Effect of Annealing Temperature on Structural, Optical and Magnetic Properties of BiFeo3 Multiferroics

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Abstract: The multiferroic materials $BiFeO_3$ nanopowders were synthesized by the wet chemical method, using the iron (III) nitrate, bismuth nitrate and citric acid. The powder was annealed at temperatures of $150℃$,$250℃$, $350℃$ and $450℃$ in air for 2 hours in a programmable box furnace with heating rate of $100℃$ per hour. The annealed powders structure, morphology were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and their optical and magnetic properties were characterised by UV-Visible (UV-Vis), photoluminescence (PL) spectrometer and vibrating sample magnetometer (VSM). The results indicate that the preparation and the properties have profound influence on the annealing temperature and the particle size. It is found that the annealing temperature of $350℃$ with $128\,nm$ size shows good dispersion without impurity. The saturation magnetization (M_s), the remanent magnetization (M_r) and the coercivity (H_C) of $BiFeO_3$ nanopowders under the annealing temperature $350℃$ are $9.81\frac{\text{emu}}{\text{g}}$, $1.79\frac{\text{emu}}{\text{g}}$ and $122.02\ \text{G}$ respectively.

Keywords: Multiferroics, $BiFeO_3$, nanopowders, annealing temperature, magnetization.

1. INTRODUCTION

Multiferroic are the class of materials that have simultaneous effects of ferroelectricity and ferromagnetism in the same material. There are a large number of electrically and magnetically polarisable materials, but only few exhibits ferroelectric and ferromagnetic ordering. Materials which are electrically and magnetically polarisable at the same time are referred as magnetoelectric materials. The multiferroic are also called magnetoelectric materials. Bismuth ferrite ($BiFeO_3$) with a pervoskite structure is a mostly widely studied multiferroic material. $BiFeO_3$ has a very high ferroelectric curie temperature($T_c = 830℃$) and shows G-type antiferromagnetism with Neel temperature of $370℃$ [1, 2]. The G-type antiferromagnetism in BiFeO3 is mainly because of each Fe^{3+} with spin up is surrounded by six nearest Fe neighbours with spin down. In multiferroic material, the ferroelectricity and magnetism are originated from different sources and the effects are independent of each other, and a small degree of coupling exists. $BiFeO_3$ is the only prototype among all other multiferroic oxides which shows both ferromagnetism and ferroelectricity in a single crystal at room temperature. The ions responsible for the production of ferroelectricity and magnetism are Bi^{3+} and Fe^{3+} ions. Since these properties are associated with different ions in the material, the preparation of pure $BiFeO_3$ has been a challenge.

Multiferroic materials can be divided into two general groups: single-phase multiferroic and composites or two phase multiferroic. Single-phase multiferroic are those in which at least two “ferroic” properties are presented within the same phase. Instead, composites are multiphase systems in which each phase presents a different “ferroic” property. In composite multiferroic magnetoelectric coupling occurs indirectly via strain. The reports can be found in which an enhancement of several orders of magnitude in the magnetoelectring coupling [3, 4] in single-phase multiferroic are more. However, a single-phase multiferroic with a strong coupling between its ferroelectric and its ferroelectric orders could allow an easier control of the magnetic nature through electric fields.

These excellent properties make $BiFeO_3$ suitable for applications in range of devices based on spintronics, magnetoelectric sensors, electrically driven magnetic data storage and recording devices, magnetocapacitve devices, non-volatile memories, etc [5]. In the present work, the effect of annealing temperature on the structural, optical and magnetic properties of the synthesised $BiFeO_3$ nanoparticle have been investigated.

2. MATERIALS AND METHODS

$BiFeO_3$ nanoparticles have been prepared by wet chemical method [6] using metal nitrates and citric acid as a chelating agent. Bismuth nitrate ($Bi(NO_3)_3$, $5H_2O$), ferric nitrate ($Fe(NO_3)_3$, $9H_2O$) and citric acid ($C_6H_8O_7$) all were used with purity 99.9% or higher and without further purification. These compounds were taken in stoichiometric ratios in a glass beaker and heated at 80℃ on a hot plate for about 20 minutes with constant stirring with cleaned glass rod to mix them together. Then the mixture was heated at 150℃, for combustion and reaction of the mixture to form brown colour precursor. The precursor was grounded into powder using mortar and pastel. It had also been reported to prepare $BiFeO_3$ by same technique by using tartaric acid as chelating agent [7]. Precursor powder was annealed using high purity alumina crucibles in air at 150℃,250℃,350℃, and 450℃, for 2 hours inside a programmable box furnace with heating rate 100℃, per hour and then slowly cooled down to room temperature. The crystal structure and the morphology of annealed sample were investigated using X-ray powder diffraction (XRD) and the scanning electron microscope (SEM). The optical properties were obtained by UV-Vis and PL spectrometer. The magnetic properties were measured at room temperature using a vibrating sample magnetometer.

