Bandgap engineering of cobalt-doped bismuth ferrite nanoparticles for photovoltaic applications

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Abstract. The bandgap energy range of multiferroic bismuth ferrite is 2.2–2.7 eV, making it a promising candidate for photovoltaic (PV) applications. But its efficiency is still very low (<2%). This report thus focusses on the application of bismuth ferrite (BFO) engineered with cobalt (Co) doping and on the tuning of its bandgap energy (E_g). BiFeO₃ is a unique multiferroic material that simultaneously displays both ferromagnetic and ferroelectric properties at room temperature. Co doped with pure BiFeO₃ (BiFe_(1-x)Co_xO₃; $x = 0, 0.05, 0.1$ and 0.15) was synthesized by the sol–gel method and annealed at 600°C. X-ray diffraction shows the well-arranged crystalline structure and peaks of pure and doped-BiFeO₃ nanoparticles. A suitable reduction of E_g has been observed for Co-doped BiFeO₃, which may be appropriate for the effective use in PV solar cells. Thermogravimetric analysis and differential scanning calorimetry were used to investigate the thermal decomposition character of the xerogel powder and the pattern of pure and doped BiFeO₃ phases. Field emission scanning electron microscopy images show the surface crystallography of pure and Co-doped BiFeO₃. Co-doped BiFeO₃ has considerably reduced the crystallite and particle size of the samples. We have calculated the E_g of pure and doped BiFeO₃ using a UV–Vis–NIR spectrophotometer and the results show the important reduction of E_g (1.60 eV) of the Co-doped samples, which may have potential applications in PV solar cells.

Keywords. Bandgap; multiferroic; nanoparticles; photovoltaic cells; sol–gel.

1. Introduction

All over the world, the power sector is facing challenges. Therefore, significant efforts have been made to study a wide range of materials that could be used in photovoltaic (PV) solar cells to develop an alternative renewable energy source [1–3]. BiFeO₃ (BFO) shows ferroelectric or anti-ferroelectric and ferromagnetic or anti-ferromagnetic properties simultaneously in the same phase. Consequently, an induced electric field can give rise to magnetization and an external magnetic field can stimulate electric polarization. Multiferroic materials are of low cost, stable and easily available. The electrical properties like bandgap of oxide materials are tunable by using the doping or co-doping procedure. This makes BFO a promising candidate for application in PV cells. The ferroelectric oxides have been investigated for more than thirty years for their PV effect. The PV effect is directly related to the non-centrosymmetry of a unit cell, as a result the asymmetries in electron excitation, recreation and scattering processes [4–6]. But the efficiency (η) of a PV solar cell

was observed to be very less due to low current densities (10^{-9} A cm⁻²) and the large E_g for these materials. It was asserted that E_g in the range of 2.2–2.7 eV for BFO should be explored as an alternative material for PV solar cells [7,8]. The rare earth metals doped in BFO entered a less impurity phase and the particle size became smaller, but the bandgap was not yet reduced significantly [9]. But doping of transition metals may be a possible option for reducing E_g .

Here, a trivalent transitional metal ion Co²⁺ was selected to replace Fe³⁺ cations in BFO. Pure BFO, doped-BiFe_{0.95}Co_{0.05}O₃ (BFCO-5), BiFe_{0.9}Co_{0.1}O₃ (BFCO-10) and BiFe_{0.85}Co_{0.15}O₃ (BFCO-15) nanoparticles were synthesized and annealed then the structure, morphology and E_g were investigated in detail for the samples.

2. Sample preparation

The pure and doped BFO nanoparticles were synthesized by the sol–gel method. Stoichiometric amounts of Bi(NO₃)₃·

$5\text{H}_2\text{O}$ of 99% purity (Merck, India) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ of 98% purity (Merck India) along with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ of 97% purity (Merck, India) were liquefied in 400 ml deionized water as a sol form. Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) was used as the chelating agent and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) was used as the polymerization agent. The details of the sol–gel process can be found elsewhere [10]. The gel was heated at 120°C for 24 h to obtain xerogel. Then, the xerogel was grinded to form a powder. This powder was annealed at 600°C for 2 h in a high temperature furnace. The heating/cooling rate was maintained at 3°C min^{-1} . The main reaction occurred in the furnace and the nanopowder samples were grinded again to ultimately obtain nanoparticles for characterization.

