Journal of Nano- and Electronic Physics
Vol. **12** No 5, 05015(6pp) (2020)

Журнал нано- та електронної фізики
Том **12** № 5, 05015(6cc) (2020)

Structural and Optical Characterization of Multiferroic $BiFeO_3$ Nanoparticles Synthesized at Different Annealing Temperatures

Naimur R. Niloy*, M.I. Chowdhury, S. Anowar, J. Islam, M.M. Rhaman

Department of Electrical and Electronic Engineering, Ahsanullah University of Science and Technology, Dhaka, Bangladesh

(Received 09 July 2020; revised manuscript received 15 October 2020; published online 25 October 2020)

Multiferroic $BiFeO_3$ (BFO) synthesis without any secondary phase is a big challenge. In this work, BFO nanoparticles were prepared using the sol-gel method at three different annealing temperatures. In order to observe the structure of prepared nanoparticles, X-ray diffraction (XRD) was used. The lucid crystalline structure of pure BFO nanoparticles was confirmed by the XRD pattern. In XRD pattern of these BFO nanoparticles, a secondary phase ($Bi_2Fe_4O_9$) was observed. A phase shift was noticed with increasing annealing temperature. To scrutinize the grain morphology of synthesized nanoparticles, field emission scanning electron microscopy (FESEM) was performed. Energy dispersive X-ray spectroscopy (EDS) analysis had also been done for three different annealing temperatures. With increasing annealing temperature from 500 to 700 °C, particle size increased from 151 nm to 318 nm and crystallite size increased from 30.6 nm to 54.3 nm. In order to measure diffuse reflectance, a UV/Vis/NIR spectrophotometer was used and then optical band gap (E_g) was determined. Band gap energy increased from 1.96 eV to 2.04 eV for the increment of annealing temperature from 500 to 700 °C. The annealing temperature of 500 °C was found to be the optimal condition for synthesizing $BiFeO_3$ nanoparticles.

Keywords: Band gap, Nanoparticles, FESEM, Sol-gel, X-ray diffraction.

DOI: 10.21272/jnep.12(5).05015 PACS numbers: 82.75.Fq, 81.07. − b

1. INTRODUCTION

Ferroelastics, ferroelectrics and ferromagnets are the primary ferroics in the classification of ferroics according to thermodynamics. Multiferroic materials possess more than one property of ferroics simultaneously in the same phase [1]. This entails their possession of spontaneous deformation, spontaneous polarization and spontaneous magnetization which can be adjusted through applied stress, applied electric field and applied magnetic field, respectively [2, 3]. The characteristics of multiferroics as noted above are favorable for an extensive range of applications. Among single-phase ABO_3 (perovskite type) multiferroics, $BiFeO_3$ (T_{CE} = 1110 K, T_N = 670 K) and $BiMnO_3$ (T_{CE} = 105 K, T_C = 450 K) are mostly studied [2]. According to studies, at the temperature below 1110 K, $BiFeO_3$ acts as a ferroelectric and it also acts as antiferromagnetic with a Neel temperature of 670 K [4]. $BiFeO_3$ can be synthesized using various methods like sol-gel (Pechini method), hydrothermal, microwave (where annealing temperature may vary from 400 °C to 800 °C), high energy ball milling etc. [5]. However, synthesis of single-phase $BiFeO_3$ without any secondary phases such as Bi_2O_3, Fe_2O_3, $Bi_2Fe_4O_9$, $Bi_{25}FeO_{39}$ etc. is a big challenge with conventional methods [6]. And this multiferroic $BiFeO_3$ exhibits variation of secondary phases, which are found at different annealing temperatures in sol-gel method. The main concern for $BiFeO_3$ preparation should be to keep as few secondary phases as possible, since these secondary phases cause leakage current. Generally, in order to prepare bulk BFO materials, solid-state reactions or rapid sintering of the liquid phase of Bi_2O_3 and Fe_2O_3 are carried out. In recent times, for the preparation of BFO nanoparticles, wet chemical methods have acquired significant recognition [7]. It can be said that multiferroic bismuth ferrite ($BiFeO_3$) which has optical band gap energy in the visible region, offers a rousing opportunity to discover materials for PV application. The further reduction of properties like particle size and band gap of bismuth ferrite is possible, introducing doping into it [8, 9]. The reduction of particle size is significant as our primary objective is to obtain the lowest possible band gap [10]. This phenomenon makes $BiFeO_3$ a prospective contender for application in PV cells [11]. In this paper, the procedure for obtaining pure BFO powders, the structural properties and band gap characterization of BFO have been delineated. A detailed comparison had been carried out to find out the optimal temperature for pure BFO nanostructure preparation using the sol-gel method.

