

Study on the ferroelectric and magnetic properties of $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ polycrystalline ceramics dependence on the Mn content

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Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.05, 0.1, \text{ and } 0.15$) ceramics were fabricated by a Sol-gel method together with calcination at an elevated temperature. The crystal structures of samples were analyzed by X-ray diffraction (XRD). The dependences of the ferroelectric, dielectric, and magnetic properties of samples on Mn contents were thoroughly investigated. The XRD patterns indicated that as increasing Mn content in samples, the unwanted impurity phases such as $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_{36}\text{Fe}_{24}\text{O}_{57}$ are markedly decreased. Polarization-electric field (P-E) hysteresis loops observed for all the samples indicated that the permanent polarization (P_r) and the coercive field (E_c) were significantly improved due to Mn substitution. With an increase of Mn content, the value of dielectric constant of samples also increased. In addition, symmetric magnetic hysteresis (M-H) loops in samples indicated that they were magnetic ordered materials, and the saturated magnetization (Ms) of the $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramics increased with an increase of Mn content.

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Introduction

In recent years, great attention has paid to single-phase BiFeO_3 (BFO) multiferroic materials crystallized in ABO_3 -type perovskite structure with the $R3c$ space group at room temperature, which display the co-existence of various competing orderings, such as ferromagnetic, ferroelectric, antiferromagnetic, as well as elastic orders [1, 2]. The characteristics of BFO multiferroics promise potential applications in advanced magnetoelectric devices and ferroelectric random access memories (FeRAMs) with smaller volume and larger capacity [3]. Though as promising as BFO multiferroic materials are, the main problem with BFO materials is the large leakage current, which gives high depolarization field and thus affects stable and low-voltage operation of FeRAMs [4]. It has been reported that the small amounts of Fe^{2+} and oxygen vacancies [V_{O}^{2-}] may be responsible for the high leakage currents in BFO [5]. Based on this assumption, site engineering technique by substitution of a small amount of impurity atoms is an effective way to reduce the leakage current due to nonstoichiometric compositions of BFO [6]. As a result, several atoms, including Ti [7], Cr [8], Co [9] and Mn [10], atoms have been substituted for Fe atoms (B site), aiming to restrain the valence fluctuation of Fe

atoms and thus to reduce the leakage current. Among them, the substitution effect of Mn atoms is most pronounced in the reduction of the leakage current in Mn-doped BFO (BFMO) films. So far, ferroelectric properties of Mn-substituted BFO thin films synthesized by chemical solution deposition [11-12] or sputtering [13] have been reported. Especially, J.H.Kim et.al [14] investigated the variations of electrical and ferroelectrical properties such as the coercive field, the remanent polarization, and the leakage current with the thickness of Mn-substituted BFO thin films. In order to explore Mn-substituted BFO ferroelectric materials' optional application for the future FeRAMs with high-density and low operation voltage, detailed studies on the structural, ferroelectric, magnetic, dielectric properties, and leakage current characteristics should be further carried out.

In this work, the structural, ferroelectric, dielectric properties, and magnetic characteristics of Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.05, 0.1, \text{ and } 0.15$) ceramics fabricated by a metal ion complex precursor solution method together with calcination at an elevated temperature have been thoroughly discussed.

Experimental

Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.05, 0.10, \text{ and } 0.15$) ceramics were fabricated by a sol-gel method. Bismuth nitrate [$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$] (Aldrich, 99.99%), Ferric nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], and Manganese acetate Tetrahydrate [$\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$] were used as the raw

