Structural and optical properties of Bi$_{1-x}$A$_x$FeO$_3$ (A = Sr, Ca; $0.40 \leqslant x \leqslant 0.55$)
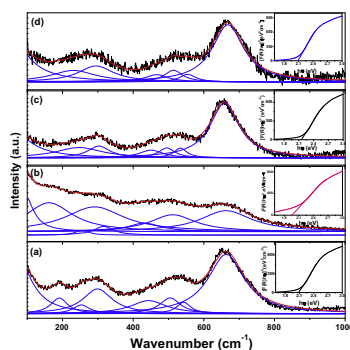
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Samita Thakur, O.P. Pandey, K. Singh *

School of Physics & Materials Science, Thapar University, Patiala 147004, India

HIGHLIGHTS

- Sr^{2+}/Ca^{2+} substituted BiFeO$_3$ are synthesized and characterized.
- Substitution has profound effect on structural and optical properties.
- Bi$_{0.45}$Sr$_{0.55}$FeO$_3$ exhibits lowest optical band gap.

GRAPHICAL ABSTRACT

ABSTRACT

The effect of Sr^{2+} and Ca^{2+} cation substitution on BiFeO$_3$-type (Bi$_{1-x}$A$_x$FeO$_3$; A = Sr, Ca; $0.40 \leqslant x \leqslant 0.55$) ceramics are investigated for structural and optical properties. X-ray diffraction patterns confirmed that Ca^{2+}/Sr^{2+} substitution facilitates the formation of tetragonal phase instead of rhombohedral phase as observed in undoped BiFeO$_3$ (BFO). The iodometric titration results show that substitution of Sr^{2+} has higher tendency to form oxygen vacancies than Ca^{2+} substituted samples. On the other hand, Ca^{2+} substitution shows opposite trend. The FT-IR and Raman spectra show shift in the peak positions towards higher wavenumber and diffused bands with the increasing concentration of substituent. The parameters like band gap energy, Urbach energy has been calculated from the UV–visible spectra. Sr^{2+} substituted samples show higher structural distortion and low optical band gap values which can be correlated to the higher oxygen vacancies and low Fe^{4+} content as compared to Ca^{2+} substituted samples.

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Introduction

Among various multi-ferroic materials, undoped and doped BiFeO$_3$ (BFO) is widely studied compound due to simultaneous existence of ferro-electricity with Curie temperature of 830 °C and anti-ferromagnetism with Neel's temperature of 370 °C [1–3]. In addition to multi-ferroic properties, BFO can also be used in variety of devices because of its interesting optical and photocat-alytic properties [4,5]. However, undoped BFO exhibits secondary phase as an impurity which restricts its applications. The forma-tion of secondary phase can be suppressed by proper doping at A and B or both the sites of BiFeO$_3$ (ABO$_3$) [6,7]. Thus, the main focus of most studies is on the use of dopants such as rare earth metals, transition metals and alkaline earth metals to improve the differ-ent properties of BFO. Doping at both sites (A and B sites) gives rise to oxygen non-stoichiometry and conversion of Fe^{3+} into Fe^{2+}/Fe^{4+} to maintain the charge neutrality of the system. The aliovalent substitution such as Ba^{2+}, Pb^{2+}, Sr^{2+} and Ca^{2+} at bismuth site creates oxygen vacancies and transforms Fe^{3+} to Fe^{4+}. It will affect the

* Corresponding author. Tel.: +91 1752393130; fax: +91 1752393005.
E-mail address: kusingh@thapar.edu (K. Singh).

degree of off-centring of FeO_6 octahedra and thus also dielectric and magnetic properties of BFO [2,8–10]. In addition to this, it also results in stabilization of low symmetric crystal structure which can improve the megnetoelectric and optical properties of the doped BFO. On the other hand, the doping also generates many controversies in scientific community related to the structural variation and defect chemistry. In most of the studies, Sr^{2+}, Ca^{2+}, Pb^{2+} and Ba^{2+} doped $BiFeO_3$ ceramics are indexed with rhombohedral structure [11–14]. Contrary to these reports, other researchers have claimed the cubic, orthorhombic and triclinic structure for different doped $BiFeO_3$ systems [15–17]. Similarly, Pokalitov et al. [18] and Li et al. [19] have reported the cubic structure (pm-3m) for $0.20 \leqslant x \leqslant 0.67$ whereas, Varshenay et al. [20] have reported the tetragonal structure (P4/mmm) of $Bi_{1-x}Sr_xFeO_3$ ($0.1 \leqslant x \leqslant 0.25$) system.

The variation in crystal structure with various dopants and their concentration influences the properties such as electric, magnetic and optical properties. As optical band gap is strongly influenced by the defects and generation of oxygen vacancies [21,22]. So, it will be interesting to investigate the effect of higher dopant concentration on the optical properties. Moreover, the change in oxidation state of Fe^{3+} to Fe^{2+}/Fe^{4+} may also influence the optical properties. The motivation of the present work is to investigate the effect of two different substituent cations Ca^{2+} (1.12 Å) and Sr^{2+} (1.26 Å) in which one is smaller in size to the parent cation and second is larger than parent cation Bi^{3+} (1.17 Å) on the structural and optical properties. The correlation between the structure and different properties is established based on the nature of two different substituents and their concentration.

