EFFECT OF HEAT TREATMENT REGIMES ON THE PHASE FORMATION AND PARTICLE SIZES OF NANOPOWDERS $BiFeO_3$ PREPARED BY Sol-Gel METHOD

© 2016 г. PHAM MAI AN[1], S.V. MEDNIKOV[2], LUU THI NHAN[3], VU THI TUYET[1], LE THI THU HIEN[1]

[1]Thai Nguyen University of Education, Thai Nguyen province, Vietnam,
[2]Volgograd State Technical University, Volgograd, Russia,
[3]Hanoi University of Industry, Hanoi, Vietnam
e-mail: phammaian@dhsptn.edu.vn, vl28_pa@yahoo.com

1. Introduction

Bismuth ferrite $BiFeO_3$ (BFO) is one of the most widely researched single-phase multiferroic materials which exhibits ferroelectricity (T_C ~ 1100 K) and antiferromagneticity (T_N ~ 640 K) simultaneously above room temperature [1,2]. Because of its high Curie and Néel temperatures, bismuth ferrite, especially nanosized BFO systems, is considered as highly promising multiferroic material for applications in the design of sensors, memory devices, optical filters, microwave and satellite communications, spintronic devices, etc. BFO nanoparticles also show good photocatalytic activities in visible-light region due to narrow band gap (2.1-2.7eV) [3], which can be used as novel visible-light responsive photocatalysts for degradation of organic pollutants or for H_2 generation from water.

It is generally known that the particle size, morphology and phase formation of BFO particles would significantly influence its applications. BFO nanoparticles are being prepared by other methods as the solid state reaction, mechano-chemical method, hydrothermal technique, solution chemistry methods, sol-gel method, etc [2,3]. Each method has advantages and disadvantages. Nevertheless, obtaining a pure single-phase product with small particle size and high uniformity has been problematic so far. Recently, in some researches sol-gel techniques with different hydrolysis catalysts were developed to synthesize the BFO nanoparticles [3,4]. However, these studies have some differences in synthesis process. Therefore, the processing parameters should be controlled carefully to obtain the required crystalline phase, morphology as well as particle size. In this paper, we present our work on synthesis of $BiFeO_3$ nanopowders prepared by sol-gel method using metal nitrates and citric acid.

2. Experimental

BFO powders were synthesized by sol-gel method using bismuth nitrate $Bi(NO_3)_3.5H_2O$ (purity ≥ 99%), iron nitrate $Fe(NO_3)_3.9H_2O$ (purity ≥ 98,5%), citric acid monohydrate $C_6H_8O_7.H_2O$ (purity ≥ 99,5%). Firstly, $Bi(NO_3)_3.5H_2O$ and $Fe(NO_3)_3.9H_2O$ in stoichiometric proportions (1/1 molar ratio) were stirred in distilled water for 30 minutes, and then citric acid was added cautiously into the solution under stirring condition. The ammonia solution was added drop-wise into the mixed solution to keep pH level between 8 and 10. The solution was stirred continuously at room temperature for 15 hours. Then, temperature of the solution was increased to 90 ºC and maintained until wet-gel was obtained. In the next step, wet-gel was dried at 120 ºC to obtain dry gel. Finally, this dry gel was calcinated in Lenton furnace at different temperatures and in different time periods. The obtained products were light brownish powders.

X-ray diffraction (XRD) patterns of the BFO powders were recorded by a diffractometer D8 Advance – Bruker with Cu-Kα radiation. A morphology of $BiFeO_3$ powder particles was investigated with scanning electron microscope (SEM) S4800 – NIHE.

3. Results and discussion

Analyses of the XRD data of powders after calcination at 500 ºC for 3h, 5h, 8h 10h, 12h, 14h confirmed that BFO phase was formed when the sample was sintered for 5 hour and more. However, in all samples impurity phases (Fe_3O_3, Fe_3O_4, Bi_2O_3) was still considerable and BFO phase composition was quite low.