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materials of the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramics. 2-methoxyethanol [$\text{C}_3\text{H}_8\text{O}_2$] and Glacial acetic acid [CH_3COOH] was used as the solvent and stable agent, respectively. Bismuth nitrate and Ferric nitrate were dissolved at room temperature in 2-methoxyethanol with nominal glacial acetic acid under constant stirring, respectively. The former was referred to as the bismuth precursor solution and the latter was referred to as the iron precursor solution. For the bismuth precursor solution, an excess of 5 wt% Bi was added to the solution for compensating some unavoidable bismuth oxide loss during the thermal treatment. Appropriate quantities of Fe and Bi precursor solutions together with adding Manganese Acetate Tetrahydrate was mixed and homogenized by constant stirring. Finally, 2-methoxyethanol was added to the mixed solutions and gets the expected $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ precursor concentration. Subjected to fully stirring and aging, the $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ precursor solutions were successfully fabricated. Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ powders with $x = 0, 0.05, 0.10,$ and 0.15 were obtained via the baking of the $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ precursor solutions at the temperature of 108°C and the calcinating at 550°C for half an hour. The resulting powders were milled in attritor with zirconia balls for several hours. Finally, the formed powders were then pressed into pellets and sintered again at 650°C for 15 minutes, and then cooled rapidly to room temperature.

The crystal structure properties of $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.05, 0.10,$ and 0.15) ceramics synthesized in this study were investigated by θ - 2θ method of XRD with a $\text{CuK}\alpha_1$ ($\lambda = 0.15406\text{ nm}$) source at 40 kV and 30 mA using a multi-purpose XRD system (D/MAX-RB). The magnetic measurements were carried out using a vibrating sample magnetometer (VSM) (Lakeshore 7407). For electrical measurements, silver was coated on the surface of the $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramic pellets (sintered at 550°C for 15 minutes). The ferroelectric hysteresis loops and leakage current behaviors of the Ag/ $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ /Ag ceramic capacitors were obtained using a ferroelectric tester (Radiant Technologies, Precision LC). The dielectric constant and the dissipation factors were measured by using an HP4294A impedance analyzer. The high-frequency capacitance-voltage characteristics of the samples were measured using Keithley 590 CV analyzer at one MHz with a bias sweep rate of 0.2 V/s. All the measurements were performed at room temperature.

Results and Discussion

Fig. 1 shows the XRD patterns of the Mn-substituted $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.05, 0.1,$ and 0.15) polycrystalline ceramics. It can be seen that majority of the peaks belong to rhombohedrally distorted perovskite BiFeO_3 phase with the space group R3c indexed by the pattern of the pure BFO. The peaks of well-documented impurity phases such as $\text{Bi}_2\text{Fe}_4\text{O}_9$ (Fe-rich phase) and

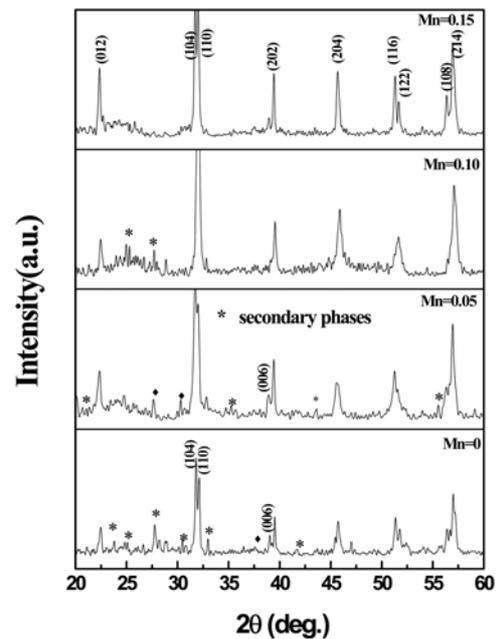


Fig. 1. XRD patterns of the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ with various Mn content $x = 0, 0.05, 0.10,$ and 0.15 .

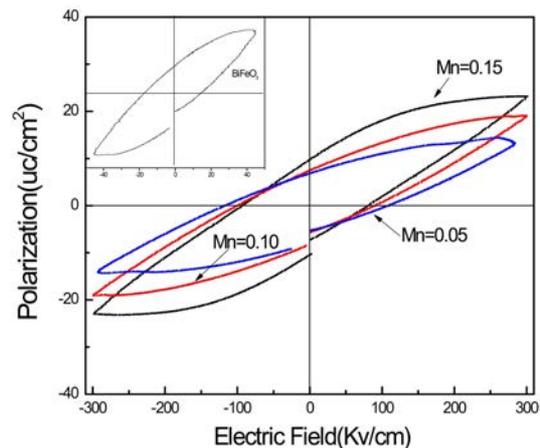


Fig. 2. Polarization electric field (P-E) hysteresis loops of the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ with various Mn content $x = 0, 0.05, 0.10,$ and 0.15 .

