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Multiferroic properties of Y-doped $BiFeO_3$

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ABSTRACT

$Bi_{1.04-x}Y_xFeO_3$ ceramics with x up to 0.30 were prepared by a tartaric acid modified sol–gel method. The crystal structure transformed from rhombohedral (R3c) to orthorhombic ($Pn2_1a$) with increasing Y doping concentration, which was confirmed by the X ray diffraction (XRD) and Raman measurements. With increasing Y doping concentration x, the leakage current was effectively suppressed, and the room temperature ferromagnetism was strongly enhanced with increasing x to 0.30. Clear room temperature ferromagnetism with saturate magnetization of about 0.31 emu/g and ferroelectric properties with 25 μC/cm^2 under electric field of 120 kV/cm have been observed in orthorhombic $Bi_{0.74}Y_{0.30}FeO_3$, suggesting the potential multiferroic applications.

1. Introduction

Multiferroics refers to the materials which simultaneously exhibit at least two of the ferroic properties, such as ferroelectric, ferromagnetic and ferroelastic order parameters, in a single phase [1]. Recently, most of the researches on multiferroics focused on the magnetoelectric (ME) coupling driven by the prospect of controlling polarization by the magnetic field and magnetization by electrical field [2]. However, the multiferroic materials are very rare [3]. Till now, $BiFeO_3$ (BFO) is the only multiferroic material with ferroelectric and antiferromagnetic orderings above room-temperature (T_C = 1103 K, T_N = 643 K), which makes it the most promising candidate for practical applications [4]. $BiFeO_3$ has canted G-type antiferromagnetic spin structure with a weak ferromagnetic moment (~0.02 μ_B/Fe) [5], and there is a superimposed cycloidal modulation with a period of about 62 nm, thus the macroscopic magnetization has been averaged to zero [6]. The magnetization is very weak which inhibits the observation of linear magnetoelectric effect [7].

Much work has been done to improve the ferroelectric and ferromagnetic properties, such as adding small amount of addictives [8], preparing epitaxial films [9]. Ion substitution with large difference in ionic radius is thought to be an effective method to improve the ferromagnetism at room temperature [10].The effect of transition metal ion, such as Mn [8], Y [11,12], added in $BiFeO_3$ with small amount have been studied. The radius of Y^{3+} (1.04 Å) is smaller than Bi^{3+} (1.17 Å) [13], which can be expect to induce lattice distortion to enhance magnetic property. But contradicted results have been reported on Y-doped $BiFeO_3$. Bellakki et al. reported that the magnetization increased with increasing Y concentration to 0.05 and decreased sharply with further increasing Y concentration up to 0.10 [11]. Wu et al. got better magnetic properties with Y doping concentration of 0.10 than 0.05 [12].

In this letter, we study the structural and multiferroic properties of $Bi_{1.04-x}Y_xFeO_3$ with x up to 0.30. A sudden improvement of ferromagnetism and better ferroelectric properties were observed with x of 0.30, which has been attributed to structural transition from rhombohedral (R3c) to orthorhombic ($Pn2_1a$) by Y substitution [14].

2. Experimental

$Bi_{1.04-x}Y_xFeO_3$ ($0 \leqslant x \leqslant 0.30$) ceramics were synthesized by a tartaric acid modified sol–gel method. The $Bi(NO_3)_3{\cdot}5H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Y(NO_3)_3{\cdot}5H_2O$ and Tartaric acid, which are analytical grade, were dissolved in distill water in proper proportions, with excess 4% Bi for compensating the loss during sintering. The solution was dried in air at 150 °C, and then sintered at 600 °C for 2 h. The obtained powders were grinded and pressed into small discs with diameter of 13 mm, sintered at 700 °C for 30 min. The crystal structure was characterized using X ray diffraction (XRD) with Cu Kα radiation. Raman measurement was performed on a Horiba Jobin Yvon LabRAM HR 800 micro-Raman spectrometer with 785 nm excitation source under air ambient condition at room temperature. The field dependent magnetization (M–H) was measured by a vibrating sample magnetometer. The ferroelectric polarization of the samples was measured at room temperature using Radiant Technologies' Precision II ferroelectric tester using silver paste as electrodes.