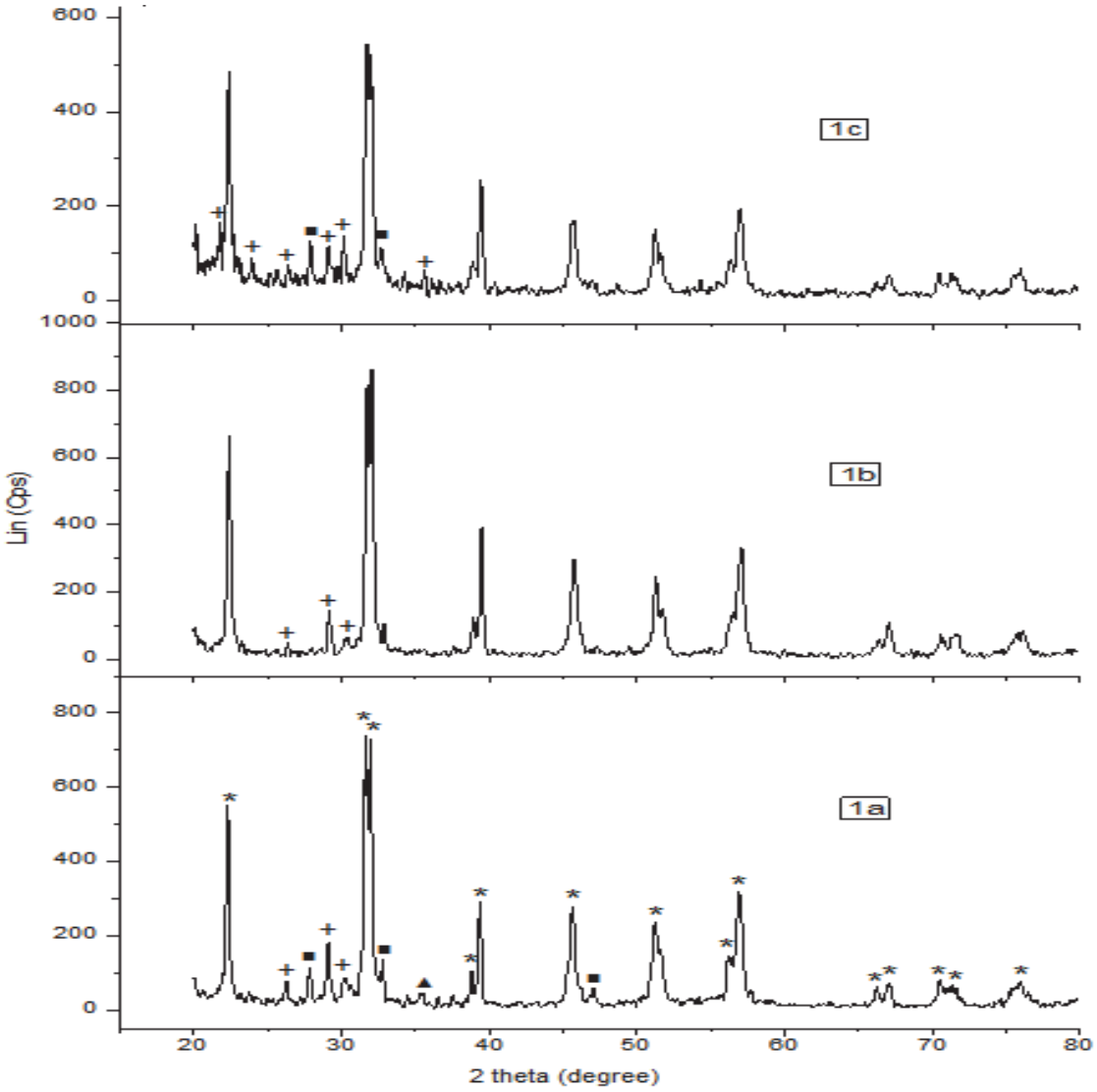

Fig. 1. Room temperature XRD patterns of BFO powders calcinated at 600 ºC for 10 hours (1a), 12 hours (1b), 14 hours (1c) (∗ - $BiFeO_3$; + - Fe_3O_4; ▲ – Fe_2O_3; ■ – Bi_2O_3).

Fig. 1 shows XRD patterns of BFO powders calcinated at 600 ºC for 10h, 12h and 14h. These peaks in Fig. 1 belong to rhombohedrallly distorted perovskite structure (R3c space group) of $BiFeO_3$ (marked with ∗) and some impurity phases. In the sample heated for 12h (1b) have only Fe_3O_4-impurity phase and it have less peaks compared with other samples. In samples cancinated for 10h (1a) and 14h (1c) are also reported Fe_2O_3 and Bi_2O_3 impurity phases.

XRD patterns of BFO powders calcinated at 700 ºC for 8h, 10h and 12h are showed in Fig. 2. Results revealed that sample heated for 10h (2b) has the best quality.

The cause of the existence of inpurity phases in samples heated at 500 ºC or at 600 ºC for 10h and 700 ºC for 8h are thought to be the formation of secondary phases [5-7]. As the calcination temperature (in the same period of time) or time period (at 600 ºC and 700 ºC) increased, the $BiFeO_3$ phase emerged out abundantly and became stronger. However, when calcination temperature and length of time would be above a limit, the impurity phases increased. It can be due to overcoming thermal stability of material.

