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Influence of Dy and Cu doping on the room temperature multiferroic properties of $BiFeO_3$

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ABSTRACT

A series of $Bi_{1-x}Dy_xFe_{0.98}Cu_{0.02}O_3$ (x=1%, 2%, 3%, 4%, 5%) nanoparticles were prepared by sol–gel method. X-ray diffraction patterns reveal that the undoped and doped samples crystallize in rhombohedral structure. Enhanced magnetic properties are observed for the doped nanoparticles as compared to undoped $BiFeO_3$ (BFO) and when Dy substitution to Bi site is increased, the saturation magnetization (M_s) and remnant magnetization (M_r) show a remarkable increase. The Dy and Cu doping has improved the ferroelectric properties of the BFO. The measured magnetoelectric effect shows remarkable enhancement for the doped BFO as compared to the undoped BFO. The measured magnetic and ferroelectric properties of the doped samples has demonstrated that Dy and Cu doping can significantly improve the multiferroic properties of $BiFeO_3$.

1. Introduction

The multiferroic materials has evoked tremendous research activity in single phase and composite materials due to the coexistence and coupling of ferroelectric and magnetic orders [1–3]. This coupling interaction which is named as the magnetoelectric (ME) coupling has led to various possibilities in the applications of mutual control and detection of electrical polarization and magnetism. Dielectric polarization of a material under a magnetic field or an induced magnetization under an electric field requires the simultaneous presence of long-range ordering of magnetic moments and electric dipoles. Among the single phase multiferroic materials, $BiFeO_3$, known as BFO, is a special type of single phase multiferroic as it exhibits room temperature multiferroic properties and it keeps fascinating the scientific community to explore the possibilities to refine and improve its properties in order to make it suitable for applications in memory devices, spintronics and sensors [4,5]. At room temperature, BFO crystallizes in a rhombohedral distorted perovskite structure (space group R3c) with no inversion center.

In BFO while Bi^{3+} ions occupy the cubo-octahedral positions, Fe^{3+} ions are in octahedral coordination. The larger displacement of Bi^{3+} ions compared to the Fe^{3+} due to Bi active lone pair electron enables the O ions to effectively fourfold coordinated to two Bi^{3+} ions and two Fe^{3+} ions. The cations are displaced from their ideal positions relative to the anions along the [111] direction. In addition, the oxygen octahedra are rotated around the [111] direction, alternately clockwise and counterclockwise. $BiFeO_3$ is ferroelectric below 830 °C but does not exhibit a saturated polarization versus electric field loop at room temperature mainly due its high Curie temperature and high leakage current. It is antiferromagnetic below the Neel temperature which is about 370 °C [6–8]. $BiFeO_3$ has a spin-modulated cycloidal magnetic structure with modulation period of ~62 nm. Due to the long period modulated magnetic structure, net macroscopic magnetization is canceled. The presence of a space modulated spin structure is considered to inhibit the linear magnetoelectric (ME) effect. The oxygen vacancies are due to the highly volatile nature of $BiFeO_3$. Cationic substitution at Bi site and at Fe site is proved to be effective in controlling the oxygen vacancies and the leakage current so as to improve the ME coupling of BFO.

Several studies have been reported that when rare earth elements such as Dy, La, Nd, Sm, Pr and Gd are doped in Bi site and transition metals such as Cu, Mn, Cr, Zr, Ti and Sc are doped in Fe site, magnetic and electrical properties for $BiFeO_3$ are enhanced [9–12]. But the investigations on the doping of the nonmagnetic metal such as Zr, Zn and Cu in Fe site are sparsely found in the literature. In the case of substitution by nonmagnetic metal ions, better results have been reported. For instance, Wei reported that Zr doped $BiFeO_3$ showed an enhanced ferromagnetism [13] and Xu et al. demonstrated that Zn doped $BiFeO_3$ exhibited paramagnetic properties [14]. As far as the authour's best knowledge, no investigations on Dy and Cu simultaneously doped $BiFeO_3$ nanoparticles are reported till now. The extensive literature search

