Structural evolution and enhanced magnetization of Bi$_{1-x}$Pr$_x$FeO$_3$

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Abstract

The structural, ferroelectric, vibrational, and magnetic properties of polycrystalline Bi$_{1-x}$Pr$_x$FeO$_3$ ($0 \leq x \leq 0.50$) powders are investigated by the measurements of X-ray diffraction, X-ray photoelectron spectroscopy, Raman scattering spectroscopy, and magnetization at room temperature. Our results reveal that the rare-earth ion Pr substitution at Bi site causes the structural transformations from rhombohedral $R3c$ phase to orthorhombic $Pbam$ phase at $x \approx 0.15$, and then to orthorhombic $Pnma$ phase at higher Pr concentration $x \approx 0.25$, accompanying the ferroelectric–antiferroelectric–paraelectric phase transition. Measurements of magnetic properties confirm that Pr substitution can improve the magnetization of BiFeO$_3$ before approaching the first phase transition. We find that an inverse behavior occurs after passing a maximum across the antiferroelectric–paraelectric phase boundary. We also obtain the unique switching behavior in low magnetic field of Bi$_{0.75}$Pr$_{0.25}$FeO$_3$ from the field dependence on magnetization, indicating the existence of the antiferromagnetic ordering.

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1. Introduction

In recent years, much attention has been paid to the multiferroic materials which display ferroelectricity, ferromagnetism and/or ferroelasticity simultaneously in a single phase [1], owing to their interesting physical phenomena and considerable potential applications in data storage, sensors and actuators, etc. [2–4]. Among these multiferroics materials, bismuth ferrite (BiFeO$_3$) has been extensively explored because of its ferroelectric transition temperature and antiferromagnetic Néel temperature well above the room temperature [5]. BiFeO$_3$ is a rhombohedrally distorted perovskite with space group $R3c$ (Ref. [6]) and described as an $a^-a^-a^-tilt$ system in which the FeO$_6$ octahedra rotate around the $\langle11\rangle_p$ (where $p$ = pseudocubic) direction [7]. However, the local short-range order of BiFeO$_3$ is G-type antiferromagnet with a cycloid spatial spin modulation with a period of 62 nm [8]. In this way, each Fe$^{3+}$ spin is surrounded by six antiparallel spins on the nearest Fe neighbors, preventing the observations of noticeable magnetization [9]. On the other hand, the ferroelectricity of BiFeO$_3$ mainly arises from the Bi site atoms [10] which are not located exactly in the middle between the FeO$_6$ octahedra as a result of the off-center displacement of Bi$^{3+}$ caused by the presence of 6s lone pair electrons [11]. In the Bi-based perovskites, the 6s$^2$ electrons of Bi$^{3+}$ hybridize with 2s and 2p of oxygen to form a space-filling localized lobe, which in turn pushes away its neighboring atoms causing a structural distortion [12]. Both effects help to induce ferroelectricity [11,13]. However, it is always difficult to obtain the spontaneous polarization in bulk BiFeO$_3$ or the good saturated hysteresis loop $P-E$ due to the large leakage current [14].

