



Sr and Pb co-doping effect on the crystal structure, dielectric and magnetic properties of BiFeO₃ multiferroic compounds



Xueyou Yuan, Lei Shi^{*}, Jiying Zhao, Shiming Zhou, Yang Li, Changzheng Xie, Jianhui Guo

Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui, 230026, People's Republic of China

ARTICLE INFO

Article history:

Received 10 January 2017

Received in revised form

23 February 2017

Accepted 27 February 2017

Available online 28 February 2017

Keywords:

BiFeO₃

Sr/Pb co-doping

Dielectric property

Magnetization

ABSTRACT

Bi_{1-x}(Sr_{1/2}Pb_{1/2})_xFeO₃ (0.10 ≤ x ≤ 0.30) multiferroic compounds have been synthesized by a conventional solid-state reaction. The influences of A-site Sr/Pb co-doping on the structure, dielectric and magnetic properties of BiFeO₃ are investigated systematically. X-ray diffraction reveals that the crystal structure of Bi_{1-x}(Sr_{1/2}Pb_{1/2})_xFeO₃ transforms from the rhombohedral symmetry (space group *R3c*) to the cubic symmetry (space group *Pm3̄m*) with Sr/Pb concentration increasing. Meanwhile, the intensities of Bi–O bond vibrations continuously decrease and finally disappear. The RT polarization versus electric field (P–E) curves confirm the ferroelectric nature for all the samples. Furthermore, it is found that the dielectric constant and dielectric loss tangent of the samples measured in the frequency range of 100–10⁷ Hz decrease drastically at room temperature. A considerable reduction in the leakage current is observed for BFO with Sr/Pb doping content increasing. The ferromagnetic property enhances with the Sr/Pb substitution increasing, which is ascribed to the cooperation of the Fe²⁺–O–Fe³⁺ double exchange interaction and the effective suppression of antiferromagnetic cycloidal spin structure caused by the crystalline structure transformation. All results indicate that the Sr and Pb co-doping can effectively improve the magnetic and high-frequency dielectric properties of the multiferroic BiFeO₃ compounds.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Multiferroic materials, which display two or more order parameters (ferroelectricity, ferromagnetism, and ferroelasticity) simultaneously, have attracted an intense interest due to their rich physics and potential applications, such as sensors, spintronics, information storage and multiple-state memory devices [1–6]. However, multiferroic materials coupled ferroelectricity and ferromagnetism are scarce, and most of them show their multiferroic properties well below room temperature (RT). Among them, BiFeO₃ (BFO) is one of the rare single-phase multiferroic materials above RT because of its high Curie temperature (*T*_C ~ 1103 K) and Néel temperature (*T*_N ~ 643 K) [7,8]. The stoichiometric BFO possesses a rhombohedrally distorted perovskite structure with polar *R3c* symmetry represented by an antiphase rotation of the adjacent FeO₆ octahedra (Glazer notation *a*[−]*a*[−]*a*[−]) [9] and G-type antiferromagnetic structure. In BiFeO₃, the off-center distortion derives from the stereoactive lone pair of electrons of Bi³⁺ ions. The

hybridization between Bi 6s and O 2p is responsible for the ferroelectricity, and the Fe–O–Fe superexchange interactions mainly dominate the ordered magnetic structure [10–13]. Although the macroscopic magnetization originated from the Dzyaloshinsky–Moriya (DM) interaction is permitted in *R3c* symmetry, any net magnetization would be cancelled out, since a cycloidal spatially modulated spiral spin structure with a period of approximately 62 nm is superimposed onto the G-type antiferromagnetic spin ordering [14–16]. Thus, the linear magnetoelectric effect (ME) is very weak, which limits its practical application. The improvement of ferromagnetism is a key factor for the enhancement of the ME. It is well known that A-site rare-earth substitutions could result in suppression of inhomogeneous cycloid spin structure. For instance, enhanced magnetization has been observed in Bi_{1-x}RE_xFeO₃ (RE = La, Pr, Nd, Gd, Sm, Ho, Tb, Dy etc.) ceramics [17–22]. Meanwhile, spontaneous magnetization is also observed in the diamagnetically substituted Bi_{1-x}A_xFeO_{3-δ} (A = Ca, Sr, Pb, Ba) compounds [23–28]. It is noteworthy that the magnetic field induced polarization (*P*_r = 96 μC/cm², at 10 T) in Bi_{0.75}Sr_{0.25}FeO_{3-δ} compounds is close to the highest value reported in BFO based systems [29]. In contrast to the situation of the rare-earth

^{*} Corresponding author.