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reveals that a few reports on Dy doped BFO, Dy and La doped BFO are recently reported. Shuxia Zhang et al. demonstrated that $Bi_{1-x}Dy_xFeO_3$ (x=0, 0.05, 0.10, 0.15) nanoparticles exhibits weak ferromagnetism [15]. Jian Mei Xu et al. studied the magnetic properties of $Bi_{1-x}Dy_xFeO_3$ (x=0, 0.05, 0.15, 0.2) nanoparticles and showed that $Bi_{1-x}Dy_xFeO_3$ (x=0, 0.05, 0.15, 0.2) nanoparticles exhibits weak ferromagnetism [16]. Results of Qian et al. on the magnetic property of $Bi_{0.8}Dy_{0.2-x}La_xFeO_3$ nanoparticles show that when the La doping concentration ranges from 0 to 0.20, the average ionic radius of the Bi-site increases and effective magnetic moment at Bi site decreases. Their result shows that the magnetization of $Bi_{0.8}Dy_{0.2-x}La_xFeO_3$ is higher compared to $Bi_{1-x}Dy_xFeO_3$ nanoparticles [9]. C.M. Raghavan et al. reported that in (Nd, Cu) co-doped $BiFeO_3$ thin films, significantly leakage current density is reduced and they have observed increased remnant polarization as compared to pure $BiFeO_3$ thin films [17]. So, the substitution of Dy and Cu can possibly enhance the magnetic and ferromagnetic properties of BFO and hence in the present work, we have doped Dy at Bi site and a nonmagnetic metal Cu at Fe site in $BiFeO_3$ host lattice to investigate the influence of Dy and Cu on the room temperature (RT) multiferroic properties. Hence, we have synthesized $Bi_{1-x}Dy_xFe_{0.98}Cu_{0.02}O_3$ (x=1%, 2%, 3%, 4%, 5%) nanoparticles by sol–gel method and investigated the doping effect of Dy and Cu on the structure, morphology, magnetic properties, ferroelectric properties and magnetoelectric properties of the $BiFeO_3$. In what follows the symbols BFO, BDFCO1, BDFCO2, BDFCO3, BDFCO4 and BDFCO5 are used for $BiFeO_3$, $Bi_{0.99}Dy_{0.01}Fe_{0.98}Cu_{0.02}O_3$, $Bi_{0.98}Dy_{0.02}Fe_{0.98}Cu_{0.02}O_3$, $Bi_{0.97}Dy_{0.03}Fe_{0.98}Cu_{0.02}O_3$, $Bi_{0.96}Dy_{0.04}Fe_{0.98}Cu_{0.02}O_3$ and $Bi_{0.95}Dy_{0.05}Fe_{0.98}Cu_{0.02}O_3$ respectively.

2. Experimental details

BFO and BDFCO (1,2,3,4 and 5%Dy) nanoparticles were synthesized by sol–gel method. BDFCO (1,2,3,4 and 5) nanoparticles were prepared keeping the Cu concentration at 2% doping level while Dy concentration was varied at 1%, 2%, 3%, 4%, 5%. Analytical grade bismuth (III) nitrate pentahydrate (assay 98% Merck), ferric nitrate (assay 98% Merck), dysprosium (III) nitrate pentahydrate (assay 99.9% Alfa Aesar), copper (II) nitrate trihydrate (assay 99% Merck) citric acid anhydrous (assay 99.5% Merck) and nitric acid (assay 70% Merck) were used as starting materials. Double distilled water was used to prepare the experimental solutions. All the chemicals used were of analytical reagent grades, which do not require further purification. The double distilled water was used as solvent for all the prepared solutions. Stoichiometric amounts of the required starting materials were dissolved in dilute nitric acid and double distilled water. Citric acid which works as a chelating agent was added in 1:1 M ratio with metal nitrates and the mixture was stirred at 90 °C for 6 h. At the end of combustion, brownish powder obtained were calcined at 800 °C for 4 h. In order to prepare $Bi_{1-x}Dy_xFe_{0.98}Cu_{0.02}O_3$ (x=1%, 2%, 3%, 4%, 5%) pellets, a known quantity of poly vinyl alcohol (PVA) was added and ground well to disperse the PVA throughout the sample. Subsequently, the powder was pelletized using hydraulic pelletizer with applied weight of 6 tones and sintered at 600 °C for 3 h. These pellets were used for the ferroelectric characterization and for the measurement of magnetoelectric effect of all the samples.