2. EXPERIMENTAL

Employing the sol-gel method, pure bismuth ferrite nanoparticles had been synthesized. Reagents used in this work were glacial acetic acid (CH_3COOH), bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), citric acid ($C_6H_8O_7$), iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) and ethylene glycol ($C_2H_6O_2$). To synthesize 2 g of bismuth ferrite nanoparticles, 3.1013 g of $Bi(NO_3)_3 \cdot 5H_2O$ and 1.2914 g of $Fe(NO_3)_3 \cdot 9H_2O$ had initially been dissolved in 800 ml water. The water used in the experiment was deionized. The individual concentration of both the reagents was maintained at 0.025 M. For the polymerization and chelating agent, ethylene glycol ($C_2H_6O_2$) and citric acid ($C_6H_8O_7$) were used, respectively. Then obtained solution was stirred continuously. To form the crystalline black-reddish solution, it was heated at 80-85 °C for 7.5 h. After obtaining the solution,

* naimurniloy@gmail.com

ethylene glycol was added to it. In order to initiate the polymerization reaction, the resultant solution was heated at 90-95 °C and after 3-4 min a gel was developed with robust boiling and smoking. To obtain the xerogel, the gel was dried in a drying oven at 100 °C for 20-24 h. When the drying was done, the obtained xerogel was grinded into small pieces. Then these powders were annealed at 500, 600 and 700 °C separately. Those had been annealed for 2-2.5 h in a high-temperature furnace to obtain BFO nanoparticles. The heating rate was maintained at 3-3.5 °C/min. The annealed samples were then crushed again in order to finally get the 2 g of desired nanoparticles for characterization.

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction (XRD)

The characterization of nanoparticles was done by X-ray diffraction (XRD) (Empyrean, Malvern Panalytical) at around 25 °C. For XRD, scanning limit had been kept from 10° to 70°. The X-ray beams diffracted on the nanoparticle samples were of high-intensity. The XRD patterns for BFO nanoparticles at 500, 600 and 700 °C were obtained after washing with CH_3COOH [12, 13] as can be seen in Fig. 1a. To support the formation of $BiFeO_3$ nanoparticles, the powder samples were heated at 500 °C to 700 °C for 2 h. Generally, nitric acid (HNO_3) was used to eliminate the secondary phase ($Bi_2Fe_4O_9$) which was composed during the preparation of $BiFeO_3$ nanopowders. Small trails of the secondary phase ($Bi_2Fe_4O_9$) were found at 27°, similar secondary phase was also found in other work [14]. This secondary phase was shown in the XRD patterns. The HNO_3 could dissolve the secondary phase of $BiFeO_3$. So, glacial acetic acid (CH_3COOH) was used for washing. The crystalline nanoparticles from the synthesized samples were clearly confirmed by XRD patterns. The secondary phase ($Bi_2Fe_4O_9$) in $BiFeO_3$ is a major disquiet. BFO containing particles Bi^{3+} and/or Fe^{3+} participates in creating this type of secondary phase which also consists of Bi^{3+} and/or Fe^{3+} ions. For the formation of secondary phase, off-stoichiometric and metastable nature of $BiFeO_3$ is considered to be the primary cause. Considering the application point of view, secondary phase increases leakage current and decreases ferroelectric property. So, this secondary phase must be as minimum as possible. From Fig. 1a, it can be said that BFO nanoparticles at 500 °C have less secondary phase than at 600 °C and 700 °C. Using (012), (104) and (110) reflection planes, crystallite size (D) was calculated from the Scherrer equation:

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

Here, β represents the full width at half maximum (FWHM), k has the value of 0.9 which is a dimensionless constant, θ is the Bragg angle and λ represents the X-ray wavelength (~ 1.542 Å). The magnified (012) diffraction peak in Fig. 1b shows that when annealing temperature increases, the FWHM decreases. With the decrease in the FWHM, crystallite size increases.

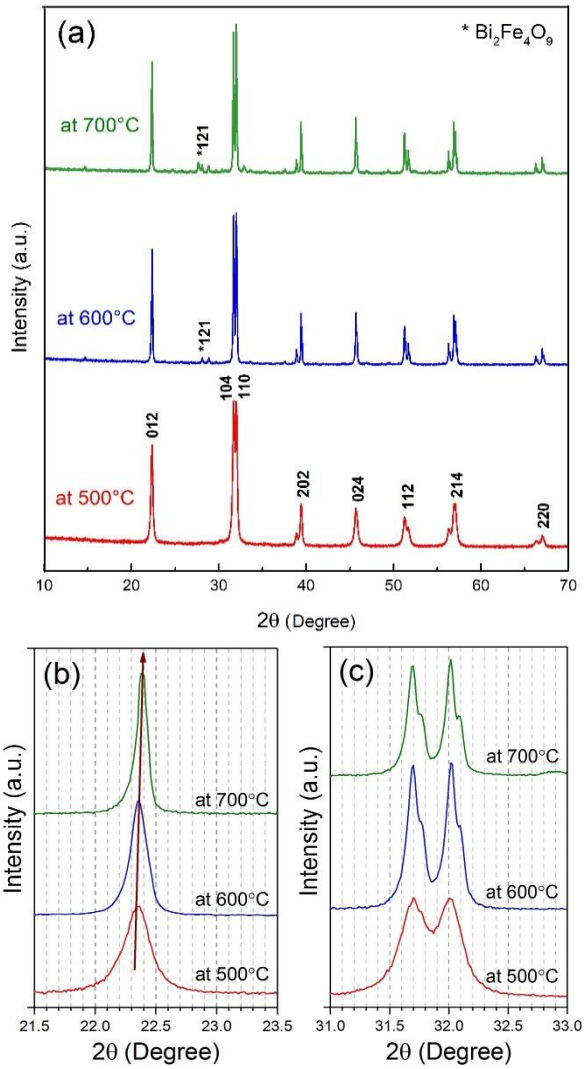

Fig. 1 – (a) XRD patterns of $BiFeO_3$ nanoparticles after washing with CH_3COOH; (b) enlarged XRD patterns of (012) peak; (c) enlarged XRD patterns of (104) and (110) peaks

It has also been observed from the magnified (012) diffraction peak that with increasing temperature, the primary phase (012) of $BiFeO_3$ becomes stronger. A shift in the peak (012) position had also been noticed. The peak at about $2\theta = 22.25°$ shifts from left to right with the increment of annealing temperature. From magnified (104) and (110) diffraction peaks in Fig. 1c, it is observable that two peaks become strong and well-shaped with increasing annealing temperature.

3.2 Field Emission Scanning Electron Microscopy (FESEM)

In Fig. 2, micrographs of BFO powder annealed at 500, 600 and 700 °C for 2-2.5 h are shown. FESEM (JSM-7600F) had been done to characterize the obtained nanoparticles at different annealing temperatures. It had been observed that with increasing annealing temperature, particle size increased. In this mechanism, attainment of a uniform particle size distribution is quite difficult.

