www.vbripress.com, www.amlett.org, DOI: 10.5185/amlett.2013.fdm.82 Published online by the VBRI press in 2013

Investigation on magnetic behaviour of $BiFeO_3$: SPIN glass view point

V. M. Gaikwad, S. A. Acharya*

Department of Physics, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, India

*Corresponding author. E-mail: saha275@yahoo.com

Received: 06 January 2013, Revised: 21 April 2013 and Accepted: 01 May 2013

ABSTRACT

Field cooled (FC) and zero field cooled (ZFC) magnetization measurements of Bismuth Ferrite ($BiFeO_3$) multiferroic obtained by microwave-assisted gel combustion method are reported. The structural investigation of sythesized and calcined sample is done by XRD and the obtained data is well fitted with Rietveld refinement using full-pro software suite. M-H hysterisis shows that BFO nanoparticles exhibit ferromagnetic properties at room temperature, which is unusally observed in BFO. The M-T plot at H = 1 and 2 kOe shows that the FC and ZFC magnetization curve start to differ at below 331K and 236 K respectively with sharp cusp around 124 K revealing spin glass behaviour of $BiFeO_3$. Both ferromagnetic properties and spin-glass-like behavior are observed in BFO nanoparticles. Ferromagnetic behavior is attributed to a partial destruction in nanoparticles of the long-wavelength cycloid spin structure expected in bulk BFO. Spin-glass-like behavior is assigned to diffusion of domain walls, with possible contributions from pinning of the cycloid spin structure at the nanoparticle surface. Copyright © 2014 VBRI press.

Keywords: $BiFeO_3$; microwave-assisted synthesis; spin glass; magnetic.

Vishwajit M. Gaikwad has completed his B.Sc. in 2009 from R.T.M. Nagpur University and M. Sc. in Physics in 2011 from same university. He worked as JRF under Major Research Project of UGC, New Delhi, India. At present, he is pursuing doctoral degree from R.T.M. Nagpur University as JRF under the scheme of Rajiv Gandhi National Fellowship provided by UGC, India. His Ph.D. topic is on "Development of Room Temperature Composite Multiferroics". He has currently 3 research papers to his credit.

Smita A. Acharya did Ph.D. at R.T.M. Nagpur University. She completed her postdoctoral work at Pune University. Her main research activity includes synthesis of ceramics in different morphology at nanoscale and studies their impact on physical properties. Her current research are focused on synthesis of semiconductor nanostructure, solid electrolyte for SOFC, Fe and Mn based perovskite multiferroic by soft chemical route for different applications view point. She has published more than 25 research papers in various reputed international journals.

Introduction

Spin glass materials are currently progressive field of research and spin glass state is most complex kind of condensed state of matter. Microscopically, the spin glass state is a configuration of spins frozen into a more or less random pattern. There exists a distinct freezing or glass temperature, T_f or T_g, below which the random, frozen state is established. The typical features of spin glasses are spin freezing (very small magnetization relaxation time), cusp in temperature dependence magnetization, irreversible behavior of magnetization below freezing temperature **[1-2]**. Spin freezing state may be dominantly influenced by nanosize effect of materials in general.

In recent years, considerable attention has been devoted to the investigation of low temperature magnetic properties of the $BiFeO_3$ (BFO) in spin glass view point **[3]**. BFO is single phase multiferroic exhibit Ferroelectric (Tc~1103 K), G-type antiferromagnetic (T_N ~643 K) order **[4-9]**. This is due to the fact that below the particle size 62 nm, there is an enhancement in both ferroelectric and magnetic polarization because of the breaking of helical ordering or incomplete rotation of spins. The decrease in particle size below 62 nm may give rise to the suppression of modulated spin structure which shifts spin glass phase transition temperature towards higher side **[3,19]**. This makes us highly curious to syntheized BFO at nanoscale (particle

size < 65 nm) and study their low temperature magnetic behaviour. So, in the present work, we synthesized $BiFeO_3$ by microwave assisted gel combustion route. The structure was confirmed by XRD. The low temperature magnetic behaviour of as-synthesized BFO was investigated in spin-glass view point. This spin glass behavior of BFO can be exploited in the field of spintronics and the devices based on it.