Many attempts have been made to improve the ferroelectricity and magnetization in BiFeO$_3$. The effective way to improve the magnetic properties is to offer internal [14–30] and/or external [31–34] stresses to BiFeO$_3$. The internal stress provided by the substitution of rare-earth cations at the Bi-site of BiFeO$_3$ can effectively modulate the crystal structure parameters and destroy the cycloid spin structure. The effect of cation substitution can lead to the release the locked magnetic moment and the improvement of magnetization [14–22]. However, some researchers considered that the enhanced magnetization can be partly attributed to the existence of Fe$^{4+}$ ion and/or the impurity phase Bi$_{25}$FeO$_{39}$ [23,24]. Therefore, there is still a debate of the mechanism of the magnetization improvement. For ferroelectric property, the recent investigations on Bi$_{1-x}$Re$_x$FeO$_3$ (Re = La [25], Nd [26,27], Sm [28,29], Gd [30]) systems showed that an alike PbZrO$_3$ orthorhombic $Pbam$ structure with antiferroelectricity appeared stably between the rhombohedral $R3c$ and the orthorhombic $Pnma$ phase boundaries. It is found that the obtained range of $Pbam$ phase in Bi$_{0.75}$Re$_{0.25}$FeO$_3$ compounds is very narrow due to the smaller ionic radius of Re$^{3+}$ ion substitutes [26,27,30]. Consequently, it can be assumed that the substitution of Pr$^{3+}$ with larger ionic radius (1.32 Å) at Bi-site...
will display a wider and more stable configuration of Pbam phase. However, there were very few papers focusing on the Pr-doped BiFeO$_3$ system [35–37], and none of them discovered the PbZrO$_3$-like orthorhombic Pbam phase. Kumar et al. [35] found that the structure transition from rhombohedral R3c to triclinic P1 in Bi$_{1-x}$Pr$_x$FeO$_3$ (0 ≤ x ≤ 0.15). Moreover, all reports [35–37] showed that both the polarization and dielectric constant increase with increasing Pr substituted concentration x. It was attributed to the reduction of oxygen vacancies resulting from the substitution of high valence Pr$^{4+}$ for Bi$^{3+}$, and the lattice distortion derived from the difference in ionic radius and electronic structures between Pr and Bi ions [35–37]. However, the simple influence of structural distortion on the ferroelectric property is still under debate.

In this paper, we aim to exhibit clear images of Pr substituted BiFeO$_3$ compounds within the concentration range of 0 ≤ x ≤ 0.5 through the investigations of the structural, ferroelectric, vibrational, and magnetic properties. The high quality samples enable us to understand better about the relations among the structure, ferroelectricity, and ferromagnetization. We show the evidence for the existence of an antiferroelectric orthorhombic Pbam phase between ferroelectric orthorhombic R3c and paraelectric orthorhombic Pnma phases. There is giant magnetization improvement approaching the polar–antipolar–nonpolar phase transitions.

2. Experimental

Bi$_{1-x}$Pr$_x$FeO$_3$ powders were synthesized by a tartaric acid (C$_4$H$_4$O$_6$) modified sol–gel technique. Appropriate amounts of Bi(NO$_3$)$_3$·5H$_2$O, Pr(NO$_3$)$_3$·6H$_2$O, and Fe(NO$_3$)$_3$·9H$_2$O, were dissolved in dilute nitric acid, and calculated amounts of tartaric acid were added as a complex agent. The resultant solution was evaporated and dried at 150 °C with continuous stirring to obtain xerogel powders. Then the xerogel powders were ground in an agate mortar and subsequently preheated to 300 °C for 1 h to remove excess hydrocarbons and NO$_3$ impurities. Finally, all samples were further annealed at 600 °C for 2 h. Phase analysis and investigation of the crystal structure were performed by x-ray diffraction (XRD) technique using a Bruker D8 ADVANCE diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) (ESCA Kratos AUD) was used to determine the oxidation states of Fe and Pr ions in the Bi$_{1-x}$Pr$_x$FeO$_3$ powders. Raman spectra were recorded in backscattering geometry with a LABRAM Jobin–Yvon spectrometer using a He–Ne laser of wavelength 633 nm. Magnetic properties were measured by using the Physical Properties Measurement System (PPMS, Quantum Design) at room temperature.

