



Synthesis and characterization of Zn substituted BiFeO₃ nanostructures

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ABSTRACT

Bismuth ferrite solution (BiFeO₃) and doped BiFeO₃ (BiFe_{0.9}Zn_{0.1}O₃) nanoparticles were synthesized by co-precipitation method. The XRD pattern of the synthesized nano composites revealed the formation of single phase distorted rhomboherdral structure. The shape of the synthesized nanoparticles was shown with an agglomerated irregular surface. The band at 556 and 851 cm⁻¹ in the FTIR spectrum is expounded to the Fe-O stretching, Bi-O/Fe-O stretching of BiFeO₃ units.

KEYWORDS: BiFeO₃, BiZnFeO₃, Multiferroic, Nano structures, particle size, EDS & FT-IR.

1. INTRODUCTION

The development and application of new materials have a significant impact not only on human life as a whole but also on the industrial and economic development of a nation or society. Multiferroic materials exhibit ferroelectricity, ferromagnetism and ferroelasticity due to the ordered coupling of electric, magnetic and structural parameters [1, 2]. They have numerous applications in spintronic devices, magnetic recording media, information storage and sensors [3]. Among the all the multiferroics, Bismuth ferrite (BFO) is a wide focused material due to its rhomboherdral perovskite structure with ferroelectric curie temperature (T_c)~1103K and G-type anti-ferromagnetic Neel temperature T_N ~ 643 K [4] Recent advances within the field of BFO based on multiferroics for device applications leading towards

“ultimate memory device” which mixes the most effective functionalities of Fe RAM and MRAMs, upgrade the writing speed as well as reducing the particular energy consumption[5]. BFO is regarded as the building blocks for future nano devices such as gas-sensing [6], photographic chemical action [7] and photovoltaic property [9]. Doping at A-site affects the Centro symmetry of FeO₆ octahedral, produce chemical element vacancies and results in a modification in multiferroic properties of BFO [9]. The current work was focused on the facile chemical precipitation methodology in the synthesis of BFO with Ba and Zinc-doped nanoparticles at A-site and B-site of BFO crystal structure respectively. The replacement could suppress the formation of Fe²⁺ and oxygen vacancies necessity of charge compensation.

2. EXPERIMENTAL PROCEDURE:

Bismuth ferrite solution (BiFeO_3) [10] and doped BiFeO_3 ($\text{BiFe}_{0.9}\text{Zn}_{0.1}\text{O}_3$ and $\text{Bi}_{0.9}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Co}_{0.1}\text{O}_3$) nanoparticles were synthesized by co-precipitation method. Bismuth nitrate [$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$] (99.99%, Sigma-Aldrich), iron nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] (Purity>99.99%, Sigma-Aldrich), Barium chloride [$\text{BaCl}_2 \cdot 6\text{H}_2\text{O}$] (Sigma Aldrich), Zinc nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] (98%, Sigma-Aldrich) nitric acid (Merck), ethylene glycol and potassium hydroxide (Merck) were used.

Initially, 4.8g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 1N HNO_3 at 60°C and 4.03g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added under the stirring condition (300 rpm at 60°C for 2h) so as to get a homogeneous solution. To the present reaction mixture 50 mL of ethylene glycol was mixed as a stabilizing agent. KOH was added drop wise to produce a co-precipitation reaction and the pH was adjusted to ~12 sequentially to complete the nucleation of BiFeO_3 nano powder. The obtained precipitate was further more stirred for 2h at 70°C , then neutralized to pH ~7 to get rid of the un-reacted ions and finally it was washed with ethanol. The resulted nano powder was dried in a hot air oven at 80°C for 10h.

Further, the powder was calcinated at 500°C for 3h to obtain the pure phase of BiFeO_3 nanoparticles. 8g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 3.63g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.12g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 150 ml distilled water under constant stirring at 60°C for 1h and 50 ml of ethylene glycol was mixed as a stabilizing agent. Later, the reaction mixture was precipitated with binary compound aqueous KOH solution, pH was adjusted to ~12 and the stirring was continued for 2h at 70°C . The precipitate was neutralized with H_2O , ethanol and filtered.

The obtained nanoparticles were dried at 80°C for 10h and calcinated at 500°C for 3h. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (4.3g) and BaCl_2 (0.6g) were dissolved in 150mL H_2O . To the obtained solution, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (3.63g) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.12g) were added under constant stirring at 60°C for 1h. After that 50mL of ethylene glycol was added as stabilizing agent for controlling the nucleation of metal ions. Then the binary compound aqueous KOH was added to precipitate the reaction mixture, during which the pH was adjusted to ~12 and then kept stirring for 2h at 70°C . In this reaction, the precipitating agent (KOH) enhances the rate of reaction

in the formation of nanoparticles at pH ~12. The final product was washed thoroughly by using distilled water, ethanol and dried at 80°C for 10h. The dried powder was calcinated at 500°C for 3h to get fine crystalline nano powder and it was used for further studies.

