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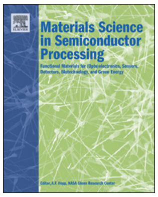

Effect of structural phase transition on magnetic and optical properties of co-substituted bismuth ferrite

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ABSTRACT

Beside the disappearance of characteristics superlattice reflections for *R*3*c* space group as (1 1 3) at $2\theta=37.8^{\circ}$, the typical reflections of *Pbnm* space group as (1 1 1) at $2\theta=25.42^{\circ}$ as well as their new superlattice reflections such as (0 2 1), (0 2 3) and (2 2 1) at $2\theta=34.14^{\circ}$, 47.69° and 47.82° which are characteristic of the antiparallel cation displacements has appeared for 7.5% of co-substitution (Eu in Bi site and Mn in Fe site) in $BiFeO_3$. Morphological phase boundary has been observed around 7.5% of co-substitution which have enhanced remnant magnetization about 20 times that of pure one and it could be due to the suppression of cycloid spin structure and spin canting at the surface of nanocrystallites. Further increase in co-substitution percentage ($>7.5\%$) leads to the reduction of remnant magnetization due to the appearance of collinear antiferromagnetic ordering in the *Pbnm* space group which becomes significant for higher co-substitution percentage. The analysis of diffuse reflectance spectra which shows the point group symmetry breaking from O_h to C_{3v} supports the modification in local FeO_6 environment and structural transition.

1. Introduction

$BiFeO_3$ (BFO) is a promising room temperature multiferroic material because it shows the ferroelectric order as well as G-type canted antiferromagnetism well above room temperature ($T_c \sim 1103$ K and $T_N \sim 643$ K) [1]. It has received attraction of several research groups due to its possible technological applications in multistate memory devices, spintronic devices, magnetically modulated transducers, ultrafast optoelectronic devices and sensors [2–5]. The crystal structure for BFO at room temperature is described by rhombohederally distorted perovskite structure with *R*3*c* space group. This space group allows the antiphase octahedral tilting and ionic displacement from the centrosymmetric position along $[1\ 1\ 1]_C$ direction of the parent cubic perovskite unit cell. The ferroelectricity in this compound arises due to the off-centre structural distortions of cations whereas the magnetism due to local spins. The symmetry of *R*3*c* space group allows canted antiferromagnetism due to Dzyaloshinky–Moriya (DM) interaction but the superposition of cycloid spin structure with the periodicity of ~62 nm prevents net magnetization which leads to net zero magnetization [6–9]. The small coercivity and magnetoelectric coupling constant limits its application in multiple state memory devices. Recently, it was reported that the high ferroelectric and ferromagnetic polarization or large magetoelectric coupling constant at room temperature can be achieved through A- site and/or B-site substitution in BFO [10–15]. It has been observed that the rare earth substitution at A-site could suppress the cycloid spin structure and induces structural transition from rhombohedral to orthorhombic symmetry [10,14,15]. This structural phase transition significantly enhances the magnetization as well as magnetoelectric interaction. It is difficult to prepare pure

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phase $BiFeO_3$ ceramics because it has narrow temperature range for phase stabilization. Several research groups have tried to prepare phase pure by chemical route and the solid state route followed by leaching with nitric acid [16,17]. The former route is found to be better compared to the later one in terms of reproducibility and phase purity. Hence, the chemical route of synthesis has been adopted for preparing all the materials.

The oxygen octahedra tilting leads to oxygen atom displacements which cause a doubling of the unit cell axes. It produces extra reflections known as superlattice reflections, which lie on half integral reciprocal lattice planes. The distorted perovskite can be precisely analyzed by observing the change in weak superlattice reflections which results from in-phase/anti-phase tilting of neighbouring BO_6 octahedra. The octahedral tilts have been described by Glazer [18] in terms of three component tilts about the three tetrad axes namely a, b, and c of the BO_6 octahedron. The tilt about a given axis induces tilt of opposite sense about the other two tetrad axes which results in the doubling of the corresponding unit cell parameters. The octahedra along the tilt axis in neighboring unit cells may tilt "in-phase" ($-$ve tilt) or "anti-phase or out of phase" ($+$ve tilt). The tilting angle is 0° for a ideal cubic perovskite ($Pm\bar{3}m$ space group). The $R3c$ space group belongs to the $a^-a^-a^-$ tilt system with anti-phase component tilts of equal magnitude about the three pseudocubic $\langle 1\,0\,0\rangle$ directions. It lead to the appearance of the superlattice reflections due to the doubling of all the three pseudocubic cell parameters, whose Miller indices with respect to the doubled cubic cell correspond to odd-odd-odd integers [18,19]. The presence of superlattice reflections in XRD patterns of BFO with indices as (3 1 1) at $2\theta = 37.8°$ (which is (1 1 3) with $k \neq l$ in hexagonal frame of reference as in the present manuscript) suggests the BFO in $R3c$ space group.