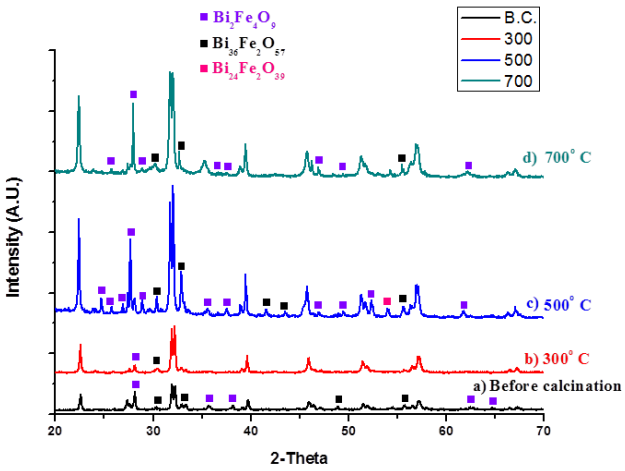

Fig. 1. XRD patterns of $BiFeO_3$: (a) Before calcination (b) Calcinated at 300^0C (c) 500°C and (d) 700°C.

Table 1. Percentage of impurity phases exists in BFO sample with different calcination temperature.

Impurity phase	Bi_2Fe_4O9 (%)	$Bi_{36}Fe_2O_{57}$ (%)	$Bi_{24}Fe_2O_{39}$ (%)
Before calcination (At room temperature)	75	3	0
300°C	2	1.6	0
500°C	62.7	39.8	1.4
700°C	74.13	3.4	0

Experimental

In present work, BFO was synthesized by gel combustion microwave-assisted route. Precursors for synthesis were procured from Sigma-Aldrich USA and used as raw materials without further purification. Analytical grade Bismuth nitrate [$Bi(NO_3)_3.5H_2O$, 99.9% pure], iron nitrate [$Fe(NO_3)_3.9H_2O$, 99.9% pure] and citric acid [$C_6H_8O_7$, 99.9% pure] Bismuth nitrate [$Bi(NO_3)_3.5H_2O$] and iron nitrate [$Fe(NO_3)_3.9H_2O$] in stoichiometric proportions (1:1 mol ratio) were dissolved in diluted nitric acid (HNO_3) solution with citric acid ($C_6H_8O_7$) at a molar ratio of 6:1 with $Bi(NO_3)_3.5H_2O$. The pH value of the reaction was adjusted by adding liquor ammonia. During the sol-gel process, citric acid was hydrolyzed in the solution to induce $(C_6O_7H_5)^{3-}$ as a complexing agent, which can complex with Bi^{3+} and Fe^{3+} cations. After adjusting pH at 5.5, the solution was proceed in microwave refluxing system at power 210 W for 10 minutes until it becomes black. Then the resultant solution was combusted at 300 W microwave power to obtained dark brown powder. The powder further calcined at 300°C for 2h and used for further characterization.

X-ray powder diffraction was performed on as-synthesized and calcined powder using Bruker AXS D8 Advance X-ray diffractometer equipped with copper target (λ_1,CuKα_1 = 1.5405 A^0). The data were collected with a step size of 0.067° and step time of 10 s. Thermogravimetry Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out on a simultaneous TGA/DTA apparatus (Perkin Elmer, Dimond TG/DTA, USA) at a heating rate of 10^0C/min. Magnetic measurements were performed using a Vibrating Sample Magnetometer (Model 14T-VSM) at temperature (2- 350 K).

