Enhancement of Magnetic Properties of Nanocrystalline $BiFeO_3$ Synthesized by a Facile Sol-Gel Auto-Combustion Process

Mehedi Hasan, Md. Fakhrul Islam

Abstract*— In this study a facile sol-gel auto-combustion methodology has been used to synthesize nearly pure $BiFeO_3$ (BFO) nanocrystals at relatively low temperature. An optimum synthesis condition has been established to obtain particles with spherical shape and uniform size distribution. Well crystallized BFO nanoparticles of average particle size 26 nm have been confirmed by X-ray diffraction analysis. Size and morphology of the synthesized materials are observed using Field emission scanning electron microscope (FESEM). Magnetic hysteresis loop measurement of BFO nanoparticles shows substantial improvement in saturation magnetization with a value of ~ 6.5 emu/g compared to 0.1 emu/g for the bulk antiferromagnetic sample. The origin of the magnetic property can be attributed to the size confinement effect for the particles with size less than 62 nm, period of the spiral modulated spin structure.

Index Terms*— $BiFeO_3$, ferromagnetism, nanoparticles, sol-gel auto-combustion.

I. INTRODUCTION

Recently there is intriguing interest in the emerging novel group of materials called multiferroics because of their promising applications in fundamental research and various possible technological schemes. Due to the simultaneous coexistence of ferroelectric, ferromagnetic and ferroelastic phases these materials exhibit collective responses to the electric, magnetic and stress fields. Therefore, these materials have potential applications in magnetic and ferroelectric devices [1]. At the same time, the coupling between two order parameters provides an addition degree of freedom in device design. The perovskite BFO is the most interesting in the family of very few single phase multiferroics because of its high phase transition temperatures (i.e. Curie temperature~ 830°C and Neel temperature~370°C) [2]. Since its discovery in the 1960s, difficult synthesis of BFO and its very low magnetic moment are the mostly reported weaknesses which have hampered its potential applications [3]. G type antiferromagnetism with a spiral spin structure having a period of 62 nm subdues any net magnetization in bulk BFO [4-7]. Several approaches to improve the magnetization in BFO ceramics have been reported in previous work [7]. A number of studies on different parameters such as A or B site substitution and co-doping have been investigated to improve magnetic properties [7-10]. Recent approaches have focused on developing novel structural formulations such as zero-, one-, and two-dimensional (0-D, 1-D, and 2-D) nanostructures of BFO materials [5, 6].

Revised Version Manuscript Received on June 20, 2015.

Mehedi Hasan, Department of Glass and Ceramic Engineering, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh.

Dr. Md. Fakhrul Islam, Department of Glass and Ceramic Engineering, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh.

The antiferromagnetic ordering can be broken if the size of the BFO nanostructures be less than the spiral period order (62 nm). Enhanced magnetization for BFO has been reported in nanoparticles [11], nanowires [12] and thinfilms [13], which is thought to be originated from the destruction of the spiral spin structure and uncompensated spins at surface [5]. However there is intense study, a fundamental understanding of structure-property correlations for BFO is still lacking. Specifically, the nature of the magnetic response on particle size is of great interest. Thus, in this paper, we systematically investigate the effect of reduced particle size on magnetic properties of BFO powders. Up to now, several wet chemical routes have been developed for the synthesis of BFO powders [14-16]. In this work a facile sol-gel auto-combustion route is reported to prepare BFO nanoparticles at relatively low annealing temperature.

II. EXPERIMENTAL

A. Materials and Synthesis

The BFO powders were prepared by sol-gel auto-combustion method as described below. Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) and iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) were taken in a suitable stoichiometry and dissolved in 400 ml with individual concentration of 0.025 M. The citric acid as chelating agent was then added into the nitrate solution in such a manner that the molar amount of citric acid and metal nitrates was 1:1. The solution was then stirred and heated at 75-80°C for 6-8 hrs to form a sol. Aqueous ammonium hydroxide was used to adjust the pH between 1-2. Subsequently appropriate amount of ethylene glycol was added to the solution as polymerization agent and as well as surfactant agent. Afterwards the solution was gently evaporated at around 85°C to obtain a viscous gel. The resultant gel was still heated at that temperature to dry up and initiate sudden combustion reaction with vigorous fuming. After the completion of the combustion reaction the resultant powders were annealed at 400°C to obtain homogenous BFO nanoparticles. A portion of the powder was also annealed at temperature as high as 800°C to obtain bulk BFO sample.

