Observation of Spin Reorientation Transitions in Lead and Titanium-Modified BiFeO₃ Multiferroics

Ashwini Kumar, Poorva Sharma, Qi Li, Fujun Qiu, Jianhui Yan, Jingyou Tang, and Guolong Tan

1Key Laboratory of Multifunctional Materials, School of Electrical and Electronics Engineering, Luzhou Vocational and Technical College, Luzhou, Sichuan–646000, China
2School of Physics, Southeast University, Nanjing-211189, China
3Institute of New Materials, Wuhan University of Technology, Wuhan-430070, China

Correspondence should be addressed to Ashwini Kumar; ashu.dhanda2@hotmail.com and Poorva Sharma; poorva@nuaa.edu.cn

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We report the synthesis and basic characterization details of bulk Bi₁₋ₓPbxFe₁₋ₓTixO₃ (x = 0.05 and 0.1) polycrystalline samples, which have been synthesized using the conventional solid-state route. We studied the effects of partially doping of Pb and Ti ion on structural, vibrational, and magnetic properties of multiferroic BiFeO₃. X-ray diffraction (XRD) was used for crystallographic studies, followed by Rietveld refinement, and phase formation of the compounds was confirmed, which indicates that the sample has rhombohedral (R3c, 100%) symmetry for x = 0.05 and R3c (98%) + P4mm (2%) symmetry for x = 0.1. X-ray absorption spectroscopy has been probed at Fe L₂,3 and O K edges to determine the valence (charge) state of Fe in BiFeO₃. Interestingly, the magnetic measurement results revealed the existence of spin reorientation transition in Pb and Ti-modified BiFeO₃, which indicates that the BiFeO₃ samples studied may find promising applications in memory and spintronic devices.

1. Introduction

A good understanding of the structure-property relationships can be used to develop new functional materials and devices. In recent years, multiferroics have great interest because in these materials, the electrical polarization emerges caused by the symmetry destruction of magnetic structure at magnetic ordering temperature. Rhombohedral distorted perovskite multiferroic BiFeO₃ (BFO) prepared under conventional synthesis conditions showed rich variety of subtle interaction among spin, charge, orbital, and lattice degrees of freedom. BFO shows G-type antiferromagnetic spin configuration below to Neel temperature (TN) = 643 K and a ferroelectric order at around Curie temperature (TC) = 1103 K [1, 2]. The ferroelectric perovskite PbTiO₃ (PTO) is a well-known tetragonal-distorted perovskite, with a space group of P4mm, TC = 763 K, and a large anisotropic thermal expansion [3]. The tetragonal symmetry is obtained below TC, where PTO belongs to the space group P4mm, while above TC, the cubic (Pm3m) symmetry describes the system [4]. These perovskite materials have attracted great interest due to their low-cost synthesis, interesting physical properties, and potential applications [5, 6]. In addition, due to the observation that ultrafast spin rotation times have possible industrial applications, the spin orientation transition (SRT) in antiferromagnetic insulators has attracted the attention of researchers [7–10]. SRTs above and below room temperature have been reported in BiFeO₃ [2, 10]. However, single crystal magnetic and neutron scattering studies have not yet revealed this reorientation transition in BiFeO₃ and are therefore questioned [2, 10, 11].