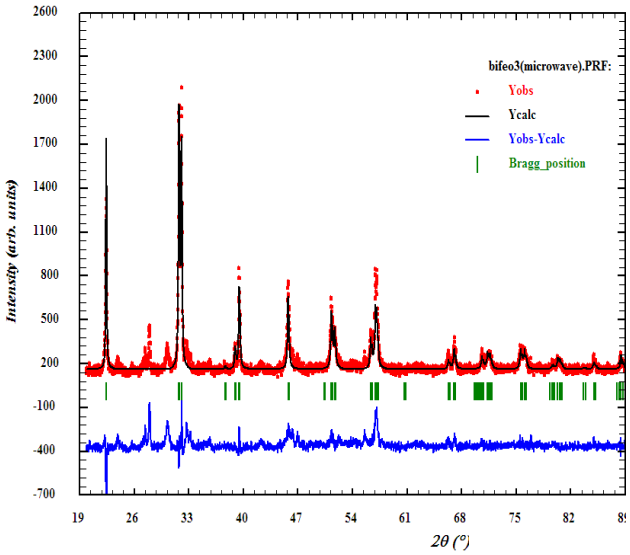

Fig. 2. Rietveld refinement of XRD patterns of BFO sample.

Table 2. XRD reitveld parameters compared with calculated and JCPDS data.

Parameters	$BiFeO_3$ (Rietveld)	$BiFeO_3$ (calculated)	$BiFeO_3$ (JCPDS)
χ^2	6.63	-	-
Rp	12	-	-
Rwp	16	-	-
Lattice parameters	a= 5.57 A^0, b=5.57 A^0, c = 13.85 A^0	a= 5.54 A^0, b=5.54 A^0, c = 13.85 A^0	a= 5.63 A^0, b=5.63 A^0, c = 13.86 A^0

Result and discussion

The XRD of as-synthesized and calcined BFO are shown in **Fig. 1** (**a** & **b,** respectively). XRD pattern of as-synthesized BFO depicts the existance of impurity phases such as $Bi_{24}Fe_2O_{39}$, $Bi_{36}Fe_2O_{57}$, $Bi_2Fe_4O_9$; while after calcination at 300°C, most of the impurity phases are disappeared; but still there are two impurities phases ($Bi_2Fe_4O_9$ and $Bi_{36}Fe_2O_{57}$) are present at very low concentration (2% and 1.6%, respectively) with pure rhombohedral (*R3c*) phase of BFO. Most of the diffraction peaks are matched with JCPDS card No. 20-0619 of the pure phase of BFO.

By increasing calcination temperature above 300°C, impurities phases ($Bi_2Fe_4O_9$, and $Bi_{36}Fe_2O_{57}$) concentrations are found surprisingly increasing with introduction of new phase ($Bi_{24}Fe_2O_{39}$). Calcination temperature and different phases related to BFO are summarized in **Table 1**. Hence for further characterization, 300°C calcined BFO was used. The average crystallite size of BFO was found to be 28 nm by XRD. The Rietveld refinement of XRD patterns for BFO was carried using full-pro software suite as shown in **Fig. 2**. The structural parameters refined by Rietveld analysis are tabulated in **Table 2**.

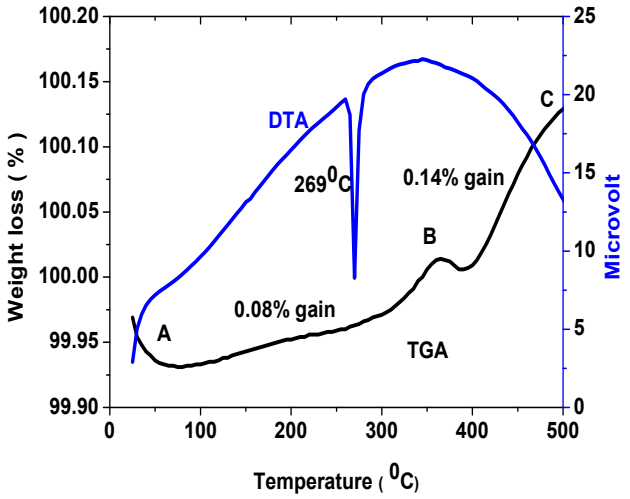

Fig. 3. TGA-DTA spectra of BFO.