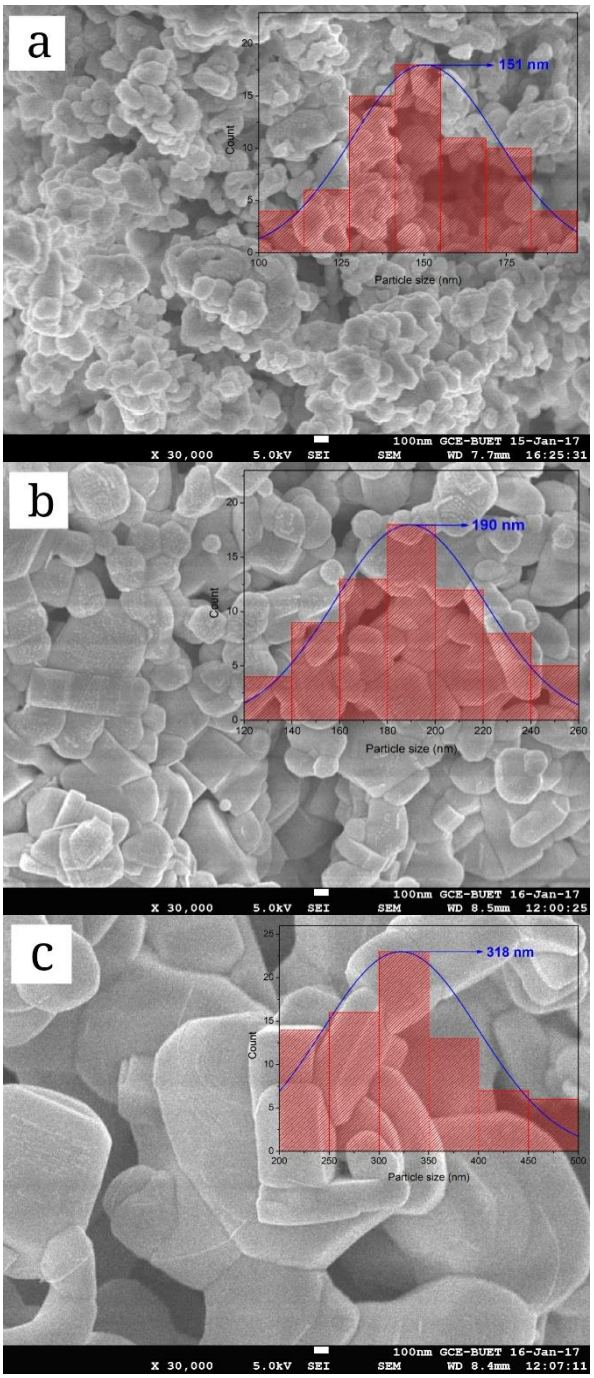

Fig. 2 – FESEM micrograph images and particle size distribution histograms of BFO nanoparticles at (a) 500 °C, (b) 600 °C, (c) 700 °C

The Energy Dispersive X-ray Spectroscopy (EDS) is a chemical analysis technique used jointly with FESEM. The EDS analysis is used to determine the homogeneity and the elemental distribution of synthesized nanocomposite. In Table 1, weight and atomic ratio of BFO has been shown. In Fig. 3, it has been observed from the EDX spectrum that bismuth ferrite nanoparticles prepared at 500 °C have the highest amount of oxygen (O), nanoparticles annealed at 600 °C have the highest amount of bismuth (Bi) and nanoparticles annealed at 700 °C have the highest amount of iron (Fe) compared to nanoparticles prepared at two other temperatures.

