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Role of (La, Gd) co-doping on the enhanced dielectric and magnetic properties of $BiFeO_3$ ceramics

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Abstract

The effect of the La^{3+} and Gd^{3+} co-doping on the structure, electric and magnetic properties of $BiFeO_3$ (BFO) ceramics are investigated. For the compositions ($x=0$ and $0 \le y \le 0.15$) in the perovskite structured $La_xGd_yBi_{1-(x+y)}FeO_3$ system, a tiny residual phase of $Bi_2Fe_4O_9$ is noticed. Such a secondary phase is suppressed with the incorporation of 'La' content (x). The magnitude of dielectric constant (ε_r) increases progressively by increasing the 'La' content from $x=0$ to 0.15 with a remarkable decrease of dielectric loss. For $x=0.15$, the system $La_xGd_yBi_{1-(x+y)}FeO_3$ exhibits highest remanent magnetization (M_r) of 0.18 emu/g and coercive magnetic field (H_C) of ~1 T in the presence of external magnetic field of 9 T at 300 K. The origin of enhanced dielectric and magnetic properties of $La_xGd_yBi_{1-(x+y)}FeO_3$ and the role of doping elements, La^{3+}, Gd^{3+} has been discussed.

Keywords: C. Dielectric properties; C. Magnetic properties; Ceramics; Ball milling

1. Introduction

The well-known perovskite oxide, which exhibits both magnetism and ferroelectricity at room temperature is $BiFeO_3$ (BFO). Being a single-phase multiferroic material, BFO exists in a rhombohedrally distorted perovskite structure with $R3c$ space group. In this crystal structure, BFO exhibits high Curie temperature ($T_C = 1103$ K) and Néel temperature ($T_N = 643$ K) [1]. Co-existence of these two order parameters results into the observation of magneto electric (ME) effect in the system, in which electric polarization can be switched using applied magnetic field and vice versa, i.e. mutual control of magnetization and polarization [2]. Due to ME effect and its large remanent polarization at room temperature, it is considered as a promising candidate for application in new kind of storage devices. However, synthesis of single phase BFO is hard due to (i) the narrow temperature window of phase formation [3,4], (ii) large leakage current in BFO ceramics induced by impurities, (iii) non-stoichiometry and oxygen vacancies makes it difficult to achieve good ferroelectric properties. Moreover, antiferromagnetic nature of BFO is one of the major obstacles to obtain large ME effect and hence prevent its effective usage. The doping mechanism [5,6] and optimized preparation approach of BFO [7,8] helps certain extent to overcome aforementioned impediments. The net magnetization in BFO originates from the canted spin structure of Fe^{3+} atoms while the net polarization is mainly a result of the stereo-chemically active of $6s^2$ lone pair electrons in Bi^{3+} [9]. The site doping with elements having similar radii are expected to improve the multiferroic properties of BFO. There are many reports on the single site doping, either at A-site or B-site in BFO [10–13]. A-site doping with the La and Ba is effective to improve the dielectric constant, reducing leakage current and to achieve good P–E loops [14,15]. The B-site doping with ions such as Ti and Mn results in improved magnetic properties, observation of weak ferromagnetism, etc. [16,17]. The control over both the order parameters can also be

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achieved simultaneously by co-doping at A and B site at the same time. In this framework, A and B sites of ABO_3 type BFO are co-doped with, for instance, Bi^{3+} ions by La^{3+} or Nd^{3+} and Fe^{3+} ions by Mn^{4+}, Ce^{3+}, V^{5+}, Ti^{4+} ions have found a growing interest as they seem to improve the electric and magnetic properties simultaneously [18–20]. However, the doping at B-site dilutes the Fe magnetic ions and reduces magnetization; moreover, A-site doping with magnetic ion not only introduces strain into the system but also superimposes additional magnetic contributions into the system. So far, there are reports, mostly on the co-doping at A and B sites of BFO simultaneously, focusing on the phase stabilization and leakage current. However, A-site substitution by some ions with smaller ionic radius can induce more closing in the Fe-O-Fe bond angle accompanying the structural changes, which leads to more reliable multiferroic at room temperature. Furthermore, there are very few reports on the A-site co-doping in BFO system, investigating its multiferroic properties. For example, the co-doping of La^{3+}, V^{5+} in the A-site of BFO results into the enhanced dielectric and ferroelectric properties of BFO ceramic [20]. Also, when BFO films are co-doped with La^{3+}, Ni^{2+} [21] and La^{3+}, Nb^{5+} [22], a reduction in the leakage current is observed with an improvement in ferroelectric properties. In case of 15% co-doping of La, Ho at A-site of BFO system, an improvement in the polarization and a weak ferromagnetism is reported [23]. However, there are very limited reports on the improvements of magnetic properties of the A-site co-doped BFO [23–25]. It is reported that A-site co-doped with (La, Pr) and (La, Sm) results in the structural phase transition to anti-polar orthorhombic phase, which leads to a weak ferromagnetism in the system [24,25]. In the literature, it is well established that the substitution of La in Bi-site is efficient in stabilizing the perovskite phase [26], reducing leakage current [14] and enhancement of magnetic properties in BFO [27,28]. The Gd, a rare-earth magnetic element doping is very effective to increase the magnetization at A-site of BFO [29]. It is interesting to investigate the effect of A-site co-doping of La and Gd on the ferroelectric and magnetic properties of the BFO materials in order to combine the advantages of La and Gd doping.

