Synthesis, structure and optical properties of lithium and zinc doped BiFeO$_3$ by sol gel method

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Abstract. BiFeO$_3$ is one of the multiferroic materials and have a wide range of application. For that reason, pure BiFeO$_3$ (BFO), Li and Zn doped BFO were synthesized by sol-gel method. Structure and optical properties of BiFeO$_3$ were characterized by using X-ray diffractometer and UV-Vis spectrophotometer. Pure BiFeO$_3$ and single phase Li-doped BiFeO$_3$ were detected from XRD pattern. Two-phase were identified in Zn doped BiFeO$_3$. The Structure parameters of the three samples seem altered. Doping Li and Zn decrease crystal parameter. The Energy gap was calculated from the UV-Vis absorbance pattern, and pure BiFeO$_3$, Li and Zn doped BiFeO$_3$ have energy gaps 2.81, 3.19 and 4.82 eV respectively. The decrease of crystallite structure caused by the doping would raise the band gap energy.

1. Introduction
Multiferroic materials have great importance due to a wide range of functional applications and their interesting fundamental physics [1]. This materials combines two or more primary ferroic orderings out of ferroelectricity, ferromagnetism and ferroelasticity [2,3]. The most interesting thing about these materials is their promising candidate for many photonic applications, electro-optical modulation, infrared detection, and photoconduction [4]. Mostly studied single-phase ABO$_3$ type perovskite multiferroics are BiFeO$_3$ (BFO), BiMnO$_3$ (BMO) and some rare earth manganites like YMnO$_3$ [5].

Among them, BFO is one of the most promising candidate that retains ferroelectric ($T_C \sim 825^\circ$C) along with G-type antiferromagnetic (Neel temperature, $T_N \sim 360^\circ$C) observed at room temperature [6,7]. The structure possesses rhombohedrally distorted perovskite with space group R3c and the refine lattice parameters described as $a_{\text{hex}} = 5.5820$ Å, $c_{\text{hex}} = 13.8758$ Å, $V_{\text{hex}} = 374.429$ Å$^3$ at standard conditions [8]. This material is synthesized in various forms like bulk, nanoparticles and thin films [9–11]. Furthermore, bulk form of BFO offers insignificant electric and magnetic moments. So, it is beneficial to synthesize the form of BFO in thin films or nanoparticles which size is less than period of cycloid modulation, i.e. 64 nm [12].

As a most investigated multiferroic, the practical applications of BFO had limitation caused by an instability composition and their defect. Nevertheless, the ratio phase-pure synthesis of the BFO is a stimulating strain. The solid-state reaction of Bi$_2$O$_3$ and Fe$_2$O$_3$ at high temperature become the conventional synthesized of BFO. However, kinematics reaction of this method suggests that stability
of the temperature is very small and leads to impurity phases like Bi$_2$FeO$_6$ and Bi$_2$ZnFeO$_{19}$ [13]. Various methods have been reported for the synthesis of BFO nanoparticles, like co-precipitation, micro-emulsion technique, mechanochemical, hydrothermal, sol–gel and solution combustion route, by wet chemical in low temperature [14,15]. Besides, several literature describe auto-combustion route but it is rare to find collective studies for structural and optical properties of BFO nanoparticles. Out of these, BFO has a small band gap lying in visible region, so it finds potential application as a visible light photo-catalyst [16]. For the integration of doped BFO into its functional structures, it is also crucial to investigate the stability of BiFeO$_3$, and to study the impact of possible parasitic phases on the optical properties.

Therefore, the purpose of this work is to synthesize stoichiometric phase BFO doped Li and Zn nanoparticles at low temperature via sol-gel auto-combustion route as a simple method to investigate structural and optical properties while maintaining the structure of BFO.

