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Effect of Annealing on Structural and Morphological Properties of Bismuth Ferrite ($BiFeO_3$) Nanoparticles

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Abstract

Bismuth ferrite ($BiFeO_3$/ BFO) nanoparticles with controlled particle size were synthesized via ethylene-glycol based auto combustion sol-gel method. The effect of the variation in the annealing temperature with time, on the structural and morphological properties of the sample was investigated. The as prepared samples were characterized by X-ray powder diffraction, to investigate the crystal structure and size of crystal. Different functional groups present in the sample were confirmed from Fourier transform infrared spectroscopy (FTIR). The surface morphology and elemental composition of the nanoparticles were investigated by scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). The thermal decomposition of the sample was examined by Thermogravimetric analysis (TGA).

Keywords: Bismuth ferrite ($BiFeO_3$/BFO), sol-gel method, nanoparticles

Introduction

Bismuth iron oxide ($BiFeO_3$/ BFO) is a single-phase multiferroic material which exhibit both the ferroelectric and antiferromagnetic ordering well above the room temperature [1]. Due to these unique properties, it has received a lot of interest in various fields such as magnetic storage, sensors, spinotronic devices etc [2]. However practical applications of BFO are restricted due to its low magnetization because of G-type antiferromagnetic nature below its Neel temperature. The ferroelectric value of BFO is also less as compared to many standard ferroelectric materials due to its high leakage behavior.

The high leakage behavior in BFO is due to the presence of defects like oxygen vacancies, variable states of Fe (Fe^{2+} and Fe^{3+}), Bi vacancy and formation of secondary phase during synthesis process [3]. Various syntheses methods like solid state [4], sol-gel [5], hydrothermal [6], soft-chemistry route [7] etc., are used for the formation of pure BFO. In BFO, the structural distortion can be induced by applying high pressure [8] or by doping [9] which in turn affects the multi ferroic properties. Instead of its multiferroic properties, BFO can be considered as visible light photocatalyst because of its wide band gap energy ($\sim$ 2.0 - 2.8 eV) and good chemical stability [10]. Guo et al. had reported an improved photo catalytic activity in Gd-doped BFO nanoparticles by degrading rhodamine B (RhB) under visible light illumination [11]. Di et al. have synthesized $BiFeO_3$ samples with different morphologies by hydrothermal method and functionalized BFO particles with Ag. They showed an improvement of RhB degradation by Ag-decorated BFO compared to non-decorated BFO under sunlight [12]. The potential use of BFO and doped BFO in the degradation of different types of organic dyes such as methylene blue [13], methyl orange [14] and congo red [15] are reported. In this article BFO nanoparticles are synthesized by auto combustion sol-gel method. The effects of annealing on the structural and morphological properties are investigated.

Methodology

For the synthesis of $BiFeO_3$ nanoparticles, the sol gel method is adopted. The starting materials used for the synthesis are bismuth nitrate ($Bi(NO_3)_3.5H_2O$), iron nitrate ($Fe(NO_3)_3.9H_2O$) and ethylene glycol. All precursors are purchased from Loba Chemie (AR grade) and used without further purification. The typical procedure for the synthesis is as follows

Bismuth nitrate penta hydrate is dissolved in ethylene glycol is used as a solvent. The resultant mixture is stirred for 30 min. Further, the iron nitrate nonahydrate is added into the resulting homogeneous mixture and stirred for 90 min at 90°C for the formation of gel. The ratio of Bi:Fe is 1:1. The formed gel is dried and annealed at 600 °C for 6 hr and 8 hr respectively. The samples are further characterized by X-ray diffractometer in the range of 20 - 80° at the scan rate of 5° per min using Rigaku D/max with Cu-kα anode (λ = 1.54056 Å). Further, the confirmation of the sample is examined from Fourier transform infra-red spectroscopy (FT-IR). Scanning electron microscope (SEM) images are obtained using JEOL at an operating voltage of 120 kV.

