



Influence of divalent Ni and trivalent Cr ions on the properties of ytterbium modified bismuth ferrite



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ABSTRACT

Different concentrations of Ni²⁺ and Cr³⁺ ions are individually doped in the Fe site of Bi_{0.95}Yb_{0.05}FeO₃ and its effect on structural, band gap, magnetic and electrical properties of bismuth ferrite is analyzed. Samples are synthesized using citrate based sol-gel method. XRD pattern of all the samples confirmed the formation of BFO with rhombohedral crystal structure. Reflectance spectra of the samples show band corresponding to charge transfer and *d-d* transitions in Fe. The direct band gap of the samples is calculated using Kubelka-Munk theory. When compared to Yb modified BiFeO₃, an enhancement of magnetization is observed in the Ni co-doped samples and variation with increase in Cr concentration is seen. All the Ni co-doped samples display high leakage behavior, whereas 1, 3 Cr co-doped samples show low leakage and an increase is observed for 5% Cr concentration. The conduction mechanism responsible for the leakage behavior in the Ni co-doped and Cr co-doped samples is found to be different. Ferroelectric measurements show ferroelectric behavior in all the samples. In Ni co-doped samples, the conducting nature has an influence on observed ferroelectric behavior.

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1. Introduction

Multiferroic materials are in which at least two of ferroics i.e., ferroelectricity, magnetism and ferroelasticity coexist at a certain range of temperature within the same phase [1]. However, the existence of multiferroic materials is very rare, due to the opposite requirements relating to the electronic configuration of *d*-orbital for ferroelectricity and ferromagnetism [2]. Among the multiferroics, BiFeO₃ (BFO) has attracted a lot of attention due to its coexistence of ferroelectricity and magnetism above the room temperature [3]. At room temperature BFO have rhombohedrally distorted perovskite structure with space group *R3c* [4]. BFO is a G-type antiferromagnetic and has spiral spin structure with an incommensurate long wavelength period of ~62 nm, which does not allow net magnetization [5]. The observation of low spontaneous polarization in BFO when compared to many standard ferroelectrics is one of the disappointing factors. The high leakage current in BFO also hinders its practical application for the devices. The high leakage current in BFO is due to the formation of bismuth or oxygen vacancies or formation of impurities during the

synthesis. The formation of oxygen vacancies is mainly due to the bismuth volatility or hopping of Fe from Fe³⁺ to Fe²⁺ [6,7].

In order to overcome the inherent problems in BFO, doping has been chosen as the more convenient way. The substitution of lanthanide/alkaline elements in the A-site (i.e., in the place of Bi) and transition metals at B-site (i.e., in the place of Fe) respectively are used to enhance the multiferroic properties and to lead a way for device fabrication [8–10]. The substitution of di- or tri- or tetra-valent ions in the place of A/B-site also plays a major role. The substitution of divalent ions in the place of A-site may increase the oxygen vacancies [11]. However, in some cases it has been reported that divalent ions in A-site enhances the multiferroic properties [12,13]. Lanthanides (e.g. La, Eu, Gd, Ho and Yb) have been chosen as the most effective in partial replacement of Bi to increase the stability of the compound and enhance the multiferroic properties [14–18].

Yb doped BFO ceramics synthesized by rapid phase liquid sintering exhibits enhanced ferroelectric properties and low leakage current [18]. There are few reports on the effect of magnetic and electrical properties by Ni doping but not much work on ferroelectric and conduction behavior [19,20]. It is reported that Cr doped BFO thinfilm and nanoparticles shows excellent magnetic particles [21,22] and its influence on the electrical properties are

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investigated [23]. Rajput et al. reported the ferroelectric and leakage current by varying the concentration of La and Ni in BFO thin films. With Ni co-doping, an increase in leakage current, low polarization and a well-saturated hysteresis loop are observed [24]. An improved multiferroic properties and strong magnetoelectric coupling are noticed for (Pr, Cr) co-doped BFO nanotubes compared to Pr and Cr singly doped BFO [25]. Recently, we studied multiferroic and leakage current mechanisms in (Nd, Ni) co-doped BFO [26]. Therefore, co-doping is proven to tailor the multiferroic properties of BFO, which is important for basic understanding and practical application. To the best of our knowledge, there are no reports on the Yb and Ni/Cr co-doped BFO.