Bhattacharjee et al. reported a clear indication of SRT in (1 – x) BFO-(x) PTO solid solution using magnetization and neutron scattering studies over a small composition range (0.27 < x < 0.31) [10]. The spin reorientation present in (1 – x) BFO-(x) PTO is different
from the SRT in RFeO$_3$, but it appears to be Morin transition in hematite. Gaikwad et al. also observed two magnetic anomalies around 124 and 213 K from low temperature infrared absorption spectra and magnetization data, which are related to the spin reorientation of Fe$^{3+}$ ions and spin glass state [2]. The local structure of the FeO$_6$ octahedra has distortion and provides a mark for robust spin-phonon coupling in the BFO along with spin reorientation of Fe$^{3+}$ [2]. Zhu et al. [12] reported the presence of a morphotrophic phase boundary (MPB) area in a series of $(1-x)$ BFO–xPTO solid solutions. In these solid solutions, the tetragonal phase, rhombohedral phase, and an orthorhombic phase existed at the same time with a large tetragonality in the tetragonal phase segment. The tetragonal symmetry had huge anisotropy [13, 14]. According to the first principle calculations, the hybridization between the electronic states of cations and anions is crucial to ferroelectricity [14, 15]. Sati et al. [16] studied the effect of varying Pr and Ti codoping concentration on the structural, magnetic, vibrational, and impedance characteristics of BiFeO$_3$ synthesized by the conventional solid-state reaction method. Rietveld-refined XRD patterns indicate that as the doping concentration increases, a compositional driven crystal structure transformation from rhombohedral to an orthorhombic phase existed. Dielectric measurements showed the enhancement in dielectric properties with reduced dielectric loss with increase in doping concentration. Impedance analysis confirmed that with the increase of Pr and Ti concentrations in BiFeO$_3$, the decrease in electrical conductivity was attributed to the enhancement of barrier performance, resulting in the suppression of the lattice conduction path due to lattice distortion. Due to coding, the magnetic properties of the material are improved, attributed to the breakdown of the balance between antiparallel sublattice magnetization of Fe$^{3+}$ ions and the collapse of the spatially modulated spin structure caused by the structural transformation [16].

Here, we report the synthesis and analysis of structural and magnetic properties of polycrystalline Bi$_{1-x}$Pb$_x$Fe$_{1-x}$Ti$_x$O$_3$ ($x=0.05$, 0.1) samples. Rietveld refinement method has been used to analyze the structural parameters. We have been studied the effect of Pb and Ti ions doping on structural, vibrational, and magnetic properties in BiFeO$_3$. Polycrystalline ceramics of Bi$_{1-x}$Pb$_x$Fe$_{1-x}$Ti$_x$O$_3$ ($x=0.05$ and 0.1) are abbreviated as BPFTO-05 and BPFTO-10, respectively, for further communication.

2. Experimental Details

The polycrystalline Bi$_{1-x}$Pb$_x$Fe$_{1-x}$Ti$_x$O$_3$ ($x=0.05$ and 0.1) samples were prepared by the conventional solid-state route. High-purity oxides such as Bi$_2$O$_3$ (99.99% purity), Fe$_2$O$_3$ (99.9% purity), PbO (99.99% purity), and TiO$_2$ (99.99% purity) were used as starting reagents. Starting reagents were carefully weighed and mixed in stoichiometric ration in an agate mortar for 6 hours using high-purity alcohol as a medium and then calcined at 650°C for 6 hours. The leaching process was carried out with distilled water and HNO$_3$ to remove impurities from the samples. The precipitated precursor particles at the bottom were collected, and the excess salts at the top layer were discarded. Pour out the particles repetitively with distilled water and HNO$_3$ to eliminate impurities. Then, the washed particles were dried at room temperature and further calcined at 700°C for 5 hours [17, 18]. XRD measurements were carried out with CuK$_\alpha_1$ (1.5406Å) radiation using a Bruker D8 Advance X-ray diffractometer and analyzed with the Rietveld refinement method [17]. The Raman spectrum was carried out by “Jobin-Yvon Horiba LABRAM (System HR800)” spectrometer with a 488 nm excitation source equipped with a Peltier cooled CCD detector (1024 × 256 pixels of 26 microns)” [17]. DC magnetization measurements were performed using the physical property measurement system (Quantum Design, PPMS-9). Zero-field cooling (ZFC) and field cooling (FC) processes were used to acquire the temperature dependence of magnetization [19]. XAS was used at normal incidence using the linearly polarized light and in the total electron yield mode at photoelectron station of Beijing Synchrotron Radiation Facility (BSRF), Beijing. The resolution of XAS is 0.3 eV [20].