The $Pbnm$ space group belongs to tilt system of $a^-a^-c^+$ in which the component tilts about the [1 0 0] and [0 1 0] pseudocubic directions correspond to anti-phase" rotation of the neighboring oxygen octahedra, whereas the octahedral are rotated "in phase" about the [0 0 1] direction. The in-phase tilt results in doubling along two of $\langle 1\,0\,0\rangle$ directions perpendicular to the tilt axis which gives rise to superlattice reflections with odd–odd–even indices with respect to the doubled pseudocubic cell and antiphase tilt leads to superlattice reflections with odd-odd-odd indices. The supperlattice reflections may also results from the antiparallel displacement of "A-site" cations in the neighbouring unit cells which are represented by even–even–odd indices [18,19].

Reddy et al. has observed the weak ferromagnetic ordering induced in BFO by Eu substitution at A-site [20]. Moreover, Liu et al. have demonstrated that Eu^{3+} ions were more effective to increase the M_r of BFO than other rare earth ions such as La^{3+}, Nd^{3+} and Sm^{3+} [21]. The Mn substitution at Fe site of BFO has been reported to inhibit the grain growth which resulted in reduced particle size [22] and improve the magnetic as well as electric properties [23]. Chauhan et al. have reported the structural phase transition in 15% Mn substitution in Fe site of BFO due to the distortion in the rhombohedral structure which leads to significant enhancement in magnetization [24]. The improved ferroelectricity in Eu and Mn co-substituted BFO thin films have been reported by Do et al. [25]. Another motivation for the present manuscript is the quantification of multiple crystal symmetries using XRD technique which has been used to observe the corresponding modification in physical properties [26–30]. This technique has been used for establishing the correlation between the crystal structure and physical properties in the present manuscript. There is a lack of detail study on correlation between crystal structure and magnetic properties of Eu and Mn co-substituted BFO. As the BFO is known for its multiferroic application prospects, it is needed to explore the magnetic properties and details of crystal structure to find the device applications. Apart from this, Eu^{3+} and Mn^{3+} have been chosen as substituent ions because it is magnetically active and could enhance the magnetic properties through the magnetic exchange coupling between Eu^{3+} & Fe^{3+}, Eu^{3+} & Mn^{3+} and Fe^{3+} & Mn^{3+}. The present article reports detailed investigation on correlation between crystal structure transition and magnetic properties.

2. Materials and methods

$Bi_{1-x}Eu_xFe_{1-x}Mn_xO_3$ with $x = 0.000$, 0.015, 0.025, 0.050, 0.075, 0.100, 0.150 and 0.200 were named as BEFM-0, BEFM-015, BEFM-025, BEFM-05, BEFM-075, BEFM-1, BEFM-15 and BEFM-2 respectively which have been prepared by the tartaric acid modified sol–gel technique [31]. The starting materials as bismuth nitrate, iron nitrate, europium oxide, manganese acetate and tartaric acid (purity $\geq 99.0\%$) were weighted in stoichiometric proportion. The molar ratio of metal nitrates to tartaric acid was taken as 1:2. The resulting material was thoroughly grinded and annealed using alumina crucibles in the air environment at 700 °C for 3 h inside a programmable box furnace and then slowly cooled down to room temperature.

The crystallographic phases of all the samples were analyzed by the powder X-ray diffraction (XRD) study using 18 kW Cu-rotating anode based Rigaku TTRX III diffractometer, Japan) with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å) operating in the Bragg-Brentano geometry in a 2θ range of 10°–120° at a scan step of 0.01°. Microstructural properties of all samples were investigated by using Hitachi S-4800 Field Emission Scanning Electron Microscopy (FE-SEM), operating at an accelerating voltage of 10 kV and equipped with energy-dispersive X-ray spectroscopic capability. The particle size was observed with the help of JEM-200, JEOL transmission electron microscope (TEM) at an accelerating voltage of 200 kV. Room temperature Raman spectra were measured in the backscattering geometry using confocal micro-Raman spectrometer (Seki Technotron Corp. Japan) with the 514.5 nm laser line as excitation source by STR 750 RAMAN Spectrograph using a 100× microscope. Fourier Transform Infrared (FT-IR) Spectra were recorded at room temperature using the Perkin Elmer (model 400) in the range from 400 to 1200 cm^{-1}. The diffuse reflectance spectroscopy has been carried out by using Perkinelmer LAMBDA 35 UV–visible spectrophotometer in the range from 200 to 1100 nm. The room temperature magnetic measurements were carried out by Quantum Design