3. RESULTS AND DISCUSSION

3.1. Structural and Morphological Analysis.

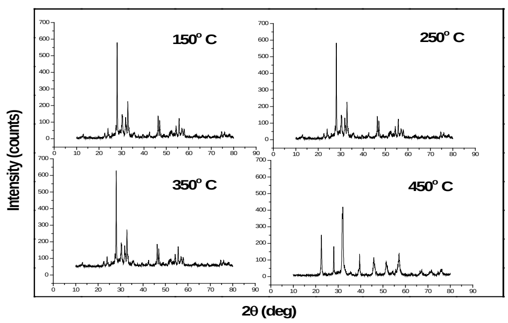


Figure 1: X - ray diffraction patterns of the annealed powders of $BiFeO_3$

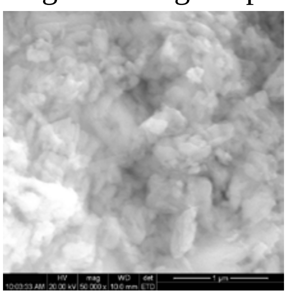
Figure.1 shows the XRD patterns of the prepared powders annealed at different temperatures of 150℃,250℃,350℃, and450℃, The Peaks can be indexed to the rhombohedral structure of $BiFeO_3$ which is in good agreement with literature results (i.e. JCPDS#20-0169). The prominent peaks in XRD plot are indexed to various hkl planes, indicating formation of $BiFeO_3$. The sample annealed at 450℃ is having many extra peaks other than $BiFeO_3$ whereas that prepared at 350℃ is less impurity peaks. Besides these prominent peaks, some other peaks of low intensity are also observed, which do not belong to $BiFeO_3$. The full width at half maxima (FWHM) of (200) plane at annealing temperature of 350℃ have lower value which indicates the structural improvement in the material. Table. 1 shows the structural parameters from the XRD measurement as a function of annealing temperature.

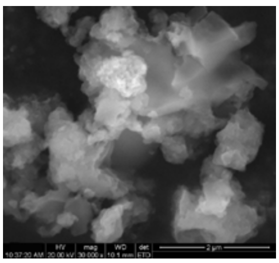
Annealing Temperature (℃)	Observed 2θ (degree)	JCPDS (20-0169) 2θ (degree)	FWHM	(h k l)
150	28.07	28.97	0.2069	(100)
250	32.67	32.84	0.5294	(110)
350	47.34	47.15	0.0445	(200)
450	40.67	40.26	0.1445	(111)
	55.70	55.73	0.2620	(211)

Table 1 Compared and Observed values of 2θ and d spacing values

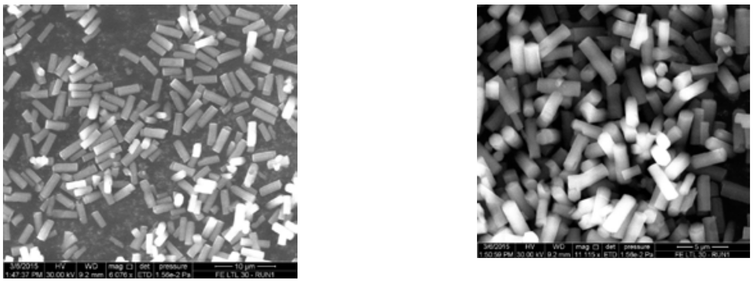
3.2 Scanning Electron Microscope (SEM)

The synthesized bismuth ferrite nanoparticles were characterized by using the SEM for revealing their surface morphology at different annealed temperatures. The SEM microstructure of all samples is given in figure. The sample in fig 2. (a) is in agglomerated form and it has no definite shape and size. The microstructure of the sample annealed at 350℃ shows appearance sharp blocks of definite shapes and sizes as shown in fig.2.(c). The particle size estimated from SEM images for the $BiFeO_3$ sample is about 100 nm for annealed temperature of 150℃, 112nm for the annealed temperature of 250℃, 128 nm for the annealed temperature of 350℃, and 120 nm for the annealed temperature of 450℃. The proportional increase in particle size with increasing annealing temperature is also confirmed by the surface morphology studies.





(a) (b)



(c) (d)

Figure 2: Surface morphology using SEM at annealing temperatures of (a) 150℃ (b) 250℃ (c) 350℃ (d) 450℃ .

3.3 UV – Vis measurements and Photoluminescence (PL)

The band edge emission increases with respect to increase in the annealing temperature and thereby decreases in the energy gap. The optical band gap as shown in Table.2 calculated by uv-visible and photoluminescence will agree with each other. The reported value of optical band gap of $BiFeO_3$ range from 2.3 to 2.8eV. The optical band gap decreases with increasing annealing temperature [8]. Further the annealing temperature changes in grain size as evidenced from the SEM observation, which in turn changes the band gap.