3. Results and Discussion

3.1. Structural Study. Figure 1 shows the X-ray diffraction pattern for Bi$_{1-x}$Pb$_x$Fe$_{1-x}$Ti$_x$O$_3$ ($x=0.05$, 0.1) samples which are abbreviated as BPFTO-05 and BPFTO-10, respectively. X-ray diffraction data suggest that BPFTO-05 sample possesses rhombohedral structure with the R3c space group. All the obtained diffraction peaks completely match the standard crystal data corresponding to JCPDS file 86–1518 [17], while the sample BPFTO-10 shows the mixed phase (R3c, 98% + P4mm, 2%) symmetry [21], it matches with the reference data (JCPDS file number 72–1832) completely, except for low-intensity impurity peaks near 2θ = 27.86° and 29.04° related to Bi$_2$Fe$_3$O$_9$. The peak splitting is decreasing in BPFTO-10 in comparison to BPFTO-05 [22] results coexistence of two phases. The tetragonal phase had large anisotropy [23]. Thorough important crystallographic parameters acquired through the refinements are given in Table 1.

3.2. Rietveld Refinement of XRD Data. The room temperature XRD patterns of BPFTO-05 and BPFTO-10 ceramics were refined using FullProf software, as shown in Figures 2(a) and 2(b). In the refining process, lattice parameters and profile parameters were refined, while atomic positions and anisotropic displacement parameters were fixed to the values given by earlier reports [24]. The calculated XRD patterns of these two samples are in good agreement with the experimentally observed XRD data with mostly small R values as given in Table 1. The lattice coordinates of the samples are given in Table 2. For BPFTO-05, the refined lattice parameters such as $a = 5.5785\text{Å}$ and...
temperature.

Also, the fracture type surface in the BPFTO-10 shows dense structure with nonuniformity in the size of ions highly influenced the morphology of BFO. Micrograph polycrystalline-prepared sample, and the dopant Pb and Ti micrographs clearly exhibits flakes such as morphology of micrograph for BPFTO-05 and BPFTO-10 samples. SEM

3.3. SEM Micrograph Analysis. Figure 3 shows the SEM micrograph for BPFTO-05 and BPFTO-10 samples. SEM micrographs clearly exhibits flakes such as morphology of polycrystalline-prepared sample, and the dopant Pb and Ti ions highly influenced the morphology of BFO. Micrograph shows dense structure with nonuniformity in the size of flakes. Also, the fracture type surface in the BPFTO-10 sample was noticeably more granular, demonstrating expressively stronger internal stresses, perhaps due to the higher tetragonal distortion for this composition [22, 26]. For both the samples, an inhomogeneous grain growth was found that resulted in notable residual porosity. The average crystallite size for BPFTO-05 is about 0.8–1 μm and for BPFTO-10 is 0.5–0.8 μm. The average crystallite size can be reduced by adding Pb and Ti ions BiFeO3 attributed to the distinct ionic size of Pb2+ and Ti4+ ions than Bi3+ in BiFeO3.

Table 1: Details of Rietveld-refined XRD parameters for Bi1-xPbxFet-xTiyO3 (x = 0.05 and 0.1) samples.

| Parameters          | x = 0.05 | x = 0.1 |
|---------------------|----------|---------|
| 2θ range (deg.)     | 20°–80°  | 20°–80° |
| Step size (deg.)    | 0.02     | 0.02    |
| Wavelength          | 1.5406 Å | 1.5406 Å |
| Number of refined parameters | 25          | 21            |
| Space group         | R3c (99%) | R3c (99%) * P4mm (1%) |
| a (Å)               | 5.5865 (3) | 5.5854 (5)/4.5854 (5) |
| b (Å)               | 5.5865 (3) | 5.5854 (5)/4.5854 (5) |
| c (Å)               | 13.8757 (3) | 13.8953 (3)/5.9453 (4) |
| Volume (Å3)         | 374.451 (1)/125.021 (2) | 374.488 (1)/125.012 (2) |
| Rf                  | 3.68     | 4.05/59.1 |
| Rinteg              | 4.48     | 5.12/91.9 |
| Rexp                | 12.4     | 12.0    |
| Rsint               | 6.94     | 9.37    |
| Rg                  | 14.3     | 20.0    |
| χ²                  | 2.89     | 1.638  |
| GOF                 | 1.7      | 1.3     |

Figure 1: X-ray powder diffraction (XRD) pattern of Bi1-xPbxFet-xTiyO3 (x = 0.05 and 0.1) bulk ceramic at room temperature.

c = 13.8547 Å and crystalline angles, i.e., α = β = 90°, γ = 120°, match well with rhombohedral R3c symmetry described in another reports [17, 25].