3. Experimental results and discussion

3.1 TGA and DSC

The xerogel powders were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (model: NETZSCH STA 449F3, Germany). Figure 1 shows the TGA–DSC curves of pure and Co-doped BFO for BFCO-5 xerogel powders and it is evident that the doped BFO curves show a right shift of about 9°C . Both samples were heated up to 600°C and then cooled down to room temperature. Initially, the weight loss was 19 and 26% up to 193 and 202°C , respectively, due to the dryness of the xerogel powders of pure and doped BFO, respectively. It is shown that a sharp major loss of 54 and 40% was observed aligned with peaks in the weight loss curves, respectively. An insignificant weight loss was observed in the curves between 400 and 600°C . This can be explained as being caused by the elimination of entrapped gases from the porous powder xerogel [11]. The pure and doped BFO peaks associated with the quick weight loss may be ascribed to the decomposition

Figure 1. TGA–DSC analysis curve of pure BFO and Co-doped BFO xerogel powder.

Figure 2. XRD patterns of: (a) BFO, (b) BFCO-5, (c) BFCO-10 and (d) BFCO-15 nanoparticles.

Table 1. Structural properties of pure and Co-doped BFO nanoparticles acquired from Rietveld refinement.

Samples	BFO	BFCO-5	BFCO-10	BFCO-15
Space group	<i>R3c</i>	<i>R3c</i>	<i>R3c</i>	<i>R3c</i>
Lattice parameters	$a = 5.57764(35) \text{ \AA}$ $c = 13.86421(87) \text{ \AA}$ $v = 373.531(24) \text{ \AA}^3$	$a = 5.57589(40) \text{ \AA}$ $c = 13.85796(99) \text{ \AA}$ $v = 373.129(27) \text{ \AA}^3$	$a = 5.57554(27) \text{ \AA}$ $c = 13.85374(66) \text{ \AA}$ $v = 372.968(18) \text{ \AA}^3$	$a = 5.57544(21) \text{ \AA}$ $c = 13.85312(54) \text{ \AA}$ $v = 372.937(15) \text{ \AA}^3$
Density (g cm^{-3})	8.3428	8.3518	8.3554	8.3561
<i>R</i> (expected) (%)	4.16776	3.94974	3.95436	3.89819
<i>R</i> (profile) (%)	4.48905	3.68386	3.55777	3.81668
<i>R</i> (expected profile) (%)	5.72454	4.78561	4.87354	5.53319
Bragg <i>R</i> factor (%)	2.52525	1.84456	0.77354	1.08788
Goodness of fit	1.37353	1.21163	1.23245	1.41942

Table 2. Average particle size, crystal size, lattice strain and bandgap energy of BFO, BFCO-5, BFCO-10 and BFCO-15 nanoparticles.

Samples	BFO	BFCO-5	BFCO-10	BFCO-15
Particle size (nm)	176	166	132	110
Crystallite size (nm)	68.3	52.9	49.2	45.2
Lattice strain (%)	0.186	0.241	0.257	0.280
Bandgap (eV)	2.1	1.85	1.8	1.6

of the polymer backbone of the compound and the combustion of most of the organic materials [11,12]. Both peaks can be attributed to NO_3^- decomposition, uncompensated COO^- groups of $\text{C}_6\text{H}_8\text{O}_7$ and some other groups like O-H and C-H . No peaks were identified above 220°C . This indicates that the decomposition of NO_3^- and all other organic phases are nearly completed. The benefit of using $\text{C}_6\text{H}_8\text{O}_7$ as an alternative to other composite agents is that pure and doped BFO phases can be obtained at lower temperatures [13,14].

3.2 XRD

The nanoparticles were characterized by X-ray diffraction (XRD) (model: PANalytical EMPYREAN) at room temperature. The high intensity X-ray beams were diffracted on the samples for the scanning limit from 10 – 70° . Figure 2a–d shows the XRD patterns for BFO, BFCO-5, BFCO-10 and BFCO-15 nanoparticles. XRD patterns clearly confirmed the crystalline nanoparticles from the synthesized samples. The Rietveld refinement of nanoparticles was conducted using the High Score Plus Software. It is clearly seen that all the peaks of the doped BFO nanoparticles matched well with the crystalline structure of undoped BFO and showed a rhombohedral lattice with the space group *R3c*. Small traces of the secondary phase ($\text{Bi}_2\text{Fe}_4\text{O}_9$, orthorhombic with the *Pbnm* space group) were found at 28° , marked by (*) on the XRD patterns. The apparently unavoidable secondary phases seen during the synthesis of the BFO-based materials by the sol–gel method have been reported in several papers [15,16].

