

Phase Formation, Microstructure and Magnetic Properties of BiFeO₃ Synthesized by Sol-Gel Auto Combustion Method Using Different Solvents

P. Ahmadi, S. Alamolhoda* and S. M. Mirkazemi

School of Metallurgy and Materials Engineering, Iran University of Science & Technology (IUST), Narmak, 13114-16846, Tehran, Iran.

(*) Corresponding author: alamolhoda@iust.ac.ir

(Received: 05 January 2016 and Accepted: 03 August 2016)

Abstract

In this research nano particles of bismuth ferrite (BiFeO₃) were synthesized by sol-gel auto-combustion route. The effect of water and ethylene glycol solvents were studied on phase constituents, magnetic properties and microstructure of the bismuth ferrite by X-ray diffraction (XRD), scanning electron microscope (SEM) and vibration sample magnetometer (VSM) techniques. XRD results displayed formation of bismuth ferrite in both samples. Also lateral phases such as Bi₂O₃ and Fe₃O₄ was formed in the sample synthesized with aqueous solvent. Using ethylene glycol as solvent the amount of formed Bi₂O₃ and Fe₃O₄ phases would be reduced. SEM results showed refinement of particles to the sizes less than 100nm, more uniformity in particle size distribution and also reduction of their aggregation in the sample synthesized with ethylene glycol in comparison with the sample synthesized in aqueous solvent. VSM results of the combustion products show reduction of M_s value from 11.83emu/g to 10.61emu/g using ethylene glycol. After heat treating of the samples at 650°C, M_s values reach to 4emu/g and 2emu/g in the samples synthesized at aqueous and ethylene glycol solvents respectively. Changes in phase constituents, Microstructure and Magnetic properties have been discussed.

Keywords: Bismuth ferrite, Sol-gel auto-combustion, Magnetic properties, Nano particles.

1. INTRODUCTION

Bismuth ferrite (BiFeO₃) is a well-known multiferroic material that has antiferromagnetic and ferroelectric properties simultaneously [1, 2]. Multiferroic materials have a high potential for application in multi-mode memories in which information could be saved both electrical and magnetically. Also these materials could be used in microwave applications and sensors [3, 4]. This material can also be used as photocatalytic material because of its small band-gap [5]. Many efforts have been made to synthesize single phase BiFeO₃. However, pure single phase BiFeO₃ is still difficult to obtain [6]. Chemically synthesized magnetic Nanoparticles recently have been attracted much

attention due to their unique magnetic properties derived from their small particle size and uniform size distribution [7, 8]. Bismuth ferrite nano particles were synthesized with methods such as hydrothermal [9] co-precipitation [10], sol-gel [11], microemulsion [12], mechano-chemistry [13] and sol-gel auto-combustion [14]. Sol-gel auto-combustion method is a method that provides the possibility of raw materials molecular scale mixing. In addition it is a facile and cost-effective method that provides fine and homogeneous powder particles [8, 15, 16]. There are some efforts to synthesize BiFeO₃ by sol-gel auto-combustion method. Carvalho et al. [17] were prepared BiFeO₃ by the sol gel combustion method

using urea as fuel. They observed $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_{25}\text{FeO}_{39}$ as lateral phases. Single phase BiFeO_3 were not obtained even after calcination of the sample at 800°C . Qi et al. [6] were also synthesized BiFeO_3 powders by sol-gel auto-combustion method using solutions of 2-methoxyethane, metal nitrate and citric acid. Their product has $\text{Bi}_{25}\text{FeO}_{40}$ lateral phase which was removed by leaching of the sample. Bao et al. [18] were obtained pure phase BiFeO_3 powders by sol-gel auto-combustion after calcining at 650°C for 2h and leaching by HNO_3 . B. Dhanalakshmi et al. [19] were also synthesized undoped and Mn doped BiFeO_3 nanoparticles by sol-gel auto combustion method and observed presence of lateral phases in the samples.