E-mail address: shil@ustc.edu.cn (L. Shi).

substitutions, the cycloid spin structure and the crystal structure change simultaneously in diamagnetical substitutions. Besides, since their similar electronic structure to that of Bi ions, Pb ions can be introduced at the A-site as a donor dopant to reduce Fe^{3+} to Fe^{2+} ions [30], which is presumably compensated by oxygen vacancies. Moreover, the existence of Pb^{4+} ions can compensate the valence change caused by Sr^{2+} dopant.

In this paper, Sr and Pb co-doped polycrystalline BFO compounds have been synthesized by a conventional solid-state reaction and the crystal structure, dielectric property and magnetization are systematically investigated. It is found that Sr and Pb co-doped BFO compounds exhibit enhanced magnetization and high-frequency dielectric properties at RT, which implies that Sr/Pb co-substitution is one of the effective ways for improving the ferromagnetic and the high-frequency dielectric properties of BFO-based compounds.

2. Experimental details

Polycrystalline $\text{Bi}_{1-x}(\text{Sr}_{1/2}\text{Pb}_{1/2})_x\text{FeO}_3$ ($x = 0.10, 0.18, 0.20, 0.30$) samples were prepared by a rapid two-stage solid-state reaction started from the high purity oxides of Bi_2O_3 , Fe_2O_3 , SrCO_3 and PbO . The raw oxides were first homogenized for 2 h in an agate mortar and then annealed at 825°C for 30 min in air. After mixed and grinding, the mixture was pressed into disks with 10 mm in diameter and about 1 mm in thickness. The disks were sintered at 920°C for 15 min. The rapid synthesis method was used to prevent extensive evaporation of Bi_2O_3 and PbO and to avoid any impurity. The phase structures of the compounds were characterized by X-ray diffraction (XRD) at RT using a Rigaku TTR III X-ray diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.54187 \text{ \AA}$) radiation and the Raman spectra in the backscattering geometry were measured on a JY LABRAMHR Raman spectroscopy with an Ar^+ ($\sim 514.5 \text{ nm}$) laser as an excitation light source. The valence state of Fe ions was investigated by X-ray photoelectron spectroscopy (XPS, ESCA-LAB25Xi, Thermo, USA). The dielectric characters were measured with an impedance analyzer (HP 4294A, Agilent, USA) in the frequency range from 100 Hz to 10 MHz at RT. The temperature dependent magnetizations for all samples were collected by Superconducting Quantum Interference Device (SQUID) from Quantum Design. The magnetization hysteresis (M-H) curves of the compounds were recorded on a Vibrating Sample Magnetometer (VSM, Quantum Design, USA) at RT in the fields between $-2 \text{ T} \leq H \leq 2 \text{ T}$.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of $\text{Bi}_{1-x}(\text{Sr}_{1/2}\text{Pb}_{1/2})_x\text{FeO}_3$ ($0.10 \leq x \leq 0.30$) compounds at RT. It is found that all the compounds are single phase without a detectable secondary phase within the limit of X-ray detection, which is typically 1%. The splitting peaks at 2θ of about 32° , 39° , 52° , and 57° , indexing to the rhombohedral structure (space group $R3c$), trend to merge and form single diffraction peaks with Sr/Pb co-doping content increasing. The enlarged portion of the XRD patterns around 32° is shown in Fig. 1(b), where the (104) peak shifts toward a higher angle and combines with the (110) peak to form a broadened peak, suggesting that the crystal structure transforms from rhombohedral to cubic structure (space group $Pm\bar{3}m$) with Sr/Pb co-doping content increasing. The lattice parameters of $\text{Bi}_{1-x}(\text{Sr}_{1/2}\text{Pb}_{1/2})_x\text{FeO}_3$ ceramics are listed in Table 1, which are similar to the results observed in $\text{Bi}_{1-x}\text{Sr}_x\text{FeO}_3$ and $\text{Bi}_{1-x}\text{Pb}_x\text{FeO}_3$ solid compounds [31,32]. All diffraction peaks shifting to higher angles indicates the decreases of the lattice constant and unit cell volume, which can be attributed to the decrease of A-site average ionic radius, indicating that it is Pb^{4+}

($0.775 \text{ \AA}$) ion rather than Pb^{2+} ($1.19 \text{ \AA}$) ion is induced, because only the average ionic radius of Pb^{4+} and Sr^{2+} ($1.18 \text{ \AA}$) ions is smaller than that of Bi^{3+} ions ($1.03 \text{ \AA}$).