Result and Discussion

1. X-ray Diffraction (XRD)

The crystal structure and phase formation of $BiFeO_3$ nanoparticles was identified by X-ray diffraction spectrometer (XRD) with Cu-kα irradiation. Figure 3.1 shows the XRD patterns of as prepared BFO nanoparticles annealed at 600 °C for 6 hr and 8 hr. From XRD patterns of BFO, it was observed that all the diffraction peaks from the sample prepared at 600°C corresponds to the reflections from different planes of rhombohedral BFO which are consistent with the reported values. (JCPDS No-01-071-2494) with space group R3c having lattice parameters as a = b = 5.5876 Å and c =13.86 Å. This confirms the formation of perovskite BFO with rhombohedral crystal structure along with some impurities such as Bi_2O_4 which are indicated by asterisks (*) [16]. The presence of secondary phase is due to the kinetics of BFO formation in a narrow temperature range [17]. It was also observed that, the impurity phase gets reduced in the sample annealed at 8 hr.

2. Fourier Transform Infra-red spectroscopy (FT-IR)

In order to confirm the crystallinity and different functional groups present in the synthesized BFO sample using ethylene glycol as a solvent, the FTIR spectra was examined. Fig.3.2 shows, the FTIR spectra of BFO sample annealed at 600 °C for 6 hr in the range of 400-4000 cm^{-1}. For the sample, the band range around 400-600 cm^{-1} corresponds to metal-oxygen bond and

confirms the existence of perovskite structure for the entire sample. The IR peaks below 1000 cm^{-1} (such as 427.26, 558.75, 813,921) cm^{-1} were corresponding to the vibration's bonds of Bi-O or Fe-O respectively. The vibration of Fe-O at 427.26 cm^{-1} and stretching vibration O-Fe-O at ~ 558.75 cm^{-1} is present in the octahedral FeO_6 group [18]. The band present at 3457.51 cm^{-1} is a result of antisymmetric and symmetric stretching of H_2O and O-H bond groups. A strong band at around 1412 cm^{-1} is due to the trapped nitrates [19].

