Structural phase transition and magnetic properties of Er-doped BiFeO$_3$ nanoparticles

Y T Li$^{1,2}$, H G Zhang$^1$, X G Dong$^1$, Q Li$^{1,3}$, W W Mao$^2$, C L Dong$^2$, S L Ren$^2$, X A Li$^2$ and S Q Wei$^3$

$^1$Physics Department, Southeast University, Nanjing, 211189, P. R. China
$^2$College of Science, Nanjing University of Post and Telecommunications, Nanjing, 210046, P. R. China
$^3$National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, 230029, P. R. China

E-mail: qli@seu.edu.cn

Abstract. The structural phase transition and local structural distortion of Er-doped BiFeO$_3$ nanoparticles have been discussed in order to understand the variation of magnetic properties in this system. The X-ray diffraction patterns and X-ray absorption fine structure of these samples demonstrate that there is structural phase transition and no obvious local structural distortion with the increasing of doping concentration. Unfortunately, no ferromagnetic properties have been observed even at a lower temperature. And the X-ray absorption spectra of Fe 2p core level of these samples are totally same, especially the energy positions do not shift which means the consistent valence states of Fe ions.

1. Introduction

The compound BiFeO$_3$ with electrical and magnetic ordering is one of the potential materials in novel storage media and spintronics devices [1]. It behaves ferroelectric properties at room temperature since its ferroelectric phase transitional temperature is 836ºC, which is testified by the observation of ferroelectric/ferroelastic single domain by polarized light microscopy [2]. Although the ferroelectric nature of BiFeO$_3$, it is actually antiferromagnetic ordering above room temperature. Thus, many researchers are engaged in releasing the ferromagnetism from space-modulated spin structure. As to spin structure of BiFeO$_3$, there are partially filled 3d orbits of Fe$^{3+}$ ion which lead to G-type canted antiferromagnetic order with an incommensurately space-modulated spin structure along the (110)$_h$ direction on a long wavelength of 62 nm [3, 4]. In order to obtain good ferromagnetic properties at room temperature, many ways have been taken by researchers to destroy the modulated spin structure, such as substitution for A-site by rare-earth element with different ion radius [4] and preparation of thin film deposited on different substrates [5].

In our paper, the samples Er-doped BiFeO$_3$ nanoparticles have been prepared by sol-gel method in order to investigate the influence on magnetism of structural distortion caused by Er$^{3+}$ ions (ion radius 0.088 nm) doping. Moreover, there is little literature until now studying the relationship between magnetism and local structure distortion for Er-doped BiFeO$_3$. Our results demonstrate that no obvious ferromagnetic properties have been observed even at lower temperature, although the structural phase transition and local structural distortion have been caused by Er ions doping.
2. Experiment
Polycrystalline Bi$_{1-x}$Er$_x$FeO$_3$ ($x = 0, 0.05, 0.1, 0.15$) nanoparticles have been prepared by sol-gel method. Highly pure Bi$_2$O$_3$, Er$_2$O$_3$, Fe(NO$_3$)$_3$·9H$_2$O powders were mixed into mixture solution by dilute nitric acid with appropriate composition. Tartaric acid as organic complex was put into the mixture, then preheated at 80 ºC for 4 h until dissolution. The solution was heated at 140 ºC for 5 h. The formed gel precursor was dried at 250 ºC. The target product was obtained by annealing the precursor at 550 ºC for 2 h.

The crystalline qualities of the samples were assessed using X-ray diffractometer (D/Max 2000) with Cu$\text{K}_{\alpha}$ radiation at room temperature. The corresponding images of the resulting nanoparticles were obtained via scanning electron microscopy (SEM, HITACHI S4800). The Magnetizations with a function of temperature and magnetic field were performed by PPMS (Quantum Desgin-9). X-ray absorption fine structure (XAFS) spectra of Fe $K$-edge of samples were measured at beamline U7C at National Synchrotron Radiation Laboratory (NSRL), University of Science and Technology of China (USTC). X-ray absorption spectra (XAS) of Fe $2p$ core level of those samples were measured at Beijing Synchrotron Radiation Facility (BSRF).

3. Results and Discussion

The X-ray diffraction (XRD) patterns are shown in Fig. 1 that there is single-well phase with BiFeO$_3$ perovskite structure and no obvious secondary phase is detected in Bi$_{1-x}$Er$_x$FeO$_3$ ($x = 0, 0.05, 0.1, 0.15$). It also notes that the structural phase transition occurs by increasing doping concentration of Er ions, which is also consistent with the results in literature [4, 6]. For samples $x=0, 0.05$, they belongs to rhombohedral lattice type with $R3c$ space group. The structural transformation begins when $x = 0.1$, a transitional state with triclinic structure is tended to be shown. As $x = 0.15$, an orthorhombic lattice structure with $Pn2_1a$ space group is transformed.