3. Results and discussion

All XRD patterns were refined well using the Fullprof Rietveld method. Fig. 1 shows the results of selected XRD measurements of Bi$_{1-x}$Pr$_x$FeO$_3$ (x = 0.04, 0.20, 0.50) powders. There is no trace of routine impurity phases such as Bi$_2$Fe$_2$O$_5$, Bi$_2$Fe$_5$O$_9$ and/or Pr$_2$O$_3$ in all samples, indicating a balanced proportion between Bi/Pr and Fe. BiFeO$_3$ is well defined as rhombohedral R3c symmetry at room temperature, and the unit cell parameters are a = b = 5.57036 Å and c = 13.84314 Å. For Pr-substituted concentration x ≤ 0.125, the XRD patterns can be well refined using a polar rhombohedral R3c model as shown in Fig. 1(a). There are some new diffraction peaks appearing around 2θ ≈ 17.7°, 28.9° and 33.0° at x = 0.15, which indicate a structure transition. A thorough analysis of the diffraction spectra indicated the second phase can be well described using the PbZrO$_3$–orthorhombic Pbam structure symmetry which is characteristic of $\sqrt{2}a \times \sqrt{2}a \times 2a$ (where a is the pseudocubic lattice parameter, a ~ 4 Å) supercell [38]. The space group Pbam combines antiphase rotations of theBO$_6$ octahedra described by a–a c$^\parallel$ tilting system with antipolar displacements of Pb ions along the (110)$_p$, where p is pseudocubic axis [26,38]. The fit at 0.15 ≤ x ≤ 0.25 with Pbam was very satisfactory, in which we replaced the Pb ions with Bi and Pr ions in the PbZrO$_3$ space group model. This confirms the phase transition observed around x = 0.15 is from rhombohedral R3c symmetry to orthorhombic Pbam phase accompanying a ferroelectric–antiferroelectric phase transition. With increasing the Pr concentration x, the characteristic peaks (110), (130) and (112) of the orthorhombic Pbam phase disappeared above x = 0.25, while the characteristic diffraction peak around 25° of Pnma appeared. It suggests another structure transformation from Pbam to Pnma. The selected Bi$_{0.50}$Pr$_{0.50}$FeO$_3$ sample is well refined using a Pnma cell with a = 5.57675 Å, b = 7.814 Å, and c = 5.49668 Å. The space group Pnma is a centrosymmetry structure with a paraelectric ordering, and has an a–a c$^\parallel$ tilting system with $\sqrt{2}a \times \sqrt{2}a \times \sqrt{2}a$ supercell [39], which implied that the second structure transition accompanied the antiferroelectric–paraelectric phase transition.

Notably, the existence range of Pbam phase in Bi$_{1-x}$Pr$_x$FeO$_3$ (0.15 ≤ x ≤ 0.25) powders is broader than that in Bi$_{1-x}$Nd$_x$FeO$_3$ and Bi$_{1-x}$Sm$_x$FeO$_3$ [26,27,30]. There was even no single Pbam phase existed particularly in Bi$_{1-x}$Gd$_x$FeO$_3$ and Bi$_{1-x}$Dy$_x$FeO$_3$ samples [23,30]. This is attributed to the radius of Pr$^{3+}$ ion (1.32 Å) is larger than Nd$^{3+}$ (1.31 Å), Sm$^{3+}$ (1.28 Å), Gd$^{3+}$ (1.27 Å), and Dy$^{3+}$ (1.24 Å) ions. Also it is the nearest one to the radius of Bi$^{3+}$ ion.
The size of the dopant has significant impact on the structural distortion. With equivalent substituted concentration, the smaller Re$^{3+}$ ion substitution will cause larger lattice distortion, which is attributed to a chemical-like pressure effect caused by the smaller radii of the isovalent Re ions. It has been reported that the Pbam phase was also found in pure BiFeO$_3$ by an external hydrostatic pressure during decompression [40]. The Pbam phase of Bi$_{1-x}$Pr$_x$FeO$_3$ ($A=$La,Nd,Sm) has been identified as the antiferroelectric PbZrO$_3$ structure [26,27,30,41,42]. The structural distortions within the cell can be considered as antipolar Pb displacements and antiphase rotations of the O octahedral described by an $a - c$ tilting system [43]. The combination of these two structural distortions gives rise to anti-ferroelectricity. The same Pbam structure of our Bi$_{1-x}$Pr$_x$FeO$_3$ (0.15 $\leq$ $x$ $\leq$ 0.25) samples accounts for its anti-ferroelectric characteristic as observed in similar systems.

