Multiferroic properties in Mn-modified $0.7\text{BiFeO}_3 - 0.3(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics

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Abstract

The $0.7\text{BiFeO}_3\text{-}0.3(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3 + x \text{ wt.}\% \text{MnO}_2$ ($x = 0.0 - 0.7$) multiferroic ceramics were fabricated by a solid state reaction method. Effects of Mn doping on phase structure, microstructure, dielectric, ferroelectric, and magnetic properties were systematically investigated. It was found that all ceramics showed pseudocubic phases. Dense microstructure along with perfect grains and clear grain boundaries were obtained in all ceramics. A relaxor behavior was observed in all ceramics and Mn doping could promote this behavior. In the case of Mn modifying, significantly lower dielectric loss values along with higher T_c could be obtained compared with un-doped system. The lower leakage current density J values and relatively higher resistivity R values showed that better electric insulation was achieved by Mn modification. The optimal ferroelectric and magnetic properties were obtained at proper amount of Mn modification with $x = 0.2 - 0.4$.

Keywords: A. Ceramics, B. Magnetic properties, D. dielectric properties, D. Ferroelectricity, D. Multiferroics.

1. Introduction

Materials that have combined different performances of ferroic orders such as (anti)ferromagnetism, (anti)ferroelectricity and (anti)ferroelasticity simultaneously are known as multiferroics. These multiferroics show opportunities for promising applications in information storage, sensors, spintronic and actuator devices [1-4]. As one of the very few single-phase multiferroics, BiFeO₃ (BFO)-based perovskite materials have attracted considerable attention in recent years due to their high Curie temperature (T_c) of 830 °C and high antiferromagnetic Néel temperature (T_N) of 370 °C [5,6]. It is known that for BFO-based multiferroics, the Bi ion with $6s^2$ lone pair electrons can move away from the centrosymmetric position in its oxygen surroundings then lead to ferroelectricity, while the magnetism originates from the partially filled d orbitals of Fe ion [7-10]. However, there are several drawbacks that hamper the practical technological applications of BFO-based multiferroics [11].

One drawback lies in that the fabrication of single-phase BFO is very difficult. BFO has a rhombohedral distorted perovskite structure in the space group $R3c$ at room temperature. Preparation of bulk BFO is usually accompanied by the presence of some impurity phases such as Bi₂Fe₄O₉, Bi₃₆Fe₂₄O₅₇ and Bi₂₅FeO₄₀ [11,12]. Moreover, BFO ceramics generally exhibit high dielectric loss and high conductivity, which are typically attributed to the reduction of Fe³⁺ to Fe²⁺ during sintering process and the formation of oxygen vacancies for charge compensation [13]. Therefore it is difficult to pole the BFO ceramics with impurity phases to measure their piezoelectric

properties and obtain the saturated polarization hysteresis loop of ferroelectrics. So, in order to improve the ferroelectric and ferromagnetic performances of bulk BFO-based ceramics, poor perovskite phase stability and low high-field electrical resistivity should be initially considered and solved.

At present, introducing other stable ABO_3 perovskites (such as $BaTiO_3$, $SrTiO_3$, and $Bi_{0.5}Na_{0.5}TiO_3$) into BFO to form solid solution becomes an effective way to suppress the appearance of secondary impurity phase and also enhance the electrical properties [14-16]. Specially, the extensively studied $BiFeO_3$ - $BaTiO_3$ solid solutions have been considered as the most interesting and promising multiferroic system. It is reported that the morphotropic phase boundary (MPB) between rhombohedral and pseudocubic phases locates at the composition of $0.70BiFeO_3$ - $0.30BaTiO_3$. [7]. L. F. Zhu et al. employed $Bi(Mg_{1/2}Ti_{1/2})O_3$ in the $0.70BiFeO_3$ - $0.30BaTiO_3$ system to enhance the electrical properties. High $d_{33} = 154$ pC/N was achieved in the $0.66BiFeO_3$ - $0.30BaTiO_3$ - $0.04Bi(Mg_{1/2}Ti_{1/2})O_3$ ceramics due to the MPB effect [17]. X. N. Zhu et al. studied the ferroelectricity, piezoelectricity and ferromagnetism in the $BiFeO_3$ -($Ba_{0.75}Ca_{0.25}$) TiO_3 multiferroic ceramics. The enhanced remnant magnetization of 0.07 emu/g at 300K was found in the MPB composition of $0.07BiFeO_3$ - $0.03(Ba_{0.75}Ca_{0.25})TiO_3$ ceramics [18]. Although the perovskite structure becomes stable and the MPB effect can be induced through forming $BiFeO_3$ - $BaTiO_3$ solid solutions, the low insulation resistance problem needs to be solved before studying the ferroelectric and ferromagnetic properties of bulk ceramics. It has been suggested that a small amount of MnO_2 doping can not only increase the resistivity,