To ascertain Sr/Pb doping level in the BFO compounds, EDX analyses were done on all of them. The representative energy dispersive spectra of $\text{Bi}_{0.8}(\text{Sr}_{1/2}\text{Pb}_{1/2})_{0.2}\text{FeO}_3$ and $\text{Bi}_{0.7}(\text{Sr}_{1/2}\text{Pb}_{1/2})_{0.3}\text{FeO}_3$ compounds are shown in Fig. 2, confirming the presence of expected amounts of Bi, Sr, Pb, Fe and O in the samples. The atomic ratios of Bi: Sr: Pb: Fe are approximately 0.732: 0.095: 0.086: 1 and 0.68: 0.146: 0.131: 1 for $\text{Bi}_{0.8}(\text{Sr}_{1/2}\text{Pb}_{1/2})_{0.2}\text{FeO}_3$ and $\text{Bi}_{0.7}(\text{Sr}_{1/2}\text{Pb}_{1/2})_{0.3}\text{FeO}_3$ compounds, respectively, which are very close to the expected values and trend.

Raman spectra of $\text{Bi}_{1-x}(\text{Sr}_{1/2}\text{Pb}_{1/2})_x\text{FeO}_3$ ($0.10 \leq x \leq 0.30$) compounds were measured at RT, as shown in Fig. 3. The standard Raman modes of the rhombohedral BFO are given as: $\Gamma = 4A1 + 9E$ [33–35]. It can be found that four A1 modes and seven E modes appear in the Raman spectra of the compounds except the sample with $x = 0.30$. With increasing x , the intensity of Raman A1 modes decreases and the peak becomes slightly broader. It was reported that the low frequency A1-1, A1-2, A1-3 and E-3 ($\sim 278 \text{ cm}^{-1}$) phonon modes are governed by the Bi–O covalent bonds [34], while the E modes at high frequency are related to the changing of Fe–O bonds [36]. Here, the intensity decreases of A1-1, A1-2, A1-3 and E-3 modes indicate the disorder increase of the local structure (or the element arrangement) at Bi-site induced by the Sr/Pb co-doping [37]. While $x = 0.30$, some Raman peaks corresponding to A1 modes disappear and only three broader peaks can be observed. J. Bielecki et al. reported that A1-1 and A1-2 modes are related to the structural distortions away from the ideal cubic $Pm\bar{3}m$ structure [38]. From this point, the disappearance of A1 modes for $x = 0.30$ sample reveals that the structure of $\text{Bi}_{0.7}(\text{Sr}_{1/2}\text{Pb}_{1/2})_{0.3}\text{FeO}_3$ ceramics has become into cubic one with space group $Pm\bar{3}m$, which is consistent with the above-mentioned XRD results. Besides, the Raman peak positions move to higher frequency with increasing Sr/Pb content, which is attributed to the lower mean mass of Sr and Pb ions in contrast with that of Bi ions. To reveal the possible valence of Pb ions in $\text{Bi}_{1-x}(\text{Sr}_{1/2}\text{Pb}_{1/2})_x\text{FeO}_3$ ceramics, the Raman spectra of $\text{Pb}(\text{NO}_3)_2$ and PbO_2 were measured and shown in Fig. 3 simultaneously. By comparison, it can be found that the spectra of Pb/Sr co-doped samples at lower frequency closely coincide with that of PbO_2 , suggesting again that the valence of Pb ions is +4. Meanwhile, the intensity increase and blue shift of E-9 mode with the increment of Sr/Pb co-doping content can be easily observed, which indicates the Fe–O bond shortening along with

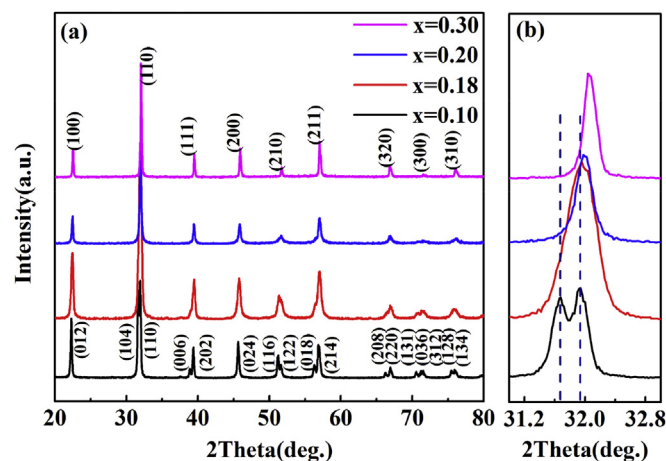


Fig. 1. (a) XRD patterns for $\text{Bi}_{1-x}(\text{Sr}_{1/2}\text{Pb}_{1/2})_x\text{FeO}_3$ compounds; (b) enlarged view of XRD patterns at the range of 2θ from 31° to 33° .

Download English Version:

<https://daneshyari.com/en/article/5459494>

Download Persian Version:

<https://daneshyari.com/article/5459494>

[Daneshyari.com](https://daneshyari.com)