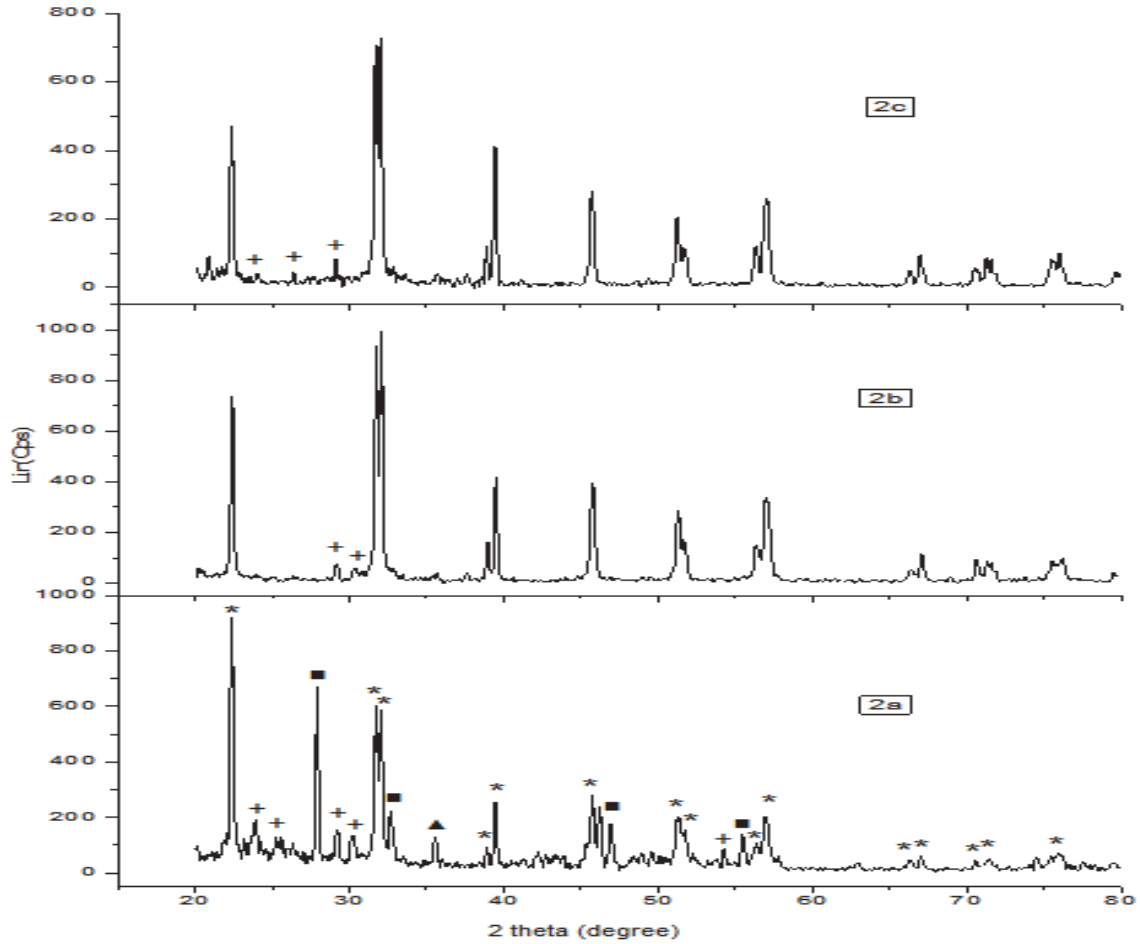

Fig. 2. Room temperature XRD patterns of BFO powders calcinated at 700 ºC for 8 hours (2a), 10 hours (2b), 12 hours (2c) (∗ - $BiFeO_3$; + - Fe_3O_4; ▲ – Fe_2O_3; ■ – Bi_2O_3).