but also significantly improve the magnetic properties [19-21], whereas, it is also noted that the piezoelectric properties (d_{33} and k_p) suffer from deterioration after MnO_2 doping in the $0.67\text{BiFeO}_3\text{-}0.33\text{Ba}0.7\text{Ca}0.3\text{TiO}_3$ ceramics [22]. Through studying the effects of density and grain size on piezoelectric properties caused by the sintering conditions, H. W. Joo et al. found that the deterioration of piezoelectric properties in MnO_2 doping $0.75\text{BiFeO}_3\text{-}0.25\text{BaTiO}_3$ ceramics was mainly due to the smaller grain size ($< 1 \mu\text{m}$) associated with the sintering behavior [23]. By carefully controlling the sintering temperature and dwell time, Y. Li et al. obtained high electric insulation and enhanced electric properties ($d_{33} = 144 \text{ pC/N}$, $M_r = 0.099 \text{ emu/g}$) in the modified $0.705\text{BiFeO}_3\text{-}0.275\text{BaTiO}_3\text{-}0.02\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 + 1 \text{ mol\% MnO}_2$ system [24].

In our previous work, the $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ (BCZT) with excellent piezoelectricity was added in BFO to form the $(1-x)\text{BFO}\text{-}x\text{BCZT}$ solid solutions in the range of $0.05 \leq x \leq 0.95$ [25]. It was found that a morphotropic phase boundary existed when $0.20 \leq x \leq 0.30$ and the optimal ferroelectric and magnetic properties were obtained when $0.30 \leq x \leq 0.35$. So in this work, the solid solution $0.7\text{BiFeO}_3\text{-}0.3(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ was chosen as multiferroic materials, and MnO_2 was added as a modifier to improve the sintering ability, enhance the electric resistivity to obtain good ferroelectric and magnetic properties. The effects of MnO_2 on the phase structure, microstructure, dielectric relaxor behavior, ferroelectric, and magnetic properties of $0.7\text{BiFeO}_3\text{-}0.3(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ system were systematically studied, and possible mechanisms were additionally discussed.

2. Experimental procedures

$0.7\text{BiFeO}_3\text{-}0.3(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3 + x \text{ wt.}\% \text{MnO}_2$ (abbreviated as $0.7\text{BFO-}0.3\text{BCZT} + x \text{ wt.}\% \text{MnO}_2$, $x = 0.0 - 0.7$) ceramics were prepared by the conventional solid state reaction method. The precursor oxides Bi_2O_3 (99%), Fe_2O_3 (99%), BaCO_3 (99%), CaCO_3 (99.99%), ZrO_2 (99%), TiO_2 (99%) and MnO_2 (98%) were carefully weighed in stoichiometric ratio and wet mixed thoroughly by ball-milling in alcohol for 24 h. After the slurry was dried, the mixture was calcined at 850°C for 3 h in a covered corundum crucible. The obtained powders were mixed with 5 wt% binder and compacted into disk-shaped pellets with a diameter of 15.0 mm and thickness of 1.0 mm under 100 MPa. To reduce the volatilization of bismuth oxide during sintering process, the pellets were buried in calcined powder of the same composition in closed crucibles and sintered at $940\text{-}980^\circ\text{C}$ with a heating rate of $5^\circ\text{C}/\text{min}$. Finally, silver electrodes were placed on the top and bottom surfaces of the sintered ceramics and fired at 840°C for 30 min.

