

An investigation of the ferroelectric and magnetic properties of Nd-doped $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ polycrystalline ceramics fabricated by a sol-gel technique

Changchun Chen*, Zhonghai Tang, Gui Wang, Chunhua Lu and Zhongzi Xu

College of Materials Science and Engineering, Nanjing University of Technology, NO.5 Xinnofan Road, Nanjing 210009, China

Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$, and 0.15) ceramics were fabricated by a sol-gel method. The crystal structures of Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$, and 0.15) ceramics were analyzed by X-ray diffraction (XRD). The effects of the Nd content on the ferroelectric, dielectric, and magnetic properties of these $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics were thoroughly investigated. The XRD patterns indicated that with an increase of the Nd doped content in $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics, 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. Clear polarization-electric field (P-E) hysteresis loops were observed for all the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics and the shape of the P-E loop of the $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics was significantly improved due to the Nd substitution. In addition, slim magnetic hysteresis (M-H) loops in the $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics were also observed, and the saturated magnetization (M_s) of the $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics also increased with an increase of the Nd content.

Key words: Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics, Ferroelectric properties, Magnetic properties, Sol-gel

Introduction

In recent years, great attention has been paid to single-phase BiFeO_3 (BFO) multiferroic materials crystallized in the 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 a smaller volume and larger capacity [3]. As promising as BFO multiferroic materials are, there are some issues to be overcome such that their leakage current is large at room temperature (RT) and their coercive field (E_c) is high. These issues affect the stable and low-voltage operation of FeRAMs [4]. It has been reported that small amounts of Fe^{2+} and oxygen vacancies [V_{O}^{2-}] could be responsible for the high leakage currents in BFO material [5]. Based on this assumption, a site engineering technique by the substitution of a small amount of impurity atoms is used to reduce leakage currents of BFO [6]. So far, several atoms including Mn [7], Ti [8], and Cr [9] atoms have been substituted for Fe atoms (B sites), aiming to restrain the valence fluctuation of Fe atoms and thus to reducing the leakage current. On the other hand, Bi atoms (A sites) substitution with non-volatile

rare earth ions like La or Nd to control the volatile nature of Bi and to suppress the generation of oxygen vacancies for charge compensation have been employed in BFO multiferroic materials [10, 11]. It has also been demonstrated that the partial substitution of La or Nd at the Bi site of BFO helps in eliminating the secondary phase (pyrochlore) along with a structural phase transition improving ferroelectric properties and also helps in release the latent magnetization locked within the spin cycloid [12]. Although multiferroic properties of Nd-substituted BFO of both bulk ceramics and thin films have been reported in the literature [13, 14], detailed studies on the structural, ferroelectric, magnetic, and dielectric properties are needed. Moreover, Nd-substituted BFO ceramics investigated in the literature were synthesized by a conventional solid state reaction sintering route at atmospheric pressure or a rapid liquid phase sintering method. As is known, fine powders derived from a sol-gel method are usually more homogenous and reactive due to atomic level mixing than those prepared by the conventional solid-state reaction method. Therefore, in this study, the structural, ferroelectric, dielectric properties, and magnetic characteristics of the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$, and 0.15) ceramics fabricated by a metal ion complex precursor solution method (a sol-gel method) together with calcination at elevated temperature are thoroughly discussed.

Experimental

Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$, 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 %),

*Corresponding author:
Tel : +86-25-83587242
Fax: +86-25-83587242
E-mail: changchunchen@hotmail.com