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3. Results and discussion

Fig. 1 shows the XRD patterns of $Bi_{1.04-x}Y_xFeO_3$ ($0 \leqslant x \leqslant 0.30$). It can be clearly seen that the $BiFeO_3$ exhibit R3c structure without any impurity phases. All the peaks shift to higher angles gradually with increasing doping concentration of Y, due to the smaller radius of Y^{3+} (1.04 Å) than Bi^{3+} (1.17 Å) [13]. With 0.10 Y doping, a small peak marked by the arrow can be observed which becomes stronger with increasing Y doping concentration, indicating the structural transformation. Furthermore, with increasing Y doping concentration above 0.20, the (104) and (110) peaks changes to four peaks. Similar XRD pattern has been observed by Zhang et al. in the Eu doped $BiFeO_3$, which has been attributed to the orthorhombic structure with space group $Pn2_1a$ [14]. However, recently, Wu et al. attributed the orthorhombic structure of $BiFeO_3$ with higher Y doping concentration to space group Pnma [12]. $Pn2_1a$ space group is non-centrosymmetric [14], while Pnma space group is centro-symmetric [12]. With the observation of ferroelectricity in $Bi_{0.74}Y_{0.30}FeO_3$ which will be discussed later, we conclude that the space group for orthorhombic $Bi_{1.04-x}Y_xFeO_3$ is $Pn2_1a$.

Details of the structural evolution with ion substitution on $BiFeO_3$ can be expressed more explicitly through Raman spectra. Fig. 2 shows the Raman spectra of $Bi_{1.04-x}Y_xFeO_3$. According to the group theory, 13 Raman active modes can be expected for the R3c rhombohedral $BiFeO_3$ [15]. However, not all modes can be clearly observed at room temperature [16]. Three peaks at 140, 172, and 218 cm^{-1} can be assigned to A_1(LO) phonons, and peaks located at 261 and 274 are associated with E(TO) phonons [8]. With 0.10 Y substitution, the $Bi_{0.94}Y_{0.1}FeO_3$ shows almost the same Raman spectra as $BiFeO_3$, indicating that the main phase is in R3c structure. However, the peak intensities decrease, and the A_1 modes shift to higher frequency (A_1(LO), A_1(2LO), A_1(3LO) at 146, 174, and 223 cm^{-1} respectively). The low frequency modes of A_1(LO), and A_1(2LO) are closely related to the Bi-O bond vibrations [8]. The Raman modes shift to higher frequency with increasing pressure which compresses the lattice unit cell [17]. With further increasing Y doping concentration to 0.20, the three A_1(LO) and two E(TO) modes disappear, while the intensity of three new modes (310, 522 and 618 cm^{-1}) becomes stronger. The Raman spectra are quite different from that of the $BiFeO_3$ in space group of Pnma [12]. Similar spectra have been reported by Dai et al. on Eu-doped $BiFeO_3$ [18]. The structural refinement has confirmed the space group of orthorhombic Eu-doped $BiFeO_3$ is $Pn2_1a$ [14],

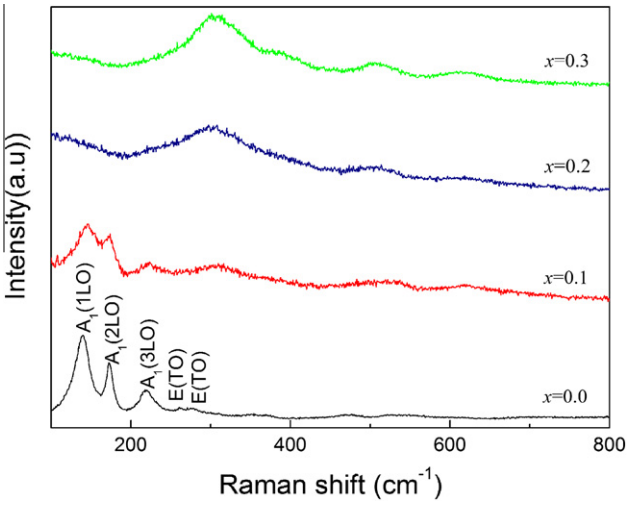

Fig. 2. Raman spectra of $Bi_{1.04-x}Y_xFeO_3$ (x = 0, 0.10, 0.20, 0.30).

suggesting the space group of orthorhombic $Bi_{1.04-x}Y_xFeO_3$ should be $Pn2_1a$.

