tan δ = 2 %, ε_r = 843) and excellent ferroelectric properties composed by a higher remanent polarization P_r (P_r = 25.9 μC/cm^2) and lower coercive field E_C (E_C = 2.54 kV/mm) at room temperature. Moreover, the two characteristic dielectric peaks can be observed in this ceramics.

Key Words: Lead-free ceramics, Piezoelectrics, Ferroelectrics, MnO_2.

INTRODUCTION

The development of lead-free piezoelectric ceramics have attracted much attention result from environmental issues associated with lead. Bismuth sodium titanate, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) was first discovered by Smolenskii and Aganovskaya in 1960[1], is an attractive A-site complex-perovskite lead-free piezoelectric ceramics due to its relatively large remanent polarization (P_r = 38 μC/cm^2) and high Curie temperature (T_c = 320 ºC)[2-4]. To enhance electrical properties, various types of compounds were added into $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) to form solid solutions. However, few studies are available on the effect of MnO_2 on electrical properties of the $(Bi_{0.5}Na_{0.5})_{0.9}Ba_{0.07}Sr_{0.03}TiO_3$ (BNBST) ceramics.

EXPERIMENTAL

The ceramics with the composition $(Bi_{0.5}Na_{0.5})_{0.9}Ba_{0.07}Sr_{0.03}TiO_3$ + x (mol %) 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 ºC 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 ºC for 3 h in air. Silver paste was fired on both sides of the samples at 700 ºC for 10 min as the electrodes for the electrical measurements. The samples were poled in 80 ºC silicon oil bath by applying the direct current electric field of 5 kV/mm for 0.5 h. The electrical properties of all ceramics were measured more than a day later.

RESULTS AND DISCUSSION

As shown in Fig. 1(a), the piezoelectric constant d_{33} value increases with increasing x, reaching maximum value (157 pC/N) at x = 0.25, then decreases with further increase of x. Similarly to d_{33}, k_p also reaches maximum value (33 %) at x = 0.25. The results indicate that the optimal piezoelectric properties can be obtained at the composition x = 0.25. Fig. 1(b) shows dielectric properties of the BNBST-Mn ceramics at 10 kHz as a function of x. It can be found that the relative permittivity ε_r reaches the maximum value of 843 at x = 0.25 and the dielectric loss tan δ reaches a minimum value of 2 % at the same point. Meantime, as compared to the pure $Bi_{0.5}Na_{0.5}TiO_3$ ceramic, this figure also shows that the ceramics possess an better mechanical quality factor Q_m of BNBST-Mn ceramics, the maximum values (364) is also achieved at x = 0.25.

Fig. 2(a) shows that 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

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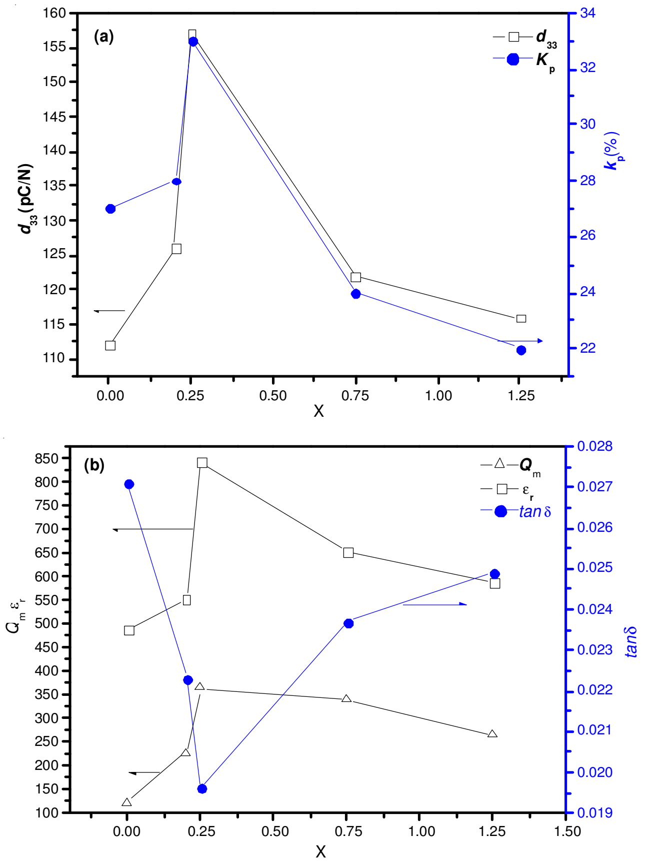

Fig. 1. Piezoelectric and dielectric properties of the BNBST-Mn ceramics as a function of x

