

Hybridization between microstructure and magnetization improvement in lead and RE co-doped BiFeO₃

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Abstract: The crystal structure, magnetic and electrical properties of Bi_{0.96}Pb_{0.04}FeO₃ and Bi_{0.92}Pb_{0.04}RE_{0.04}FeO₃ (RE=La, Sm, Dy and Yb) polycrystalline samples were prepared by the flash autocombustion technique. X-ray diffraction (XRD) measurements show that the rare-earth doped compositions crystallized in rhombohedral symmetry of space group *R3c*. The undoped sample consisted needle shape particles while rare earth substitution preferred platelet like particles as clarified from high resolution transmission electron microscopy (HRTEM). Morphological features were examined using field emission scanning electron microscopy (FESEM). Magnetization measurements showed that Yb³⁺ samples possessed the highest room temperature saturation magnetization while when Bi³⁺ ions were substituted by La³⁺ ions, a smaller *M_S* (0.28 emu/g) was obtained. The coexistence of ferroelectric and magnetic transitions was detected using DSC and χ_M , indicating the multiferroic characteristics of Bi_{0.92}Pb_{0.04}RE_{0.04}FeO₃ crystallites. The Néel temperature shifted upwards with decreasing the ionic radius of rare earth ion. Nice correlation was established between microstructure, morphology and magnetic properties in view of the contribution of magnetocrystalline and shape anisotropy in the magnetic parameters values.

Keywords: BiFeO₃; multiferroic; rare earths; anisotropy; dielectric; conductivity; Neel temperature

Multiferroic materials, in which electric and magnetic ordering coexists in a single phase, have attracted a lot of attention. Indeed, the coupling between the corresponding order parameters opens interesting perspectives for the novel designing applications in fields of microelectronics and spintronics^[1,2]. Spontaneous magnetization in BiFeO₃ can be induced via lanthanide^[3,4] or alkaline-earth/lead^[5,6] substitution. It has also been shown that partial substitution of A-site cation in BFO by lanthanide elements (La, Sm, etc.) leads to improved ferroelectric properties and magnetization^[7,8]. The latter has been explained by collapse of cycloidal spin structure of BiFeO₃ by A site substitution by Sm, La, etc. resulting in a uniform canted antiferromagnetic order and therefore significantly improving the multiferroic properties by intensifying the magneto-electric interaction^[7,8].

BiFeO₃ is reported to be a rhombohedrally distorted perovskite with space group *R3c* at room temperature in which the Bi³⁺ ions occupy the cubo-octahedral positions and Fe³⁺ ions in octahedral coordination. BFO is antiferromagnetic and the spin ordering is G-type. Superimposed on the antiferromagnetic ordering, there is a spiral spin structure in which the antiferromagnetic axis rotates through the crystal with an incommensurate long-wavelength period of ~62.0 nm^[9]. The existence of the spa-

tially modulated spin structure prevents the observation of any net magnetization and linear magnetoelectric effect^[10]. Recently, many promising methods have been tried to suppress this spin configuration, such as high magnetic field^[11,12], epitaxial constraint^[13,14], or doping with rare-earth ions^[15–18].

In our previous work, magnetization improvement was achieved at different levels via La doping in BiFeO₃ quantum dots (QDs)^[19]. The detailed spectroscopic characterization and the fluorescence of this series of QDs were published earlier^[20]. Another reported work was focused on conductivity enhancement of BFO through Ag doping which affected strongly the morphology, microstructure as well as physical properties^[21]. We chose Pb as substituent Bi_{0.92}Pb_{0.04}RE_{0.04}FeO₃ owing to small number of publications on BFO doped by Pb the expense of Bi ions which enhance the the electric and magnetic properties at room temperature^[22]. Here, in this piece of research, we continued our examinations on the A-site cation size variation by changing the rare earth element itself (the number of 4f electrons of the lanthanide) to better exploitation of the multifunctional nature of the multiferroic under investigation. In this paper, we reported on the synthesis of single phase (Bi_{0.92}Pb_{0.04}RE_{0.04}FeO₃, RE=La, Sm,

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Dy and Yb) by flash autocombustion technique. The crystalline structure, microstructure, morphology, magnetic and physical properties were investigated. Fruitful correlation between microstructure and magnetization would be established to recommend multifunctional applications of such doped nano multiferroics.