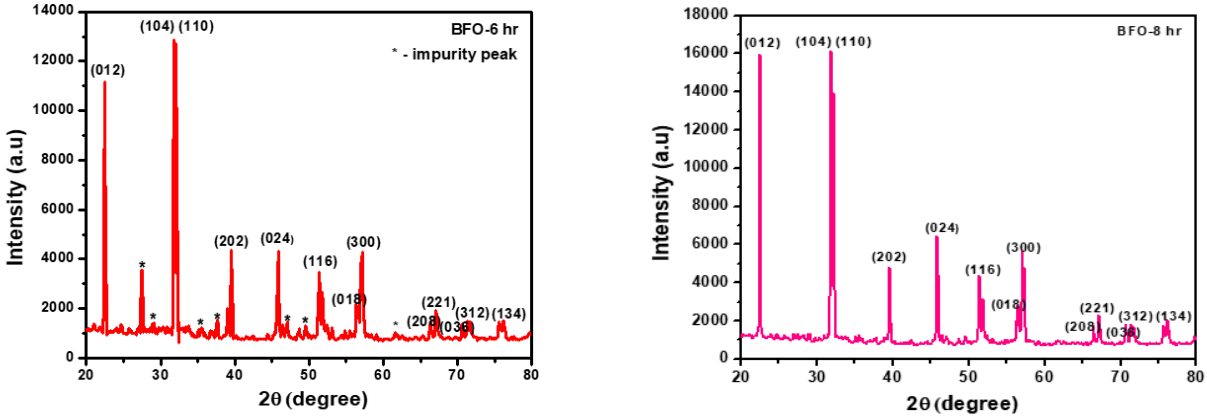


Fig 3.1 XRD pattern of BFO sample annealed at 600 ˚C for 6 hr and 8 hr

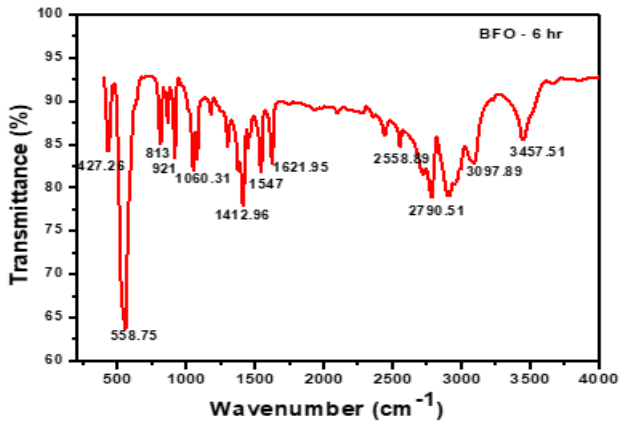
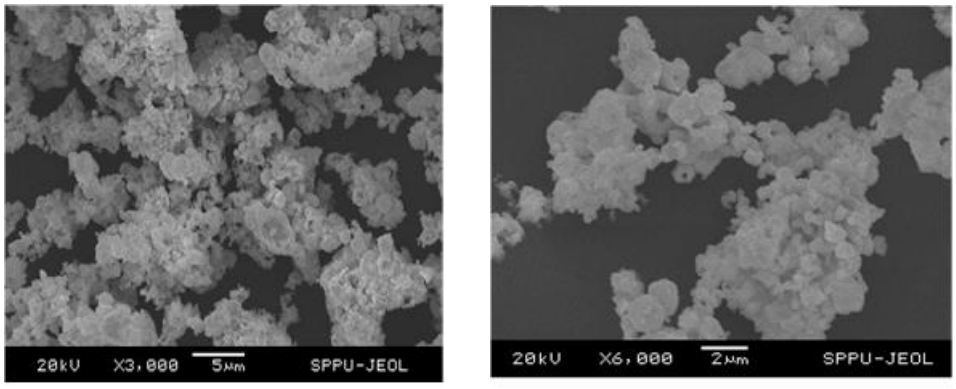


Fig 3.2: FTIR spectra of BFO annealed at 6hr



a-BFO - hr 6 b-BFO-8 hr

Fig 3.3 SEM images and EDS spectrum of BFO sample annealed at 600 ˚C a) 6 hr b) 8 hr

Spectrum processing :

Peak possibly omitted : 0.250 keV

Processing option : All elements analyzed (Normalised)

Number of iterations = 3

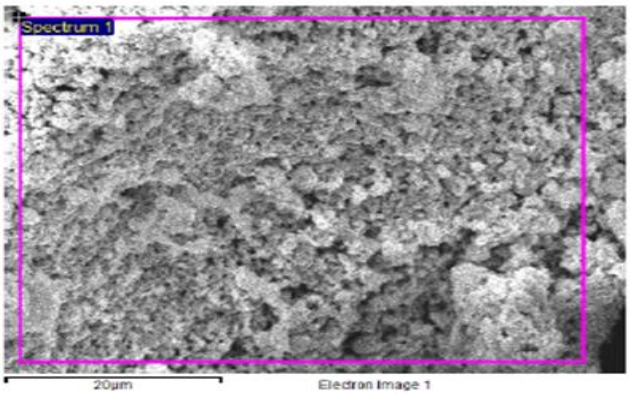
Standard :

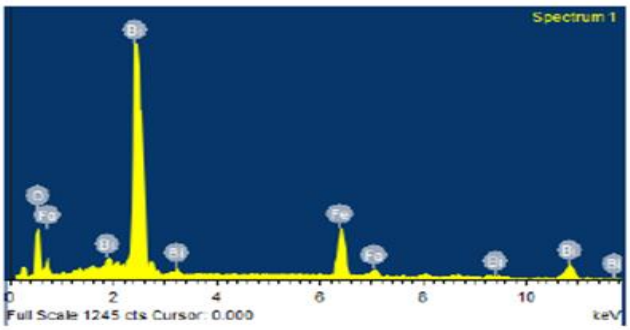
O SiO2 1-Jun-1999 12:00 AM

Fe Fe 1-Jun-1999 12:00 AM

Bi Bi 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	27.67	77.51
Fe K	11.87	9.53
Bi M	60.46	12.97
Totals	100.00	





a.EDS-BFO -6hr

Spectrum processing :

Peak possibly omitted : 0.252 keV

Processing option : All elements analyzed (Normalised)