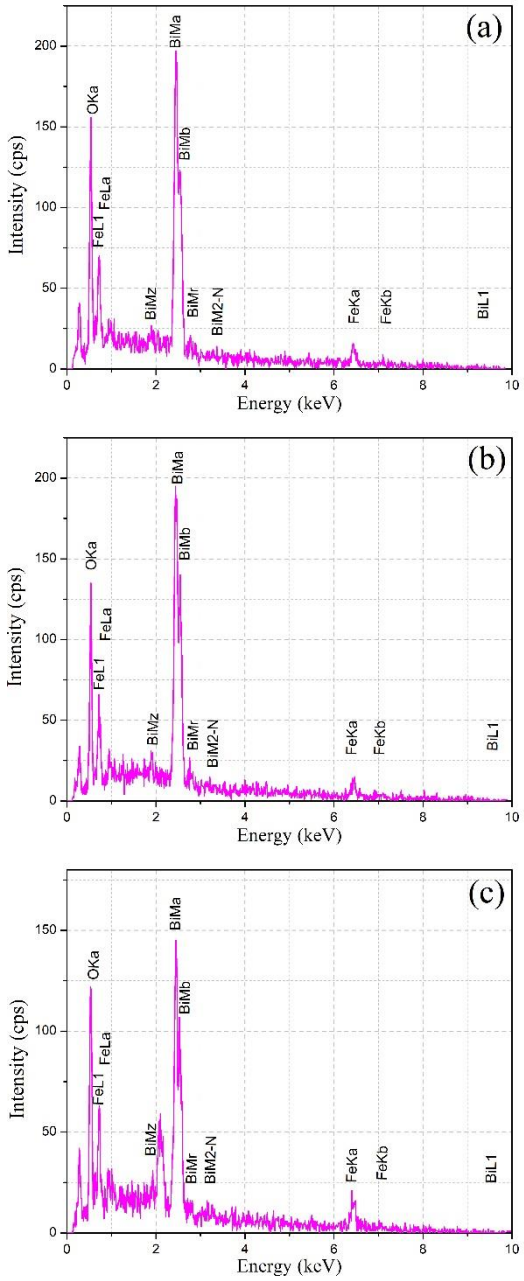

Fig. 3 – EDS analysis of BFO nanoparticles at: (a) 500 °C, (b) 600 °C, (c) 700°C

The sizes of the particles were calculated from the FESEM micrographs using ImageJ software. It was found that the crystallite size which was roughly calculated from XRD data was found to be smaller than particle size obtained from the FESEM micrographs. As the ratio of volume to surface area of the nanoparticles is lower, this leads to agglomeration and results in assembling several crystallites into a particle [15]. From Table 2, it is observable that with increasing annealing temperature from 500 °C to 700 °C, crystallite size increases from 30.6 nm to 54.3 nm and particle size increases from 151 nm to 318 nm.

Table 1 – EDS weight and atomic ratios of pure BFO nanoparticles which were annealed at 500, 600 and 700 °C

$BiFeO_3$ composite	Bismuth (Bi)		Iron (Fe)		Oxygen (O)	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
Prepared at 500 °C	72.30	25.18	15.77	20.56	11.93	54.26
Prepared at 600 °C	76.36	28.78	12.86	18.14	10.78	53.08
Prepared at 700 °C	62.73	21.65	27.87	35.99	9.40	42.36

It had been observed from Fig. 2 that the particle sizes obtained from the FESEM micrograph are consistent with the XRD results. This indicates that the nanoparticles are single crystalline. When nanoparticles are annealed up to 600 °C, the shape of the observed nanoparticles is almost rounded which is uniformly distributed. But cubic morphology was seen for the BFO samples annealed at 700 °C. Using VESTA software, the hexagonal unit cell of pure BFO nanoparticles was constructed from crystal information file (CIF). The unit cell structure of $BiFeO_3$ nanoparticles annealed at 600 °C had been shown in Fig. 4.