ferric nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], and neodymium acetate [$\text{C}_6\text{H}_9\text{NdO}_6$] were used as the raw materials of Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics. 2-Methoxyethanol [$\text{C}_3\text{H}_8\text{O}_2$] and glacial acetic acid [CH_3COOH] were used as the solvent and stabilizing agent, respectively. Bismuth nitrate and ferric nitrate were dissolved at room temperature in 2-methoxyethanol with a nominal amount of glacial acetic acid under constant stirring, respectively. The former was referred to as the bismuth precursor solution and the later was referred to as the iron precursor solution. For the bismuth precursor solution, an excess of 5 wt% Bi was added to the solution aiming at compensating for some unavoidable bismuth oxide loss during the thermal treatment. Appropriate quantities of Fe and Bi precursor solutions together with the addition of neodymium acetate was mixed and homogenized by constant stirring. Finally, 2-methoxyethanol was added to the mixed solutions and gave the expected $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ precursor concentrations. Subjected to full stirring and aging, the $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ precursor solutions were successfully made. These Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ powders with $x = 0, 0.05, 0.1$, and 0.15 were obtained via the baking of the $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ precursor solutions at a temperature of 108°C and the calcination at 550°C for half an hour. The resulting powders were milled in an attritor with zirconia balls for several hours. Finally, the powders formed were pressed into pellets and sintered again at 650°C for 15 minutes, and then cooled rapidly to room temperature.

The crystal structures of the synthesized $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$, and 0.15) powders were investigated by the 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 surface morphology of $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0.1$) ceramics was examined by a scanning electron microscope (SEM, JSM-5900). The magnetic measurements were carried out using a vibrating sample magnetometer (VSM) (Lakeshore 7407). For electrical measurements, silver was coated on the surfaces of the $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$, and 0.15) ceramic pellets (then sintered at 550°C for 15 minutes). The ferroelectric hysteresis loops and leakage current behaviors of the films were obtained using a ferroelectric tester (Radiant Technologies, Precision LC). The dielectric constant and the dissipation factor were measured using an HP4294A impedance analyzer. The high frequency capacitance-voltage characteristics of the samples were measured using a Keithley 590 CV analyzer at 1 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 Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$, and 0.15) ceramics. It can be seen that majority of the peaks belong to a

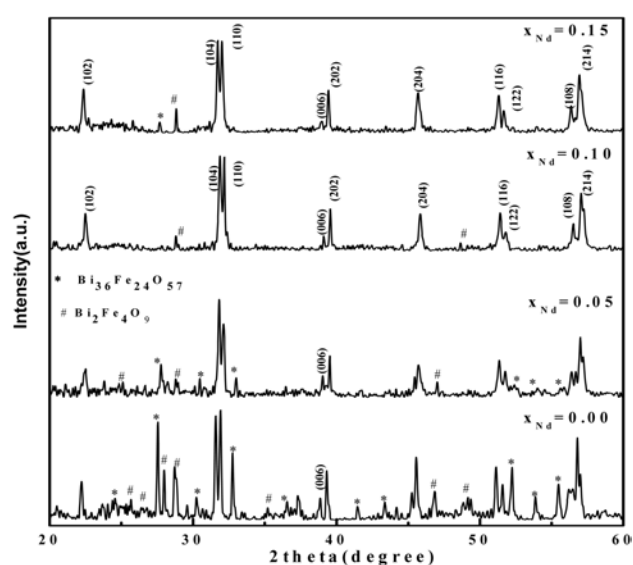


Fig. 1. XRD patterns of the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ with various Nd contents $x = 0, 0.05, 0.1$, and 0.15 .

rhombohedrally distorted perovskite BiFeO_3 phase with the space group $R3c$ indexed by the pattern of pure BiFeO_3 . The peaks of impurity phases such as $\text{Bi}_2\text{Fe}_4\text{O}_9$ (labeled as hash) and $\text{Bi}_{36}\text{Fe}_{24}\text{O}_{57}$ (labeled as asterisk) owing to a Bi deficiency were detected from all the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$, and 0.15) ceramics. With an increase of the Nd content in $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics, 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 $P4mm$ occurs in the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$, and 0.15) ceramics, which is indicated by the decrease of the peak intensity of the (006) peak positioned around 40° [15]. This transition maybe is due to the smaller ionic radius of Nd^{3+} ($1.109'$, eight coordination) than that of Bi^{3+} ($1.17'$, eight coordination). The slight shifting of diffraction peaks in the pattern of Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0.05, 0.1$, and 0.15) compared with those of Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0.0$) (BFO) toward a high angle, indicates that the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ maintains the same tetragonal $P4mm$ structure as that of BFO but with a slight lattice distortion due to the Nd doping.