The phases of obtained ceramics were analyzed by using X-ray diffraction (XRD, D/max-2550/PC, Rigaku, Japan) using $\text{CuK}\alpha$ ($\lambda = 0.15406 \text{ nm}$) radiation in the range of $20^\circ \leq 2\theta \leq 80^\circ$ with a scanning rate of $8^\circ/\text{min}$. The microstructures of the natural surface of the as-prepared samples were observed by scanning electron microscopy (Quanta 200, Philips, Netherlands). The temperature-dependent dielectric properties of the samples were obtained by measuring the capacitance (C) and loss ($\tan \delta$), using an LCR meter (Agilent E4980A, Penang, Malaysia). The P - E hysteresis loops, P - E hysteresis at different temperatures, and leakage current density were recorded using a

precision materials measuring system (Premier II, Radiant Technologies, Inc.). Room temperature magnetic hysteresis loops were measured under a magnetic field of 10,000 Oe using a superconducting quantum interferometric device (SQUID) magnetometer (Quantum Design, America).

3. Results and discussion

The room temperature x-ray diffraction (XRD) patterns for 0.7BFO-0.3BCZT + x wt.% MnO_2 ceramics ($x = 0.0 - 0.7$) are shown in Fig.1. All the samples are well crystallized and exhibit a single phase without any second phase. The XRD results indicate that the formation of impurity phases in BFO can be effectively suppressed by the addition of BCZT and the modification of MnO_2 . All samples show a pseudocubic crystal structure, as no peak splitting or superlattice reflections is observed. The XRD results show that addition of MnO_2 cannot cause obvious change in the crystal structure along with the change of composition. Considering the fact that the radii of Mn ions (Mn^{2+} : 0.67Å, Mn^{3+} : 0.64Å, and Mn^{4+} : 0.53 Å) are much smaller than those of A-site ions (Ba^{2+} : 1.35Å, Ca^{2+} : 0.99Å, and Bi^{2+} : 1.38Å), and closer to those of B-site ions (Ti^{4+} : 0.68Å, Zr^{4+} : 0.79 Å, and Fe^{3+} : 0.645Å), it is suggested that Mn ions may prefer to substitute for the B-site ions (Ti^{4+} , Zr^{4+} or Fe^{3+}) to form a stable perovskite structure. Moreover, according to the present reports, MnO_2 will convert into Mn_2O_3 and Mn_3O_4 at 650°C and 980°C, respectively, when it is sintered in air [26]. The corresponding change of valence state from Mn^{4+} to Mn^{3+} has also been observed and verified in Mn doped $(\text{K}_{0.5}\text{Na}_{0.5}\text{Li}_{0.065})\text{NbO}_3$ ceramics using synchrotron x-ray absorption spectroscopy [27]. In our cases, all ceramics

were sintered in the temperature range of 940-980 °C in air, so it is possible that the Mn ions may have Mn^{3+} chemical states for all compositions. In addition, the reaction between Mn^{3+} and Fe^{2+} ($\text{Mn}^{3+} + \text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + \text{Fe}^{3+}$) effectively restrains the conversion of Fe^{3+} to Fe^{2+} , and leads to the appearance of Mn^{2+} in the doped ceramics. Then it is reasonable that there are three kinds of Mn ions in the obtained ceramics: Mn^{2+} , Mn^{3+} and Mn^{4+} . The presence of multivalent Mn ions will significantly affect the electric properties and be discussed in the later part.

Fig. 2 shows the SEM microstructural images of 0.7BFO-0.3BCZT + x wt.% MnO_2 ceramics ($x = 0.0 - 0.7$). As shown in Fig.2, all the obtained ceramics exhibit dense structure along with perfect grains and clear grain boundaries. It can be seen that the doping of MnO_2 is an effective way to suppress the grain growth of ceramics. The average grain size of the un-doped ceramics is about 8 μm , while the doped ceramics with $x = 0.7$ show smaller grain size of about 1 μm . As mentioned above, since Mn ions have multivalences (+2, +3 and +4) and may occupy B-site to form a stable perovskite structure. In 0.7BFO-0.3BCZT+ x wt.% MnO_2 system, the substitution of B-site ions (Ti^{4+} or Fe^{3+}) by Mn cations with lower valences (Mn^{3+} or Mn^{2+}) can result in the existence of oxygen vacancies to compensate the charge imbalance [23], which can slow down the ion motion and result in a lower rate of grain growth[28].