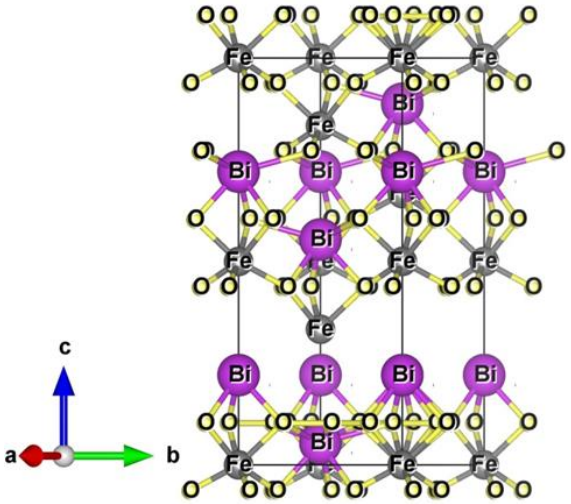

Fig. 4 – Unit cell representation of pure BFO nanoparticles annealed at 600 °C

3.3 Band Gap of BFO

$BiFeO_3$ is very effective as an irradiator of visible light because its band gap energy is small. It is widely known that the photovoltaic absorption capability of $BiFeO_3$ is immediately interconnected to its structure of electrons. In order to calculate the band gap energy, photovoltaic absorption phenomenon is important [16]. With the help of the diffuse reflectance spectra, the optical band gap (E_g) of BFO nanoparticles was measured by a UV/Vis/NIR spectrophotometer (PerkinElmer Lambda 1050). To compute E_g of all BFO, the Kubelka-Munk equation had been used. The diffuse reflectance values had been converted to the Kubelka-Munk function using this equation:

$$F(R) = \frac{(1-R)^2}{2R}, \tag{2}$$

where R represents the diffuse reflectance. Fig. 5 illustrates the $[F(R)h\nu]^2$ vs. $h\nu$ (energy, eV) plots for every BFO nanoparticle. The intersection of the tangent at $[h\nu[F(R)]^2 = 0$ shows the band gap energy (eV) [17]. It mostly plots the violet to red solar radiation which has wavelength range from 380 nm to 750 nm that can hit the substance with energy sufficient for removing electrons from infirm bonds. Those dislodged electrons produce electric current. The ultraviolet and infrared rays have wavelength range of 10-380 nm and 750-1,000,000 nm respectively. These rays are absorbed as heat energy. The energy of light is calculated by $E = hc/\lambda$. Infrared rays do not have notable energy to displace the electrons because the energy of light (E) is inversely proportional to the wavelength (λ). Thus, we only considered the range of wavelengths from 200 nm to 800 nm to capture the data. In Table 2, the values of E_g for BFO nanoparticles annealed at 500, 600 and 700 °C are shown.

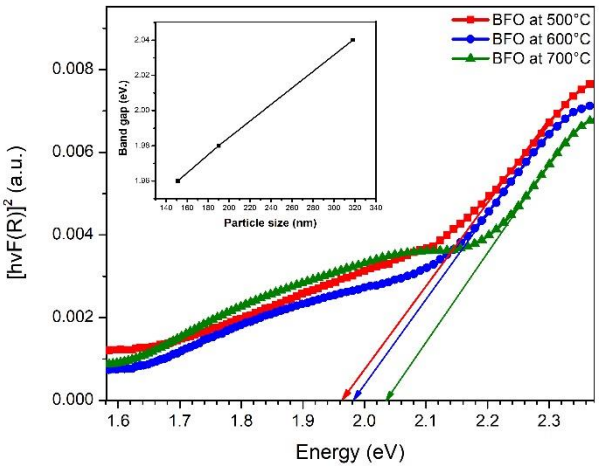

Fig. 5 – $[F(R)h\nu]^2$ vs. $h\nu$ for BFO nanoparticles annealed at 500, 600 and 700 °C. Inset figure shows the dependence of band gap energy (eV) on particle size (nm)

$$W \infty \frac{\cos\omega}{d^{3.5}_{(\mathrm{Fe-O})}}. \tag{3}$$

The experimental formula shows that bandwidth (W) is dependent on the Fe–O–Fe bond angle and Fe–O bond length, where