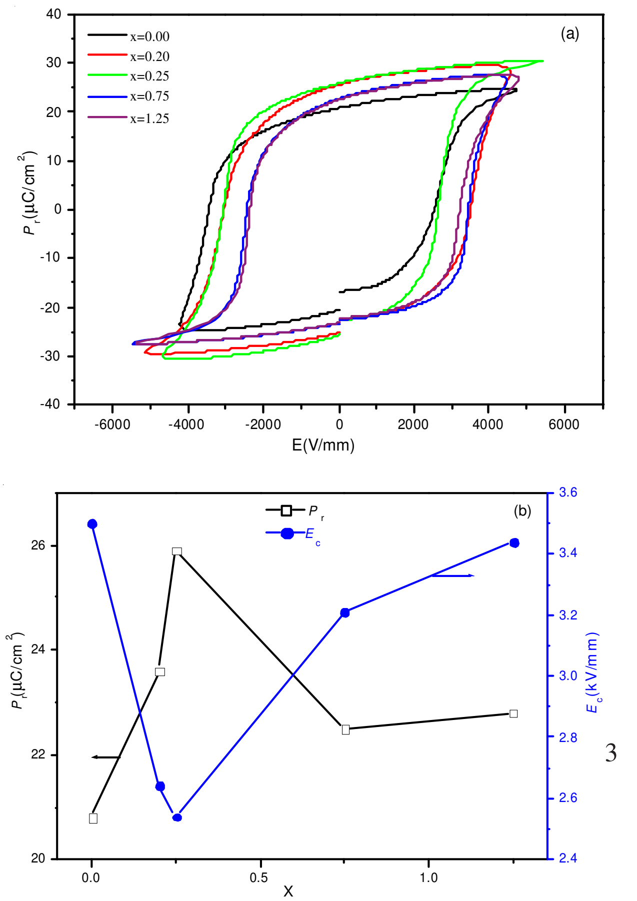

Fig. 2. (a) P-E hysteresis loops of the BNBST-Mn ceramics; (b) Remanent polarization P_r and coercive field E_C of the BNBST-Mn ceramics

quickly, giving a maximum value of 25.9 μC/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. 3(a) shows two abnormal dielectric peaks at 10 kHz 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 lead-free piezoelectric ceramics possess relatively higher Curie temperature (T_c = 392 ºC). Fig. 3(b) shows that the compositions at x = 0.25 exhibit a lower depolarization temperature, which implies a reduction of the stability of ferroelectric domains, due to the incompatibility of their crystal lattices.

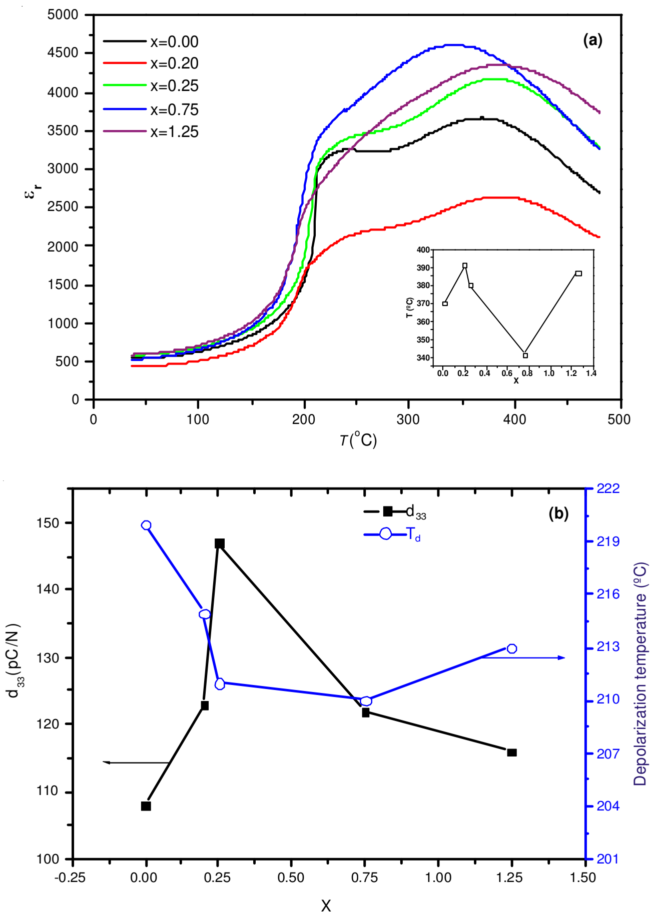

Fig. 3. (a) Temperature dependence of dielectric constant for the BNBST-Mn ceramics at 10 kHz; (b) piezoelectric constants and depolarization temperatures of BNBST-Mn ceramics as a function of x

Conclusion

A new lead-free ceramics $(Bi_{0.5}Na_{0.5})_{0.9}Ba_{0.07}Sr_{0.03}TiO_3$ + x (mol %) MnO_2 were prepared by the conventional mixed oxide method. At x = 0.25, the BNBST-Mn ceramics exhibiting optimal electrical properties. Moreover, 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 μC/cm^2) after the introduction of Mn^{2+} and Mn^{3+} into the BNBST.

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