Fig. 3 illustrates the room temperature M–H curves of $Bi_{1.04-x}Y_xFeO_3$. Linear curve was observed for $BiFeO_3$, confirming the antiferromagnetic properties. With 0.10 and 0.20 Y doping, no significant changes have been observed. With increasing x up to 0.30, a clear hysteresis loop can be observed, indicating the ferromagnetic properties. The remnant magnetization (M_r = 0.09 emu/g) and saturate magnetization (M_s = 0.31 emu/g) of $Bi_{0.74}Y_{0.30}FeO_3$ increase significantly compared to those values of $BiFeO_3$. It should be noted that Y^{3+} is nonmagnetic ions. Thus Y doping will not contribute to the enhanced ferromagnetism directly. The observed ferromagnetism can only come from the Fe^{3+}–O^{2-}–Fe^{3+} superexchange interaction. Recently, Yuan et al. studied the Y-doped $LuFeO_3$, and attributed enhanced ferromagnetism to the structural modification on the FeO_6 octahedra by Y doping [19]. $YFeO_3$ is a canted antiferromagnet with weak saturate magnetization of about 0.18 emu/g, which is smaller than that of $Bi_{0.74}Y_{0.30}FeO_3$ (0.31 emu/g). Furthermore, the coercivity of $YFeO_3$ (970 Oe) is much larger than that of $Bi_{0.74}Y_{0.30}FeO_3$ (150 Oe) [20]. Thus the possible contribution from the impurity phase of $YFeO_3$ can be excluded, and the sudden improvement of the ferromagnetism in

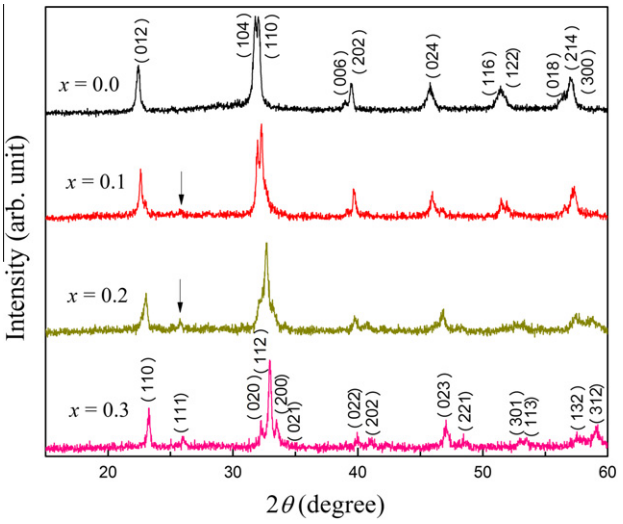

Fig. 1. XRD patterns of $Bi_{1.04-x}Y_xFeO_3$ (x = 0, 0.10, 0.20, 0.30).

