Structural, spectroscopic, and dielectric characterizations of Mn-doped 0.67BiFeO₃–0.33BaTiO₃ multiferroic ceramics

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Abstract: 0.67BiFeO₃–0.33BaTiO₃ multiferroic ceramics doped with x mol% MnO₂ ($x = 2$ –10) were synthesized by solid-state reaction. The formation of a perovskite phase with rhombohedral symmetry was confirmed by X-ray diffraction (XRD). The average grain sizes were reduced from 0.80 μm to 0.50 μm as increasing the Mn-doped levels. Single crystalline nature of the grains was revealed by high-resolution transmission electron microscopy (HRTEM) images and electron diffraction patterns. Polar nano-sized ferroelectric domains with an average size of 9 nm randomly distributed in the ceramic samples were revealed by TEM images. Ferroelectric domain lamellae (71° ferroelectric domains) with an average width of 5 nm were also observed. Vibrational modes were examined by Raman spectra, where only four Raman peaks at 272 cm^{-1} (E -4 mode), 496 cm^{-1} (A_1 -4 mode), 639 cm^{-1} , and 1338 cm^{-1} were observed. The blue shifts in the E -4 and A_1 -4 Raman mode frequencies were interpreted by a spring oscillator model. The dielectric constants of the present ceramics as a function of the Mn-doped levels exhibited a V-typed curve. They were in the range of 350–700 measured at 10³ Hz, and the corresponding dielectric losses were in range of 0.43–0.96, approaching to 0.09 at 10⁶ Hz.

Keywords: multiferroic ceramics; dielectric properties; Raman spectra; microstructure

1 Introduction

Recently, multiferroic materials have received much attention due to their promising applications in novel electronic devices (e.g., multiple-state memories and

new data-storage media), since multiferroics with multiple (charge, spin) order parameters can offer an exciting way of coupling between the electronic and magnetic orderings [1,2]. Besides the potential applications, the fundamental physics of multiferroic materials is also interesting and fascinating. However, it is generally difficult to find materials that are magnetic as well as ferroelectric because ferroelectricity occurs as the metal ions have empty d-orbitals, whereas a partly filled d shell is necessary

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for magnetism to occur in transition metal ions [3]. As one except, BiFeO₃ is perhaps the only multiferroic material that is both magnetic and strong ferroelectric at room temperature, which has been widely investigated in the past few years [2]. However, the inherent problems in BiFeO₃ such as high leakage current, structural instability, and the formation of multiphase system during the synthesis, have limited its applications [4]. To solve these problems, some attempts have been made including small dopants (e.g., lanthanides such as La, Ce, Eu) at the Bi/Fe sites to improve the dielectric properties of BiFeO₃ [5,6]. There are also several reports on the synthesis of solid solution of BiFeO₃ with other ABO₃ perovskite materials such as BaTiO₃ [4,7–9] and PbTiO₃ [10] to stabilize the perovskite structure and enhance the electrical insulating properties of BiFeO₃. For example, in the BiFeO₃–BaTiO₃ solid solution system, anomalous dielectric and magnetic behaviors were observed at concentration of 33 mol% of BaTiO₃, which was closely related to the structural transformation between the rhombohedral and cubic phases. The composition of 0.67BiFeO₃–0.33BaTiO₃ solid solution exhibited the spontaneous polarizations of 35 $\mu\text{C}/\text{cm}^2$ at room temperature [8]. Although the perovskite structure of these ceramics has been found to be stable and the spontaneous magnetic moment is increased at room temperature, the insulation resistance of BiFeO₃–ABO₃ ceramics has not been improved sufficiently and their ferromagnetism is still weak. Previous investigations on the ferroelectric and ferromagnetic properties of BiFeO₃–BaTiO₃ solid solution have demonstrated that their dielectric properties were complicated by high dielectric losses and high conductivity, which were ascribed to the valence fluctuation of Fe and the formation of oxygen vacancies [4,8]. Recently, it has been reported that Mn-doping can significantly reduce the leakage current and dielectric losses of the BiFeO₃–BaTiO₃ solid solution [11,12]. However, up to now, the effects of the Mn-doped levels on the microstructure and dielectric properties of the BiFeO₃–BaTiO₃ ceramic system are not systematically investigated, especially in the ferroelectric nanodomain structures.