In view of the slighter impurity phases detected in the $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0.1$) ceramic sample compared to those in $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0, 0.05$, and 0.15) polycrystalline ceramics samples, only the surface morphology of the $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0.1$) ceramics sample observed by SEM is shown in Fig. 2. The $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0.1$) ceramic sample has good crystallinity, as evidenced by the clear morphology and distinct boundaries of the grains. On the other hand, the well-grown larger grains and dense morphology shown in Fig. 2 also indicate that there are no macroscopic defects such as holes or cracks in $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0.1$) ceramics sample. The larger grains with denser

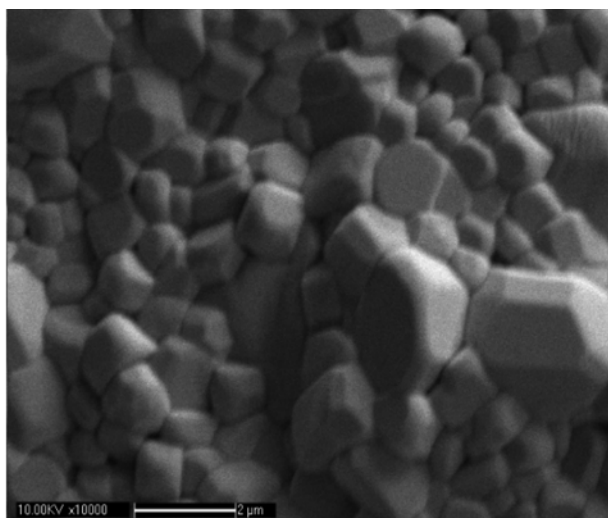


Fig. 2. SEM micrograph of the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ with Nd content $x = 0.1$.

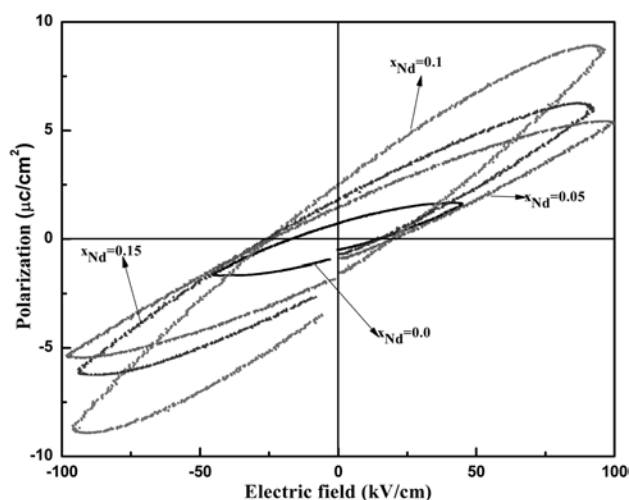


Fig. 3. Polarization electric field (P-E) hysteresis loops of the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ with various Nd contents $x = 0, 0.05, 0.1$, and 0.15 .

morphology in the $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0.1$) ceramic sample are beneficial to their electrical properties, which is also described in the literature [16].

The polarization-electric field (P-E) hysteresis loops of Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ polycrystalline ceramics with various Nd contents ($x = 0, 0.05, 0.1$, and 0.15) are shown in Fig. 3. Clear hysteresis loops are observed for all the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ polycrystalline ceramic samples, which are a typical shape for ferroelectric materials. The P-E loop shape of $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics is significantly improved due to a Nd substitution. Owing to the larger leakage current in the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramic with $x = 0$, polarization-electric field (P-E) hysteresis loops were only acquired with an applied electric field below 50 kV/cm . However, the polarization-electric field (P-E) hysteresis loops of the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramic with $x = 0.05$ was