The secondary phase in BFO is the main concern because Bi^{3+} and/or Fe^{3+} vacancies assist in creating these types of secondary phases. Table 1 shows the structural parameters for pure and Co-doped BFO nanoparticles from the Rietveld refinement data. The *R* factors fall slightly and goodness of fit values are in the range of 1.2–1.4, which indicate that the synthesized samples are appropriate. The calculated crystallite size and lattice strain are presented in table 2. From figure 2a–d, it is observed that with an increase in the Co dopant, the intensity of some peaks, (104), (112) and (220), becomes weak and the secondary phase $\text{Bi}_2\text{Fe}_4\text{O}_9$ becomes strong.

The crystallite size has been calculated using the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta}, \quad (1)$$

where β , full-width at half-maximum intensity; k , dimensionless constant with a typical value of 0.9; λ , wavelength of $\text{CuK}\alpha$ radiation with the value of $1.5418 \text{ \AA}$; and θ , Bragg angle of the diffraction peak.

The crystallite size decreases from 68.3 to 45.2 nm with an increase in the Co^{2+} doping level, because there is a difference in the ionic radius between Co^{2+} ($0.745 \text{ \AA}$) and Fe^{3+} ($0.645 \text{ \AA}$) that will lead to lattice (octahedral rotation) distortion and shrink the crystal structure. It plays a vital role in determining the optical properties of pure and doped BFO as well.

Figure 3. FESEM images of synthesized nanoparticles: (a) BFO, (b) BFCO-5, (c) BFCO-10 and (d) BFCO-15.

Lattice strain was also calculated using Bragg's law:

$$d = \frac{n\lambda}{2 \sin \theta}, \quad (2)$$

where d , lattice spacing and n , order of reflection.

Lattice strain:

$$\varepsilon = \frac{\Delta d}{d_1}, \quad (3)$$

$$\Delta d = d_1 - d_2. \quad (4)$$

A shift in peak positions was observed with Co-doped BFO. The peaks shift from right to left, causing a reduction in the interplanar spacing which in turn contributes to an increase in the lattice strain and a reduction in the crystallite size. Table 2 shows that the lattice strain increases from 0.186 to 0.28% with an increase in Co doping in BFO.

3.3 FESEM

Field emission scanning electron microscopy (FESEM) (model: JEOL JSM-7600F) was used to detect the morphology of BFO and doped BFO. Figure 3a–d shows the FESEM micrographs of BFO, BFCO-5, BFCO-10 and BFCO-15, respectively. The nanoparticles of pure and Co-doped BFO are almost spherical in shape and identical in size distribution. The particle size of FESEM was measured using the ImageJ software. The FESEM images show that the Co dopant considerably reduced the particle size of pure BFO from 176 to 110 nm as shown in table 2. This indicates that Co doping suppresses grain growth of pure BFO. The particle size may be decreased because of the mismatch of the ionic radius of Fe^{2+} and Co^{2+} . The difference in the ionic radii between Fe^{2+} (0.645 Å) and Co^{2+} (0.745 Å) subjected to a lattice deformation, which hinder crystallite nucleation, as a result, the particle size is reduced. For the sol–gel synthesis method, the complex mythology of precursor xerogel cover the nanocrystals and hinder particle agglomeration. During annealing at 600°C, the citrate complexing agents evaporate at temperatures above 300°C. The particle size measured from the FESEM micrographs was found to be larger than the crystallite size estimated from XRD analysis. Due to the higher surface area to volume ratio of nanoparticles, led to agglomeration, which resulted in the assemblage of a number of crystallites into a particle [17].

3.4 Bandgap engineering

Because of small bandgap energy, BFO is very effective as a visible-light irradiator. It is established that the PV absorption ability of BFO is directly related to its electronic structure and is considered as the key factor to calculate its bandgap energy [18]. The optical E_g of BFO nanoparticles was measured by the diffuse reflectance spectra using a

Figure 4. $[F(R)hv]^2$ vs. hv plots for BFO, BFCO-5, BFCO-10 and BFCO-15 nanoparticles.

UV–Vis–NIR spectrophotometer (Model: PerkinElmer UV–Vis–NIR Spectrometer Lambda 1050).