The structures of BiFeO_3 , $\text{Bi}_{0.9}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_3$, $\text{Bi}_{0.9}\text{Ba}_{0.1}\text{FeO}_3$, $\text{BiFe}_{0.9}\text{Zn}_{0.1}\text{O}_3$ nanoparticles were analyzed by Fourier transform infrared spectroscopy (FTIR) of Perkin Elmer Model impact 410), Bruker model ENDEAVOR D4 with $\text{Cu-K}\alpha$ radiation used to carry out the X-ray diffraction (XRD) studies at the scan rate of $0.05^\circ \text{ s}^{-1}$, Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS) studies were done by JEOL JEM 7500F at 2 keV. For the microscopy characterization the SEM samples were coated with gold by sputtering. Further, room temperature.

3. RESULTS AND DISCUSSIONS:

a) X-Ray diffraction :

The XRD pattern of the synthesized nano composites revealed that the formation of single phase distorted rhombohedral structure which can be described in the hexagonal shape frame work of area cluster. From Figure 1 that the high intensity peak of (1 1 1) at 31.9° appeared as overlapped single peak rather than peak splitting at I_{max} that could a common development in BFO nanoparticles [11]. It is important to notice that there is an observable decrease in the intensity of (111) peak in the multiferroic samples which may be due to the atomic radii variation and strain. The crystallite size was obtained by means of Scherer's equation using the most prominent peak at $2\theta=31.9^\circ$ and the data were produced in the Table 1.

In keeping with the tolerance factor of the unit cell calculations of lowest value of $\text{BiFe}_{0.9}\text{Zn}_{0.1}\text{O}_3$ when compared to the values of BiFeO_3 and $\text{Bi}_{0.9}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_3$ which is in well agreement with the average crystalline size of $\text{BiFe}_{0.9}\text{Zn}_{0.1}\text{O}_3$ (21.01nm) the highest compared to BiFeO_3 (20.65nm) and $\text{Bi}_{0.9}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_3$ (18.32 nm). [12].

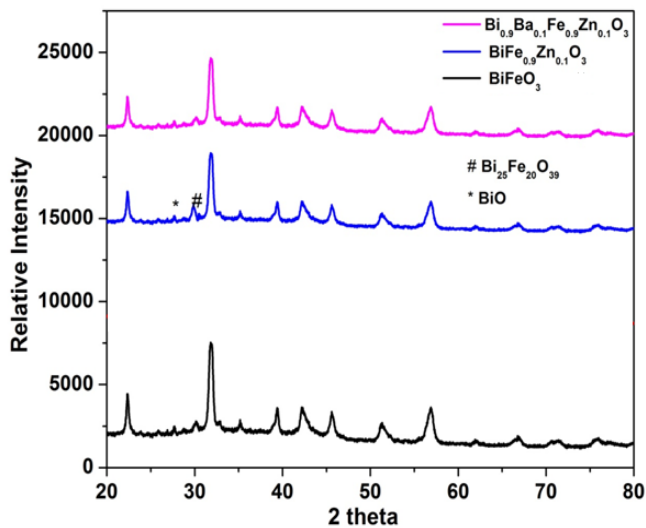


Figure 1: X-ray diffraction of synthesized nano composites

Table 1: Crystallite size, tolerance factor of synthesized nano composites

S. No.	Nanocomposite	Crystallite size (nm)	Tolerance factor(t)
1	BiFeO ₃	20.65	0.8830
2	BiFe _{0.9} Zn _{0.1} O ₃	21.01	0.7910
3	Bi _{0.9} Ba _{0.1} Fe _{0.9} Zn _{0.1} O ₃	18.32	0.8043

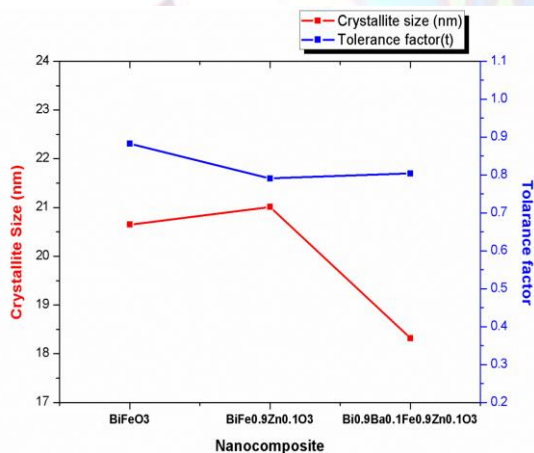


Figure 2: An illustrative analysis of Table 1 content

b) SEM/EDS:

The shape of the synthesized BiFe_{0.9}Zn_{0.1}O₃, Bi_{0.9}Ba_{0.1}Fe_{0.9}Zn_{0.1}O₃ nanoparticles were shown with an agglomerated irregular surface and the Bi_{0.9}Ba_{0.1}Fe_{0.9}Zn_{0.1}O₃ nanoparticles were in combination of BiFe_{0.9}Zn_{0.1}O₃ with other nanomaterials. The agglomerated particles appeared due to relatively large

magnetization for these small particles. The reason for agglomeration in the synthesized nanoparticles is attributed to the high surface energy of nanoparticles [13] EDS patterns of the nano composites were presented in Figure 3. It was clearly observed that there were no foreign elements in the BiFe_{0.9}Zn_{0.1}O₃ and Bi_{0.9}Ba_{0.1}Fe_{0.9}Zn_{0.25}O₃ which indicates the formation of pure phase in the nanomaterials and these results were in good agreement with the XRD studies.