Hence, we carried out a systematic study on the La and Gd co-doping ($La_xGd_yBi_{1-(x+y)}FeO_3$ (LGBFO)) samples. Here La^{3+} and Gd^{3+} partially substitute for Bi^{3+} at the A-site of BFO such that the stoichiometry of A-site doping (La+Gd) is consistently maintained at 20% thereby the stoichiometry of Bi is fixed at 80%. It is to be noted that whenever a change in La content is mentioned in the manuscript, correspondingly a change in Gd fraction occurs in order to maintain 20% doping level at A-site of BFO. The overall co-doping level is restricted to 20% for this study as this particular doping level is a critical composition and exhibits good electrical and magnetic properties for the individual doping of La, Gd [26,29]. The role of each dopant element on the structural, electrical and magnetic properties is discussed in detail.

2. Experimental details

The ceramics of $La_xGd_yBi_{1-(x+y)}FeO_3$ (LGBFO) for $(x, y)=(0, 0)$; (0.05, 0.15); (0.1, 0.1); (0.15, 0.05) are prepared by a conventional solid state reaction method. Stoichiometric ratios of Bi_2O_3, La_2O_3, Gd_2O_3 and Fe_2O_3 powders are milled thoroughly under the ethanol medium using a ball mill for 4 h. The ball milling is carried out in a Retsch single station (PM-100) planetary ball milling system in air. A 125 ml tungsten carbide vial and tungsten carbide balls with a diameter of 10 mm, 5 mm and 3 mm have been used. The milling speed is set at 350 rpm and it is stopped for every 30 min of milling for duration of 2 min to cool down the system, and the balls direction is reversed for further grinding. Then the mixture is pre-calcined at 600 °C for 30 min followed by the calcination at 820 °C for 1 h. Further, pellets are made and sintered at 800 °C for 4 h.

The crystalline structures of these ceramics are investigated using a Bruker D8 X-ray diffractometer with Cu K_α wavelength (1.5418 Å). The samples are characterized for its microstructure using Carl Zeiss Ultra 55 Field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray fluorescence (EDS) analysis has carried out for chemical composition. The Raman spectra is recorded by Horiba JobinYvon, LabRAM-HR 800 micro-Raman system equipped with an excitation wavelength of 514.5 nm and laser power of 3 mW under back scattering geometry (incident and scattered wave vectors are parallel) using 50× objective lens. To measure the electrical properties, silver electrodes are deposited on both sides of the sample discs to make capacitor geometry. Dielectric constant (ε_r) measurements are carried out using Agilent E4980A LCR meter at room temperature. Temperature dependent magnetic properties of these samples are studied using Quantum Design PPMS-VSM in the presence of an external magnetic field of 100 and 1000 Oe. Hysteresis loops are recorded at 2 K, 60 K, 200 K and 300 K by sweeping the external field between −9 T and +9 T.

3. Results and discussion

3.1. Structural analysis

The effect of La and Gd doping on the structure of BFO at A-site is analyzed using X-ray diffraction (XRD). The obtained XRD pattern of LGBFO for $x=0.05$, 0.1 and 0.15 samples is shown in Fig. 1. It is known that the XRD of pure BFO matches well with the standard data, JCPDS card no. 86-1518 and is indexed as rhombohedral structure with $R3c$ space group. As shown in Fig. 1, for all the samples of LGBFO, along with the major peaks of BFO, noticeable minor peaks corresponding to the secondary phase, $Bi_2Fe_4O_9$ (marked by asterisk #) is also observed. A small contribution from this minor phase on magnetic properties has been discussed. However, this contribution is not so remarkable because $Bi_2Fe_4O_9$ phase is not a ferromagnetic in nature at room temperature. $Bi_2Fe_4O_9$ shows AFM with T_N around 250 K [30,31]. Furthermore, the careful observation of the XRD spectrum reveals that with an increase in La doping, the percentage of the impurity phases have been suppressed with respect to the undoped sample. The weight ratios of the secondary phases are estimated using the following formula