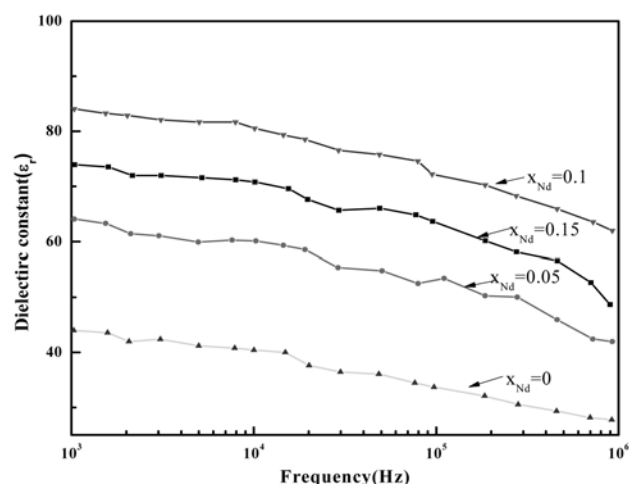


Fig. 4. Frequency dependence of the relative dielectric constant of the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ with various Nd contents $x = 0, 0.05, 0.1$, and 0.15 .

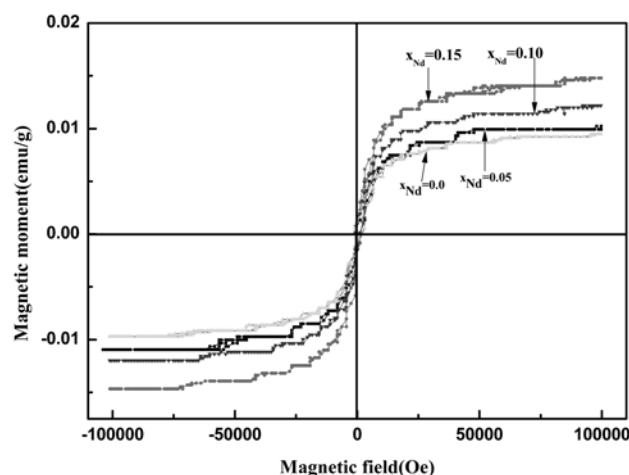


Fig. 5. Magnetization-magnetic field (M-H) hysteresis curves of the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ with various Nd contents $x = 0, 0.05, 0.1$, and 0.15 .

determined under a maximum electric field of 100 kV/cm .

The variation of the dielectric constant as a function of frequency in the range from 1 kHz to 1 MHz for the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics with various Nd contents ($x = 0, 0.05, 0.1$, and 0.15) measured at room temperature is shown in Fig. 4. It was observed that the value of the dielectric constant was found to be higher for the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics with a lower phase purity [17]. In addition, for all the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics, the value of the dielectric constant was high at lower frequencies and decreased with an increase in the frequency. Their 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 the applied field, while at high frequencies, they may not have time to undergo relaxation [18].

The magnetic hysteresis (M-H) loops of the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics with various Nd contents ($x = 0, 0.05, 0.1$, and 0.15) measured by a VSM with an in-plane mode, are shown in Fig. 5. All the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics exhibited symmetric magnetic hysteresis loops indicating that they were magnetic alloy ordered materials. The remanant magnetizations of the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics for $x = 0, 0.05, 0.1$, and 0.15 at 50000 Oe were achieved around 0.00864, 0.00985, 0.0113, 0.0138 emu/mg, respectively, showing a rise with an increase of the Nd content. This enhancement in remanant magnetization with Nd substitution might be due to the continuing collapse of the space-modulated spin structure of $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ [19].

Conclusions

In summary, the Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics with various Nd contents ($x = 0, 0.05, 0.1$, and 0.15) were synthesized by a sol-gel method. The 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 Nd content in $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics, the above-mentioned impurity phases were markedly decreased. In addition, both the remnant polarization and magnetic moment of Nd-modified $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics were improved owing to the Nd substitution in Bi sites.

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