1 Experimental

Pure and RE doped $\text{Bi}_{0.96}\text{Pb}_{0.04}\text{FeO}_3$ and $\text{Bi}_{0.92}\text{Pb}_{0.04}\text{RE}_{0.04}\text{FeO}_3$ (RE=La, Sm, Dy and Yb) were prepared by the flash autocombustion technique using high-purity bismuth nitrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, lead nitrate $\text{Pb}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, iron nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. The molar ratio of urea was calculated using charge neutrality^[12]. The chemicals were weighed in the required stoichiometric proportions and mixed manually together for 20 min and heated on a magnetic stirrer. Thermal dehydration resulted in a highly viscous liquid. On further heating at high temperature, the viscous liquid swelled and auto-ignited to produce voluminous powder. The reaction was too fast, and produced dry fine powder. This method is quite simple, fast inexpensive and exploits an exothermic, usually very rapid and self sustaining chemical reaction between the desired metal salts and a suitable organic fuel, usually urea. The obtained nanopowders were heated at 550 °C for 2 h at a heating/cooling rate of 4 °C/min. X-ray studies were carried out by an X-ray diffractometer using radiation source Cu K α radiation ($\lambda=0.15405$ nm).

The shape and morphology of the fine particles were analyzed using a high resolution transmission electron microscope (HRTEM, JEOL-1010). The scanning electron microscope for the samples was SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (energy dispersive X-ray analyses), with accelerating voltage 30 kV, magnification $\times 14$ up to $\times 1000000$.

Thermal properties were examined using differential scanning calorimetry (Shimadzu DSC-50) from room temperature to 500 °C with a rate 10 °C/min. The hysteresis and magnetization measurements were performed using a vibrating sample magnetometer (VSM; EG & G Model No 1551 (USA) with maximum applied field of 20000 Oe at room temperature.

The measurements of molar magnetic susceptibility χ_M at room temperature were carried out using Faraday's method at different magnetic field intensities. The accuracy of measuring temperature in the magnetic susceptibility measurements was ± 1 °C where the data were reproducible.

The powder was pressed into pellet form and then annealed. The two surfaces of each disc were coated using silver paste and checked for good conduction.

The LCR meter (Hioki 3532, Japan) was used to

measure the ac electrical resistivity of the investigated samples. The dielectric constant (ϵ'), dielectric loss factor (ϵ''), and ac conductivity (σ) were measured from room temperature up to 980 K at different frequencies ranging from 100 Hz to 5 MHz.

2 Results and discussion

2.1 Structural analysis

Fig. 1 shows the XRD patterns for $\text{Bi}_{0.96}\text{Pb}_{0.04}\text{FeO}_3$ and $\text{Bi}_{0.92}\text{Pb}_{0.04}\text{RE}_{0.04}\text{FeO}_3$ (where RE=La, Sm, Dy and Yb). The diffraction peaks presented by all doped samples were indexed and compared with ICDD card number 01-086-159. The broad XRD lines with small intensities indicate that, the particles are of nanosized range. All peaks were indexed according to the rhombohedral hexagonal structure $R3c$ of the BiFeO_3 structure. The lattice parameters were computed and are reported in Table 1. The lattice parameter (c) for all doped rare earth (RE=La, Sm, Dy and Yb) is constant while (a) is highest for La due to the large crystallite size and ionic radius. Accordingly, the lowest density (D_x) is obtained owing to smaller molecular weights as shown in Table 1.

BiFeO_3 is well known to possess exotic incommensurate magnetic structure^[23]. Its local spin structure is a G-type antiferromagnet, meaning that, on a local level, the magnetic properties of BFO are comparable to those of perovskite orthoferrites^[24,25]. Accordingly, the strength of the antiferromagnetic superexchange interaction is tuned by the Fe–O–Fe angle (θ); specifically, it is proportional to $\cos\theta$ ^[26–28]. In a perfectly cubic perovskite, θ

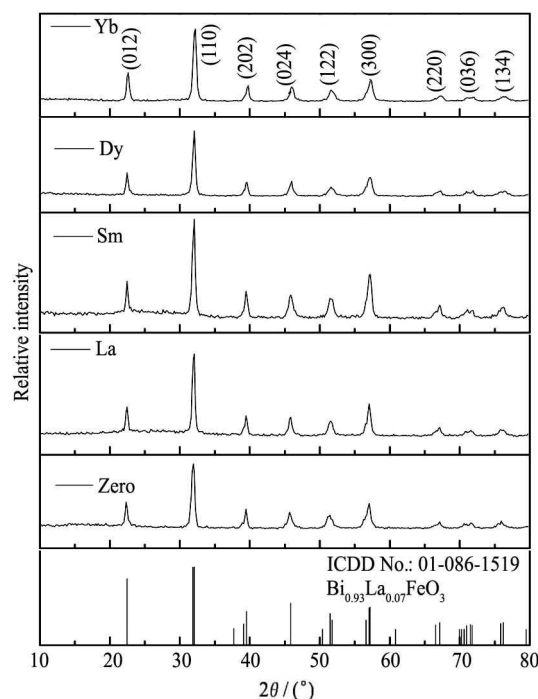


Fig. 1 X-ray diffraction pattern obtained for $\text{Bi}_{0.96}\text{Pb}_{0.04}\text{FeO}_3$ and $\text{Bi}_{0.92}\text{Pb}_{0.04}\text{RE}_{0.04}\text{FeO}_3$ (RE=La, Sm, Dy and Yb) respectively

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