Table 2 Band gap values from UV and PL measurement

Temperature(℃)	Band gap in (eV)	
	UV	PL
150	2.1956	2.2066
250	2.1733	2.1884
350	2.1577	2.1517
450	2.1022	2.1156

The emission peak around wave length 550 nm at annealing temperatures of 150℃, 250℃ as shown in Fig.3 is attributed to the distortion, defects and impurity levels in $BiFeO_3$ stoichiometry [9]. The emission peak intensity shifted below 550 nm at the annealing temperature of 350℃ shows the reduction in the impurity of energy levels. It also noted from the Table.2. that at this temperature the band gap is close in agreement with UV and PL measurements, which leads to estimate band gap of the material.

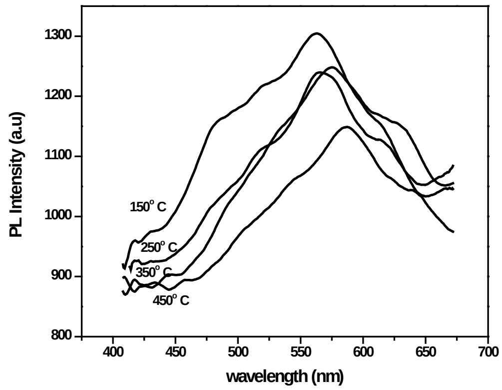


Figure 3: Photoluminescence spectra of $BiFeO_3$ under different annealing temperature

3.4 Magnetic Measurements

The magnetic properties of the products were measured at room temperature using a vibrating sample magnetometer in a maximum applied field of 12000 G. From the obtained hysteresis loops, the saturation magnetization(M_s) remanence magnetization (M_r) and coercive field (H_c) were determined for different annealing temperatures are shown in Fig.4.

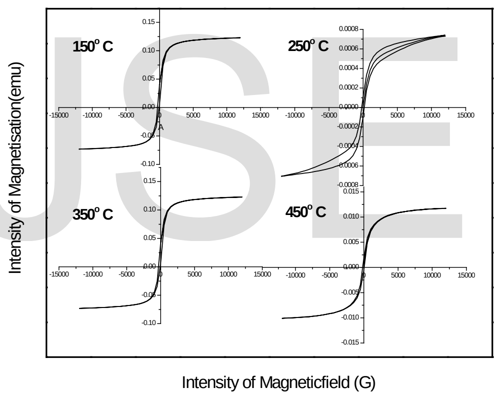


Figure 4: Magnetic hysteresis loop of $BiFeO_3$ nanopowder at different annealing temperatures

The coercive field was decreased with increasing the annealing temperature as shown Table.3. . A higher coercive field (188.78 G) was attributed to the magnetic anisotropy [10]. The decrease in the coercivity could be attributed to the increase in the particle size. The possibility of increase in magnetisation (M_s) may be due to increase in particle size. As the particle size increases, the large numbers of spins are coupled on the surface and hence (M_s) increases.

Table.3 Values of Magnetic parameter of $BiFeO_3$

Annealing Temperature °C	Magnetization $(M_s)\frac{emu}{g}$	Retentivity $(M_r)\frac{emu}{g}$	Coercivity (G)	Remanance $\left(\frac{M_s}{M_r}\right)$
150	0.072	0.010	188.78	7.20
250	0.169	0.031	147.12	5.45

350	9.81	1.79	122.02	5.48
450	1.09	0.121	113.57	9.01

The highest saturation magnetisation $\left(M_s = 9.81\frac{emu}{g}\right)$ with narrow hysteresis loop of coercive field $(122.02\ G)$ was achieved for the annealing temperature of 350℃ due to the formation $BiFeO_3$ without impurity. With the further increase of annealing temperature to 450℃ , the saturation magnetisation was decreased to $\left(M_s = 1.09\frac{emu}{g}\right)$due to the impurity phases as appease as extra peaks in XRD.

CONCLUSION

The multiferroic $BiFeO_3$ nanoparticles with particle size of good morphology have been successfully synthesized. The annealing temperature increases there will be change in the optical properties in the wavelength region of 400-600nm with variation in the band gap from 2.20 – 2.10eV. As the annealing temperature increases the ionic radius of the ferrite increases. This increases the maximum in magnetization value corresponding to the annealing temperature of 350℃ . It may be concluded that the annealing temperature of 350℃ plays very important role in the formation of pure phase of $BiFeO_3$. Further the annealing temperature influences the structural, morphological, optical and magnetic properties of multiferroic materials.

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