

Study of enhanced magnetism in Lu doped multiferroic bismuth ferrite



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ABSTRACT

In this work, the enhancement in magnetic moment in Lu doped BiFeO₃ is reported. Sol–gel synthesized Bi_{1-x}Lu_xFeO₃ ($x=0, 0.02, 0.04$ and 0.05) were characterized for their phase, magnetic properties, thermal analysis and Raman scattering studies. The X-ray diffraction study revealed the segregation of rare earth garnet as secondary phase. The presence of garnet phase was reiterated in the magnetization measurements with Curie temperature at 575 K. The DSC and the Raman spectrum once again ascertain the garnet phase in the compound. We believe that the instability in the structure with lower dopant ionic radii resulted in increase in segregation of garnet and hence enhanced the magnetic moment in rare earth doped BiFeO₃ samples. We suggest that the increase in magnetic moment with decrease in rare earth dopant ionic radii reported in the literature could have a strong correlation with the structural instability and the related secondary phase segregation.

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1. Introduction

Bismuth iron oxide (BiFeO₃) is an important class of multifunctional material among the known multiferroic oxides because of its high ferroelectric Curie temperature (1083 K) and antiferromagnetic Néel temperature (643 K) [1]. It has application potential in the field of transducers, actuators, memory devices and spintronics etc. Large switchable polarization (90 $\mu\text{C}/\text{cm}^2$) and the interesting domain structure make it an attractive candidate for ferroelectric tunnel junctions [2]. However its application potential with respect to its magnetic property has rarely been investigated. This is because of its weak magnetic characteristics. In its distorted rhombohedral structure, the spins are ferromagnetically aligned along (1 1 1) plane but the adjacent planes are antiferromagnetically aligned with slight canted angle. Hence the crystal shows weak ferromagnetism due to canted antiferromagnetic coupling between (1 1 1) planes with resultant non-zero magnetic moment in the unit cell. However, the canted magnetic moment rotates in a spiral direction and forms a spiral spin structure with a period of 62 nm which cancels out the net magnetization in the bulk [3,4]. There are several reports showing enhanced magnetism in BiFeO₃ by doping elements varying from rare earth [5–9] to alkaline

earth to transition metal series [10–13]. Several arguments are put forward to explain the enhanced magnetic behavior such as destruction of the spiral spin arrangement [5,6], the size dependent suppression of spiral spin structure [7], uncompensated spins at the surface of nanoparticles [8], ferromagnetic coupling between the rare earth and iron ions [9], and change in Fe–O–Fe bond angle etc. [14]. Besides that Fe₂O₃, Fe₃O₄, Bi₂Fe₄O₉, and Bi₂₅FeO₄₀ secondary phases could contribute to magnetization in doped BiFeO₃ [15]. Recently we have reported a strong evidence for the presence of R₃Fe₅O₁₂ garnet phase in rare earth doped BiFeO₃ that may be one of the reasons for the reported enhancement in magnetization [16]. Looking at the application potential of BiFeO₃, it is important to address this issue in an unambiguous way. In the distorted rhombohedral structure, the A-site ion can easily accommodate the higher ionic radii dopant than the one with lower ionic radii without affecting structural stability. Since the BiFeO₃ has distorted rhombohedral structure, the dopant ion with lower ionic radii can lead to structural instability and hence the higher segregation of the impurity phases which can be characterized convincingly (which is otherwise difficult to see in routine measurements). In this work we have chosen the rare earth Lu ion, which has lowest ionic radii, as the dopant and investigated the properties of Bi_{1-x}Lu_xFeO₃ ($x=0, 0.02, 0.04$ and 0.05) sample. The structural, magnetic, thermal and Raman studies are presented in this manuscript. The results clearly confirm that the enhancement in magnetic moment in rare earth doped BiFeO₃ could indeed

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originate from the segregation of the garnet $R_3\text{Fe}_5\text{O}_{12}$ as secondary phase.