Here we report on the structural, spectroscopic, and dielectric characterizations of the Mn-doped 0.67BiFeO₃–0.33BaTiO₃ multiferroic ceramics with x mol% MnO₂ ($x=2, 3, 4, 5, 6, 8, 10$), which were synthesized by the solid-state reaction route.

2 Experimental details

Multiferroic ceramics of 0.67BiFeO₃–0.33BaTiO₃ doped with x mol% MnO₂ ($x=2, 3, 4, 5, 6, 8, 10$) were prepared by a conventional solid-state reaction method. The stoichiometric amounts of the analytical-grade starting materials, Bi₂O₃ (with 5 mol% excess), Fe₂O₃, MnO₂, BaCO₃, and TiO₂ were weighted and mixed in a ball mill for 24 h in agate container with agate balls. After drying at 120 °C, the mixed powders were ground, then pressed into disc shape and pre-sintered at 850 °C for 2 h in air. Subsequently, the pre-sintered disc samples were ball-milled again for 24 h to get crushed powders. After drying, the crushed powders mixed with 5 wt% polyvinyl alcohol binders were pressed into cylindrical pellets with a diameter of 10 mm and thickness of about 2 mm. Disk pellets were sintered at 950 °C for 1 h. To measure the dielectric properties, the specimens were electroded with postfire silver paste on both sides. The dielectric properties of the sintered ceramics were measured as a function of frequency using an HP4192A impedance analyzer controlled by a computer.

The crystal structures of the sintered pellets were examined by X-ray diffraction (XRD, Philips X'Pert MRD four-circle diffractometer, Almelo, the Netherlands). To obtain the structural information of the Mn-doped 0.67BiFeO₃–0.33BaTiO₃ multiferroic ceramics from vibrational spectra, Raman scattering was carried out at room temperature with a Jobin Yvon HR800 spectrometer (JY Ltd., France), and the visible laser light (wavelength 514.5 nm) was used as the excitation source. The grain morphology, ferroelectric nanodomain structures, crystal lattice structures, and grain boundary structures were examined by a field-emission transmission electron microscopy (FEI, Titan S/TEM, operated at 300 kV).

3 Results and discussion

3.1 Phase structure

Figure 1 shows the XRD patterns of the 0.67BiFeO₃–0.33BaTiO₃ ceramics doped with x mol% MnO₂ ($x=2, 3, 4, 5, 6, 8, 10$), which indicate the formation of high-purity perovskite structure. All the XRD patterns can be indexed based on the data of BiFeO₃ with rhombohedrally distorted perovskite structure. To demonstrate the characteristic splitting of

the diffraction peaks such as (006) and (202) peaks in the XRD patterns, the local XRD pattern around $2\theta = 40^\circ$ is shown as inset in Fig. 1. From the inset, the characteristic splitting of the diffraction peaks associated with deviation from cubic symmetry can be clearly observed, although the present Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics have small rhombohedral distortions. With increasing the Mn-doped levels from 2 mol% to 10 mol%, the changes of the lattice parameters a and c of the Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics are shown in Fig. 2(a), and Fig. 2(b) demonstrates the change of the unit cell volume. Basically, the lattice parameter a is decreased with increasing the Mn-doped levels, whereas the lattice parameter c is first increased at Mn-doping level of 2 mol%, then decreases, and then remains almost constant value of 1.383 nm as the Mn-doped levels are in the range of 3–10 mol%. The unit cell volume is first decreased as increasing the Mn-doped levels, and reaches a minimum value at the Mn-doped level of 8 mol%, and then increases as further increasing the Mn-doped levels. The above phenomena can be understood by considering the following reaction:

which depresses the electron hopping from Fe^{3+} to Fe^{2+} and reduces the levels of oxygen vacancies. Since the ionic radius of Mn^{3+} ions (72.0 pm, coordination number 6 (low spin)) is smaller than that of Fe^{2+} ions

Fig. 1 XRD patterns of the $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics doped with x mol% MnO_2 : (a) $x=2$, (b) $x=3$, (c) $x=4$, (d) $x=5$, (e) $x=6$, (f) $x=8$, and (g) $x=10$.