2. Experimental Methods

2.1. Sample synthesis

Bismuth ferrite (BFO) nanoparticles were synthesized by low-temperature sol-gel followed by auto-combustion route, which was based on weight percent (wt%) fraction. In this method, Bi(NO$_3$)$_3$·6H$_2$O, CH$_3$COOH·2H$_2$O, Zn granular and Fe(NO$_3$)$_3$·9H$_2$O (Sigma Aldrich, purity > 99 %) were used as starting materials according to the wt% fraction of BiFeO$_3$, Bi$_{0.96}$Li$_{0.04}$FeO$_3$ (BLFO), and Bi$_{0.7}$Zn$_{0.3}$FeO$_3$ (BZFO). First, bismuth nitrate was dissolved in 5 ml nitric acid room temperature, and then iron nitrate and other precursor was added to it. Zn solution was prepared by dissolving the granular form into 5 ml nitric acid before adding bismuth nitrate. After all of the precursors were inserted, then citric acid as a chelating agent was added in 3:1 molar ratio with precursor ions. The solution was stirred actively at 80–90°C for 2–3 hour till brown and transparent viscous gel which was subsequently kept in an oven at 120°C for 24 hour to obtain xerogel. Then, the xerogel was grounded into powders and transferred to a crucible, which was heated to 600°C with a heating rate of 10°C min$^{-1}$ and followed by cooling down naturally as the powders product. At that the heating process, the auto-combustion occurs.

2.2. Characterization

The study of BFO phase structure and nanoparticles were carried out by XRD with PANalytical Diffractometer (Model: X’Pert Pro; Cu-K$_{α_1}$, $λ = 1.5405$ Å) at room temperature. Fourier transform infrared spectroscopy (FTIR) (SHIMADZU IRPrestige-21) was used to determine the chemical bonding of the product. The UV–vis absorption spectra of the BFO nanoparticles were measured on SHIMADZU UV-2450 UV–vis spectrophotometer.

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction pattern at room temperature of BFO nanoparticles powder sintered at 600°C is shown in figure 1. All the diffraction peaks are indexed with various (h k l) planes according to rhombohedral structure. Each peak position was found to be in good agreement with the perovskite BiFeO$_3$ [ICSD 98-018-0501].

Further, hexagonal crystal structure of the BFO was confirmed by the clear splitting of peaks (1 0 4) and (1 1 0). Sharp and high intensity XRD peaks support the good crystallinity of the as-synthesized BFO nanoparticles. Traces of some low intensity peaks corresponding to secondary phases like Bi$_2$ZnFeO$_{19}$ were identified in Zn doped [17,18]. But, overall there had been a good control over the non-perovskite phases which confirms the phase purity of BFO nanoparticles. Thus, loss of Bismuth was minimized due to low temperature synthesis in this method. The Rietveld refinement was performed using HighScore software package with starting parameters for hexagonal system of basis and space group R3c. The refined unit cell parameters $a_{hex}$, $c_{hex}$ and $V_{hex}$ of all the sample are shown in table 1 respectively and have resemblance with that reported previously [8,19,20]. There is also good agreement between observed and reference XRD peak patterns (figure 1). In our case, the refinement
Goodness of Fit parameters (<1.6) and R-factors are very low compared with some previous reports ([21]. This matter had shown that the resemblance values between the doping sample structures which had made with the reference structure were much better. The obtained peaks of the powder XRD were found to be broad which is due to the nano-crystallite size of BFO. The crystallite size of the BFO nanoparticles was calculated using Scherrer formula [22],

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

(1)

3.2. Vibrational studies

To understand the vibrational properties of the BFO nanoparticles, their FTIR spectrum was also measured, as shown in figure 2. In which, a two absorption peaks at 548 and 432 cm\(^{-1}\) were also observed, which are assigned to the Fe-O stretching vibration mode along the Fe-O axis and the bending vibration mode, respectively. These two peaks are the characteristics of octahedral FeO\(_6\) groups in the perovskite compound and reveal the existence of BFO phase [10,23].