Figs. 3 show the temperature dependence of relative dielectric constant (ϵ_r) for 0.7BFO-0.3BCZT + x wt.% MnO_2 ceramics ($x = 0.0 - 0.7$) measured at different frequencies. All the ceramics show frequency-dependent and broadened dielectric

permittivity peaks. The dielectric permittivity peaks corresponding to the maximum relative dielectric constant (ϵ_m) are associated to the ferroelectric to paraelectric phase transition, which is corresponding to the Curie temperature (T_c). T_c is frequency-dependent and T_c shifts to higher temperature with increasing frequency, indicating the relaxor behavior for all samples. The variations of $\tan\delta$ with temperature for all 0.7BFO-0.3BCZT + x wt.% MnO_2 ceramics show similar trend, that is, all samples show relatively constant $\tan\delta$ below T_c . Above T_c , the monotonous increase in $\tan\delta$ can be attributed to the scattering of thermally activated charge carriers and some defects in the samples.

To analyze the effects of Mn content on the relaxation characters of 0.7BFO-0.3BCZT + x wt.% MnO_2 ceramics, the modified Curie-Weis law is described as follows: [29]

$$\frac{1}{\epsilon_r} - \frac{1}{\epsilon_m} = \frac{(T - T_m)^\gamma}{C} \quad (1)$$

Where γ and C are constant with $1 \leq \gamma \leq 2$. The degree of relaxor behavior can be estimated by the parameter γ . For normal ferroelectrics, $\gamma = 1$ and ϵ_r above T_c obeys the Curie-Weis law. While for an ideal relaxor ferroelectric, $\gamma = 2$ and the ϵ_r above T_c deviates from the Curie-Weis law. Through fitting curves of the $\ln(1/\epsilon_r - 1/\epsilon_m)$ versus $\ln(T - T_m)$ plots for all samples, the calculated γ values are 1.45, 1.64, 1.73, 1.81, 1.87, 1.92, 1.97 and 1.98 for $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$ and 0.7 , respectively. It can be seen that with increasing x , γ increases monotonically, indicating the enhanced relaxor behavior, which are partially ascribed to the domain refinement and the weakening of long-range ferroelectric interactions caused by Mn

doping [30]. On the other hand, in Mn doped 0.7BFO-0.3BCZT ceramics, the appearance of oxygen vacancies for charge compensation caused by substituting Mn for B-site ions may disrupt the long-range ferroelectric ordering, resulting in enhanced relaxor behavior [23]. Additionally, it is known that the fine-grained BCZT-based ceramics can show higher inner stress due to 90° domain walls, and the inner stress increases with the decreasing of grain size. The higher inner stress can also promote the appearance of relaxor behavior [31-33]

The dielectric constant ϵ_r and dielectric loss $\tan\delta$ of 0.7BFO-0.3BCZT + x wt.% MnO₂ ceramics ($x = 0.0 - 0.7$) measured around room temperature at 10 kHz as a function of x are presented in Fig. 4(a). The dielectric constant ϵ_m is the maximum value of dielectric constant obtained at T_c . T_c and dielectric constant (ϵ_m) with respect to Mn content measured at 10 kHz are plotted in Fig. 4(b). Fig. 4(a) shows that the dielectric properties exhibit significant dependence on the content of Mn doping. With increasing x from 0.0 to 0.7, ϵ_r gradually decreases from 485 to 295. By doping Mn in 0.7BFO-0.3BCZT system, $\tan\delta$ decreases sharply from higher value of 0.097 at $x = 0.0$ to 0.042 at $x = 0.3$, and then maintains at about 0.035 with further increasing x to 0.7. These results indicate that Mn modification is an effective way to improve the dielectric resistivity of 0.7BFO-0.3BCZT system as that in other ferroelectric systems. According to Fig. 4(b), T_c is above 340 °C for all 0.7BFO-0.3BCZT + x wt.% MnO₂ ceramics, which is much higher than that of piezoelectric (Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O₃ ceramics. ϵ_m increases initially, reaches a maximum value of 18900 at $x = 0.2$, and then decreases with further increasing x

above 0.2. The dielectric properties show that the significantly lower dielectric loss values along with higher T_c can be achieved simultaneously in Mn modified 0.7BFO-0.3BCZT system, which is very favorable to improve the dielectric properties.