B. Characterizations and Measurements

Crystalline structures of the BFO powders were examined using an X-ray diffractometer (XRD, model 3040-X'Pert PRO, Philips). The high-intensity X-ray beam was focused on the sample in the scanning range from 10° to 70°. The average crystallite size (d) was calculated from the XRD patterns using the Scherrer formula, $d = k\lambda/\beta\cos\theta$, where k is the dimensionless shape factor with a typical value of about 0.9, λ is the wavelength of Cu Kα radiation with the value of 1.5418 Å, θ is the Bragg angle for the (102) diffraction peak and β is

Published By:
Blue Eyes Intelligence Engineering
& Sciences Publication Pvt. Ltd.

the full width at half maximum intensity (FWHM) of the corresponding diffraction peak. Particle size measurement of bulk sample is not convenient with XRD. So conventional linear intercept method was utilized to measure particle size of bulk sample.The particle morphology and distribution were observed using field-emission scanning electron microscope (FESEM, mode JSM 7600, Jeol) with accelerating voltage of 5 kV. To investigate magnetic properties, room temperature isothermal magnetization data was taken using a vibrating sample magnetometer (model VSM 7407, Lake Shore) up to applied field of 16.5 kOe.

III. Results and Discussion

Room temperature powder x-ray diffraction (XRD) pattern of the BFO nanoparticles and that of bulk sample are shown in Fig.1. XRD pattern reveals that nearly pure and well crystalline BFO nanoparticles have been synthesized at as low as 400°C. All the diffraction peaks are indexed in the rhombohedral distorted perovskite structure with space group-*R3c*. XRD patterns show the presence of small amounts of the $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$ impurity phases for both nano and bulk powders. Synthesis of BFO nanoparticles without these impurity phases is very difficult [17]. Researchers have proposed different reasons for appearance of these impurity phases. Low temperature stability of impurity phases and metastable nature of BFO are thought to be the prime reasons for the formation of impurity phases [18, 19]. However, these impurity phases have little or no effect on magnetic properties [9, 20]. The average particle size of BFO nanoparticles calculated from the XRD peak broadening is about 26 nm. The measured particle sizes and magnetic parameters of both nano and bulk powders are enlisted in table 1.

Table 1. Particle size and magnetic parameters of nano and bulk BFO powders

Annealing Temperature (°C)	Particle size (nm)	Saturation magnetization, Ms (emu/g)	Coercivity, Hc (Oe)	Exchange bias, EB (Oe)
400	26	6.5	41.3	4.0
800	863	0.1	-	-

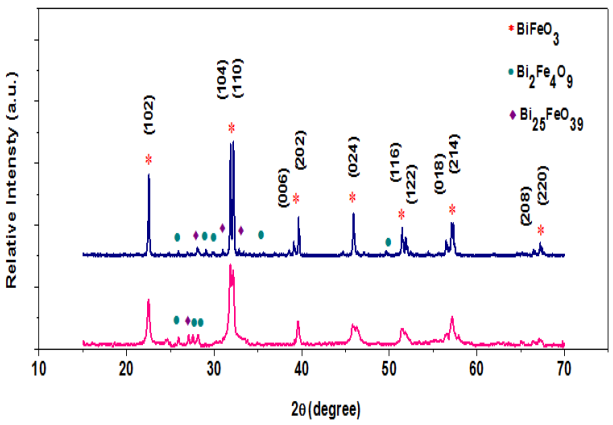

Fig.1: XRD patterns of the BFO powders annealed at 600°C and 800°C in static air.

