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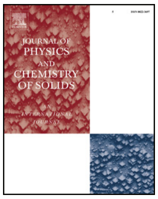

Effect of Ti substitution in place of Fe on crystal symmetries and magnetic properties of $Bi_{0.850}La_{0.150}FeO_3$

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ABSTRACT

Lanthanum (La) modified BFO crystallize to an impurity free crystal structure and enhance the multiferroic properties in BFO. The $Bi_{0.850}La_{0.150}FeO_3$ is found to be optimized composition to have very good multiferroic properties. It is also reported that the Ti^{4+} substitution significantly reduces the leakage current in BFO. Moreover, the Ti^{4+} substitution is more effective than that of magnetic cations to increase the magnetization. Hence, $Bi_{0.850}La_{0.150}Fe_{1\text{-}x}Ti_xO_3$ (x = 0.000, 0.025, 0.050, 0.100) polycrystalline samples were synthesized by the tartaric acid modified sol gel method and the effect of non-magnetic Ti substitution at the Fe-site of $Bi_{0.850}La_{0.150}FeO_3$ on crystal structure and magnetic properties has been studied. The Rietveld refinements of X-ray diffraction patterns indicate the structural transition from rhombohedral (*R3c*) to orthorhombic (*Pbnm*) with the increase in the substitution concentration. A gradual shift in the frequency of Fe-O stretching modes toward higher frequency in the FTIR spectra indicates a composition-driven structural transition. Magnetic properties of $Bi_{0.850}La_{0.150}Fe_{1\text{-}x}Ti_xO_3$ polycrystalline samples were measured at room temperature with the applied field range of ± 7 T. A significant increase in the magnetization with Ti substitution is observed from the magnetic hysteresis loops. The highest magnetic moment was observed for 2.5% Ti substitution at the Fe-site in $Bi_{0.850}La_{0.150}FeO_3$.

1. Introduction

Multiferroic materials have the considerable research interest because of its wide range of applications starting from storage systems, microelectronics and spintronics devices, magnetic sensors etc. [1,2]. However, there are a very few number of materials exhibiting multiferroic behaviour. The ferromagnetism exists in the material if partially filled d-orbital is available and ferroelectricity can be observed for the materials without electron in d-orbital [3]. Hence, these two phenomena are difficult to exist together in a single material. However there are a few materials exhibit both orderings which are known as multiferroic materials. However, most of the single phase multiferroic materials usually show the magnetic ordering below room temperature, which restrict them for technological applications. Among the very few number of known multiferroic materials, Bismuth Ferrite ($BiFeO_3$) is a well known multiferroic materials with rhombohedrally distorted structure (space group, *R3c*), which possesses simultaneous ferroelectric ordering (T_C ~*1103K*) and anti-ferromagnetic ordering (T_N ~*643K*) [1]. It is the promising candidate as future ferroelectric and magnetoelectric material in technological applications. The ferroelectric polarization in $BiFeO_3$(BFO) arises due to the structural distortions induced by Bi^{3+} ($6s^2$) lone pairs and, the super-exchange interactions of Fe^{3+}-O-Fe^{3+} causes the G-type antiferromagnetic ordering [4]. Both the phenomena are totally independent from each other in BFO. However, BFO has certain inherent issues like preparation of pure phase of it, high leakage current [5,6], high dielectric loss, low remnant polarization, weak magnetoelectric coupling effect and a wide difference in ferroic transition temperatures etc. [7], which restrict it for practical applications. BFO has very narrow temperature range of phase stabilization and, as well as easy crystallization to secondary phases ($Bi_2Fe_4O_9$, $Bi_{25}FeO_{39}$ etc.) make difficult to prepare the BFO [8,9]. The presence of secondary phases and oxygen vacancies (generated due to the interconversion between Fe^{2+} and Fe^{3+} states) leads to high leakage current in BFO at room temperature. BFO show very weak ferromagnetism (i.e. deviate from its antiferromagnetic order) due to the presence of spiral modulated spin structure with a periodicity of ~62 nm [5]. This behaviour does not allow to saturate the magnetization and restrict the observation of linear magnetoelectric effect.