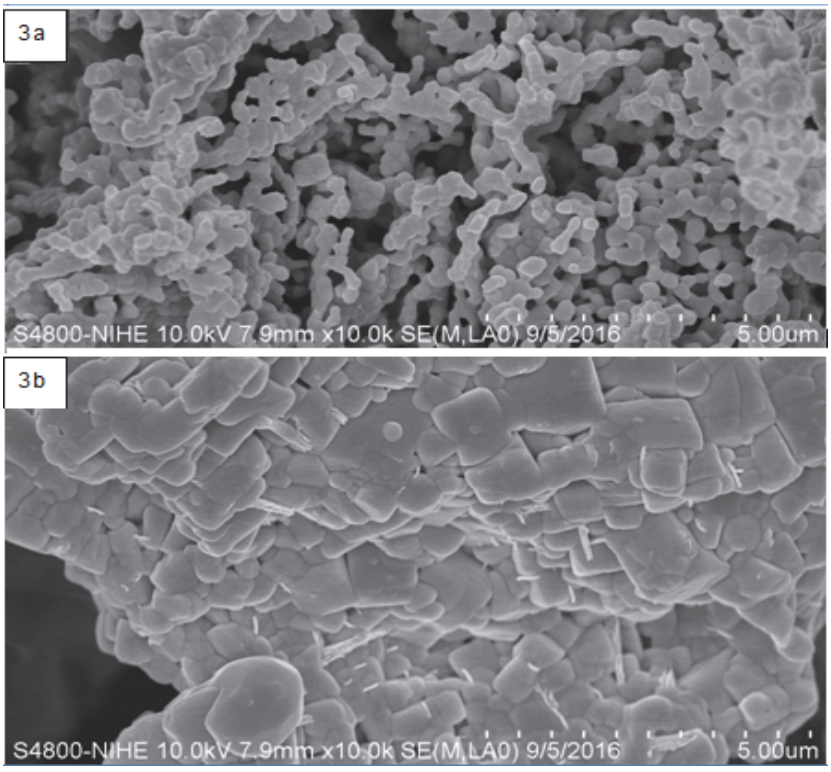

Fig. 3. SEM images of BFO powders prepared at 600 ºC for 12 hours (3a) and at 700 ºC for 10 hours (3b).

Fig. 3 shows the scanning electron microscope (SEM) images of BFO powders sintered at 600 ºC for 12 hours and at 700 ºC for 10 hours. The SEM image shows that $BiFeO_3$ particles of sample sintered at 600 ºC (Fig. 3, a) are homogeneous with the size of 200 – 250 nm. In the SEM image of sample heated at 700 ºC (Fig. 3, b), the particles coalesce into larger clusters and they are not homogeneous. Thus, although phase composition of these samples are same, but morphology of BiFeO3 powder heated at 600 ºC is better than of the sample heated at 700 ºC.

4. Conclusion

In summary, $BiFeO_3$ nanopowders were successfully synthesized by sol-gel method using citric acid. The phase analysis of the samples was carried out by X-ray diffractometry (XRD). A morphology of $BiFeO_3$ powder particles was investigated with scanning electron microscope (SEM). The results show that the phase composition of the samples and the powder particle morphology strongly depend on the synthesis parameters - temperature and sintering time period. In all synthesized samples, BFO phase composition of powders calcinated at 600 ºC for 12 hours and at 700 ºC for 10 hours were highest, powder morphology of sample heated at 600 ºC was the best.

REFERENCES

1. *P. Fischer, M. Polomskya, I. Sosnowska, M. Szymanksi.* Temperature dependence of the crystal and magnetic structures of BiFeO3.// J. Phys. C: Solid State Phys., 13 (1980), 1931–1940.
2. *Manisha Arora, P.C. Sati, Sunil Chauhan, Sandeep Chhoker, A.K. Panwar & Manoj Kumar.* Structural, Optical and Multiferroic Properties of $BiFeO_3$ Nanoparticles Synthesized Soft Chemical Route.// J. Supercond Nov Magn, Vol. 25, No. 4 (2012), DOI 10.1007/s10948-012-1761-4
3. *T. Gao, Z. Chen, Q. Huang, F. Niu, X. Huang, L. Qin and Y.Huang.* A review: preparation of bismuth ferrite nanoparticles and its applications in visible-light induced photocatalyses.// Rev.Adv.Mater.Sci.40 (2015), 97-109.
4. *J. Wei, D. Xue.* Low-temperature synthesis of $BiFeO_3$ nanoparticles by ethylenediaminetetraacetic acid complexing sol-gel process.//Materials Research Bulletin 43 (2008), 3368-3373
5. *Archna Sagdeo, Puspen Mondal, Anuj Upadhyay, A.K. Sinha, A.K. Srivastava, S.M. Gupta, P. Chowdhury, Tapas Ganguli, S.K. Deb.* Correlation of microstructural and physical properties in bulk $BiFeO_3$ prepared by rapid liquid-phase sintering.// Solid State Sci. 18 (2013), 1–9.
6. *J. Lu, L.J. Qiao, P.Z. Fu, Y.C. Wu.* Phase equilibrium of Bi_2O_3–Fe_2O_3 pseudobinary system and growth of $BiFeO_3$ single crystal.// J. Cryst. Growth 318 (2011), 936–941.
7. *Mehedi Hasan, Md. Fakhrul Islam, Rubayyat Mahbub, Md. Sarowar Hossain, M.A. Hakim.* A soft chemical route to the synthesis of $BiFeO_3$ nanoparticles with enhanced magnetization.// Materials Research Bulletin 73 (2016), 179-186.