3.4. XAS Spectra. XAS measurements were performed on both BPFTO-05 and BPFTO-10 samples. Due to large 2p core hole spin-orbit coupling energy, the measured Fe L2,3 edge XAS spectra are divided into L3 (2p3/2) and L2 (2p1/2) regions for BPFTO-05 and BPFTO-10, as shown in Figure 4(a) [27]. When Fe ions are located at the L3 and L2 edges, strong absorption peaks appeared at the photon energies of 709.6 eV (L2g) – 710.2 eV (eg) and 722eV (L2g) – 723.8 eV (eg), respectively. The line shape of Fe L2,3 edge determines the valence state information of Fe ions [27]. We observed the prominent presence of XAS signal in Fe L2,3 edge [20]. These results indicate that the samples have the electronic configuration such as α-Fe2O3 and LaFeO3, and Fe3+ is the leading oxidation states of Fe ions. The electrostatic interaction is between O 2p and Fe 3d t2g and eg orbitals, hybridization of O 2p with Bi 6s/6p orbitals, hybridization of O 2p with Fe 4s/4p orbitals clearly exists in the prepared systems. Figure 4(b) shows the normalized OK edge XAS spectra for both of these prepared samples, which are evidently showing vacant O 2p state in the conduction band [28]. The first two bands denote the hybridization of O 2p through unoccupied Fe 3d orbitals which splits in t2g and eg initiated by the electrostatic interaction concerning the O 2p and Fe 3d orbitals [28]. Although, another band feature starting at about ~540 eV corresponds to the hybridization of O 2p with Fe 4s/4p orbitals. Improvement in the hybridization of Bi 6r2 lone pair with O 2p orbitals is liable for the enhanced ferroelectric behavior as detected in prepared samples [20, 27, 28].

3.5. Magnetic Analysis. Temperature dependence zero-field cooling, ZFC (plotted with blue circle), and the field cooling, FC (plotted with red circle), magnetic curves for both BPFTO-05 and BPFTO-10 samples are shown in Figures 5(a) and 5(b). The samples were cooled down to the temperature of 10 K without an external applied magnetic field in the ZFC mode. Then, we measured the magnetization of the sample with increase in temperature with the applied magnetic field of 0.1 T. Whereas, in the FC mode, the magnetization was measured while cooling down the sample to temperature of 10 K (as shown in Figures 5(a) and 5(b)). In the FC process, the magnetization reduces with temperature increases. Meanwhile, in the ZFC process, the magnetization takes a magnetic transition around temperature of 160 and 232 K. A noticeable anomaly is observed around 233 K in the BPFTO-05 sample in the FC mode, which reveals its AFM behavior, and is matched well with previously reported data [29, 30].
Another magnetic transition occurs below the temperature of 160 K in the ZFC mode. The obtained experimental result shows that a change in spin ordering at low temperature attributes to spin reorientation of Fe$^{3+}$ ions in BiFeO$_3$ comparable with other rare earth orthoferrites. Though, for bulk BFO single crystal, the spin reorientation has been described close to 50 K [2, 25, 31, 32]. This deviation in BFO can be attributed to the particle size effect or...
presence of flakes in SEM micrographs, which is the cause of induced strain, distortion, and lattice disorder. Below 160 K, the magnetization is observed to decrease in the ZFC curve until 50 K and then increase again until 10 K. However, in the FC curve, no significant change in the magnetization with the decrease in temperature was detected, but it changed around temperature of 232 K. The origin of observed SRT is due to the orientation of Fe$^{3+}$ spins, and the orientation of Fe$^{3+}$ spins is caused by the destruction of the antiferromagnetic spiral order. For the BFO system, the orientation of Fe$^{3+}$ spins is caused by the destruction of the magnet and PbTiO$_3$ is diamagnetic, thus as Pb and Ti ion dependence of magnetic moment [12].