In this work, different concentrations of Ni^{2+} and Cr^{3+} ions are individually co-doped in the Fe site of $\text{Bi}_{0.95}\text{Yb}_{0.05}\text{FeO}_3$ and their role on the multiferroic properties are investigated. The effect of different dopants ($\text{Ni}^{2+}/\text{Cr}^{3+}$) and its concentrations on the structural, optical band gap, magnetic, ferroelectric and leakage current density properties are studied and reported in detail here.

2. Experimental

The precursors used for the synthesis of $\text{Bi}_{0.95}\text{Yb}_{0.05}\text{Fe}_{1-x}\text{T}_x\text{O}_3$ (where T = Ni/Cr and $x = 0, 0.01, 0.03$ and 0.05) are $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. All the precursors are purchased from Alfa Aesar (India) of GR grade and used without any further purification. The synthesis is done by citrate based sol-gel method and procedure is same as described in our previous report [26], except Yb and Ni/Cr are taken in the stoichiometric ratio to Bi and Fe concentration respectively. The samples are obtained by two-step annealing process, initially the samples are pre-heated at 250°C for 2 h and later at 600°C for 4 h. The final products are used for further characterization.

The X-ray diffraction (XRD) pattern is recorded using Rigaku D/Max Ultima III diffractometer with Cu-K_α anode ($\lambda = 1.54056 \text{ \AA}$) operated at voltage of 40 kV and current 30 mA. 2θ is recorded in the range of $20\text{--}80^\circ$ with a step-size of 0.02° and a scanning speed of 2° per min. JEOL JEM1200 EX II transmission electron microscope (TEM) at an operating voltage of 120 kV is used to obtain the morphology of the samples. The diffused reflectance spectra (DRS) are recorded by Jasco V670 UV–Vis–NIR spectrometer. The magnetic measurements at room temperature are measured using Lakeshore vibrating sample magnetometer (VSM) model 7404. For electrical measurements, powders are made into pellets using pelletizer by applying a pressure of 6 tons and annealed at 600°C for 2 h and silver paste is applied both sides to make electrodes. Leakage current density and ferroelectric measurements are carried out at room temperature using Radiant Precision Premier II multiferroic test system.

In the article, $\text{Bi}_{0.95}\text{Yb}_{0.05}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$ (where $x = 0, 0.01, 0.03$ and 0.05) are denoted as Yb5, Y5N1, Y5N3, Y5N5 and $\text{Bi}_{0.95}\text{Yb}_{0.05}\text{Fe}_{1-x}\text{Cr}_x\text{O}_3$ (where $x = 0.01, 0.03$ and 0.05) are coded as Y5C1, Y5C3, Y5C5 respectively.

3. Results and discussion

X-ray diffraction pattern of all the samples are shown in Fig. 1. The diffraction patterns confirm the rhombohedral structure of BFO with space group $R3c$ and indexed using JCPDS card number 71-2494. A small impurity phase around 28° corresponds to sillenite phase or Bi_2O_3 . The average crystallite size is calculated using Scherrer equation for (012) peak and is found to be 32, 28, 24, 25, 37, 40 and 29 nm for Yb5, Y5N1, Y5N3, Y5N5, Y5C1, Y5C3 and Y5C5 respectively. In case of Ni co-doping, the average crystallite size decreases with the concentration of Ni. However, Cr doped sample