$\text{Bi}_{36}\text{Fe}_{24}\text{O}_{57}$ (Bi-rich phase) were detected in Fig.1 [15]. With an increase of the Mn content in Mn-substituted $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramic, the unwanted impurity phases such as $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_{36}\text{Fe}_{24}\text{O}_{57}$ are markedly decreased. In addition, a structural transition from rhombohedral R3c to tetragonal P4 mm occurs in the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0, 0.05, 0.10,$ and 0.15) ceramics, which is indicated by the decrease of peak intensity of the (006) peak positioned around 40° [16-17]. This is a good indication that transition metal Mn was substituted into the BFO crystal lattice.

The polarization-electric field (P-E) hysteresis loops of Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ polycrystalline ceramics with various Mn contents ($x = 0.05, 0.1,$ and 0.15) measured by the applied electric field up to 300 kV/cm are shown in Fig. 2. Due to the higher leakage current,

the P-E loop of the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ polycrystalline ceramics with Mn contents $x = 0$ only determined under a maximum electric field of 50 kV/cm is also shown in the inset of Fig.2. Clear hysteresis loops are observed for all Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ polycrystalline ceramics samples, which are typical shapes of ferroelectric materials. On the other hand, under a maximum electric field of 300 kV/cm, the coercive field (E_c) values of the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ polycrystalline ceramics for $x = 0.05, 0.1,$ and 0.15 is 110.86 kV/cm, 91.58 kV/cm, 81.38 kV/cm, respectively. And the P_r value of the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ polycrystalline ceramics for $x = 0.05, 0.1,$ and 0.15 is 13.5 mc/cm², 14.9 mc/cm², 19.6 mc/cm², respectively. That is to say, with an increase of Mn content in the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ polycrystalline ceramics, the P_r value and of $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ polycrystalline ceramics increases and the coercive field (E_c) values decreases. This larger P_r value for the $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ polycrystalline ceramics with bigger Mn content may be attributed to the possible lower concentration of oxygen vacancies induced by the Mn doping, which alleviates the domain pinning effect in the ceramics [18].

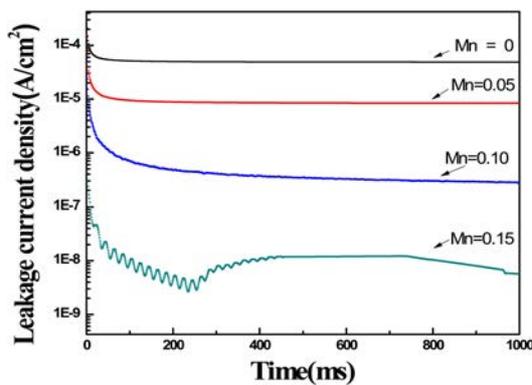


Fig. 3. Current density versus time characteristics of $\text{Ag/BiFe}_{1-x}\text{Mn}_x\text{O}_3/\text{Ag}$ ($x = 0, 0.05, 0.1,$ and 0.15) bulk ceramic capacitors measured at applied voltage of 80 kV at room temperature.

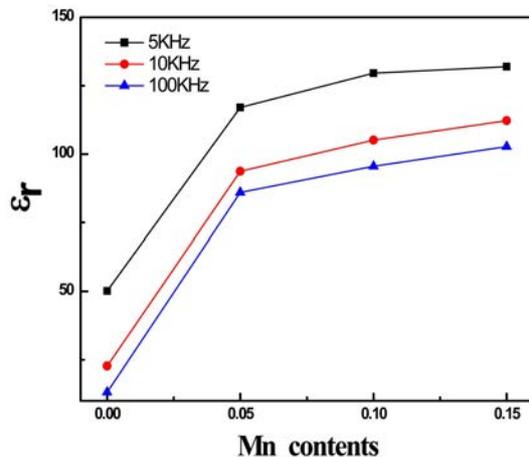


Fig. 4. Frequency dependence of the relative dielectric constant of the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ with various Mn content $x = 0, 0.05, 0.10,$ and 0.15 .