According to Gaikwad et al., “the AFM ordering results in rotation of spins, and the order parameter of this helical ordering is 62 nm. The particles having size less than 62 nm, breaking of the helical ordering of the spins along AFM, are observed. It suppresses the modulated spin structure and improves magnetization” [2]. On increasing the Pb ion substitution in BFO, there is not a prominent transition like BPFTO-05, but there is little sign of presence of magnetic transitions around temperature of 94, 174, and 224 K in BPFTO-10. Somehow, we revealed small shift in transition temperature for BPFTO-10 as compared to the BPFTO-05 sample. As it is well known that BiFeO$_3$ is an antiferromagnet and PbTiO$_3$ is diamagnetic, thus as Pb and Ti ion increases, it affects the magnetic properties obviously and may vanish the magnetic transitions completely as PbTiO$_3$ is completely ferroelectric material till it is having a tetragonal phase. According to the structural analysis, BPFTO-10 exists simultaneously in two phases rhombohedral and tetragonal near the MPB region. Consequently, it is sensible to recommend that each of these phases undergoes an antiferromagnetic ordering at a different temperature, leading to an anomaly on the temperature dependence of magnetic moment [12]. The $T_N$ for both phases decreases with the increase in $x$ across the MPB region [12]. The magnetic curve in the ZFC mode decreases first and then increases at spin reorientation region temperature, a behavior distinctly different from the FC magnetic data that continuously decrease with lowering in temperature. This behavior is evocative of weak ferromagnetism (FM) associated with magnetic glassiness or cluster glass (CG) behavior [33].

Figures 5(c) and 5(d) represent the magnetization versus magnetic field at two different temperatures of 10 and 300 K. Magnetization loops recorded at 300 K show a remnant value of ~0.004 $\mu_B$, as shown in Figures 5(c) and 5(d). This weak ferromagnetic moment or canted antiferromagnetic ordering, seeming small when compared with that of other BiFeO$_3$-based compositions such as Bi$_{0.7}$Ba$_{0.3}$FeO$_3$ [34], may take place within a tetragonal phase allowing lattice transverse softening. We can observe in Figures 5(c) and 5(d) that the magnetization loops recorded at 10 K show a very less remnant value of ~0.001 $\mu_B$ for both the samples. Magnetic moments at 10 K show true antiferromagnetic ordering in both prepared samples. However, possibly the enhancement in the resultant magnetic moment attributed to the broken cycloid spin structure caused by the variation in crystallographic arrangement with Pb and Ti doping in BiFeO$_3$ [35–38].

3.6. Raman Analysis. For the vibrational study, we probed the Raman spectroscopy at room temperature for BPFTO-05 and BPFTO-10 samples with an excitation wavelength of 514 nm, as shown in Figure 6. Distorted rhombohedral-structured BFO yields 18 optical phonon modes and which can be summarized as following irreducible representation: $\Gamma_{opt} = 4A_1 + 5A_2 + 9E$ [16]. According to the group theory, 13 modes ($R_{Raman, R3c} = 4A_1 + 9E$) are Raman active, while 5 $A_2$ modes be Raman inactive [17, 39, 40]. $A_1$ modes are related with Fe ions and $E$ modes are allied with Bi ions. The mode positions dependency on parent BFO and doped BFO is given in Table 3 [17, 39, 41]. In the present work, as obtained, ten Raman active phonon modes of BPFTO-05 and BPFTO-10 samples including $A_1-1$, $A_1-2$, $A_1-3$, $E-3$, $E-4$, $E-5$, $E-6$, $E-7$, $E-8$, and $E-9$ modes at 134 (135), 165 (166), 214.
(216), 269 (264), 308 (309), 368 (362), 475 (470), 514 (524), 542 (542), and 624 (625) cm$^{-1}$ are in good agreement with earlier reported data [41, 42]. The stereochemical activity of the Bi ion lone pair electron which is principally responsible for the change in both Bi–O covalent bonds originates ferroelectricity in BFO. It is believed that the six characteristic modes, i.e., $E$-1, $A_1$-1, $A_1$-2, $A_1$-3, $A_1$-4, and $E$-2 are accountable for the ferroelectric nature of the BFO samples [17]. As evident from the X-ray diffraction, the crystal symmetry contains rhombohedral ($R_3c$) and (rhombohedral ($R_3c$) + tetragonal phase ($P4mm$)) on subsequent doping of Pb ion and Ti ion at A-site and B-site of BFO samples, and there are changes in Raman modes as compared to BFO.