Fig. 3 shows the TGA of as-synthesized BFO, negligible weight loss of the material upto 70°C corresponding to the formation of BFO with no residues after synthesis. The weight gain of almost 0.21% is observed along the curve AC in the temperature range 70-520°C. This small weight gain may be due to the absorption of nitrogen gas supplied by the instrument. This leads to the oxidation of Fe in the atmosphere of purged gas N_2. From TGA, it is concluded that after the gel combustion of BFO, all residues were decomposed during combustion and no residues remain after that in the sample indicates that the synthesized powder is almost stable **[10]**. In DTA, a sharp endothermic peak is observed near 269°C but it is not related to any mass change. It can be due to the phase transition of impure phases in the synthesized sample. The presence of some impure phases in as synthesized sample was already confirmed by XRD which are not observed in 300°C calcined sample. So, endothermic peak in DTA related to the phase transition of impurity phases.

For the investigation of magnetic behavior of BFO, magnetic hysteresis curve was studied at 124 and 300 K. **Fig. 4** shows M-H curve of BFO at 300 K (room temperature). A slim magnetic hysteresis loop is displayed under a field of ±10,000 Oe with a weak remanent magnetization of 0.68 emu/g at 300 K. The saturation magnetization is observed at 5.16 emu/g and saturated at a field of about ±5000 Oe.

The magnetic hysterisis shows that the BFO nanoparticles exhibit ferromagnetic properties at room temperature. Same behaviour of M-H curve is also observed at 124 K (not shown here). This ferromagnetic behavior is very unusual; the BFO samples prepared so far in the forms of single crystals, ceramics or thin films have been known to exhibit antiferromagnetic properties **[4, 8, 11, 20, 21]**.

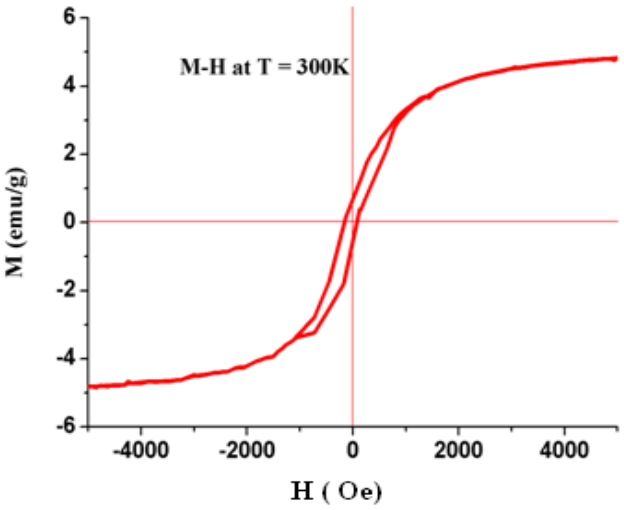

Fig. 4. M-H hysteresis curve for BFO at T=300K.

Low temperature magnetic behaviour were investigated under two condition: zero field-cooling (ZFC) and field-cooling (FC) in the temperature range of 2 to 350 K. Fig. 5 shows the temperature dependence of the ZFC and FC magnetizations under applied field H of 1 kOe and 2 kOe while warming the sample.

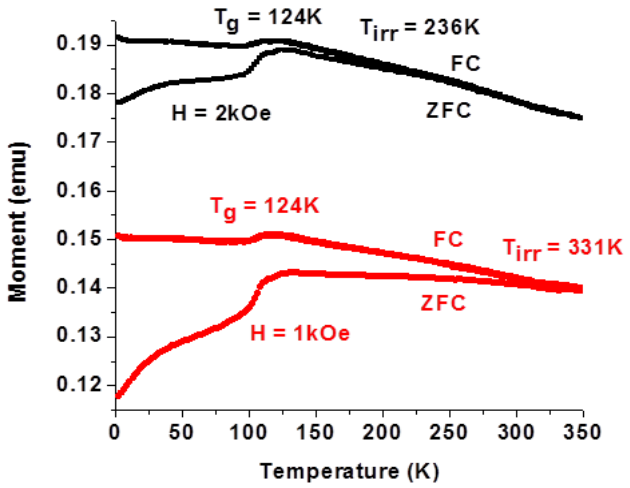

Fig. 5. Temperature dependence of magnetization at H=1kOe and 2kOe of $BiFeO_3$ Sample.