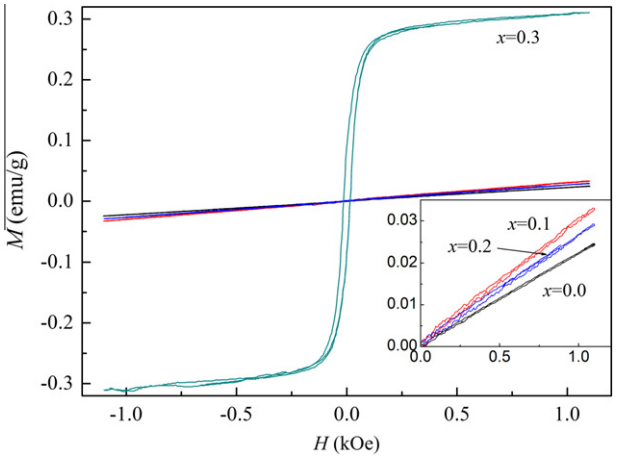

Fig. 3. Room temperature M–H curves of $Bi_{1.04-x}Y_xFeO_3$ (x = 0, 0.10, 0.20, 0.30). The inset shows the enlarged view of the M–H curves for $Bi_{1.04-x}Y_xFeO_3$ (x = 0, 0.10, 0.20).

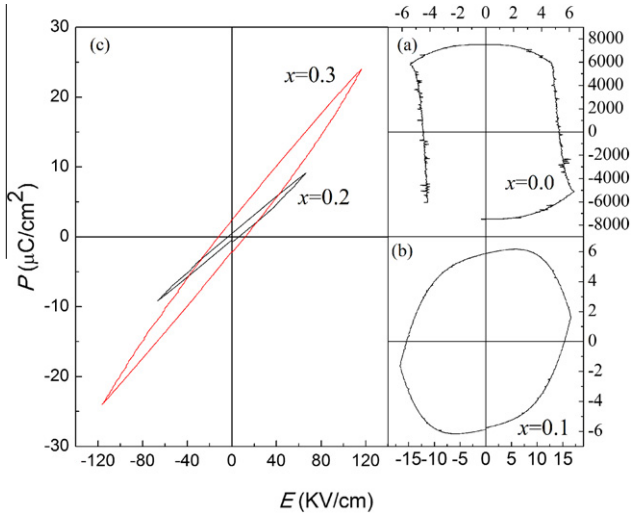

Fig. 4. Ferroelectric hysteresis loops for $Bi_{1.04-x}Y_xFeO_3$ ($x = 0$, 0.10, 0.20, 0.30) at room temperature.

$Bi_{0.74}Y_{0.30}FeO_3$ might be attributed to the suppression of the cycloidal modulation and the canted antiferromagnetic spin structure.

The ferroelectric hysteresis loops (P–E) of $Bi_{1.04-x}Y_xFeO_3$ are shown in Fig. 4. Due to the large leakage current in $BiFeO_3$, P–E curve shows rounded shape with unusual large value [21]. With increasing x to 0.10, the P–E loop is still rounded in shape, but much improved in comparison with that of the undoped $BiFeO_3$. With further increasing x, the leakage current was effectively suppressed, and the P–E loops became more and more typical, as shown in Fig. 4c. Similar phenomena have been observed in rare-earth (such as La, Nd, etc.) doped $BiFeO_3$ [22]. We were unable to obtain the exact value of the saturate polarization, due to the electrical penetration before full switching could occur, which also determine the maximum electrical field can be applied during the ferroelectric measurements. The improvement of the ferroelectric properties is due to the suppression of the leakage current, which would ascribed to the suppression of the oxygen vacancies by Y substitution for the volatile Bi [22].

4. Conclusion

In summary, $Bi_{1.04-x}Y_xFeO_3$ ($0 \leqslant x \leqslant 0.30$) ceramics were prepared by a tartaric acid modified sol–gel method. The effect of Y doping for BFO on the crystal structure, magnetic and ferroelectric properties have been investigated. XRD and Raman measurements reveal the structural transition from rhombohedral R3c of $BiFeO_3$ to orthorhombic $Pn2_1a$ with increasing x above 0.20. The doping of Y has little effect on the magnetic properties with increasing x to 0.20, while sudden improvement of ferromagnetism has been observed in $Bi_{0.74}Y_{0.30}FeO_3$. Increasing x can effectively suppress the leakage current, and clear ferroelectric hysteresis loop has been observed in $Bi_{1.04-x}Y_xFeO_3$ with $x > 0.20$. The coexistence of ferromagnetism and ferroelectricity in $Bi_{0.74}Y_{0.30}FeO_3$ suggests the potential multiferroic applications.

Acknowledgments

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