Because of these considerable challenges, there are various methodologies have been employed to improve the magnetic as well as

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electrical properties [10,11]. Also researchers have tried by preparing composites with other perovskite and/or spinel type materials as well as making thin films and heterostructures [12,13]. A transition from antiferromagnetic to weak ferromagnetic can be observed by application of high magnetic field of 20Tesla [14,15]. Also, the suppression of the spiral spin structure can be achieved by synthesizing nanoparticles smaller than the cycloid spin structures ($<$ 60 nm). Among the several kinds of methods, chemical substitution of suitable ions on the Fe and/or Bi sites of BFO is quite an effective method to improve the multiferroic properties and a stable perovskite phase. Substitution of the rare earth lanthanide ions (La^{3+}, Gd^{3+}, Nd^{3+}, Eu^{3+} etc. [16–19]) or divalent ions (Ca^{2+}, Sr^{2+},Ba^{2+},Pb^{2+} etc. [20–23]) in place of B (i.e. Bi atom) in BFO and transition metal ions (Mn^{4+}, Ti^{4+},Nb^{4+},Cr^{3+} etc. [24–28]) in place of F (i.e. Fe atom) have been reported. All these reports reveal that the magnetic and ferroelectric properties can be enhanced by substitutions in BFO. It has been reported that the substitutionin Bi site destroy the space modulated spin structure of BFO and results in a canted antiferromagnetic ordering. However, substitution in Fe site can improve both electrical and magnetic properties [29]. S Madolappa et al. have demonstrated enhanced multifunctional properties of $BiFeO_3$ with Gd and Ti substitution at the Bi and Fe sites respectively [30]. An increase in magnetization by non-magnetic Ti substitution in $Bi_{0.8}Ba_{0.2}FeO_3$ compound was obtained due to the structural modification in the material [31]. Singh et al. observed an enhancement of remnant magnetization and coercivity in Ti doped $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.5}O_3$ is due to canting of the antiferromagetically ordered spins [32].

Lanthanum (La) modified BFO stabilizes the crystal structure and nonuniformity in the spiral spin structure which enhances the multiferroic properties [33]. The $Bi_{0.850}La_{0.150}FeO_3$ is reported to be secondary phase free BFO and have enhanced magnetization due to structural distortion [34]. It is reported that the Ti^{4+}substitution significantly reduces the leakage current [25]. Moreover, the Ti^{4+}substitutionis more effective than that of magnetic cations to increase the magnetization. It has been attributed to the antiferromagnetic (AFM) alignment of the moment (of magnetic cations) with respect to Fe moment, which decreases the contribution from the overall magnetic moment. Whereas, Ti^{4+}as non-magnetic, do not cancel the magnetic moment of Fe^{3+}. If Fe^{3+} is heavily doped by Ti^{4+}, it may reduce the magnetic exchange interactions between Fe^{3+} ions and hence the magnetization decreases. As discussed above it is interesting to study the Ti^{4+} doping in place of Fe in $Bi_{0.850}La_{0.150}FeO_3$.

2. Experimental methods

2.1. Synthesis of material

The polycrystalline samples of $Bi_{0.850}La_{0.150}Fe_{1\text{-}x}Ti_xO_3$ with x = 0.000, 0.025, 0.050 and 0.100 were synthesized by the tartaric acid modified sol-gel technique [35]. Stoichiometric amounts of high purity Bismuth nitrate pentahydrate (≥98% purity, Alfa Aesar), Iron nitrate nonahydrate (≥98% purity, Alfa Aesar), Lanthanum acetate (≥99.9% purity, Alfa Aesar), Titanium dioxide (≥99% purity, Merck) and Tartaric acid (≥99.9% purity, Merck) were taken. The total metal nitrates to tartaric acid were taken in a molar ratio of 1:1. Liquid solutions of all the metal nitrates and oxides are prepared in separate beakers by dissolving in concentrated nitric acid and deionised water (milli Q grade) under constant sonication. The final solution was obtained by mixing all the solution in a single beaker along with sonication for half an hour. Finally the solution gets evaporated by heating in a hot plate at 80 °C with constant stirring of 100 rpm to obtain a viscous and brown gel. To remove the excess water from the gel, it was dried overnight at 100 °C in an oven. The resulting materials were grinded using a mortar pestle to get homogeneous mixture. The mixture was annealed at 700 °C for 3 h in the air environment inside a programmable high temperature furnace with a ramp rate of 5 °C/min using alumina crucibles.

