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Structure analysis and multiferroic properties of Zr^{4+} doped $BiFeO_3$ ceramics

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Abstract

Zr^{4+} doped multiferroic ceramics samples $BiFe_{1-x}Zr_xO_3$ ($x=0$, 0.02, 0.04, 0.06, 0.08, 0.10) were prepared by a solid state reaction method and characterized by X-ray diffraction and X-ray Absorption Fine Structure analysis. X-ray diffraction analysis showed that the characteristic peaks of samples were shifted toward a lower angle with the increase of Zr^{4+} doping concentration. It indicated that the doped Zr^{4+} ions entered into the crystal lattice. The length of Zr–O bond was calculated based on the results of X-ray Absorption Fine Structure analysis. The abnormal dielectric constant near the Neel temperature of $BiFe_{1-x}Zr_xO_3$ indirectly demonstrated the coupling between magnetic and electric properties of $BiFe_{1-x}Zr_xO_3$. The Neel temperature of Zr^{4+} doped $BiFeO_3$ was ~20 °C lower than that of the undoped $BiFeO_3$. The Neel temperature of $BiFe_{1-x}Zr_xO_3$ will be different if the doping amount of Zr^{4+} is different. However, all the prepared samples are antiferromagnetic.

Keywords: B. X-ray methods; C. Ferroelectric properties; C. Magnetic properties; E. Functional applications

1. Introduction

Multiferroic materials have attracted great attention because of two reasons. One is the potential applications in multifunctional sensors, convertors and microelectronic devices [1,2]. The other is their interesting physical problems, for example, the coupling between magnetic order parameters and electric order parameters [3,4]. As other important multiferroic materials, $BiFeO_3$ possesses ferroelectricity, anti-ferromagnetism and ferroelasticity [5]. Furthermore, $BiFeO_3$ is the only single-phase multiferroics, which has both Curie temperature (T_C, 1103 K) and Neel temperature (T_N, transition temperature from anti-ferromagnetism to para-magnetism, 643 K) above room temperature [6]. It is a good candidate for making lead-free ferroelectric memory devices due to its large spontaneous polarization (P_S, 88–100 μC/cm^2) [5] and high T_C [7,8]. However, its main drawback, the relatively high leakage current, impedes its further applications. The leakage current is caused by oxygen vacancies and Fe^{2+} in $BiFeO_3$. Oxygen vacancies come from the evaporation of Bi, and Fe^{2+} comes from the reduction of Fe^{3+}[9].

Although the impurity phases are inevitable in $BiFeO_3$ ceramic materials prepared by the solid state reaction method [6], it has been demonstrated that there is no correlation between the impurity phase intensity in XRD patterns and the leakage current [10–12]. Many methods have been tried to decrease the leakage current of $BiFeO_3$, such as aliovalent-ion-doping [9], rapid liquid phase sintering [12], thin film, etc. [7,13,14]. As for $BiFeO_3$ ceramics samples prepared by the solid state reaction method, doping is a main and convenient approach to decrease the leakage current. Decrease in the leakage current of Zr^{4+} doped $BiFeO_3$ prepared by the solid state reaction method was reported previously and the enhanced properties could be attributed to the change in the conduction mechanism and the competition of two different charge-compensation ways [15]. In this paper, the further discussions on Zr^{4+} doped $BiFeO_3$ prepared by the solid state reaction method will be carried out, such as the differences between Fe–O and Zr–O bond, and the resultant effect on the dielectric and magnetic properties.

2. Experiments

$BiFe_{1-x}Zr_xO_3$ (BFZO, $x=0$, 0.02, 0.04, 0.06, 0.08, 0.10) samples were prepared by a solid state reaction method.

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The analytical purity regents of Bi_2O_3, Fe_2O_3 and ZrO_2 were mixed in a stoichiometric ratio with 3% (mol) extra Bi_2O_3 considering its evaporation. The mixture was milled for 24 h and then calcined in the air at 600 °C for 2 h. Then the calcined powder was milled again and pressed into pellets with 15 mm diameter and 2 mm thickness at the pressure of 135 MPa. The pressed pellets were sintered at 820 °C in the air for 50 min in an alumina crucible. After sintering, the samples with the crucible were immediately taken out from the furnace.

X-ray diffraction (D8 Advance) with $CuK\alpha_1$ was used to analyze the phase of BFZO. X-Ray Absorption Fine Structure (XAFS) analysis was carried out with BL14W1 beam line in Shanghai Synchrotron Radiation Facility (SSRF). Ifeffit software was used for XAFS data processing. For the electric properties measurement, the as-sintered BFZO pellets were well polished as thin as 1 mm, and silver paste was pasted on the both sides as the electrodes. Agilent 4284A Precision LCR Meter was used to measure the dielectric properties. Magnetic properties were measured by vibrating sample magnetometer (VSM, Quantum Design).

