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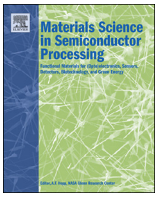

Effect of cobalt substitution on the optical properties of bismuth ferrite thin films

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ABSTRACT

Effect of cobalt substitution on the band gap and absorption coefficient of the $BiFeO_3$ thin films formed on quartz substrate by low cost spin coating method have been investigated. $BiFe_{1-x}Co_xO_3$ ($x=0$, 0.03, 0.06 and 0.10) thin films are polycrystalline and it retains the rhombohedral distorted perovskite structure up to 10 mole % of Co substitution. Smooth and compact surface morphology with uniform size particles are observed in SEM micrographs. Narrowing and broadening of band gap is observed as a function of Co content. Two strong emission peaks at ~2.51 eV and ~2.38 eV are recorded for all films with noticeable change in intensity. Results obtained from the optical absorption and photoluminescence spectroscopy experiments have shown that there exists an inverse correlation between the variation in the band gap and the concentration of oxygen vacancies. Band gap decreased by ~100 meV and absorption coefficient increased by 28% at the wavelength of 375 nm in 6 mole % Co substituted thin film and these observations are necessary requirements to improve the efficiency of photovoltaic devices.

1. Introduction

Bismuth ferrite (BFO), the only RT multiferroic material since $T_c \sim 1103$ K and $T_N \sim 643$ K, has drawn considerable attention in recent years due to its interesting physical properties and its potential applications in sensors, data storage, and spintronics [1]. More research work on BFO in the last decade have been concentrated on its magnetic and electrical properties for the improvement of magnetization, remnant polarization and piezo-electric coefficient values. Recent report of photovoltaic properties on BFO by Choi et al. has provided a new direction for research on BFO to explore it in solar cell [2]. Optical properties like (i) narrow band gap of ~2.7 eV among the ferroelectric perovskites and (ii) increased photoconductivity ($3.68 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$) which further improves with the increase in oxygen vacancy concentration make BFO a potential candidate for solar cells and opto-electronic devices [3].

Any material to be used in solar cell needs to have low band gap and high absorption coefficient to absorb maximum solar radiation. It necessitates the importance of band gap reduction. One of the possible ways to reduce the band gap is chemical substitution. Various elements have been substituted at A^{3+}-site (Nd^{3+} [4] and Eu^{2+} [5]) or B^{3+}-site (Cr^{3+} [6], Mn^{2+} ([7] and Co^{2+} [8]) of BFO thin films. What does the substitution do? Substitution of isovalent ion does not alter the charge neutrality while substitution of heterovalent ion creates an unbalance between sum of cations and anions. When a heterovalent lower charge ion than that of host cation is substituted at the lattice, creation of an anion

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vacancy (i.e. oxygen vacancy) and reduction of cations occur to maintain the charge neutrality. However, it is proved that dominant charge compensation mechanism in the divalent Ni^{2+} doped BFO thin film is the creation of oxygen vacancies (OVs) [9]. When the OVs increase, the concentration of free carriers in the film also increases. It leads to increase in density of states. Previous investigations have suggested that increase in the density of states leads to reduction in the band gap [4,7,8]. The reduction in the band gap value could be due to the existence of defect induced energy levels between the conduction band and valence band, more particularly energy levels close to the conduction band. Optical absorption spectra gives only the variation of band gap with substitution and it does not give the origin whether it is due to increase or decrease in the conduction or valence band. The energy level of the OVs lies just below the conduction band and direct measurement of the concentration of the OVs is difficult. Nevertheless, the variation in the concentration of OVs can be qualitatively related through the intensity of photoluminescence (PL) spectra. Further, PL intensity of defect level emission peak due to OVs is established to vary directly with the concentration of OVs [10]. So, PL intensity of defect level emission peak is attributed to be a measure of concentration of OVs. Recently, an inverse correlation has been observed between the variation of the band gap and concentration of OVs in ZnO through PL studies [11]. Therefore, the present study investigates the relationship between the variation of band gap and the concentration of OVs using optical absorption and PL spectroscopy.