Number of iterations = 3

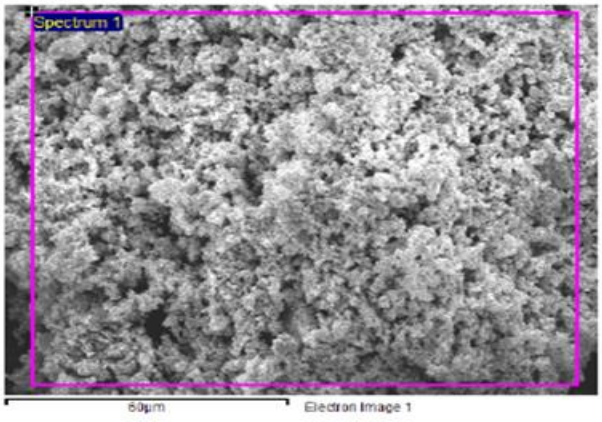
Standard :

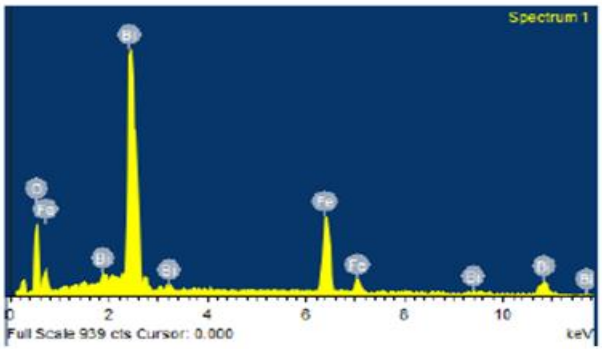
O SiO2 1-Jun-1999 12:00 AM

Fe Fe 1-Jun-1999 12:00 AM

Bi Bi 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	31.21	78.12
Fe K	16.55	11.87
Bi M	52.24	10.01
Totals	100.00	





b.EDS- BFO – 8 hr

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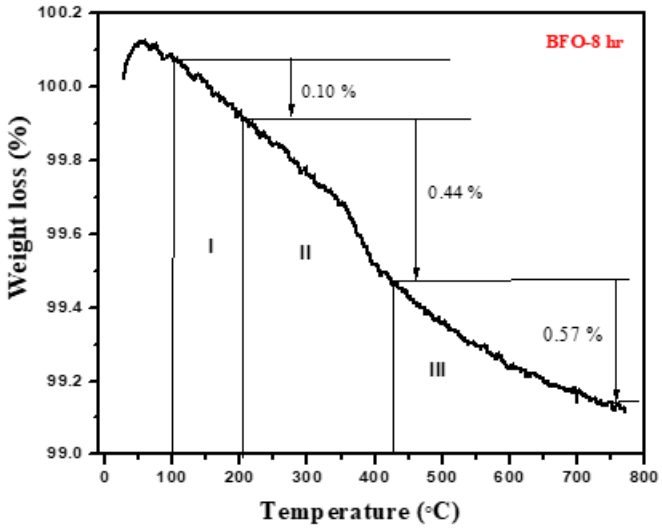

Fig 3.4 TGA curve of BFO sample annealed at 600 °C for 8 hr

3. **Scanning electron microscopy (SEM) and EDS spectra**

Figure 3.3 illustrates the SEM images and EDS spectra of BFO nanoparticles synthesized by sol gel method annealed at 600 °C for 6 hr and 8 hr respectively. From images, it is observed that the prepared particles have nearly spherical morphology as well they are in agglomerated form. The agglomeration of BFO is due to the magnetic nature of the BFO particles [20]. It was also observed that the particles are not uniformly distributed.

4. Thermogravimetric analysis

Thermo gravimetric analysis (TGA) was used to investigate the thermal degradation of the sample. From TGA curve, it is observed that 0.10% weight loss from 100 to 200 °C due to evaporation of adsorbed water from the sample. The weight loss from 200 to 750 °C is around 1% and it may be due to the loss of residual compounds after annealing, probably trapped nitrates (also confirmed from FTIR traces in 1300-1412.96 cm^{-1} range, Figure 3.2) [21].

Conclusions

The synthesis of $BiFeO_3$ through the sol gel method resulted in the formation of highly crystalline BFO perovskite. An unexpected phase was indentified in the sample annealed for 6 hr. and it may be attributed due to the pre-annealed precursor stoichiometry. SEM analysis indicates non uniform, agglomerated and nearly spherical distribution of the particles. The thermal degradation of sample shows ~ 1.5% weight loss is observed around 100 -750 °C.

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Conflicts of interest: The authors stated that no conflicts of interest.

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