Experimental techniques

The samples of $Bi_{1-x}A_xFe_xO_3$ (A = Ca, Sr; x = 0.0, 0.40 $\leqslant x \leqslant$ 0.55) were synthesized by conventional solid state reaction method using powders of Bi_2O_3 (99.9%), SrO (99.9%), CaO (99.9%), Fe_2O_3 (99.8%). These chemicals were used without further purification. The powders in their stoichiometric ratio were ground for 2 h in agate mortar pestle in acetone media for undoped $BiFeO_3$. The resulting ground powder was heat treated at 650 °C and 800 °C for 1 h with intermediate grinding. The sintered powder was treated with 10% nitric acid to leach out the secondary phase. The acid treated powder was compacted into circular disks of 10 mm diameter by applying a 12 kN/cm^2 of pressure and again heat treated at 550 °C. The more details of sample preparation are given elsewhere [23]. The as prepared sintered samples were characterized using X-ray diffraction (XRD) for the phase identification. X-ray powder diffractions study was performed at room temperature using PANalytical X'Pert PRO system with Cu Kα (1.54 Å) and Ni-filter in the range of $20° \leqslant 2\theta \leqslant 70°$ with step size of 0.013°. The oxygen stoichiometry and average oxidation state of the iron in the present studied system was calculated by iodometric titration. The titration was performed as described in literature for perovskite type oxides [24]. Approximately 0.1 g of powder sample was dissolved in 10 ml of HCl and 10% KI solution under argon atmosphere (to prevent the oxidation state of iodide ions in the air). Then the solution was titrated by 0.01 M sodium thiosulphate solution. Few drops of starch solution were added to indicate the end points when the initial transparent solution changes its color from orange to yellow. The changes in local structures of the samples were examined by Raman spectroscopy. Raman spectra of the samples were collected using a Renishaw in via Raman spectrometer with the 514.5 nm line of an Ar^+ laser at 20 mW power. The instrument was calibrated using silicon as a reference at 520 cm^{-1} within ±1 cm^{-1}. FTIR spectra were obtained at room temperature by using Perkin Elmer model RZX spectrometer in

the region 400–1200 cm^{-1}. The spectrum of each sample was normalized to the spectrum of blank KBr. The diffuse reflectance spectra of the powder samples were recorded using a double beam UV–Vis spectrophotometer (model: Hitachi U-3900H) in the wavelength range of 200–800 nm at room temperature. Approximately 3 mg of powder was used and the instrument was calibrated by using aluminum oxide for 100% reflectivity.

Results and discussion

X-ray diffraction

Fig. 1 shows the XRD patterns of $Bi_{1-x}A_xFeO_3$ (A = Ca, Sr; x = 0.0, 0.40, 0.50). The XRD results confirm that undoped $BiFeO_3$ has some phase which can be indexed as $Bi_2Fe_4O_9$ while Sr^{2+}/Ca^{2+} substituted samples are single phase except $Bi_{0.45}Ca_{0.55}FeO_3$ which has $Ca_2Fe_2O_5$ as secondary phase. In undoped $BiFeO_3$, the peak around 32° is clearly splitted and indicates the rhombohedral structure [21]. However, for the lower valent cation substitution such as Ca^{2+} and Sr^{2+}, these peaks merge and form a broad peak (as shown in Fig. 1(right)). This change in diffraction peaks indicates that rhombohedral structure of $BiFeO_3$ has been modified and reduced towards more symmetric structure like tetragonal. Moreover, the XRD peaks have been shifted as compared to pure $BiFeO_3$ due to difference in ionic radii of substituent cations and parent cation. The XRD peaks shift to higher diffraction angle in both cases. The shifting of peaks towards higher angles is quite obvious in Ca^{2+} substituted system due to smaller ionic radii of Ca^{2+} (1.12 Å) as compared to Bi^{3+} (1.17 Å). However, in case of Sr^{2+} substituted system, these peaks should shift towards lower smaller angle due to larger ionic radii of Sr^{2+} (1.26 Å) as compared to Bi^{3+}, whereas they are showing opposite trend in the present system [13,25]. This can be due to the generation of oxygen vacancies and change in oxidation state of Fe^{3+} to Fe^{4+} due to charge imbalance created by the substituent in the present system (as discussed in iodometric titration). It can be seen from Fig. 1 (right) that the XRD peaks of Sr^{2+} substituted $BiFeO_3$ system is broader as compared to Ca^{2+} doped $BiFeO_3$ system. The full width at half maxima (FWHM) of Sr^{2+} doped system for 32° reflection is 0.1578° as compared to 0.1224° of Ca^{2+} doped system. This can be attributed to higher disordering in Sr^{2+} doped $BiFeO_3$ as compared to Ca^{2+} doped systems.

X-ray diffraction peaks can also be used to calculate the crystallite size and lattice strain due to the substitution of cations and dislocations. The breadth of a XRD peak is combination of both instrument and sample dependent effects. The instrumental broadening was corrected by using following relation [26]

$$\beta_{hkl} = \left[(\beta_{hkl})^2_{measured} - (\beta_{hkl})^2_{instrumental} \right]^{\frac{1}{2}} \tag{1}$$

To calculate crystallite size, Scherer's formulae [27] has been used i.e.

$$D = \frac{k\lambda}{\beta_{hkl} \cos\theta} \tag{2}$$

where D is crystallite size, k is shape factor (0.94), λ is wavelength of Cu Kα radiation, β_{hkl} is width of peak at half maximum in radians and θ is peak position.

The crystal imperfections and dislocations in the crystal structure also induces the strain (ε) which also increases the XRD peak broadening and is related with this as follows [28]

$$\varepsilon = \frac{\beta_{hkl}}{4 \tan\theta} \tag{3}$$

From Eqs. (2) and (3) it is clear that both of them depend upon θ, but crystallite size and strain varies as $\cos\theta$, and $\tan\theta$, respectively. The distinct dependency of both effects enables us to separate the