Fig. 5(a) shows the leakage current density J of the 0.7BFO-0.3BCZT + x wt.% MnO_2 ceramics ($x = 0.0 - 0.7$) measured at room temperature as a function of the electric field E , while Fig. 5(b) gives the dependence of resistivity R on the electric field E for the 0.7BFO-0.3BCZT + x wt.% MnO_2 ceramics. According to Fig. 5(a), the leakage current density J decreases obviously with Mn doping, and all the Mn-modified 0.7BFO-0.3BCZT ceramics show lower J values of 10^{-6} - 10^{-5} A/cm² under the electric field of 30 kV/cm. As shown in 5(b), the resistivity R increases by orders of magnitude with Mn doping, and all the Mn-modified 0.7BFO-0.3BCZT ceramics show higher R values of 10^{10} - 4×10^{10} Ωcm under the electric field of 30 kV/cm, suggesting that the Mn doping is an effective way to increase the electric insulation of 0.7BFO-0.3BCZT ceramics. It has been known that the valence transformation of Fe ions from Fe^{3+} to Fe^{2+} in the BiFeO_3 creates oxygen vacancies, and thus results in the high conductivity. The higher electric insulation of the Mn-modified 0.7BFO-0.3BCZT ceramics can be attributed to the reaction between Mn^{3+} and Fe^{2+} ($\text{Mn}^{3+} + \text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + \text{Fe}^{3+}$), which effectively restrains the conversion of Fe^{3+} to Fe^{2+} . As a result, the high resistivity is obtained in the 0.7BFO-0.3BCZT + x wt.% MnO_2 ceramics, especially for the samples with $x = 0.3 - 0.4$.

Fig. 6(a) shows the polarization-electric field (P - E) hysteresis loops of 0.7BFO-0.3BCZT + x wt.% MnO₂ ceramics ($x = 0.0 - 0.7$) measured under applied field of 70 kV/cm and at room temperature. Fig. 6 indicates that all samples can exhibit ferroelectricity. The un-doped 0.7BFO-0.3BCZT ceramics possess a round ferroelectric hysteresis loop with a saturation tendency, which shows significant conductive loss in the un-doped ceramics. While the P - E loops of the Mn-doped ceramics with $x = 0.1 - 0.3$ can attain ferroelectric saturation, indicating that Mn doping can decrease the conductive loss sufficiently. In addition, with increasing x , the P - E loops become slimmer, which are consistent with the appearance of obvious ferroelectric relaxor behaviors verified by the dielectric properties [30]. The most important evidence of ferroelectricity is P - E hysteresis loop, however, there exists a certain insulation leakage in actual ferroelectrics which makes the measured P - E loops deviate from actual ones [34]. It is suggested that distinguishing the contributions of linear capacitance, electric conductivity and domain switching in current-electric field loops is an effective way to observe the reorientation of polarization and measure the ferroelectricity of materials studied. Figs. 6(b) and 6(c) show the polarization current intensity-electric field (J - E) curves for 0.7BFO-0.3BCZT + x wt.% MnO₂ ceramics ($x = 0.0, 0.2$) measured under the applied field of 70 kV/cm. The polarization current intensity of all ceramics show very broad and flat peaks at the nonergodic state, indicating ferroelectric domains reverse. In addition, comparing Fig. 6(b) with Fig. 6(c), the J - E curves of Mn-doped composition with $x = 0.2$ show relatively sharper current intensity peak than that of

un-doped one, showing the ferroelectricity can be modified by Mn doping.

The room temperature magnetization-magnetic field (M - H) hysteresis loops of the 0.7BFO-0.3BCZT + x wt.% MnO_2 ceramics ($x = 0.0 - 0.7$) were measured with a maximum magnetic field of 10 kOe, as shown in Fig. 7. The hysteresis loops indicates the ferromagnetic nature for all ceramics. The variation of the maximum magnetization (M_{max}), remnant magnetization (M_r) and coercive field (H_c) as a function of Mn content is present in Fig. 8. Both M_{max} and M_r increase with x , reach the maximum values of 0.4559 emu/g and 0.1595 emu/g at $x = 0.4$, respectively, indicating that the ferromagnetic properties of 0.7BFO-0.3BCZT + x wt.% MnO_2 ceramics can be significantly improved by appropriate Mn modification. It has been suggested that the spatially modulated spiral spin structure of BF can be suppressed by doping, actually, doping can even lead to a transition from the spinodal structure of pure BF to the homogeneous FM state [35].