In order to analyze the structural distortion quantitatively, we summarize the evolutions in the cell parameters and unit cell volume with Pr-doped concentration $x$ in Fig. 2 expressed by a pseudo-cubic cell. As can be seen, the volume decreases with increasing Pr-substituted concentration $x$ and shows two abrupt changes around $x$=0.15 and 0.3. This is due to lattice distortion resulted from the difference ionic radii between Pr$^{3+}$ (1.32 Å) and Bi$^{3+}$ (1.36 Å), and the abrupt changes are evidences of the phase transitions. Additionally, the slight reduction of $a_{pc}$ and $c_{pc}$ is observed, with increasing $x$ at the low Pr-doped concentration region. However, all the axes show clearly abrupt evolution in the ranges of 0.125 $\leq$ $x$ $\leq$ 0.15 and 0.25 $\leq$ $x$ $\leq$ 0.3. It can be explained by the occurrence of the structural transformations from rhombohedral R3c symmetry to orthorhombic Pbam phase, and finally to another orthorhombic Pnma phase. In the Pbam symmetry, the $a_{pc}$ lattice parameter begins to increase and, conversely, $b_{pc}$ decreases quickly. Nevertheless, the $c_{pc}$ axis continues to decrease. The $a_{pc}$, $b_{pc}$, and $c_{pc}$ cell parameters keep the same variation trends at the higher substitution concentration $x$=0.3–0.5, accompanying a sudden change between $x$=0.25 and 0.30. Generally speaking, these abnormal phenomena at the phase boundary can be ascribed to the largest lattice distortion and the drastic competition between two phases resulting from the Pr substitution in the Bi-site.

![Fig. 2. The substitution $x$ dependence of the unit-cell volume $V$ divided by the number of formula units per unit cell $Z$, the normalized lattices parameters of Bi$_{1-x}$Pr$_x$FeO$_3$ (0 $\leq$ $x$ $\leq$ 0.50). The cell parameters are described in a pseudocubic cell $a_{pc} = a/\sqrt{2}$, $b_{pc} = b/\sqrt{2}$, and $c_{pc} = c/\sqrt{2}$ for the R3c phase, $a_{pc} = a/2$, $b_{pc} = b/2$, and $c_{pc} = c/2$ for the Pbam phase, $a_{pc} = a/2$, $b_{pc} = b/2$, and $c_{pc} = c/2$ for the Pnma phase.](image)

![Fig. 3. X-ray photoelectron spectra of the Fe 2p line (a) and Pr 3d line (b) for Bi$_{0.925}$Pr$_{0.075}$FeO$_3$ compound.](image)
compositions. Therefore, the increased magnetization observed later cannot yet result from Fe$^{3+}$.

Raman scattering is a very informative technique to study the local distortion in ABO$_3$ system. It is sensitive to the changes of atomic displacement, the evolution of Raman modes with increasing Pr content. Unpolarized Raman spectra were carried out for all Bi$_{1-x}$Pr$_x$FeO$_3$ ($0 \leq x \leq 0.5$) powders at room temperature, as shown in Fig. 4. According to group theory, pure BiFeO$_3$ with rhombohedral R3c structure has 13 Raman active modes, illustrated as $\Gamma' = 4A_1 + 9E$ [48], while 24 Raman-active modes are corresponding to the Pbam and Pnma orthorhombic structure with $\Gamma' = 13A_g + 13B_g + 11B_{2g} + 11B_{3g}$ [49] and $\Gamma' = 7A_g + 5B_g + 7B_{2g} + 5B_{3g}$ [50], respectively. Just 13 Raman modes obtained in Pbam phase, and only 11 modes in Pnma phase are observed. The number of unpolarized Raman-active modes is about half of the polarized ones in Pbam and Pnma orthorhombic structure [51].