The Kubelka–Munk equation was used to calculate the E_g for all pure BFO and doped BFO. The diffuse reflectance data were changed to the Kubelka–Munk function by:

$$F(R) = \frac{(1 - R)^2}{2R}. \quad (5)$$

Here, R is the diffuse reflectance. Figure 4 presents the $[F(R)hv]^2$ vs. hv (bandgap energy, eV) plots for all nanoparticles. Basically, solar radiation with wavelengths ranging from 380 to 750 nm (violet to red) strikes the material with enough energy to knock electrons from their weak bonds and create an electric current. The unused wavelengths, ultraviolet (10–380 nm) and infrared (750–1,000,000 nm) do not have enough energy to dislodge the electrons and are absorbed as heat. Thus, we considered the wavelength range of 200–800 nm for capturing the data. The intersection of the tangent line at $[F(R)hv]^2 = 0$, indicates the bandgap energy, eV [19],

which is correlated with the energy (eV) difference between the valence band (VB) (O 2p) and the conduction band (CB) (Fe 3d) of BFO. The obtained values of E_g for pure BFO, BFCO-5, BFCO-10 and BFCO-15 are shown in table 2.

There are several explanations for the reduced E_g in the doped BFO. The reduction of E_g in all doped samples can be related to distortion generation in the Fe–O octahedral reordering of molecular orbitals [20]. Also, the values of E_g depend on the particle size, which means that if the particle size is small, the E_g will be reduced [21–24]. Additionally, interchanges in the Fe–O bond length and Fe–O–Fe bond angle by cation dopants play a significant role in changing one electron bandwidth (W) and hence, reportedly have an important influence on the E_g of BFO [25]. The CB edge of Co ($E_{cb} = -4.39$ eV) is less than that of Fe ($E_{cb} = -4.33$ eV) [26], which reduces the effective bandgap energy between the O 2p VB and the Fe 3d CB and thereby reducing the E_g of BFCO nanoparticles. The experimental formula shows the W with the bond length and angle:

$$W \propto \frac{\cos \omega}{d_{\text{Fe-O}}^{3.5}}, \quad (6)$$

where $\omega = 1/2\{\pi - (\text{Fe} - \text{O} - \text{Fe})\}$ and $d_{\text{Fe-O}}$ is the Fe–O bond length. E_g is correlated with W as:

$$E_g = \Delta - W, \quad (7)$$

where Δ is the invariant charge-transfer energy [27]. Also, the Fe–O orthorhombic phase bond length is much less than that of the rhombohedral phase [28]. Co doping in BFO nanoparticles can significantly increase the value of W and as a result, there is a decline in the effective value of E_g with an increase in the orthorhombic phase [29]. From table 3, one can observe that the bond angle (Fe–O–Fe) is increased and the average bond length (Fe–O) is decreased with an increase in Co doping concentration. According to the bandwidth equation, increased bond angle enlarges the value of W ; similarly, decreased average bond length also enlarges the value of W . Thus, the enhanced W decreases the value of E_g .

Table 3. Major structure, average bond length and bond angle of pure and Co-doped BFO samples.

Samples	Major constituent	Bond length Fe–O (Å)	Average bond length Fe–O (Å)	Bond angle Fe–O–Fe (°)
BFO	R3c	1.95382(3) 2.10815(3)	2.030985	154.7744
BFCO-5	R3c	1.97177(3) 2.08668(3)	2.029225	154.9686
BFCO-10	R3c	1.95121(3) 2.10215(3)	2.02668	155.6974
BFCO-15	R3c	1.87024(3) 2.15941(3)	2.014825	158.8395

4. Conclusion

Pure and Co-doped BFO samples have been synthesized by the sol–gel method. TGA–DSC analysis was conducted for the heat flow and weight loss of xerogel samples, which showed the peak shift of doped BFO by 9°C. The structure, XRD and bandgap energy have been studied successfully. The crystallite size of doped BFO by Co was found to be decreased when compared with that of pure BFO. Co-doped BFO also enhanced its optical properties, which are related to the bandgap energy. Transition metal Co-doped BFO leads to structural transformation from the rhombohedral (*R3c*) to orthorhombic (*Pn21a*) symmetry and that was found to have a considerable effect on the bandgap energy. The bandgap energy of Co-doped BFO is reduced from 2.1 to 1.6 eV. This reduced value is closely comparable to the ideal value of 1.5 eV (equivalent to the maximum theoretical power conversion efficiencies for a semiconductor-based PV solar cell) and this BFCO-15 may find prospective applications in PV devices.

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