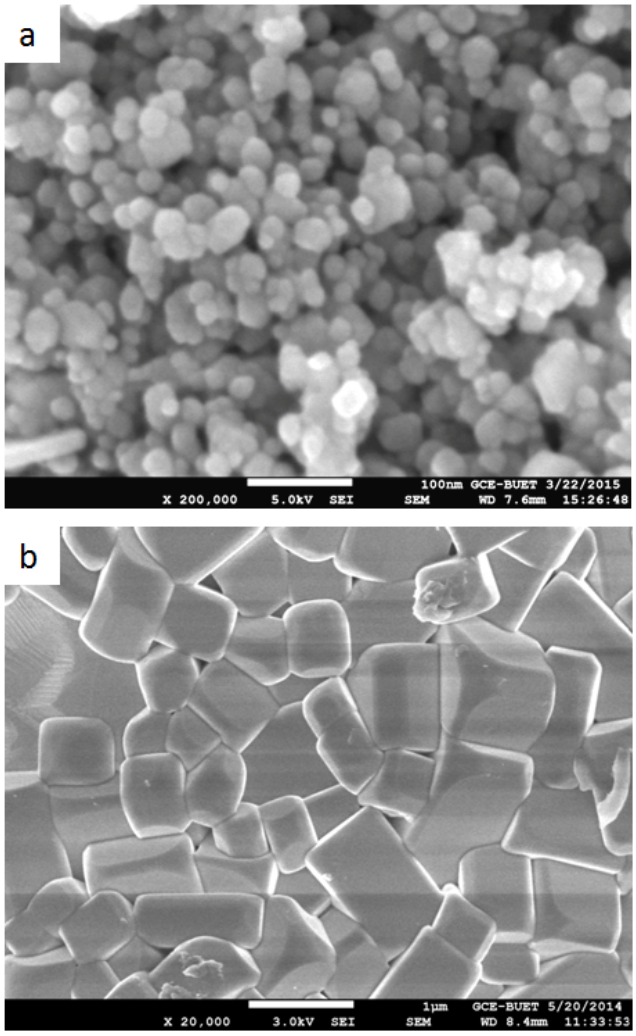

Fig. 2: FESEM micrographs of $BiFeO_3$ powders annealed at (a) 400°C and (b) 800°C

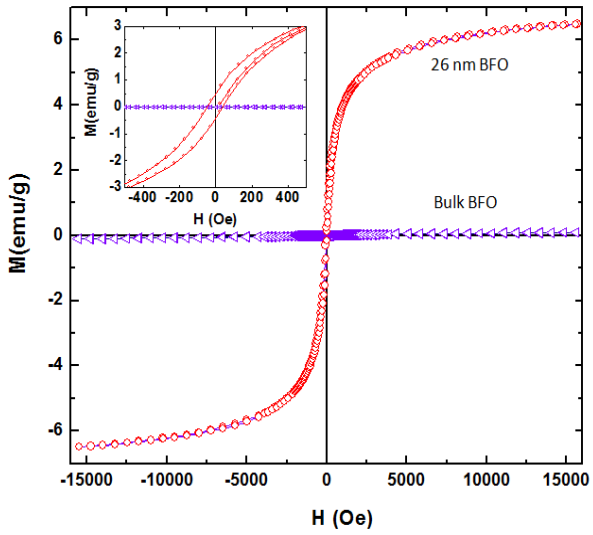

Fig. 3: Hysteresis loops for bulk and nanopowders of BiFeO3 at 300 K. The inset shows expanded plots of magnetization up to applied magnetic field of 500 Oe.

Fig. 2 shows the FESEM micrographs of nano and bulk BFO powders. It is evident from the Fig. that the particle size of nanocrystalline BFO observed in FESEM micrograph is quite compatible with that of XRD results. This suggests that the synthesized nanoparticles are single crystalline in nature [21]. Fig. 2(a) reveals that nanoparticles are nearly spherical in

Published By:
Blue Eyes Intelligence Engineering
& Sciences Publication Pvt. Ltd.