Using inorganic solvents as alcohols can play an important role in controlling the nucleation and growth of nano crystalline materials [20]. It was observed that synthesis of nano particles with in ethylene glycol rather than aqueous solvent by solvothermal method refines the particles and reduces their agglomeration [21]. In sol-gel process alcohols generally play the role of solvent and are homogenizing agent in the sol and in some cases participate in reactions [22]. Also in sol-gel processes polymerization of mineral metal salts performs in alcoholic solutions [23].

In this research nano particles of bismuth ferrite were synthesized by sol-gel auto-combustion method in aqueous and ethylene glycol solutions and the effect of the used solvent on phase constituents, magnetic properties and microstructure of bismuth ferrite was studied.

2. MATERIALS AND METHODS

In order to synthesize bismuth ferrite 2.02 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99% Merck) and 2.42 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99% Merck) were dissolved distilled water on a magnetic stirrer to make an aqueous solution. Then citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99% Merck) was added to the above mixture as a chelating agent with a nitrate to citrate ratio of 1:1. The pH

of the solution was raised to 7 by ammonia solution addition. Then proper amount of cetyl trimethyl ammonium bromide (CTAB) $\text{C}_{19}\text{H}_{42}\text{BrN}$ (99% Merck) was added to the solution as a surfactant. The resulting sol was heated at constant temperature of 80°C on magnetic stirrer to complete the formation of the gel precursor. Then the gel undergoes a self-ignition reaction to form a very fine brown foamy powder. Another sample was prepared with dissolution of raw materials in ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) rather than distilled water. The combustion products were calcined at 650°C for 2h. The samples which were synthesized in distilled water and in ethylene glycol solvents were named W and EG respectively. Phase identification of the combustion products were performed by Philips X'pert Pro X-ray diffractometer (XRD) using Cu K_α radiation ($k = 0.1541$ nm). The morphology and microstructure of the nano particles were studied by a scanning electron microscope (SEM) TESCAN model VEGA. Magnetic properties have been taken out at room temperature at the maximum applied field of 14 kOe by vibrating sample magnetometer (VSM) model MDK.

3. RESULTS AND DISCUSSION

Figure 1 shows XRD results of sample W. The combustion product consists of BiFeO_3 as the main phase and $\text{Bi}_2\text{Fe}_4\text{O}_9$, Fe_3O_4 and also tetragonal and cubic Bi_2O_3 as lateral phases. $\text{Bi}_2\text{Fe}_4\text{O}_9$ and tetragonal Bi_2O_3 phases would be disappeared after calcination of the sample at 650°C . However some amount of cubic Bi_2O_3 and Fe_3O_4 exists in the sample yet. So single phase BiFeO_3 would not be obtained in this sample.

In order to evaluate the effect of solvent on the obtained product the raw materials were dissolved in ethylene glycol. Figure 2 shows XRD results of sample EG. The combustion product of the sample EG consists of BiFeO_3 as the main phase and

$\text{Bi}_2\text{Fe}_4\text{O}_9$, cubic Bi_2O_3 , $\text{Bi}_2\text{O}_{2.3}$ and Fe_3O_4 as lateral phases.

According to the thermochemical concepts from propellant chemistry [24, 25], the elements H and C are considered reducing elements with the corresponding valencies +1, +4 respectively. The element oxygen is considered as an oxidizing element with the valency -2. Therefore ethylene glycol would be a reducing agent during the combustion process. Presence of $\text{Bi}_2\text{O}_{2.3}$ phase in the combustion product of the sample EG might be for the sake of scarcity of oxygen that happens with the combustion of ethylene glycol.

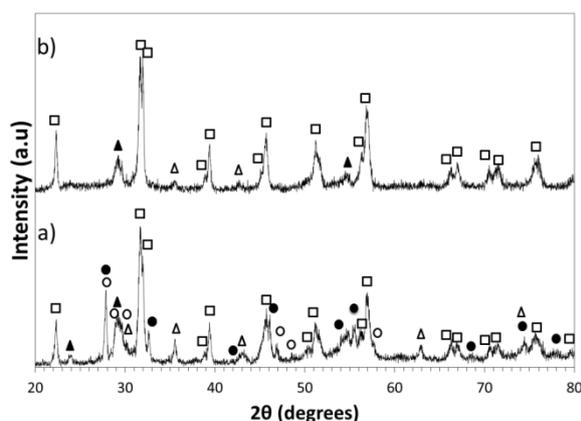


Figure 1. XRD patterns of sample W: a) combustion product and b) calcined at 650°C for 2 h. \square : BiFeO_3 , \triangle : Fe_3O_4 , \circ : $\text{Bi}_2\text{Fe}_4\text{O}_9$, \blacktriangle : cubic Bi_2O_3 , \bullet : tetragonal Bi_2O_3 .