In this work, $BiFe_{1-x}Co_xO_3$ ($x=0$, 0.03, 0.06 and 0.10) thin films were formed on quartz substrates by low cost spin coating method. Effect of cobalt substitution on the optical properties were investigated using optical absorption and PL spectra and causes for the variation in the band gap in terms of concentration of OV's are discussed. Further, lower band gap and higher absorption coefficient criterion are considered to identify the composition that is more suitable for photovoltaic properties.

2. Experimental details

2.1. Materials and synthesis

$Bi(NO_3)_2 \cdot 5H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ were used to prepare 0.3 M concentration precursor solution by dissolving it in ethylene glycol using sol–gel method. The solution was heated to 80 °C/2 h and allowed for ageing at 60 °C/12 h. Viscosity of the sol was 20 cP. Thin films were prepared on the quartz substrate, cleaned with acetone, isopropyl alcohol and de ionized water, by spin coating the sol at 4000 rpm for 20 s. Coated films were dried at 160 °C/300 s using hot plate and then pyrolized at 400 °C/600 s using tubular furnace. Spin coating, drying and pyrolysis actions were repeated to get films of required thickness and finally annealed at 600 °C/1 h.

2.2. Characterizations and measurements

Structural characterization of the films were investigated by XPert Pro PANalytical X-Ray diffractometer operating at 40 KV, 30 mA with Bragg Brentano geometry using Cu Kα radiation. A Scanning Electron Microscope (SEM) (VEGA 3 TESCON) was used to characterize the microstructures. The transmission spectra of thin films were measured at RT on a Techcomp 2301 UV–vis spectrophotometer. The photoluminescence spectra at RT were recorded on a Varian cary eclipse spectrofluorescence meter using a Xenon flash lamp as excitation source. The excitation wavelength was 330 nm.

3. Results and discussion

3.1. Structural analysis

XRD patterns of $BiFe_{1-x}Co_xO_3$ ($x=0$, 0.03, 0.06 and 0.10) thin films are shown in Fig. 1. All (h k l) peaks match with ICDD no. 86-1518 data and it indicates that thin films belong to rhombohedral distorted perovskite structure with R3c space group. Presence of all (h k l) peaks confirms that films are polycrystalline. The preferred orientation of thin film has been observed as (1 1 0). No extra peaks could be detected in Fig. 1, which indicates that films are single phase and Co ion might have substituted in BFO lattice. Further no large shift can be observed in the major peak (1 1 0) position for $BiFe_{1-x}Co_xO_3$ ($x=0.03$, 0.06 and 0.10) when compared to that of BFO. It signifies that the basic rhombohedral distorted perovskite structure has not been affected and it retains the basic structure up to 10 mole % substitution of Co ion. Crystallite size was evaluated from the (1 1 0) peaks using Debye Scherrer's equation for $BiFe_{1-x}Co_xO_3$ ($x=0$, 0.03, 0.06 and 0.10) thin films are 31 nm, 38 nm, 42 nm and 51 nm, respectively. It shows that the substitution of Co in BFO thin films leads to increase in crystallite size.

3.2. Morphological analysis

Fig. 2(a) and (b) shows the surface micrograph of the $BiFe_{1-x}Co_xO_3$ ($x=0$ and 0.06) thin films. BFCO $x=0.06$ thin film shows a homogeneous and uniform surface when

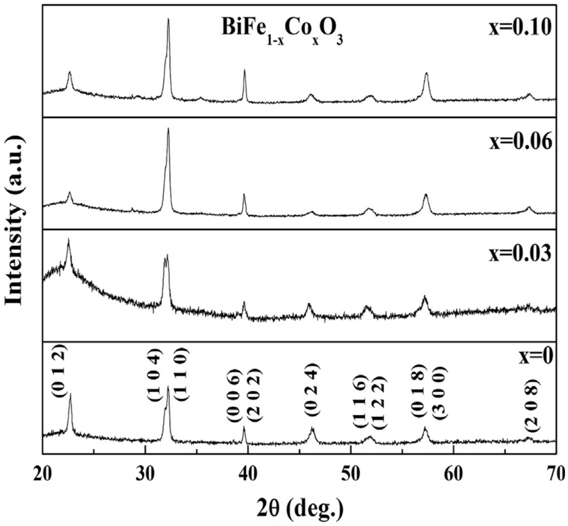

Fig. 1. Powder XRD pattern of $BiFe_{1-x}Co_xO_3$ (x=0, 0.03, 0.06 and 0.10) thin films.