shape with uniform particle size distribution. However, Fig. 2 (b) presents that bulk BFO shows somewhat stable cubic morphology which is the characteristic for this type of perovskite material [22]. The magnetization measurements of synthesized BFO powders were carried out at room temperature in order to investigate the magnetic behavior. The magnetic hysteresis loops for both nano and bulk BFO powders are shown in Fig. 3. Though bulk BFO is antiferromagnetic, a significant improvement in ferromagnetic ordering with a value of about 6.5 emu/g is reported for that of nanoparticles. Due to the presence of spiral spin structure in bulk BFO, the antiferromagnetic axis rotates through the crystal with an incommensurate wavelength of 62 nm and thereby cancels out any net magnetic moment [6]. However, in our case, the size of the synthesized nanoparticles is about 26 nm which being less than 62 nm, modifies the spiral spin structure. Thus for nanosized BFO, the substantially enhanced ferromagnetism cloud be attributed to the destruction of the spiral modulated antiferromagnetic long range order [5, 11]. Another possible source of ferromagnetism could be attributed to the ferromagnetic surface and antiferromagnetic core of the BFO nanoparticles [6]. The noticeable 4 Oe exchange bias (table 1) for the synthesized nanoparticles indicates the presence of surface spin disorder and hence ferromagnetic surface [23]. Thus for 26 nm particles the significantly high surface to volume ratio could contribute this improved ferromagnetic property.

IV. Conclusion

A facile sol-gel auto-combustion route was used to synthesize BFO nanoparticles with uniform shape and homogenous particle size distribution. Nearly pure and well crystalline BFO powders were obtained at as low as 400^0C in contrast to above 800^0C for the traditional solid-state sintering process. Magnetic hysteresis loop measurement showed substantial improvement in saturation magnetization with reported value of 6.5 emu/g for 26 nm size powder samples, whereas bulk BFO was antiferromagnetic. This significant improvement in ferromagnetic ordering may conduct further research to use BFO nano structures in the desired technological applications. For the BFO particles with size less than 62 nm, a structural anomaly arises, which could be the possible reason for improved ferromagnetic behavior in this material.

Acknowledgment

The work is supported by Bangladesh University of Engineering and Technology, Dhaka, Bangladesh. The authors would like to thank Dr. M. A. Hakim and Mr. Rubayyat Mahbub for their useful discussions concerning this manuscript. The authors also wish to thank S. N. Bose National Centre for Basic Sciences, Kolkata, India for its support with the VSM.