These alterations in crystallographic structure is ascribed the A-site and B-site disorder created by Pb and Ti ion substitution, “which leads to the shifting of Raman modes at higher and lower frequencies” with sudden disappearance of mode (E-8 in BPFTO-05 and A1-4, E-1, and E-2 in both of the prepared samples) [17]. Additional E-1 and E-2 modes at 68 and 75 cm$^{-1}$ appear in doped BFO samples, but is too weak to detect in the prepared sample. These phenomena reveal the change of Bi–O covalent bonds with increasing doping concentration as compared to BFO and induced ferroelectricity. Moreover, a shift in the Raman characteristic modes towards the higher wavenumber is noted with increasing doping concentration in prepared BPFTO ceramics as compared to pure BFO, which are due to Bi–O bond vibrations [43, 44]. This can be attributed to the lower atomic weight of Pb (207.2) compared to Bi$^{3+}$ (208.98) and Ti (47.86) compared to Fe$^{3+}$ (55.84) [17]. Furthermore, for BPFTO-05 and BPFTO-10 samples, the intensity of E-modes increase, whereas $A_1$ mode intensity decreases significantly. This might be due to some contractions in unit cell volume of the structural phase as rhombohedral ($R_3c$) and (rhombohedral ($R_3c$) + tetragonal ($P4mm$)) in BPFTO-10, respectively, and account for the fact that doping affects the

Figure 5: Temperature dependence of ZFC and FCC magnetization curve for (a) BPFTO-05, (b) BPFTO-10, (c) M-H loop for BPFTO-05, and (d) BPFTO-10.
 symmetry in BFO [16]. The two-magnon features are almost invisible in the Raman spectrum, but they are advantageous in this study. We detected the broad peak approximately at 964 (955) cm$^{-1}$ in BPFTO-05 and BPFTO-10, respectively, in the frequency region of 800–1500 cm$^{-1}$. The peak position of the scattering frequency of two-magnon may be equal to twice energy of zone boundary magnon estimated from the exchange parameters of prepared ceramics [20]. We have observed peaks at 1107 (1108) cm$^{-1}$ and 1279 cm$^{-1}$ for BPFTO-05 and BPFTO-10 samples. The above explained peaks were assigned as the two-phonon Raman scattering process of the prepared samples [45].

4. Conclusions

In conclusion, Bi$_{1-x}$Pb$_{x}$Fe$_{1-y}$Ti$_{y}$O$_{3}$ (x = 0.05, 0.1) polycrystalline bulk ceramics were synthesized by the conventional solid-state route. X-ray diffraction along with the Rietveld refinement show that BPFTO-05 and BPFTO-10 samples have (R3c) and (R3c + P4mm) symmetry, respectively, which are confirmed by Raman scattering data. Through the magnetic data, we have observed the spin re-orientation transition above 100 K. It is necessary to use advanced techniques such as neutron scattering to study the properties of observed phenomena in more detail.

Data Availability

The data used to support the findings of this study are included within the article and are available from the corresponding author upon request.

Disclosure

The manuscript is presented in abstract form at the International Conference on Minerals Metallurgy and Materials.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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