Moreover, calculation by the first principle demonstrates that the tetragonal structure with P4 mm symmetry is also beneficial for the enhancement of spontaneous polarization [19].

Fig. 3 shows current density versus time characteristics of $\text{Ag/BiFe}_{1-x}\text{Mn}_x\text{O}_3/\text{Ag}$ ($x = 0, 0.05, 0.1,$ and 0.15) bulk ceramic capacitors measured at applied voltage of 80 kV at room temperature. The current density in an undoped BFO polycrystalline ceramic is very high (on the order of 10^{-4} A/cm²). As the increase of Mn content in $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ polycrystalline ceramic, the current density of $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ polycrystalline ceramics sharp decrease. The improved breakdown characteristic is ascribed to reduction of oxygen vacancies by Mn donor doping effect [11], although addition experiments are needed to determine the chemical valence state of Mn atoms.

Variations of dielectric constant as a function of frequency in the range from 5 kHz to 100 kHz for the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramics ($x = 0, 0.05, 0.1,$ and 0.15) measured at room temperature are shown in Fig. 4. It is observed that with an increase of Mn content in $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramics, the values of dielectric constant of $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramics also increase, which are resulted from the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramics with higher Mn content having a less phase purity [20]. In addition, for all the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramics, the value of dielectric constant was high at lower frequencies and decreases with an increase in frequency. The characteristic can be explained according to the space-charge relaxation phenomena wherein at low frequencies the space charges are able to follow the frequency of applied field, while at high frequencies, they may not have time to undergo relaxation [21].

The magnetic hysteresis (M-H) loops of the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramics with various Mn contents ($x = 0, 0.05, 0.1,$ and 0.15) measured by a VSM with in-plane mode, is shown in Fig. 5. According to Fig. 5 Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramics exhibited

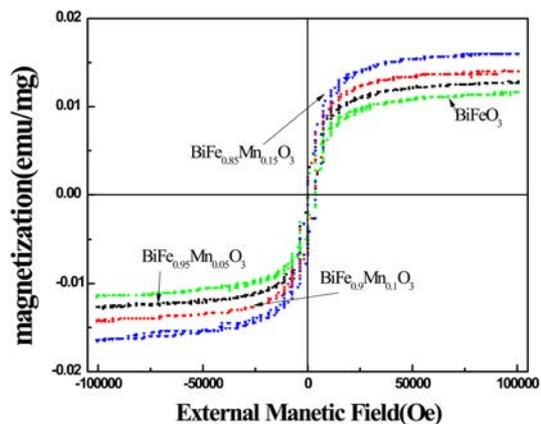


Fig. 5. Magnetization-magnetic field (M-H) hysteresis curves of the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ with various Mn content $x = 0, 0.05, 0.10,$ and 0.15 .

the symmetric magnetic hysteresis loops indicating that they were magnetic ordered materials. The remanant magnetizations of the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramics for $x = 0, 0.05, 0.1, \text{ and } 0.15$ at 50000 Oe were achieved around 0.0013, 0.0018, 0.0025, 0.0032 emu/mg, respectively, showing a rise with an increase of Mn content. This enhancement in remanant magnetization with an increase in Mn substitution might be due to the continuing collapse of the space-modulated spin structure of BMFO [22].

Conclusions

In summary, the Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramics with various Mn content ($x = 0, 0.05, 0.1, \text{ and } 0.15$) were synthesized by a metal ion complex precursor solution method together with calcination at an elevated temperature. Pure BiFeO_3 ceramic was associated with some secondary phases such as $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{36}\text{Fe}_{24}\text{O}_{57}$. With an increase of the Mn doped content in $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramics, the mentioned impurity phases are markedly decreased. In addition, breakdown characteristic, dielectric characteristic, the remnant polarization and magnetic moment of Mn-modified $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ceramics were improved owing to the Mn substitution in Bi site of BFO perovskite structure. Mn-substituted BFO ferroelectric materials should have potential application for the future FeRAMs with high-density and low operation voltage.

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