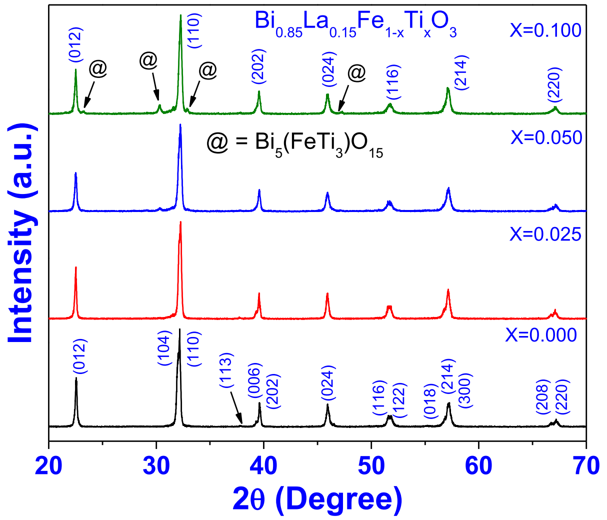

Fig. 1. XRD patterns of $Bi_{0.850}La_{0.150}Fe_{1\text{-}x}Ti_xO_3$ for x = 0.000, 0.025, 0.050 and 0.100 annealed at 700 °C.The peaks denoted by '@' symbol in the XRD pattern of x = 0.100 represents the secondary phases of $Bi_5(FeTi_3)O_5$.

2.2. Characterization technique

The crystal structure of the compounds were studied by the powder X-ray diffractometer (XRD) (Rigaku TTRX III diffractometer, Japan) with Cu-Kα radiation (λ = 1.5418 Å) at room temperature. The XRD data were collected with a wide range of Bragg's angle 2θ ($10° \leq 2\theta \leq 100°$) at a scan step of 0.01° and scan rate of 2°/min. Fourier-transform infrared spectroscopy (FTIR) (Perkin Elmer 400) was used to record the FTIR spectra at room temperature in the range of 400–1200 cm^{-1}. Superconducting Quantum Interference Device (SQUID) magnetometer, Quantum Design, Inc., USA was used to measure the magnetic hysteresis loop at room temperature with the maximum applied field of ± 7 T.

3. Results and discussions

3.1. Structural analysis

Fig. 1 shows the room temperature XRD patterns of $Bi_{0.850}La_{0.150}Fe_{1\text{-}x}Ti_xO_3$ polycrystalline samples with x = 0.000, 0.025, 0.050 and 0.100 annealed at 700 °C. There is ashift of the XRD intensity peaks around 32° towards higher 2θ value with the increase in the substitution percentage of Ti in Fe site of $Bi_{0.850}La_{0.150}FeO_3$ and it is clearly observed in Fig. 2. It is due to smaller ionic radius of Ti (605 Å) compare to that of Fe (645 Å), which will results in a decrease in the lattice constants (discussed later). The main intensity peak of $Bi_{0.850}La_{0.150}FeO_3$ at $2\theta \simeq 32°$ is the combination of two intensity peaks ((104) and (110)). It can be clearly visible by de-convoluting the peak at $2\theta \simeq 32°$ as shown in Fig. 2. With increase in the substitution percentage of Ti, the two peaks are merging into a single intensity peak (110) which is shown in Fig. 2. It suggests that, Ti is getting substituted into the lattice sites. The substitution of Ti creates lattice distortion in the compound and it increases with the increase in Ti substitution in the compound. The increasing lattice distortion leads to a structural transition from rhombohedral to orthorhombic crystal symmetry (discussed later). It can be observed from Fig. 1 that, all the peaks in the XRD pattern of $Bi_{0.850}La_{0.150}FeO_3$ are indexed to $R3c$ space group. It is interesting to note that, there is no secondary phase present in the XRD pattern which can be detected with the limit of X-ray diffraction technique. To support our results, the XRD peak intensities of all compounds are plotted in logarithmic scale and depicted in Fig. 3. This is in good agreement with the earlier report [34].