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Electron spin resonance studies and improved magnetic properties of Gd substituted $BiFeO_3$ ceramics

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Abstract

Polycrystalline $Bi_{1-x}Gd_xFeO_3$ ($x=0.00$–0.15) ceramics were prepared by solid-state reaction method. The samples preserve rhombohedral symmetry for $x \leq 0.10$ and coexistence of rhombohedral $R3c$ and orthorhombic $Pn2_1a$ symmetries for $x > 0.10$. A significant change in the phonon frequencies of A_1 modes and line widths in Raman spectra also confirms the structural transition from rhombohedral to orthorhombic for $x=0.12$ and 0.15. The improved magnetic behaviour indicates weak ferromagnetism in the samples with remnant magnetization ($2\,M_r$) of 0.145 emu/g for $x=0.15$. An asymmetric shift in the coercive field indicates the presence of exchange bias effect in samples. Electron spin resonance spectra are of the ferromagnetic resonance type at higher dopant concentration and indicate the presence of ferromagnetically coupled clusters in the samples. Optical studies in the spectral range from 1.6–5.2 eV were dominated by one doubly degenerate d–d transition and three charge transfer transitions. The optical band gap decreases from 2.25 to 2.16 eV with increasing Gd substitution due to increased lattice distortion.

Keywords: B. X-ray methods; B. Electron microscopy; C. Magnetic properties; C. Optical properties

1. Introduction

Multiferroics with magnetoelectric effect show both (anti) ferroelectric order and (anti)ferromagnetic order in the same phase and a coupling between them over certain range of temperature [1–4]. Such materials can be electrically polarized by applying an external magnetic field; alternately, an external electric field can induce magnetization in them. These multiferroic materials have wide applications in emerging electronic devices such as data storage media, multiple state memories, spin valves, spintronics, quantum electromagnets, and microelectronic devices [5,6]. $BiFeO_3$ (BFO) is one of the scarcest multiferroics exhibiting spontaneous polarization and antiferromagnetic ordering with high Curie ($T_C \sim 830\,^\circ C$) and Neel ($T_N \sim 370\,^\circ C$) temperatures having rhombohedrally distorted perovskite structure with $R3c$ space group [7]. The magnetism and ferroelectricity in BFO derive by different sublattices. Bi-O orbital hybridization due to Bi $6s^2$ lone pair is responsible for the ferroelectric instability while Fe–O–Fe antisymmetric Dzyaloshinskii–Moriya (DM) exchange gives rise to a complicated magnetic order [8]. But some limitations like evolution of impurity phases during preparation due to loss of bismuth, poor ferroelectric properties due to oxygen vacancies and very low magnetization due to modulated spiral spin structure in addition to the G–type antiferromagnetism (AFM) restrict use of the bulk BFO in real applications [9]. In order to overcome these problems much efforts have been devoted which include depositing ultra thin $BiFeO_3$ single layer or multilayer films to enhance ferroelectric property [10,11]; fabricating high quality single crystal of BFO to solve non-stoichiometric problems [12]; synthesizing BFO nanoparticles with particle size below 62 nm to achieve ferromagnetism by destroying spiral spin structure [13]. Further, the chemical substitution of rare earth ions (like Eu^{3+}, Dy^{3+}, Gd^{3+}) [14–16] or alkaline earth metal ions (like Ba^{2+}, Sr^{2+}, Ca^{2+}) [17–19] at the A site and doping of non magnetic ions (like Zr^{4+}, Ti^{4+}, Nb^{5+}) [20–22] at the B site of BFO have

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proved effective ways to enhance multiferroic properties. Among these approaches, chemical substitution doping might be a feasible way to improve the macroscopic magnetization because chemical doping of BFO can not only change the electric conductivity but also alter the magnetization behaviour by affecting the ligand field at Fe ions [23]. Moreover, the verification of cycloid suppression in A–site substituted samples has been specified by nuclear magnetic resonance (NMR) technique which has been associated with the structural transition from rhombohedral to orthorhombic [24]. This structural phase transition (in morphotropic phase boundary) significantly enhances the magnetization as well as magneto-electric interaction.

The main purpose of the present work is to improve the magnetic properties of BFO ceramics. Gadolinium (Gd) is a promising dopant for BFO system because the large difference in ionic radii of Bi^{3+} (1.17 Å) and Gd^{3+} (0.938 Å) can lead to large structural distortion and promote Gd^{3+} ions to induce inter-defect coupling for enhanced ferromagnetism [6]. In addition, gadolinium ions are magnetically active, therefore, strong magnetic interaction between the Gd^{3+}-Gd^{3+} and Gd^{3+}-Fe^{3+} ions can be expected [25]. In this paper, we have investigated the effects of Gd substitution on structural, magnetic, and optical properties of BFO ceramics.