Fig. 2 Composition dependence of (a) the lattice parameters a and c of the Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics, and (b) the volume of unit cell.

(75.0 pm, coordination number 6 (low spin)) [13], therefore as increasing the Mn-doped concentration to 8 mol%, the doped Mn^{3+} ions possessing smaller ionic radius will evidently reduce the unit cell volume; whereas as further increasing the Mn-doped levels, more Mn^{3+} (72.0 pm, coordination number 6 (low spin)) and Mn^{2+} (81.0 pm, coordination number 6 (low spin)) may substitute the Fe^{3+} (69.0 pm, coordination number 6 (low spin)) and Ti^{4+} (74.5 pm, coordination number 6) ions [13], respectively. Thus, the volume of the unit cell is increased, as demonstrated in Fig. 2(b).

3.2 Raman spectra

Figure 3 illustrates the Raman spectra of the Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ multiferroic ceramics, where only four characteristic Raman peaks near 272 cm^{-1} , 496 cm^{-1} , 639 cm^{-1} and 1338 cm^{-1} , are clearly observed. A very small Raman peak at around 870 cm^{-1} in curve (d) is due to the artifact. It is known that there are 13 Raman active modes ($4A_1+9E$) for perovskite BiFeO_3 with distorted rhombohedral ($R3c$) structure [14]. Since the Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ multiferroic ceramics have the same symmetry, the same set of the Raman active modes should be expected in the present case. However, actually only four Raman peaks are observed. It is known that the Raman spectra of crystals with relatively small unit cells and a limited number of

Fig. 3 Raman spectra of the $0.67\text{BiFeO}_3-0.33\text{BaTiO}_3$ multiferroic ceramics doped with x mol% MnO_2 : (a) $x=2$, (b) $x=3$, (c) $x=4$, (d) $x=5$, (e) $x=6$, (f) $x=8$, and (g) $x=10$.

atoms, usually exhibit all of the Raman modes (like the case of BiFeO_3), as expected from symmetry arguments. However, in a complex structure with a large number of atoms in a unit cell, experimental results account for fewer of the calculated Raman modes to appear [15]. Therefore, some Raman active modes predicted for the rhombohedral symmetry are not observed in the Mn-doped $0.67\text{BiFeO}_3-0.33\text{BaTiO}_3$ multiferroic ceramics, which is due to the too small rhombohedral distortions to activate these Raman modes, or namely the symmetry-forbidden scattering. The Raman peaks near 272 cm^{-1} and 496 cm^{-1} can be assigned to the $E-4$ and A_1-4 modes of BiFeO_3 structure, respectively. Similar Raman modes were reported previously in BiFeO_3 crystal by Fukumura *et al.* [16] (e.g., $E-4$ mode 279 cm^{-1} , and A_1-4 mode 490 cm^{-1}), and in the $0.70\text{BiFeO}_3-0.30\text{BaTiO}_3$ solid solution by Ianculescu *et al.* [17]. As shown in Fig. 3, the Raman frequencies of the $E-4$ and A_1-4 modes are shifted slightly to high frequency as increasing the Mn-doped levels up to 10 mol%. As viewed from a spring oscillator model for interatomic forces, the frequency (f) of the $E-4$ or A_1-4 Raman mode is dependent on several local factors, such as the magnitude of the force constant (k) of the spring oscillator, ionic mass (m) of the doped-element, and the specific bond length between the oxygen atom

and the doped element. So one can describe the mode frequency f by the following equation [18]:

$$f \propto \sqrt{\frac{k}{m}} \propto \frac{1}{\text{bond length between atoms}} \quad (2)$$