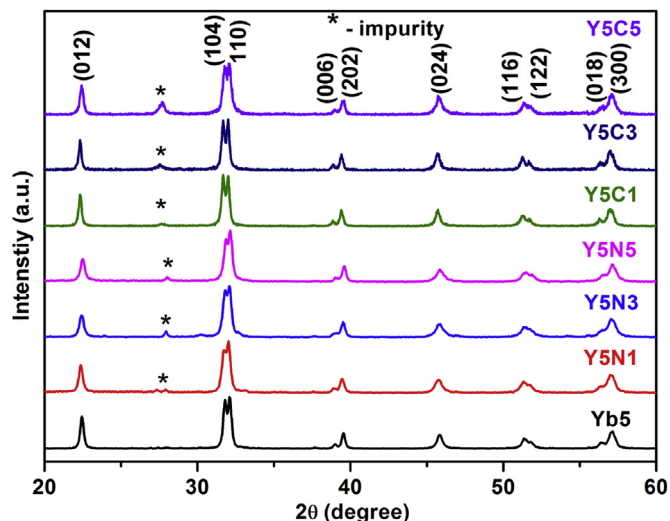


Fig. 1. X-ray diffraction pattern of $\text{Bi}_{0.95}\text{Yb}_{0.05}\text{Fe}_{1-x}\text{T}_x\text{O}_3$ (where T = Ni/Cr and $x = 0, 0.01, 0.03$ and 0.05) samples.

does not follow a uniform trend, the average crystallite size increases upto 3% and beyond which a sudden decrease is observed. Accumulation of metal ions at the grain boundaries inhibits the growth of the crystal and thereby reduces the crystallite size [27]. Rietveld refinement is performed using FullProf software [28]. The initial lattice parameters and atomic positions are taken from the previous report of Selbach et al. [29]. The parameters refined during the refinement are background, lattice parameters, FWHM and shape parameters, atomic positions and asymmetry parameters. Table 1 shows the lattice parameters, atomic positions, bond lengths, bond angles and fitting parameters. The Fe–O–Fe bond angle of co-doped samples is greater than Yb-doped BFO.

TEM images of Yb5, Y5N5 and Y5C5 samples are shown in Fig. 2. It can be seen that particles are agglomerated and no particular morphology is observed. The particle size distribution calculated using Image J software for Y5C5 sample is shown in Fig. 2(d). It is clear from the figure that majority of the particles are in the range of 20–50 nm.

The reflectance spectra transformed to the absorption spectra using Kubelka-Munk (K-M) theory is shown in Fig. 3. The bands around 250 and 360 nm correspond to charge transfer (C-T) of Bi–O. Similarly, the C-T band due to Fe–O is present around 490 nm. The transitions around 670 and 900 nm are attributed to $d-d$ crystal-field transition in Fe^{3+} which are assigned as ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ respectively [30]. As the concentration of Ni or Cr increases, the C-T of Fe–O and Fe $d-d$ transitions undergo a red shift. The peak intensity of $d-d$ transition increases gradually with the concentration of Ni or Cr. The band gap of the samples are calculated using the relation $F(R)h\nu = C(h\nu - E_g)^n$, where $F(R) = (1-R)^2/2R$ is called Kubelka-Munk Function, R is the reflectance, h is the Planck constant, ν is the frequency and E_g is the band gap [31]. The value of n is equal to 2 for the indirect band gap and is equal to 1/2 for direct band gap [32]. As BFO is a direct band gap material, n is equal to 1/2. The direct band gap is estimated by extrapolating the linear region of band tail to y-axis equal to zero from the plot $[F(R)h\nu]^2$ against energy ($h\nu$). The band gap for Yb5, Y5N1, Y5N3, Y5N5, Y5C1, Y5C3 and Y5C5 is 2.18, 2.15, 2.07, 1.98, 2.15, 2.13 and 1.99 eV respectively. The band gap decreases with the concentration of Ni/Cr. The variation of band gap with the concentration of Ni and Cr is shown in Fig. 3(b). From the figure, it is clearly seen that the band gap decreases linearly with the concentration of Ni. Upto 3% of Cr co-doped, the band gap decreases and its variation is also very

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