$$\omega = \frac{1}{2}\{\pi - (\mathrm{Fe-O-Fe})\} \tag{4}$$

and $d_{(\mathrm{Fe-O})}$ is the Fe–O bond length. E_g is connected with W as

$$E_g = \Delta - W, \tag{5}$$

where invariant charge transfer energy is represented by Δ [18]. And, bond length of the Fe–O rhombohedral phase is greater than of orthorhombic phase [19]. With increasing temperature, Fe–O–Fe bond angle decreases and Fe–O average bond length increases [20]. Ac-

cording to equations (4) and (3), decreased bond angle increases the value of ω. As a result, bandwidth (W) decreases. Similarly, increased average bond length also decreases the bandwidth value. From equation (5), it can be said that decreased W increases the value of E_g. So, eventually, E_g increases with the increment of bismuth ferrite particle size. This relation between the band gap and particle size is inserted in Fig. 5 by the obtained data, a similar result was found elsewhere [5].

Table 2 – Band gap energy, crystallite size and average particle size of BFO nanoparticles at 500, 600 and 700 °C

Samples	BFO (500 °C)	BFO (600 °C)	BFO (700 °C)
Band gap (eV)	1.96	1.98	2.04
Crystallite size (nm)	30.6	49.8	54.3
Particle size (nm)	151	190	318

4. CONCLUSIONS

$BiFeO_3$ nanoparticles were prepared using the sol-gel method and then annealed at 500, 600 and 700 °C separately. The structural properties have been analyzed through XRD and FESEM micrographs. Optical properties were studied through band gap energy. The secondary phase ($Bi_2Fe_4O_9$) in bismuth ferrite was the weakest at the annealing temperature of 500 °C. BFO nanoparticles prepared at 500 °C had more iron (Fe) than nanoparticles annealed at 600 °C that indicates higher conductivity. BFO nanoparticles annealed at 500 °C had the least particle size of 151 nm. Particle size was found to be increased with the increment of annealing temperature. Increasing particle size seems to have a significant effect on the optical band gap. With the increment of particle size, band gap energy of $BiFeO_3$ also increased. For BFO nanoparticles annealed at 500 °C, we obtained the lowest band gap energy of 1.96 eV. As its band gap energy is closer to the ideal band gap for a photovoltaic cell (~ 1.50 eV), BFO nanoparticles annealed at 500 °C with the lowest secondary phase and band gap energy can be considered for photovoltaic applications.

ACKNOWLEDGEMENTS

The authors are thankful to the Department of Glass and Ceramic Engineering, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh for experimental support.