The sample exhibit an irreversible thermomagnetization process below 236 K for 2 kOe field that is there exist an obvious difference between the ZFC curve and FC curve. The branching temperature (T_{branch}) decreases with increasing magnetic field. This type of irreversibility in magnetization is generally indicative of antiferromagnetic (AF) ordering **[12]**. However, for a simple AF no thermomagnetization hysteresis is expected. This effect is

expected as spin glass system **[13]** with a charateristics spin glass transition temperature Tg. The spin glass state generally occurs when positions of magnetic moments or sign of neighbour coupling appear in random manner. This combination of magnetic randomness and mixed interaction caused frustration and stochastic disorder in the corresponding energy landscape.

The anomaly is observed near 124 K in the present work can be related to spin reorientation, which is observed to be at higher temperature in constrast to bulk BFO single crystal, which is observed around 50 K **[3,4,17,19,20]**. There are very few reports, which have observed magnetic transition around 140 K **[8, 16]**. This deviation in nanocrystalline BFO may be attributed to nanosize effect, which is responsible for induce strain, coordination distortion and lattice disorder. This gives rise to different frustrated spin structure and high magnitude of magnetic spins-strain interaction. For the ZFC curve, decrease in magnetization below 124 K is observed, while for FC the magnetization remains almost constant with decrease of temperature for both the applied magnetic field (1 kOe and 2 kOe). The trend in variation of magnetization with temperature is due to spin reorientation transition. For BFO, the wavelength of critical spiral ordering is 62 nm, therefore particle having size greater than 62 nm, the spin reorientation transition is expected to be absent. This behavior is only observed to the nanosize less than 62 nm and found to be absent in bulk single crystal and polycrystalline samples with much larger grain size. XRD data confirmed the average particles size of BFO prepared in the present study is 28 nm.

The origin of behaviour (known as spin reorientation transition) is due to the orientation of Fe^{3+} spins which are generated by the breaking of antiferromagnetic spiral ordering and as the orientation of Fe^{3+} spins are highly field dependent therefore distortion in orientation is more with external magnetic field would change the orientation of Fe^{3+} spins toward the field direction. Due to this orientation there was an overall decrease in the magnetic susceptibility with an increase in the field. This transition was also reported by Park et al. for BFO nanoparticles, however, the dependence of this transition on the applied magnetic field was not reported earlier **[3,14,15,18-20]**.

Conclusion

In conclusion, BFO have synthesized by gel combustion microwave assisted route. Impurity phases appeared in XRD patterns of as-synthesized sample which dissappeared after calcination at 300^0C indexed rhombohedral phase with space group R3c. The average crystallite size is obtained to be 28 nm. TGA shows negligible weight loss corresponding to pure phase of $BiFeO_3$ with no residues. M-H measurements shows ferromagnetic behavior at 300K having saturation magnetization 5.16 emu/g and remanent magnetization M_r = 0.68 emu/g. Themomagnetization study indicates the spin-glass behaviour of microwave-assisted synthesized BFO. Shift in spin-glass transition temperature from 50 K for bulk to 124 K for nanocrystalline BFO is clearly observed. This deviation in nanocrystalline BFO may be attributed to nanosize induce strain, coordination distortion and lattice disorder, which result in a different frustrated spin structure and high magnitude of magnetic spins-strain interaction.

Acknowledgements

UGC-DAE CSR at Indore, India is acknowledged for providing the Magnetic characterization facility.