Due to the smaller molar weight of the Mn atoms replacing the Fe atoms with larger molar weight, the effective mass of the spring oscillator will become smaller, which results in higher vibrating frequency for the mode of $E-4$ or A_1-4 , as expected from Eq. (2). The bond length between the oxygen and the doped atom is also expected to be reduced, leading to a smaller volume of the unit cell of the Mn-doped $0.67\text{BiFeO}_3-0.33\text{BaTiO}_3$ multiferroic ceramics. This is consistent with the above XRD results. The observed Raman band centered near 639 cm^{-1} , is attributed from the symmetrical stretching vibrations of the basal oxygen ions of the MnO_6 (and perhaps FeO_6) octahedra in the Mn-doped $0.67\text{BiFeO}_3-0.33\text{BaTiO}_3$ ceramics. With increasing the Mn-doped level from 2 mol% to 10 mol%, the intensity of this Raman band is increased, as observed in Fig. 3. That can be attributed to the structural distortion of $(\text{Mn,Fe})\text{O}_6$ octahedra (i.e., Jahn–Teller distortion) due to the substitution of Fe by Mn. The very wide Raman peak near 1338 cm^{-1} , may be attributed to the random occupancy of the cations at A site by Bi/Ba, and at B site by Fe, Mn and Ti ions, and also the microscopic strains in the Mn-doped $0.67\text{BiFeO}_3-0.33\text{BaTiO}_3$ ceramics. Considering a unit cell containing either FeO_6 , TiO_6 , or MnO_6 octahedron, due to the different magnitudes of the Fe–O, Ti–O, and Mn–O bond force constants, the bond distances can fluctuate from one unit cell to the other, which lead to different characteristic vibrational frequencies for these three octahedrals, resulting in a wider Raman band [19]. Similar phenomenon was reported in the La-doped $\text{BiFeO}_3\text{–PbTiO}_3$ mixed crystal system [20].

3.3 Microstructures revealed by TEM

TEM images of typical ceramic grains in the $0.67\text{BiFeO}_3-0.33\text{BaTiO}_3$ ceramics doped with x mol% MnO_2 ($x=3, 4, 6$, and 10) are shown in Fig. 4, which demonstrate that the grains basically have rounded grain morphology. Some grains exhibit grey TEM contrast whereas others have a bright fluctuating mottled contrast, especially clear in Figs. 4(b) and 4(d). The grains contact tightly with each other and the grain boundaries are very clean; as a consequence, triple-grain boundary regions are rarely observed. The

Fig. 4 Bright-field TEM images of the typical grains in the $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics doped with x mol% MnO_2 : (a) $x=3$, (b) $x=4$, (c) $x=6$, and (d) $x=10$.

average grain size is measured to be $0.80\text{ }\mu\text{m}$ in the $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ solid solution doped with 3 mol% MnO_2 (Fig. 4(a)), and $0.60\text{ }\mu\text{m}$ for the samples doped with 4 mol% MnO_2 and 6 mol% MnO_2 , and $0.50\text{ }\mu\text{m}$ for the sample doped with 10 mol% MnO_2 . Therefore, the average grain size shows a tendency to be decreased as increasing the Mn-doped levels. That can be ascribed to the fact that the grain growth during the sintering process is suppressed by a diffusion-controlled process through the formed liquid phases by the aid of the doped MnO_2 . The HRTEM image and the selected area electron diffraction (SAED) pattern taken from a single grain in the $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics doped with x mol% MnO_2 ($x=3, 4, 6$, and 10) are shown in Fig. 5. All the HRTEM images clearly reveal two-dimensional lattice fringes (as indicated in Fig. 5), indicating well developed atomic arrangements in the Mn-doped ceramics. The SAED patterns shown as insets in Fig. 5 also demonstrate that the grains have a single crystalline nature, and their lattice constants determined from the SAED patterns match well with the XRD analysis.

Figure 6 shows the bright- and dark-field TEM images of the domain structures in the $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ solid solution doped with 3 mol% MnO_2 . Nano-sized ferroelectric domains are clearly observed in the dark-field TEM image (Fig. 6(b)), which exhibit bright TEM contrast and are

Fig. 5 HRTEM images taken from single grain in the $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics doped with x mol% MnO_2 : (a) $x=3$, (b) $x=4$, (c) $x=6$, and (d) $x=10$. The insets are the SAED patterns taken from a single grain or the fast Fourier patterns of the corresponding HRTEM images of different grains. The two-dimensional lattice fringes are indicated.