2. Materials and methods

The parent compound BiFeO_3 (BFO) and $\text{Bi}_{1-x}\text{Lu}_x\text{FeO}_3$ ($x=0, 0.02, 0.04$ and 0.05) powders are synthesized by sol-gel method. The precursors used are bismuth acetate, iron acetylacetonate and rare earth nitrates. For the synthesis, the stoichiometric amount of the required precursors are mixed and stirred vigorously for 30 min at 70°C in a magnetic stirrer until the formation of a homogeneous solution. Then 2 molar citric acid is added to the mixture as a gelating agent, stirred for 6 h until the solution turned into brown gel. The final gel is dried and preheated at 400°C for 30 min followed by calcination at 800°C for 2 h. The calcinated powder is then characterized for their phase formation by X-ray diffraction (XRD) analysis using a PANalytical X'Pert Pro X-ray diffractometer, magnetic properties by vibrating sample magnetometer (VSM) using LAKESHORE model, thermal properties by differential scanning calorimetry using NETZSCH DSC 204 F1 Phoenix and Raman studies using Horibon Vyon spectrometer.

3. Results and discussion

The XRD patterns of the parent BFO and the doped BLFO samples for 2θ ranging from 20° to 60° are shown in Fig. 1(a)–(d). BFO is indexed to rhombohedral structure with $R3c$ space group. The pattern for BFO did not reveal any visible peaks representing secondary phases. Similarly, the pattern for $x=0.02$ sample shown in Fig. 1(b) also did not reveal any visible secondary phases. On the other hand, the patterns for $x=0.4$ and $x=0.5$ samples shown in Fig. 1(c) and (d) show peaks corresponding to rhombohedral BFO along with additional peaks (marked by * symbol) representing secondary phases. These additional peaks are indexed to $\text{Lu}_3\text{Fe}_5\text{O}_{12}$ garnet phase. Note that these peaks were not visibly seen in the

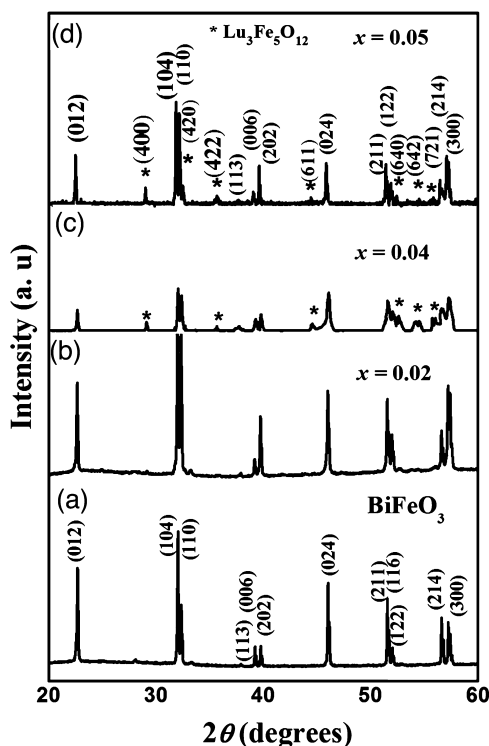


Fig. 1. XRD of pure BiFeO_3 and $\text{Bi}_{1-x}\text{Lu}_x\text{FeO}_3$ ($x=0.02, 0.04$ and 0.05) samples.