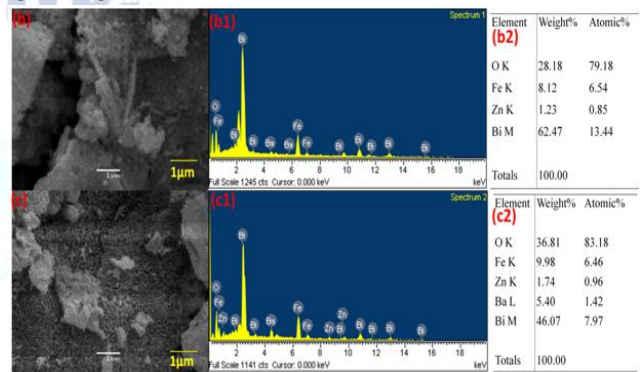


Figure 3: SEM/EDS patterns of nanomaterials BiFe_{0.9}Zn_{0.1}O₃ and Bi_{0.9}Ba_{0.1}Fe_{0.9}Zn_{0.1}O₃

c) FTIR Analysis:

The FTIR spectra of the BiFe_{0.9}Zn_{0.1}O₃, Bi_{0.9}Ba_{0.1}Fe_{0.9}Zn_{0.1}O₃ were shown in Figure 4. The band at 556 and 851 cm⁻¹ in the FTIR spectrum is expounded to the Fe-O stretching, Bi-O/Fe-O circulate stretching of BiFeO₃ units, respectively. The height that determined at 1372cm⁻¹ is attributed to the string vibration of NO₃⁻ robust vibrations [14]. However, above functional groups (of BiFeO₃) were shifted in the case of BiFe_{0.9}Zn_{0.1}O₃ (543, 848, 1386 cm⁻¹), and Bi_{0.9}Ba_{0.15}Fe_{0.9}Zn_{0.1}O₃ (529, 837, 1392 cm⁻¹) and their band become broader by Zinc, Ba ions doping respectively.

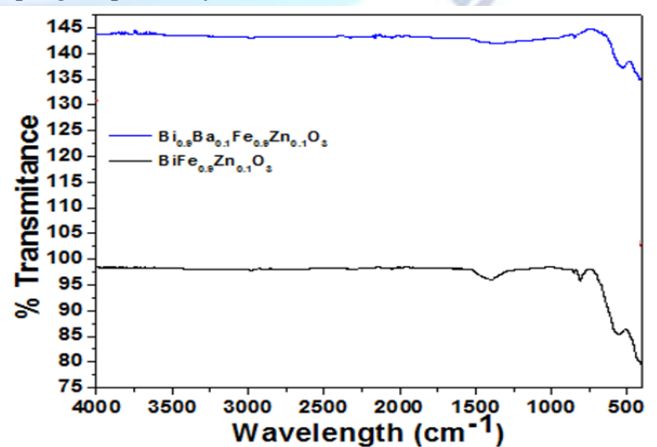


Figure 4: FT-IR Spectrum of nanocomposites Bi_{0.9}Ba_{0.1}FeO₃ and Bi_{0.9}Ba_{0.1}Fe_{0.9}Zn_{0.1}O₃

4. CONCLUSION:

In this work, Bismuth ferrite solution (BiFeO_3) [15] and doped BiFeO_3 ($\text{BiFe}_{0.9}\text{Zn}_{0.1}\text{O}_3$ and $\text{Bi}_{0.9}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Co}_{0.1}\text{O}_3$) nanoparticles were synthesized by co-precipitation method. The dried powder was calcinated at 500°C for 3h to get fine crystalline nano powder. The XRD and SEM pattern of the synthesized nano composites revealed that the formation of single phase distorted rhomboherdral structure which can be described in the hexagonal shape frame work of area cluster. The shape of the synthesized $\text{BiFe}_{0.9}\text{Zn}_{0.1}\text{O}_3$, $\text{Bi}_{0.9}\text{Ba}_{0.1}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_3$ nanoparticles were shown with an agglomerated irregular surface. It was observed by FTIR analysis that the functional groups (of BiFeO_3) were shifted in the case of $\text{BiFe}_{0.9}\text{Zn}_{0.1}\text{O}_3$ (543, 848, 1386 cm^{-1}), and $\text{Bi}_{0.9}\text{Ba}_{0.15}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_3$ (529, 837, 1392 cm^{-1}) and their band become broader by Zinc ions.

Conflict of interest statement

Authors declare that they do not have any conflict of interest.

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