Fig. 2 presents the radial structure function curves of samples $x = 0, 0.05, 0.1$ which is obtained from the normalized XAFS spectra via Fourier transformation using USTCXAFS2.0 code [8]. In this figure, the first peak at near 0.15 nm is the first nearest neighbor coordination of center atom Fe. There is no obvious change as the doping concentration increasing, although the structural phase transition is occurred. It demonstrates that the local structural distortion, especially for the Fe-O-Fe
distortion, is not significantly affected by the Er ions doping, although there is unequivocal variation of ions radius between Er ions and Bi ions.

Now that there is no obvious local structural distortion of Fe-O-Fe bonds, the space-modulated spin structure would not be destroyed based on the deduction in the part of Introduction. Therefore, the weak ferromagnetism will not be released and no room temperature ferromagnetism will be observed. The temperature dependence of magnetization of samples $x = 0.05$ and 0.1 has been measured which is shown in Fig. 4. The pure BiFeO$_3$ nanoparticle behaves paramagnetism at room temperature which will be published elsewhere [9]. Both the temperature dependence of magnetization with external field $H = 500$ Oe and magnetic field dependence of magnetization at lower temperature $T = 5$K indicate that there is no ferromagnetism observed even at lower temperature and the value of magnetization at lower temperature and higher magnetic filed is quite small, not to mention the magnetic properties at room temperature. These results are inconsistent with literatures reported [4, 6, 10], where structural phase transition occurred by ions doping at Bi-site induces room temperature ferromagnetism. In our case, although structural phase transition occurs, there is no obvious local structure distortion which will not destroy the space-modulated spin structure. From this point of view, non-ferromagnetism of the samples may be easily explained.

![Fourier transform of Fe K-edge XAFS spectra of Bi$_{1-x}$Er$_x$FeO$_3$ (x = 0, 0.05, 0.1).](image1)

**Fig. 3** Fourier transform of Fe K-edge XAFS spectra of Bi$_{1-x}$Er$_x$FeO$_3$ (x = 0, 0.05, 0.1).

![Temperature dependence of magnetization (M–T) of Bi$_{1-x}$Er$_x$FeO$_3$ (x = 0.05, 0.1) nanoparticles with an external field H= 500 Oe. The inset shows the M–H curves of Bi$_{1-x}$Er$_x$FeO$_3$ (x = 0.05, 0.1) nanoparticles at temperature T = 5 K.](image2)

**Fig. 4** Temperature dependence of magnetization (M–T) of Bi$_{1-x}$Er$_x$FeO$_3$ (x = 0.05, 0.1) nanoparticles with an external field $H= 500$ Oe. The inset shows the $M$–$H$ curves of Bi$_{1-x}$Er$_x$FeO$_3$ (x = 0.05, 0.1) nanoparticles at temperature $T = 5$ K.

![X-ray absorption spectroscopy of Fe 2p core level of Bi$_{1-x}$Er$_x$FeO$_3$ (x = 0.05, 0.1) nanoparticles at room temperature.](image3)

**Fig. 5** X-ray absorption spectroscopy of Fe 2p core level of Bi$_{1-x}$Er$_x$FeO$_3$ (x = 0.05, 0.1) nanoparticles at room temperature.
Besides the local structure distortion, variation of valence states of Fe ions is another factor to induce ferromagnetism for doped BiFeO$_3$ samples [11], even though it is not one of the necessary factors [6]. D. Kothari et al. [6] have reported the multiferroic properties of Eu doped BiFeO$_3$ which is not due to Fe multiple valence but to the structural distortions. Here, the XAS spectra of Fe 2$p$ core level at room temperature are shown in Fig. 5. It can be seen that two main peaks of 2$p_{3/2}$ and 2$p_{1/2}$ are located at energy position of 726.6eV and 713.4eV, respectively. For the two samples, the energy position of Fe 2$p_{3/2}$ is totally same, which means the same valence states of Fe ions and no variation of valence states.

In summary, only structural phase transition can not drive room temperature ferromagnetism without variation of local structural distortion and valence states of Fe ions for Er-doped BiFeO$_3$ samples.

4. Conclusion
In this paper, the structural phase transition and local structural distortion of the Er-doped BiFeO$_3$ nanoparticles have been discussed. The XRD patterns and XAFS of these samples demonstrate that there is structural phase transition but on obvious local structural distortion with the increasing of doping concentration. And the XAS of Fe 2$p$ core level of these samples are totally same, which means the consistent valence states of Fe ions. Only the structural phase transition can not drive the magnetism change of Er-doped BiFeO$_3$ nanoparticles. Perhaps there is some kind of correlation between the magnetism of doped BiFeO$_3$ and the local structural distortion and valence states of Fe ions.

5. Acknowledgement
We are indebted to NSFC for its financial support to our research projects No.10979016 and No.51172110 and to NSRL and BSRF for their beamtime. Further more, this work is also supported by Nanjing University of Posts and Telecommunications under research project No. NY211144 and No.NY208027 as well.

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