4. Conclusions

In summary, the phase structure, microstructure, dielectric, ferroelectric as well as magnetic properties of the 0.7BFO-0.3BCZT+ x wt.% MnO_2 ($x = 0.0 - 0.7$) ceramics were prepared and intensively investigated. XRD results showed that the formation of impurity phases in BFO was effectively suppressed by the addition of MnO_2 and all compositions exhibited the pseudocubic crystal structure. Dense microstructure along with perfect grains and clear grain boundaries were obtained in all samples. It was also found that Mn doping in 0.7BFO-0.3BCZT was effective in suppressing the grain growth of ceramics. According to the dielectric properties, Mn

modification in 0.7BFO-0.3BCZT system could promote the relaxor behavior, decrease the dielectric loss and also improve the Curie temperature T_c significantly. In the case of Mn doping, the ferroelectric P - E hysteresis loops changed gradually from round shape for un-doped samples to typical saturated shape, and then became slimmer at higher Mn contents. The lower leakage current density J values and relatively higher resistivity R values showed that better electric insulation could be achieved by Mn modification. Additionally, the ferromagnetic properties was enhanced significantly by Mn doping. Especially at $x = 0.4$, both the maximum magnetization ($M_{\max}$) and remnant magnetization (M_r) reached the maximum values of 0.4559 emu/g and 0.1595 emu/g, respectively. While the ceramics with optimal dielectric and ferroelectric properties were obtained at $x = 0.2$: $\epsilon_r = 463$, $\epsilon_m = 18900$, $T_c = 369$ °C, $P_r = 11.95$ $\mu\text{C}/\text{cm}^2$.

Acknowledgements

This work was supported by National Science Foundation of China (NSFC) (Grant Nos.51572163, 21401123, and 51577111), and the Natural Key Science Basic Research Plan in Shaanxi Province of China (Grant No. 2015JZ011).

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Figure Captions

Fig. 1. X-ray diffraction patterns for 0.7BFO-0.3BCZT + x wt.% MnO₂ ceramics with different x .

Fig. 2. SEM micrographs of the 0.7BFO-0.3BCZT + x wt.% MnO₂ ceramics: (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, (e) $x = 0.4$, (f) $x = 0.5$, (g) $x = 0.6$, and (h) $x = 0.7$.

Fig. 3. Temperature dependence of relative dielectric constant for 0.7BFO-0.3BCZT + x wt.% MnO₂ ceramics ($x = 0.0, 0.2, 0.4$, and 0.7) measured at different frequencies.

Fig. 4. Dielectric properties of 0.7BFO-0.3BCZT + x wt.% MnO₂ ceramics: (a) ϵ_r and $\tan\delta$ measured at 10 kHz as a function of x ; (b) T_c and ϵ_m measured at 10 kHz as a function of x .

Fig. 5. Leakage current J (a) and resistivity R (b) of 0.7BFO-0.3BCZT + x wt.% MnO₂ ceramics measured at room temperature as a function of the electric field E .

Fig. 6. (a) Loops of polarization P versus electric field E for 0.7BFO-0.3BCZT + x wt.% MnO₂ ceramics with different x measured under 70 kV/cm; (b) Room temperature polarization current intensity versus electric field loops of 0.7BFO-0.3BCZT ceramics; and (c) Room temperature polarization current intensity

versus electric field loops of 0.7BFO-0.3BCZT + 0.2 wt.% MnO₂ ceramics.

Fig. 7. Magnetic hysteresis loops for 0.7BFO-0.3BCZT + x wt.% MnO₂ ceramics measured at room temperature: $x = 0.0, 0.2, 0.4$ and 0.7 .

Fig. 8. Magnetic properties of 0.7BFO-0.3BCZT + x wt.% MnO₂ ceramics as a function of x .

Figure

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Graphical Abstract