References

[1] W. Eerenstein, N. D. Mathur, J. F. Scott, 'Multiferroic and magnetoelectric materials' Nature, Vol. 442, 2006, pp 759-765.
[2] Nicola A. Hill 'Why are there so few magnetic ferroelectrics?' Journal of Physical Chemistry B, Vol. 104, 2000, pp 6694-6709.
[3] Gustau Catalan, James F. Scott 'Physics and applications of bismuth ferrite' Advanced Materials, Vol. 21, 2009, pp 2463-2485.
[4] A. Mukherjee, S. Basu , P.K. Manna, S.M. Yusuf, M. Pal 'Enhancement of multiferroic properties of nanocrystalline $BiFeO_3$ powder by Gd-doping' Journal of Alloys and Compounds, Vol. 598, 2014, pp 142-150.
[5] Tae-Jin Park, C. Georgia Papaefthymiou, J. Arthur Viescas, R. Arnold Moodenbaugh, S. Stanislaus Wong 'Size-dependent magnetic properties of single-crystalline multiferroic $BiFeO_3$ nanoparticles' Nano Letters, Vol. 7 , 2007, pp 766-772.
[6] Fengzhen Huang, Zhijun Wang, Xiaomei Lu, Junting Zhang, Kangli Min, Weiwei Lin, Ruixia Ti, TingTing Xu, Ju He, Chen Yue, Jinsong Zhu 'Peculiar magnetism of BiFeO3 nanoparticles with size approaching the period of the spiral spin structure' Scientific Reports, Vol. 3, 2013, pp 2907.
[7] Gurmeet Singh Lotey, N. K. Verma 'Structural, magnetic, and electrical properties of Gd-doped BiFeO3 nanoparticles with reduced particle size' Journal of Nanoparticle Research, Vol. 14, 2012, pp 742.
[8] D. H. Wang, W. C. Goh, M. Ning, C. K. Ong 'Effect of Ba doping on magnetic, ferroelectric, and magnetoelectric properties in mutiferroic BiFeO3 at room temperature' Applied Physics Letters, Vol. 88, 2006, pp. 212907.
[9] Weiwei Hu, Yan Chen, Hongming Yuan, Guanghua Li, Yu Qiao, Yuanyuan Qin, Shouhua Feng 'Structure, Magnetic, and Ferroelectric Properties of $Bi_{1-x}Gd_xFeO_3$Nanoparticles' Journal of Physical Chemistry C Vo. 115, 2011, pp. 8869-8875.
[10] Won-Sik Kim, Youn-Ki Jun, Kee Hoon Kim, Seong-Hyeon Hong 'Enhanced magnetization in Co and Ta-substituted $BiFeO_3$ ceramics' Journal of Magnetism and Magnetic Materials, Vo. 321, 2009, pp. 3262–3265
[11] V. Annapu Reddy, N.P. Pathak, R. Nath 'Particle size dependent magnetic properties and phase transitions in multiferroic $BiFeO_3$ nano-particles' Journal of Alloys and Compounds, Vol. 543, 2012, pp. 206-212.
[12] Gurmeet Singh Lotey, N. K. Verma 'Multiferroic properties of Tb-doped $BiFeO_3$ nanowires' Journal of Nanoparticle Research, Vo. 15, 2013, pp. 1553.
[13] Fengzhen Huang, Xiaomei Lu, Weiwei Lin, Yi Kan, Junting Zhang,Qingdong Chen, Zhe Wang, Liben Li and Jinsong Zhu 'Thickness-dependent structural and magnetic properties of $BiFeO_3$ films prepared by metal organic decomposition method' Applied Physics Letters, Vol. 97, 2010, pp. 222901.
[14] M. Yasin Shami, M.S. Awan, M. Anis-ur-Rehman 'Phase pure synthesis of $BiFeO_3$ nanopowders using diverse precursor via co-precipitation method' Journal of Alloys and Compounds, Vol. 509, 2011, pp. 10139–10144.
[15] Yuning Huo, Yi Jin, Ya Zhang 'Citric acid assisted solvothermal synthesis of $BiFeO_3$microspheres with high visible-light photocatalytic activity' Journal of Molecular Catalysis A: Chemical, Vol. 331, 2010, pp. 15–20
[16] J. Silva, A. Reyes, H. Esparza, H. Camacho, L. Fuentes '$BiFeO_3$: A review on synthesis, doping and crystal structure' Integrated Ferroelectrics, Vol. 126, 2011, pp. 47-59.
[17] Matjaz Valant, Anna-Karin Axelsson, Neil Alford 'Peculiarities of a solid-state synthesis of multiferroic polycrystalline $BiFeO_3$' Chemistry of Materials, Vol. 19, 2007, pp. 5431-5436.
[18] J. Lu, L. J. Qiao, P. Z. Fu, Y. C. Wu 'Phase equilibrium of Bi_2O_3–Fe_2O_3 pseudo-binary system and growth of $BiFeO_3$ single crystal' Journal of Crystal Growth, Vol. 318, 2011, pp. 936-941.
[19] 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 Sciences, Vol. 18, 2013, pp. 1-9.
[20] Yijun Chen, Qingsheng Wu , Jing Zhao 'Selective synthesis on structures and morphologies of $Bi_xFe_yO_z$ nanomaterials with disparate magnetism through time control' Journal of Alloys and Compounds, Vol. 487, 2009, pp. 599–604.
[21] H. Yang , T. Xian , Z. Q. Wei , J. F. Dai ,J. L. Jiang, W. J. Feng 'Size-controlled synthesis of $BiFeO_3$ nanoparticles by a soft-chemistry route' Journal of Sol-Gel Science and Technology, Vol. 58, 2011, pp. 238-243.
[22] Jian-Ping Zhou, Ruo-Lin Yang, Rui-Juan Xiao, Xiao-Ming Chen, Chao-Yong Deng 'Structure and phase transition of $BiFeO_3$ cubic micro-particles prepared by hydrothermal method' Materials Research Bulletin, Vol. 47, 2012, pp.3630-3636.
[23] Shuai Dong, Kunihiko Yamauchi, Seiji Yunoki, Rong Yu, Shuhua Liang, Adriana Moreo, J.-M. Liu, Silvia Picozzi, Elbio Dagotto 'Exchange Bias Driven by the Dzyaloshinskii-Moriya Interaction and Ferroelectric Polarization at *G*-Type Antiferromagnetic Perovskite