3. Results and discussions

Fig. 1 (a) shows the XRD patterns of BFZO samples. All the XRD patterns indicate that it is a typical rhombohedral structure. There are two kinds of impurities in the BFZO samples, which are $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$, according to the XRD results. The impurities are due to the decomposition of $BiFeO_3$ at 720–1040 K during the cooling process from the sintering temperature [6]. As a result, the impurities are inevitable in $BiFeO_3$ prepared by the solid state reaction method. Although there are a few impurity phase (≤10%) showed in the patterns, the electrical properties of samples would not be affected [10–12]. It is found that the typical diffraction peaks are shifted toward a lower angle in Fig. 1(b) and (c). It means that Zr^{4+} ions are entered into the crystal lattice. Because the radius of Zr^{4+} ion (0.72 Å) is larger than that of Fe^{3+} ion (0.65 Å)[16], the unit cell size of BFO would be distorted and enlarged when Zr^{4+} entered into the lattice. As a result, the diffraction peaks of BFZO samples in XRD patterns would be shifted toward a lower angle. For further analysis, the neighbor coordinate conditions of Zr^{4+} ions in BFZO will be investigated by XAFS.

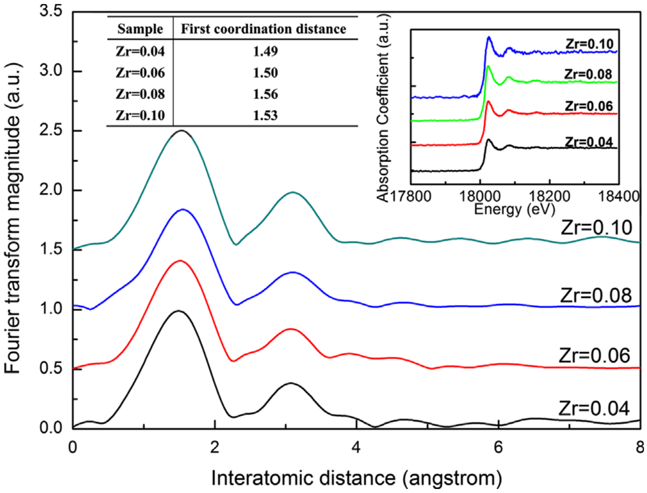
Fig. 2 shows the variation of Fourier transformed XAFS spectra of Zr K edge vs. the neighbor interatomic distance. Due to the time limitation of XAFS experiment, the sample of $x=0.02$ is not tested. The corresponding original data of X-ray absorption spectroscopies of K edge of Zr^{4+} ions are depicted in the inset of Fig. 2.

The original XAFS data are processed with Ifeffit software (free download, http://cars9.uchicago.edu/ifeffit/) based on the following theory reported by Stern, Sayer, and Lytle in 1975.[17,18]

The origin XAFS data is the relationship between $\mu(E)$ and E,

$$\mu(E) \sim E \tag{1}$$

$\mu(E)$: absorption coefficient.



Sample	First coordination distance
Zr=0.04	1.49
Zr=0.06	1.50
Zr=0.08	1.56
Zr=0.10	1.53

Fig. 2. Fourier transformed XAFS spectrum of Zr K edge.

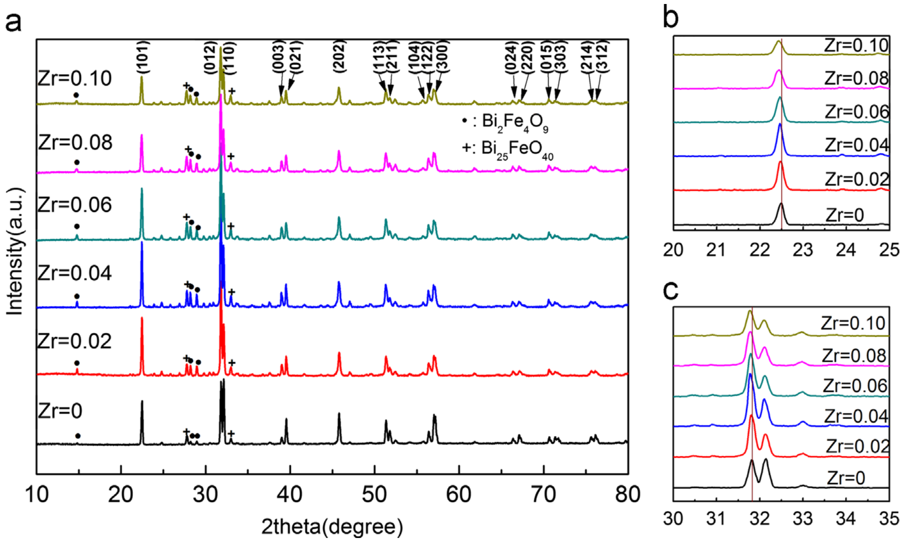


Fig. 1. The XRD patterns of BFZO.