Fig. 6 (a) Bright- and (b) dark-field TEM images of the ferroelectric domain structures observed in the $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ solid solution doped with 3 mol% MnO_2 .

randomly distributed in the ceramic sample. Their sizes are in the range of 4–16 nm with an average size of 9 nm. Such polar nano-sized ferroelectric domains in the randomly substituted mixed-crystal systems can lead to the relaxor dielectric behavior of the mixed-crystal system. Microscopic compositional fluctuations or chemical ordering over a few nanometer length scale can result in the formation of nano-sized ferroelectric domains although the XRD yields an average cubic structure consistent with the average stoichiometry. Within the nano-sized ferroelectric domains, the local structure could be different due to the chemical ordering. Furthermore,

nano-sized ferroelectric domain lamellae are also observed in the rhombohedral $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ solid solution doped with 10 mol% MnO_2 . Figure 7(a) shows the TEM image of the nano-sized ferroelectric domains lamellae, as marked by a box. The enlarged TEM image of the nano-sized ferroelectric domain lamellae is shown in Fig. 7(b), and their average width is measured to be 5 nm. The HRTEM images obtained from the local areas marked by boxes A and B in Fig. 7(b), are shown in Figs. 7(c) and 7(d), respectively. In the ferroelectric materials with rhombohedral structure like BiFeO_3 , the ferroelectric polarizations point along the $[111]_p$ (where the subscript p represents in pseudocubic setting) directions of the perovskite unit cell, with two antiparallel polarities for each direction. Therefore, eight different polar domains can be observed in BiFeO_3 with rhombohedral structure. Separating adjacent domains, there are three possible types of ferroelectric domain walls, namely 71° , 109° , and 180° domain walls [2]. Since the 109° domain energy is nearly three times that of 71° domain, the latter is observed to occur more frequently than the former [21]. As shown in Figs. 7(c) and 7(d), the angle between the

ferroelectric polarizations in the adjacent nano-sized ferroelectric domain lamellae is 70.5° , so they are named as 71° ferroelectric domains.

3.4 Dielectric properties

The dielectric constants and dielectric losses of the Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics were measured as a function of frequency at room temperature, which are shown in Figs. 8(a) and 8(b), respectively. It is noticed that all the dielectric constants and dielectric losses are decreased as increasing the frequency up to 10^5 Hz, and then remain almost constant in the frequency range of $10^5\text{--}10^6$ Hz. The fast decrease of the dielectric constants in the low frequency region (below 10^5 Hz), can be attributed to the space charge polarization induced by oxygen vacancies in the perovskite Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics [4,8,9]. The dielectric constants of Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics measured at 10^4 Hz, 10^5 Hz and 10^6 Hz as a function of the Mn-doped level, are shown as inset of Fig. 8(a). It is demonstrated that the Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics at the level of 6 mol% have the lowest value of the dielectric constant, which indicates the sample with high level of oxygen vacancies. It is assumed that the doped Mn atoms in the $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ solid solution could lead to a reaction of Eq. (1), thus suppressing the electron hopping from Fe^{3+} to Fe^{2+} ions and reducing the concentrations of the oxygen vacancies due to the donor doping with Mn. However, since the Mn atoms enter into the B-site of perovskite structure in the $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ solid solution, there is also the possibility of substitution for Ti atoms at B-site, which can be represented as

The above reaction can lead to the formation of oxygen vacancies, resulting in high dielectric loss and fast decrease of the dielectric constant at low frequency region through the space charge polarization mechanism. Therefore, in the Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics, the concentrations of oxygen vacancies are controlled by the balance between the reactions of Eqs. (1) and (2). At low Mn-doped levels, Mn atoms prefer to depressing the electron hopping ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$) and reducing the concentrations of oxygen vacancies via reaction of Eq. (1), whereas at high Mn-doped levels, some Mn atoms can substitute

Fig. 7 (a) TEM image of nano-sized ferroelectric domains lamellae (with average width of 5 nm) observed in the $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ solid solution doped with 10 mol% MnO_2 , and (b) enlarged TEM image of the nano-sized ferroelectric domain lamellae. (c) and (d) HRTEM images of the nano-sized ferroelectric domain lamellae obtained from the local areas marked by boxes A and B in (b), respectively.