Published By:
Blue Eyes Intelligence Engineering
& Sciences Publication Pvt. Ltd.

Interfaces' Physical Review Letters, Vol. 103, 2009, pp. 127201.

Mehedi Hasan had completed his B.Sc in 2013 in Materials and Metallurgical Engineering and M.Sc in 2015 in Glass and Ceramic Engineering from Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh. He began his academic career with the Department of Glass and Ceramic Engineering, BUET as a Lecturer from 2013. His publication record is given below:

1) Rubayyat Mahbub, Takian Fakhrul, Md. Fakhrul Islam, **Mehedi Hasan**, Arman Hussain, M. A. Matin, M. A. Hakim "Structural, Dielectric, and Magnetic Properties of Ba-Doped Multiferroic Bismuth Ferrite" Acta Metallurgica Sinica, 2015 (Received)
(Available online at http://link.springer.com/journal/40195)

2) Md. Fakhrul Islam, **Mehedi Hasan**, M. Hasanuzzaman "Development of Ceramic Candle Filters by Slip Casting Process", Key Engineering Materials Journal, Volume 608 (2014), pp: 85-90

Dr. Md. Fakhrul Islam received his first class honours B.Sc. Engineering degree in Metallurgical Engineering in 1986 from Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh and also the M. Sc. Engineering degree in 1988 from the same University. He began his academic career with the same department as a Lecturer in 1989 and was promoted to Professor in 2006. He completed his Ph. D. at University of Manchester – Institute of Science and Technology (UMIST), UK in 1995. He is the current head of Department of Glass and Ceramic Engineering, BUET, Dhaka, Bangladesh. His publication record in high quality peer-reviewed (SCI listed) journal papers like Scripta Materiala reflects his potentiality and leadership qualities in research. Some of his recent publications are listed below:

1. Md. Fakhrul Islam, Rubayyat Mahbub, Adnan Mousharraf, "Effect of Sintering Paramateres and Ta2O5 Doping on the Microstructure and Dielectric Properties of BaTiO3 Based Ceramics", Key Engineering Materials Journal, Volume 608, 2014, page: 247-252.
2. Md. Fakhrul Islam, M.H. Rizvi, T.A. Khan, M. Hasanuzzaman, "Development of Ceramic Candle Filters by Slip Casting Process", in the proceedings of International Conference on Traditional and Advanced Ceramics, Bangkok, Thailand, 2013.
3. Adnan Mousharraf and Md. Fakhrul Islam, "Effect of Ta2O5 doping on the microstructure and dielectric properties of BaTiO3 based ceramics", International Journal of Automotive and Mechanical Engineering, Volume 7, January-June 2013, page: 840-849.
4. Rubayyat Mahbub, Md. Sazzad Hossain, Md. Fakhrul Isalam "Structural Characteristics and Dielectric Properties of Tantalum Oxide Doped BaTiO3 Based Materials", Materials Engineering - Materiálové inžinierstvo Journal, Volume 20, 2013, page: 45-54.
5. Shahida Akhter, D. P. Paul, M. A. Hakim, S. Akhter, D. K. Saha, B. Anjuman, and F. Islam, "Microstructure and Complex Permeability Spectra of Polycrystalline Cu-Zn Ferrites", Journal of Scientific Research, Volume 4 (3), 2012, page: 551-560.

Published By:
Blue Eyes Intelligence Engineering
& Sciences Publication Pvt. Ltd.