In order to understand the relationship between the frequency of Raman modes and the Pr concentration $x$, we fitted the Raman spectra with Lorentzian shapes. Fig. 5 shows the Pr concentration $x$ dependence of the frequency shifts of Raman active modes. For pure BiFeO$_3$, there are 13 Raman modes in accordance with previously theoretical results. It is notable that all the modes shift slowly in the low substituted range $0 \leq x \leq 0.125$, which illustrate the structures are stable and just distort slightly. The peaks located 121, 136, 170, 215, and 260 cm$^{-1}$ in pure BiFeO$_3$ are described as $E'$-1, $A_1$-1, $A_2$-2, $A_1$-3, and $E$-2 modes, respectively, which are governed by the relative motion of A-site cations against the oxygen octahedrons. They shift slowly to higher frequency with increasing Pr content $x$. This is due to the decrease of the Bi–O bond caused by gradually replacement of Pr$^{3+}$ at Bi-site. As Pr content increases from 0.125 to 0.15, one dramatic shift can be found in the vibrational modes in the region of 200–300 cm$^{-1}$. Another abrupt change is that a new peak at around 650 cm$^{-1}$ appears at $x=0.15$. These phenomena are attributed to the larger lattice distortion at the phase transition boundary, resulting from the drastic competition between the rhombohedral R3c symmetry and orthorhombic Pbam phase. In the Pr concentration range of $0.15 \leq x \leq 0.25$, the two peaks near 375 and 405 cm$^{-1}$ shift to higher frequency and get closer to each other gradually with increasing concentration $x$. It is striking that the two highest frequency modes, about 609 and 652 cm$^{-1}$, shift separately at first and then get close. A larger sudden frequency shifts is observed at $x=0.30$. Between $x=0.25$ and 0.30, the prominent feature in the Raman spectra is the superposition of the modes around 397 and 409 cm$^{-1}$ and merger of the modes around 610 and 642 cm$^{-1}$, respectively. The vibrational mode around 407 cm$^{-1}$ assigned as $A_{3g}$ symmetry, connected with (101) distortion of the FeO$_6$ octahedral [52], is the intrinsic modes of the orthorhombic Pnma phase [53], revealing the occurrence of the Pbam–Pnma transformation. The phase boundary determined based on Raman scattering technique results is in good agreement with the results from XRD patterns.

Fig. 6 shows the magnetic hysteresis loops of the selected Bi$_{1-x}$Pr$_x$FeO$_3$ ($x=0.0, 0.15, 0.4$, and 0.5) samples with a maximum applied magnetic field of 8.0 T at room temperature. It is well known that the pure BiFeO$_3$ has a G-type antiferromagnetic

![Fig. 4. Raman scattering spectra of Bi$_{1-x}$Pr$_x$FeO$_3$ ($0 \leq x \leq 0.5$) compounds at room temperature.](image1)

![Fig. 5. The Pr substituted concentration $x$ dependence of frequency shifts of Raman active modes of Bi$_{1-x}$Pr$_x$FeO$_3$ ($0 \leq x \leq 0.5$) compounds.](image2)

![Fig. 6. Room temperature $M$–$H$ curves of Bi$_{1-x}$Pr$_x$FeO$_3$ ($x=0.0, 0.15, 0.4$, and 0.5). The inset shows Pr composition $x$ dependent remnant magnetization.](image3)
ordering with a spatially modulated spiral spin structure, leading to null macroscopic magnetization. However, our BiFeO$_3$ powders show a narrow ferromagnetic hysteresis loop with a remanent magnetization $M_r \approx 0.029$ emu/g. The spontaneous magnetization should result from the uncompensated spin magnetic moments due to the grain size of particles smaller than 62 nm. The obvious openings in the hysteresis loops of Bi$_{1-x}$Pr$_x$FeO$_3$ ($0 < x < 0.2$) confirm that the magnetic properties are improved owing to the Pr substitution at the Bi site. The inset of Fig. 6 presents the measured magnetization value ($M_r$) as the function of the Pr concentration $x$. For $x \leq 0.125$, the remanent magnetization of Bi$_{1-x}$Pr$_x$FeO$_3$ samples increases gradually with increasing Pr substituted concentration $x$. A dramatic enhancement in the remanent magnetization appears in the range of $x=0.125\sim0.15$, accompanied with the structural crossover from R$3c$ phase to Pbam symmetry. In the antipolar Pbam phase ($0.15 < x < 0.3$), the $M_r$ values are very large, which is several times larger than those obtained for the pure BiFeO$_3$. According to the neutron diffraction technique, the enhancement of magnetization could be attributed to the increasing periodicity of spiral spin structure suppressed by Pr substitution, releasing partially latent magnetic moments locked within the cycloid spin structure [54,55].