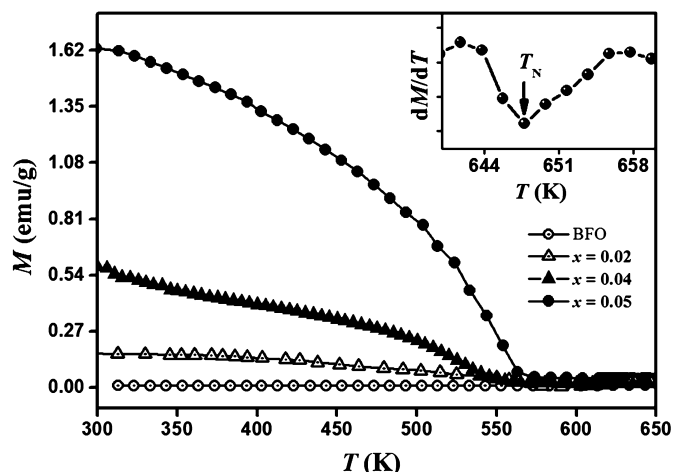


Fig. 2. Temperature (T) dependent magnetization (M) curve from 300 K to 600 K for BiFeO_3 and $\text{Bi}_{1-x}\text{Lu}_x\text{FeO}_3$ ($x=0.02, 0.04$ and 0.05) samples under 500 G magnetic field. dM/dT versus T of BiFeO_3 is shown in the inset.

reported [16] BFO doped with rare earth ion such as Ho, Er and Y whose ionic radii are higher than Lu^{3+} ion.

Temperature (T) dependent magnetization (M) for BFO and the doped BFO samples measured from 300 K to 680 K under an applied field of 500 G are shown in Fig. 2. All the doped samples show an increase in magnetization starting at 575 K down to 300 K. But, no such anomaly is observed for bare BFO as shown in the graph. The paramagnetic to ferromagnetic transition observed around 575 K is nearly matching with the ferromagnetic Curie temperature of $\text{Lu}_3\text{Fe}_5\text{O}_{12}$ garnet [17]. The antiferromagnetic Néel temperatures for both BFO and BLFO samples (retrieved from dM/dT versus T curve shown in the inset of Fig. 2 for BFO sample) are around 647 K which is matching with the bulk BFO sample.

We have performed the magnetization versus field at 300 K for all the samples. For comparison, we show the data for $x=0.05$ sample along with the data for Ho, Er and Y doped BFO samples in Fig. 3. From the graph it is inferred that the magnetic moment of Y^{3+} , Ho^{3+} , Er^{3+} and Lu^{3+} doped BFO are 0.43 emu/g, 0.56 emu/g, 0.60 emu/g, and 0.67 emu/g at 0.8 kOe, respectively. The magnetization is enhanced with decrease in dopant ionic radii with the maximum magnetization observed for Lu doped sample having the least ionic radii. The ionic radii of Bi^{3+} , Y^{3+} , Ho^{3+} , Er^{3+} and Lu^{3+} by considering the 6 coordination number of the ions are 1.17 Å,

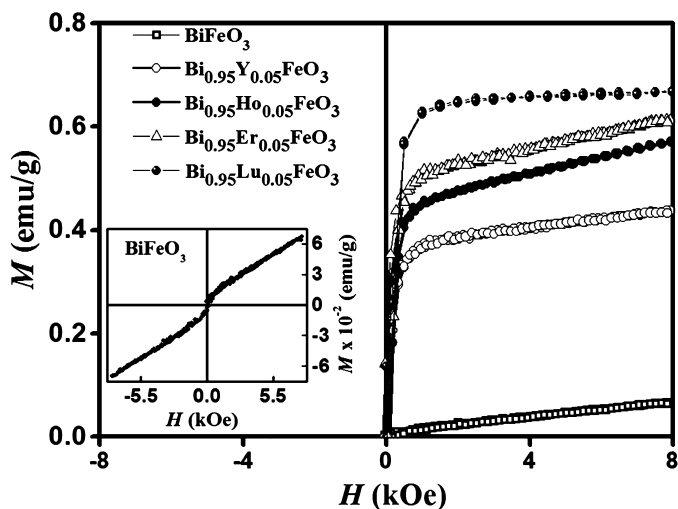


Fig. 3. M versus H measured at 300 K for bare BiFeO_3 and doped BiFeO_3 samples.

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