Reference

1. R. Palai, H.Hutinen, J.F.Scott and R.S. Katiyar, Physical Review B, **2009**, 79, **DOI:** 10.1103/physRevB.79.104413
2. John E. Greedan, J.Mater.Chem, **2001**,11, 37-53, **DOI**: 10.1039/b003682j
3. Adhish Jaiswal et al, J.Phys. Chem C, **2010**, 114, 2108-2115, **DOI :** 10.1021/jp910745q
4. Manoj K. Singh, W. Prellier, M. P. Singh, Ram, S. Katiyar and J. F. Scott, PHYSICAL REVIEW B, **2008**, **77**, **DOI**:10.1103/PhysRevB.77.144403
5. Vladimir Tuboltsev, Alexander Savin Wataru Sakamoto,Atsushi Hieno,Toshinobu Yogoc, J. Mater. Chem., **2011**, 21, 781–788, **DOI**: 10.1039/c0jm02273j
6. Shin Nakamura, Susumu Soeya, Naoshi Ikeda, and Midori Tanaka, J. Appl. Phys. ,**1993**, 74. **DOI**: 10.1063/1.354179
7. James F. Scott, Ratnakar Palai, Ashok Kumar, Manoj K. Singh, Nishit M. Murari, Naba K. Karan, and Ram S. Katiyar, J. Am. Ceram. Soc., **2008**, 91, 1762–1768. **DOI**: 10.1111/j.1551-2916.2008.02404.x
8. Gustau Catalan and James F. Scott, Adv. Mater. , **2009**, 21, 2463–2485. **DOI**:10.1002/adma.200802849
9. Qingyu Xu,Shengqiang Zhou, D. Wu, Marc Uhlarz, Y. K. Tang, Kay Potzger, M. X. Xu and Heidemarie Schmidt, JOURNAL OF APPLIED PHYSICS, **2010**, 107 **DOI**:10.1063/1.3406150
10. Robert J. Hanrahan, Jr. and Darryl P. Butt, Oxidation of Metals, **1997**, 48,pp 41-58, **DOI:** 10.1007/BF 01675261
11. D. Lebeugle, D. Colson, A. Forget, Phys Rev. B 76, 2007, **DOI:** 10.1103/PhysRevB.76.024116
12. N. Hill and N.A. Spaldin, Magnetic Materials (Cambridge university Press, Cambridge 2003)
13. K.H. Fischer, J.A. Hertz, and D. Edwards, spin Glasses (Cambridge University Press, Cambridge, 1991
14. Tae-Jin Park, Georgia C. Papaefthymiou, Arthur J. Viescas, Arnold R. Moodenbaugh, and Stanislaus S. Wong, LETTERS 2007 Vol. 7, No. 3 766-772. **DOI:**10.1021/nl063039w
15. K.K.Mishra, A.T.Satya, A.Bharathi, V.Sivasubramanian, V.R.K.Murthy et al., J.Appl.Phy., **2011**, 110. **DOI**:10.1063/1.3673240
16. SAT Red fern, Can Wang, J.W.Hong, G.Catalon and J.F.Scott, J.Phy:Condens Matter, **2008,** 20, **DOI :** 10.1088/0953-8984/20/45/452205
17. Manoj K. Singh, Ram S. Katiyar, W.Prellier and J.F.Scott, J.Phys.Condens Matter, **2009** , **DOI** : 10.1088/ 0953-8984/21/4/042202r
18. F.M. Bai, J.L. Wang, M. Wutting, Appl Phys Lett 86, 2005. **DOI :** 10.1063/1.1851612a
19. Ching-Jung Cheng, Chengliang Lu, Zuhuang Chen, Lu You, Lang Chen et al, Appl. Phys. Lett. , **2011**, 98, **DOI**: 10.1063/1.360006422ha
20. Hiroshi Naganuma and Soichiro Okamura, JOURNAL OF APPLIED PHYSICS, **2007**, 101, **DOI**: 10.1063/1.2711279
21. Manoj K Singh, Ram S Katiyar and J F Scott, J. Phys.: Condens. Matter, 2008, 20 **DOI**:10.1088/0953-8984/20/25/2522031963,