2. Experimental

$Bi_{1-x}Gd_xFeO_3$ ceramics with $x=0.00$, 0.03, 0.06, 0.10 0.12, and 0.15 were synthesized via solid state reaction method. The high purity Bi_2O_3, Fe_2O_3 and Gd_2O_3 (purity 99.99%, Sigma Aldrich) were used as starting materials. The stoichiometric amount of oxides was mixed thoroughly for 4 h. These mixed powders were calcined at 700 °C for 2 h. The calcined powders were pressed into discs of 10 mm diameter and 1 mm thickness at a pressure of 10 Torr in a hydraulic press with polyvinyl alcohol as a binder. The prepared pellets were sintered at 820 °C for 2 h to get desired phase. The phase purity and crystal structure were examined by X-ray diffraction (XRD) technique using XRD–6000 Shimadzu diffractometer with CuKα radiation. The morphology of the samples was studied with the help of scanning electron microscope (SEM). The phonon modes were measured by Renishaw Raman spectrometer with 514.5 nm argon ion laser. The magnetization as a function of applied field was measured using a Vibrating Sample Magnetometer (VSM, Lakeshore VSM 7410). The room temperature electron spin resonance (ESR) spectra were recorded on Bruker EMX spectrometer. UV–Visible diffuse reflectance spectrum (UV–Vis DRS) of the samples were measured by Ocean optics UV–Visible 4000. Infrared spectra were recorded on a Fourier transform infrared (FTIR) spectrometer (Perkin Elmer Spectrum BX-II).

3. Results and discussion

3.1. Rietveld analysis

Fig. 1 shows Rietveld refined XRD patterns for $Bi_{1-x}Gd_xFeO_3$ ceramics. A rhombohedral perovskite structure with space group *R3c* can be indexed in pure BFO (JCPDS card no.71-2494). Due to metastable nature of BFO and its chemical kinetics of formation it is always coupled with some impurity phases like $Bi_2Fe_4O_9$ and $Bi_{24}Fe_2O_{39}$. Impurity phases gradually decreases with increasing Gd concentration and they almost disappear for $x > 0.03$. The refinement results obtained for $x=0.0$–0.10 samples confirm that they possess rhombohedral structure belonging to *R3c* space group. However, few small peaks appear related to orthoferrite $GdFeO_3$ phase for $x=0.12$ sample and intensity of these peaks

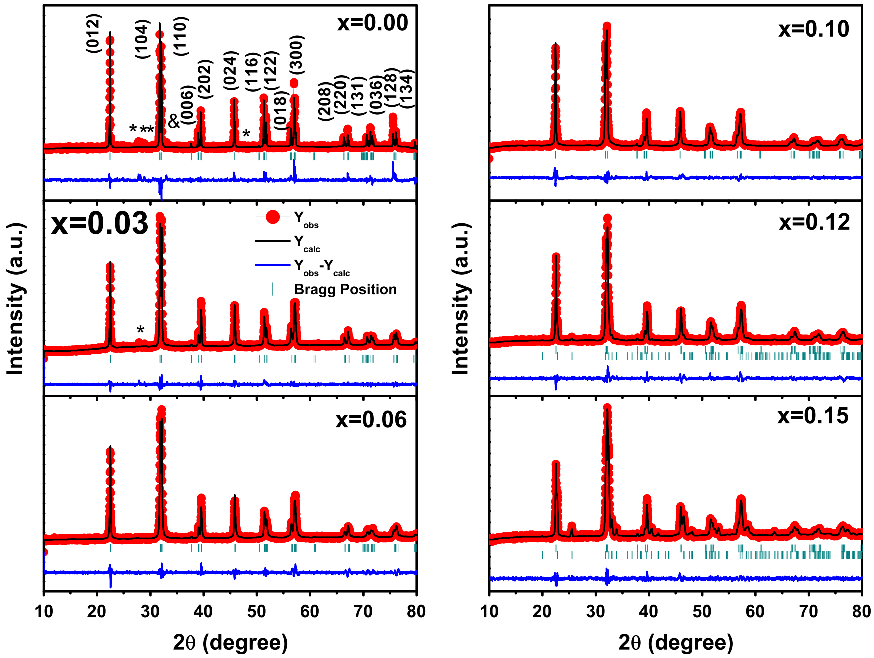

Fig. 1. Rietveld refined XRD patterns for $Bi_{1-x}Gd_xFeO_3$. The asterisk * and & represent $Bi_2Fe_4O_9$ and $Bi_{24}Fe_2O_{39}$, impurity phases, respectively.