Ti atoms at B-site, creating oxygen vacancies via reaction of Eq. (3). That is the reason why the dielectric constants of Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics as a function of the Mn-doped levels exhibit a V-typed curve. The dielectric constants (measured at 10^3 Hz) for the $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics doped with 4 mol% and 10 mol% MnO_2 are in the range of 600–700, which are much higher than that for the $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics doped with x mol% MnO_2 ($x=3, 5$, and 6) (dielectric constants in the range of 350–475). However, the dielectric losses of the $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics doped with 4 mol% and 10 mol% MnO_2 are also very high, which are in the range of 0.8–0.9 (measured at 10^3 Hz) (Fig. 8(b)). Considering the trade-off between the dielectric constant and dielectric loss of the Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics, the optimized Mn-doped level is determined to be 3 mol%, which has both relatively higher dielectric constant and smaller dielectric loss, as demonstrated in Fig. 8.

Fig. 8 (a) Room-temperature dielectric constants and (b) dielectric losses of the $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics doped with different levels of MnO_2 as a function of the measured frequency. Inset in (a) is the dielectric constants of the Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics as a function of the Mn-doped level.

4 Conclusions

Perovskite $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ multiferroic

ceramics doped with x mol% MnO_2 ($x=2, 3, 4, 5, 6, 8, 10$), have been synthesized by the solid-state reaction. Their structural, spectroscopic, and dielectric properties were well characterized. XRD patterns revealed that the Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics were rhombohedral phase, and their lattice parameters a and c , and the volume of the unit cell, were closely dependent upon the Mn-doping contents. The Raman spectra revealed that only four characteristic Raman peaks near 272 cm^{-1} ($A_1\text{-}4$ mode), 496 cm^{-1} ($E\text{-}4$ mode), 639 cm^{-1} , and 1338 cm^{-1} , were observed; whereas some other Raman active modes predicted for the rhombohedral symmetry were not observed due to the too small rhombohedral distortions in the present multiferroic ceramics. A slight blue shifts in the frequencies of the $E\text{-}4$ and $A_1\text{-}4$ Raman modes were observed as increasing the Mn-doped levels, which could be interpreted by using a spring oscillator mode. TEM images revealed that the grains basically had rounded grain boundaries, and their average grain sizes were decreased from $0.80\text{ }\mu\text{m}$ to $0.50\text{ }\mu\text{m}$ with increasing the Mn-doped levels from 3 mol% to 10 mol%. The grains had a single crystalline nature as confirmed by HRTEM images and SAED patterns. Dark-field TEM images showed that the polar nano-sized ferroelectric domains with average size of 9 nm were randomly distributed in the ceramic sample. In addition, nano-sized ferroelectric domain lamellae with an average width of 5 nm were also revealed by HR-TEM images, which were identified as 71° ferroelectric domains. The dielectric constants and dielectric losses of the Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ multiferroic ceramics were decreased fast as increasing the frequency in the low frequency region (below 10^5 Hz), and then they remained stable in the frequency range of $10^5\text{--}10^6$ Hz. These phenomena were ascribed to the space charge polarization induced by the oxygen vacancies in the ceramic system. The dielectric constants of Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics as a function of the Mn-doped levels exhibited a V-typed curve. The dielectric constants (measured at 10^3 Hz) of the Mn-doped $0.67\text{BiFeO}_3\text{--}0.33\text{BaTiO}_3$ ceramics were in the range of 350–700, and the dielectric losses in the range of 0.43–0.96 (at 10^3 Hz), which approached to 0.09 at 10^6 Hz.

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