The Pr substitution can only suppress but cannot destroy the spin cycloid structure completely as the substituted concentration of Pr is below 0.25, and results in a limited increase of the magnetic properties. However, with further increasing $x$ ($x \geq 0.3$), the $M_r$ decreases quickly after passing a maximum value $0.246$ emu/g at $x=0.25$. It means that the spiral spin structure is destroyed completely at $x=0.25$. The decrease of magnetization for $x \geq 0.3$ is believed to happen due to further decrease in the extent of canting of spin structure, allowing a more perfect antiferromagnetic order [19,56].

It is more interesting that the magnetic hysteresis loop of $x=0.50$ shows a metamagnetic behavior at low applied field as shown in Fig. 6. This is so called 'switching behavior' found in Y doped BiFeO$_3$ system at low and room temperature [17,57]. This is a distinctive character of applied field induced alignment of spins in an antiferromagnetic order system opening the hysteresis loop. This phenomenon confirms the perfect antiferromagnetic structure existing within the orthorhombic Pnma phase of our Bi$_{1-x}$Pr$_x$FeO$_3$ powder system. The switching behavior is a special observation at room temperature for the multiferroic classiﬁcation, and makes it probable candidate for obtaining better magnetoelectric coupling. However, this quite fascinating magnetic behavior of multiferroic materials is required to be further researched on both macroscopic and microscopic horizons.

4. Conclusions

We have successfully synthesized the single phase Bi$_{1-x}$Pr$_x$FeO$_3$ ($0 \leq x \leq 0.5$) powders by the modiﬁed sol–gel method. Pr substitution at Bi-site of BiFeO$_3$ has caused the compositional-driven structural transformations from rhombohedral $R3c$ phase to orthorhombic Pbam phase in the region of $x=0.125\sim0.15$, then into another orthorhombic Pnma phase at $x=0.30$. The structural crossovers were also conﬁrmed by the abrupt evolution of the cell parameters and active vibrational modes at the phase boundaries. These structural transitions brought about an appearance of antiferroelectric ordering in the PbZrO$_3$-like Pbam symmetry ($0.15 \leq x \leq 0.25$) between the ferroelectric R$3c$ phase ($x \leq 0.125$) and paraelectric Pnma phase ($x > 0.25$). We observed the magnetization enhanced gradually with increasing the Pr concentration resulting from the spiral spin magnetic moments suppressed by Pr substituted in initial R$3c$ phase. The dramatic increases at the phase transitional edges are attributed to the complete destruction of the spiral spin structure. Interestingly, the magnetization decreased quickly with further increase of Pr doped content after passing the maximum $M_r$ value at $x=0.25$. In fact, the suppressed helical spin arrangement was broken absolutely at the antipolar phase transition, and changed into well perpendicular antiferromagnetic ordering. Moreover, the unique switching behavior in low magnetic field is the most interesting observation of the magnetic field dependence of magnetization of Bi$_{0.5}$Pr$_{0.5}$FeO$_3$, which is attributed to the perfect antiferromagnetic ordering for $x=0.5$. We expect such a behavior would provide a new possible candidate for obtaining better magnetoelectric coupling.

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