REFERENCES

1. H. Schmid, *Ferroelectrics* **162**, 317 (1994).
2. C.N.R. Rao, C.R. Serrao, *J. Mater. Chem.* **17**, 4931 (2007).
3. M.M. Rhaman, M.A. Matin, M.N. Hossain, M.N.I. Khan, M.A. Hakim, M.F. Islam, *J. Phys. Chem. Solids* 109607 (2020).
4. I. Sosnowska, T.P. Neumaier, E. Steichele, *J. Phys. C: Solid State Phys.* **15**, 4835 (1982).
5. M.A. Matin, M.M. Rhaman, M.N. Hossain, F.A. Mozahid, M.A. Hakim, M.H. Rizvi, MF. Islam, *Trans. Electr. Electron. Mater.* **20**, 485 (2019).
6. M.M. Rhaman, M.A. Matin, M.A. Hakim, M.F. Islam, *Mater. Res. Express.* **6**, 125080 (2019).
7. M. Arora, M. Kumar, *Mater. Lett.* **137**, 285 (2014).
8. M.M. Rhaman, M.A. Matin, M.N. Hossain, F.A. Mozahid, M.A. Hakim, M.H. Rizvi, M.F. Islam, *J. Electron. Mater.* **47**, 6954 (2018).
9. M.M. Rhaman, M.A. Matin, M.N. Hossain, F.A. Mozahid, M.A. Hakim, M.F. Islam, *Bull. Mater. Sci.* **42**, 190 (2019).
10. P.C. Sati, M. Arora, S. Chauhan, M. Kumar, S. Chhoker, *J. Phys. Chem. Solids* **75**, 105 (2014).
11. M.A. Matin, M.M. Rhaman, M.A. Hakim, M.F. Islam, *Bull. Mater. Sci.* **43**, 167 (2020).
12. X. Xu, T. Guoqiang, R. Huijun, X. Ao, *Ceram. Int.* **39**, 6223 (2013).
13. J. Liu, M. Li, L. Pei, J. Wang, B. Yu, X. Wang, X. Zhao, *J. Alloy Compd.* **493**, 544 (2010).
14. M.M. Rhaman, M.A. Matin, M.A. Al Mamun, A. Hussain, M.N. Hossain, B.C. Das, M.A. Hakim, M.F. Islam, *J. Mater. Sci. Mater. Electron.* **31**, 8727 (2020).
15. S. Gupta, M. Tomar, A.R. James, V. Gupta, *J. Mater. Sci.* **49**, 5355 (2014).
16. S. Irfan, Y. Shen, S. Rizwan, H.C. Wang, S.B. Khan, C.W. Nan, *J. Am. Ceram. Soc.* **100**, 31 (2017).
17. P.S.V. Mocherla, C. Karthik, R. Ubic, M.S.R. Rao, C. Sudakar, *Appl. Phys. Lett.* **103**, 022910 (2013).
18. M. Medarde, J. Mesot, P. Lacorre, S. Rosenkranz, P. Fischer, K. Gobrecht, *Phys. Rev. B* **52**, 9248 (1995).
19. H.M. Tütüncü, G.P. Srivastava, *Phys. Rev. B* **78**, 235209 (2008).
20. M. Hasan, M.F. Islam, R. Mahbub, M.S. Hossain, M.A. Hakim, *Mater. Res. Bull.* **73**, 179 (2016).

Структурні та оптичні характеристики мультиферроїчних наночастинок $BiFeO_3$, синтезованих при різних температурах відпалу

Naimur R. Niloy, M.I. Chowdhury, S. Anowar, J. Islam, M.M. Rhaman

Department of Electrical and Electronic Engineering, Ahsanullah University of Science and Technology, Dhaka, Bangladesh

Синтез мультиферроїчного $BiFeO_3$ (BFO) без будь-якої вторинної фази є великою проблемою. У роботі наночастинки BFO готували методом золь-гелю при трьох різних температурах відпалу. Для спостереження за структурою підготовлених наночастинок застосовували рентгенівську дифракцію (XRD). Яскраво-кристалічна структура наночастинок чистого BFO була підтверджена рентгенограмою. На рентгенограмі наночастинок BFO спостерігалась вторинна фаза ($Bi_2Fe_4O_9$). Зміщення ліній від фази було помічено із збільшенням температури відпалу. Для детального вивчення морфології зерна синтезованих наночастинок було проведено автоелектронну скануючу

мікроскопію (FESEM). Метод енергодисперсійної рентгенівської спектроскопії (EDS) також проводили для трьох різних температур відпалу. Зі збільшенням температури відпалу з 500 до 700 °C розмір частинок збільшився із 151 нм до 318 нм, а розмір кристалітів збільшився з 30,6 нм до 54,3 нм. Для вимірювання дифузного відбиття використовували спектрофотометр UV/Vis/NIR, а потім визначали оптичну ширину забороненої зони (E_g). Енергія забороненої зони зросла з 1,96 еВ до 2,04 еВ при збільшенні температури відпалу з 500 до 700 °C. Встановлено, що температура відпалу 500 °C є оптимальною умовою синтезу наночастинок $BiFeO_3$.

Ключові слова: Ширина забороненої зони, Наночастинки, FESEM, Золь-гель, Рентгенівська дифракція.