The phase identification was performed for the pure and doped $BiFeO_3$ nanoparticles by X-ray diffractometer with an X Pert Pro X-ray diffractometer (PANalytical) with Cu K_α radiation of wavelength 1.5404 Å at the scanning rate of 0.02 min^{-1} in the range of 2θ being 10°–90°. The magnetization hysteresis (M–H) loop of undoped and (Dy and Cu) co-doped $BiFeO_3$ nanoparticles were obtained at room temperature using vibrating sample magnetometer (EG&G PARC VSM 155). The ferroelectric hysteresis (P–E) loops of the undoped and (Dy and Cu) co-doped $BiFeO_3$ were traced at room temperature at various electric fields using the Ferroelectric loop tracer (Marine India Pvt. Ltd). The magneto-electric effect of the prepared samples were measured using the Magneto Electric Coefficient Measurement System (Marine India Pvt. Ltd).

3. Result and discussion

3.1. Structural analysis

The XRD patterns of BFO, BDFCO1, BDFCO2, BDFCO3, BDFCO4 and BDFCO5 nanoparticles are shown in Fig. 1. The XRD patterns reveal that the crystal structure of all undoped and doped samples are in the perovskite based rhombohedral structure (space group R3c) of $BiFeO_3$ and the XRD peaks are in accordance with JCPDS data card no. (86–1518). It is evident that doping has not distorted the crystal structure. However, small trace of impurity phases corresponding to $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ appear for all the doped compounds. The phase of $Bi_2Fe_4O_9$ appear at 14.75°, 20.01°, 33.59° and 37.07° and phase of $Bi_{25}FeO_{40}$ appear at 27.61° and 27.58°. Such phases are not visibly seen for undoped BFO. The broad diffraction peaks indicate that crystallite sizes are in the nanometer scale. The variation in the intensity of XRD peaks of doped samples speculates that doping has occurred effectively. A small shift of the XRD peaks towards the lower angle side for the doped sample is seen in the inset of Fig. 1 and this indicates the incorporation of Dy and Cu. The average crystallite size of all nanocrystalline samples is calculated from the broadening of the X-ray diffraction peaks. The average crystallite size was calculated by Scherrer's formula.

$$d = \frac{0.9\lambda}{\beta \cos\theta}$$

where θ is the Bragg's angle, β is the full width half maximum and λ=1.5404 Å. The average crystallite size of BFO, BDFCO1, BDFCO2, BDFCO3, BDFCO4 and BDFCO5 are 31 nm, 69 nm, 69 nm, 65 nm 59 nm and 58 nm respectively. In the case of doped samples, the average crystallite size is found to decrease as Dy dopant level increases [18].

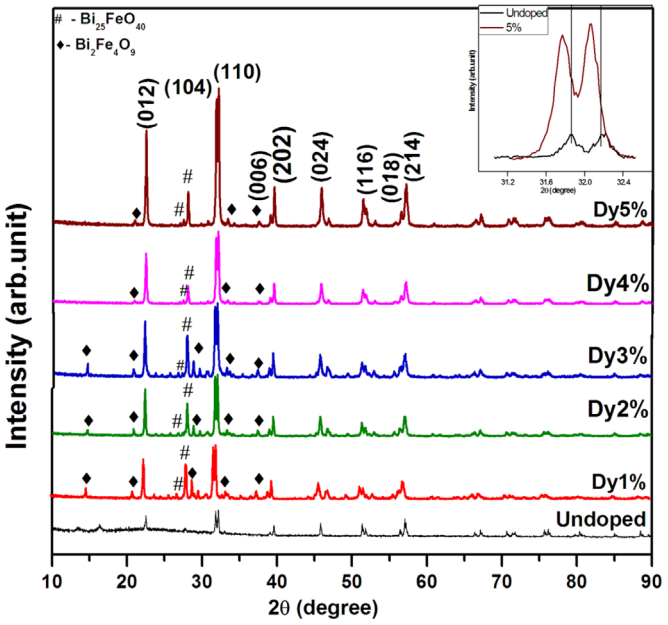

Fig. 1. X-Ray diffraction patterns of BFO and BDFCO (1,2,3,4 and 5) samples.