![Figure 1. X-ray diffraction pattern of BiFeO\(_3\), Bi\(_{0.96}\)Li\(_{0.04}\)FeO\(_3\), and Bi\(_{0.9}\)Zn\(_{0.1}\)FeO\(_3\) nanoparticles at room temperature.](image)

**Table 1.** Identification of crystallite size (D), lattice parameter (a = b, c), unit cell volume (V), crystallite density (ρ), residuals of the weighted pattern (R\(_{wp}\)), pattern profile (R\(_p\)) and goodness of fit (GOF) phase structure of BiFeO\(_3\), Bi\(_{0.96}\)Li\(_{0.04}\)FeO\(_3\), Bi\(_{0.9}\)Zn\(_{0.1}\)FeO\(_3\).

|                | BiFeO\(_3\) (BFO) | Bi\(_{0.96}\)Li\(_{0.04}\)FeO\(_3\) (BLFO) | Bi\(_{0.9}\)Zn\(_{0.1}\)FeO\(_3\) (BZFO) |
|----------------|-------------------|------------------------------------------|----------------------------------------|
| D [Å]          | 1938.700          | 1237.400                                 | 997.100                                |
| a= b= c [Å]    | 5.580             | 5.579                                    | 5.578                                  |
| c [Å]          | 13.874            | 13.872                                   | 13.868                                 |
| V [Å\(^3\)]    | 374.157           | 373.948                                  | 373.805                                |
| ρ [g cm\(^{-3}\)] | 8.330             | 8.330                                    | 8.340                                  |
| iFeO\(_3\) [%] | 100.0             | 100.0                                    | 63.6                                   |
| i\(_{23}\)FeO\(_{40}\) [%] | 0.0              | 0.0                                      | 36.4                                   |
|                | 4.878             | 4.422                                    | 6.083                                  |
|                | 1.599             | 1.165                                    | 1.040                                  |
3.3. Optical properties

For semiconductor materials, energy bandgap can be determined by their optical absorption performance. The UV-Vis diffuse reflectance spectra of the BFO nanoparticles were collected and converted to absorption spectra by Kubelka-Munk (K-M) method, as shown in figure 3. The optical bandgap of the BFO nanoparticles can be deduced from the plot of $F(R)^2$ versus $eV$, as shown in the inset of figure 3. The linear plot indicated the value of $n$ is 1, which means the BFO nanoparticles possess a direct band gap. The band gap ($E_g$) of BFO, BLFO, and BZFO nanoparticles were determined to be 2.81, 3.19 and 4.82 eV, which is comparable to the values reported previously ($E_g = 2.21$ eV) [10]. These $E_g$ value were higher and gained with the doping presence, made the sample more isolative, which give benefit to attenuate the leak current. Moreover, from the spectrum we can see that the $E_g$ properties were assigned in the UV light region, let it become the potential candidate for UV-photocatalytic applications [24].

![Figure 2. FTIR spectra of BiFeO$_3$ (BFO), Bi$_{0.96}$Li$_{0.04}$FeO$_3$ (BLFO), and Bi$_{0.9}$Zn$_{0.1}$FeO$_3$ (BZFO).](image)

![Figure 3. UV–vis optical absorbance spectrum of BiFeO$_3$, Bi$_{0.96}$Li$_{0.04}$FeO$_3$, Bi$_{0.9}$Zn$_{0.1}$FeO$_3$ and [inset] calculated band gap ($E_g$) of their properties.](image)
4. Conclusions

In conclusion, phase-pure BFO nanoparticles have been synthesized using low temperature sol-gel followed by auto-combustion route. Phase purity and crystal size of the BFO nanoparticles were confirmed by XRD studies. Higher energy gap and reduced leakage current have been achieved which is a direct consequence of suppression of oxygen vacancies. Moreover, the assigned $E_g$ properties in the UV light region had let all the sample becomes potential candidate for UV-photocatalysis applications. Hence, this method can be useful for synthesizing highly resistive and uniform-sized BFO nanoparticles for various applications.

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