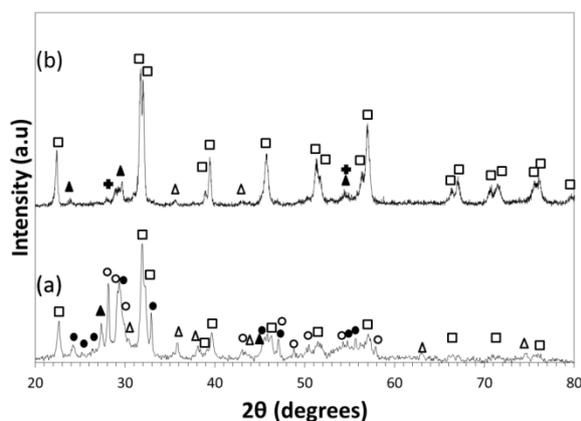


Figure 2. XRD patterns of sample EG: a) combustion product, b) calcined at 650°C and c) calcined at 750°C for 2 h. \square : BiFeO_3 , \bullet : $\text{Bi}_2\text{O}_{2.3}$, \circ : $\text{Bi}_2\text{Fe}_4\text{O}_9$, \blacktriangle : cubic Bi_2O_3 , \triangle : Fe_3O_4 and \times : BiO .

Ethylene glycol is a good dispersive medium for starting reactants. The two hydroxyl groups of this capping agent can hold free Bi^{2+} and Fe^{3+} ions tightly in the solution. Therefore metal ions would be distributed in the sol more uniformly [26]. The better interaction between the ions in the sol and also higher amount of released heat as a result of presence of ethylene glycol provides a proper condition for formation of higher amount of $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase in the combustion product. After calcination of this sample at 650°C the lateral phases are cubic Bi_2O_3 , Fe_3O_4 and BiO phases. The relative intensity of the main peak of Bi_2O_3 in the calcined samples are equal to 30% and 17% in samples W and EG respectively representing formation of lower amount of lateral phases in sample EG after calcination.

Figure 3 shows SEM images of the samples W and EG calcined at 650°C . As it could be observed, using ethylene glycol as solvent causes remarkable reduction in particle size and particle size distribution. Presence of lower amount of Bi_2O_3 in sample EG after calcination might be due to smaller particles formed in the combustion product of sample EG. This could facilitate formation of BiFeO_3 during calcination.

The reason of differences in particle size and morphology is the difference in physical properties of the solvents such as viscosity, dielectric constant and thermal conductivity. Increasing of dielectric constant and thermal conductivity and decreasing of the viscosity of solvent, would increase the solubility and diffusion velocity of ions in the solvent. This increases the particle size [21]. Dielectric constant of water and ethylene glycol at 20°C is equal to 80.1 and 37.7 and their viscosity values at 25°C are equal to 0.89mPa.s and 20mPa.s respectively [27, 28]. So it is expected that the obtained particle size for the sample synthesized in aqueous solvent be greater. Reduction of dielectric constant reduces the solubility and the degree of decomposition of the

salts in alcoholic solvent than aqueous solvent. This reduction declines the compactness of the ionic layer and the thickness of the electrical layer around the solid species. As a result the electrostatic repulsion between the solid species would be increased. This increment prevents the agglomeration of the formed solid species in the sol [29]. Also the reduced solubility as a result of reduced dielectric constant causes a very high degree of supersaturation. Therefore, rapid nucleation would be occurred by consumption of complexes at the nucleation stage. It should be mentioned that the complexes are formed between metallic ions and citric acid that undergo esterification with ethylene glycol to initiate the formation of Fe–O–Bi bonds during gelation [30]. Ultrafine particles of BiFeO₃ would be obtained after combustion.

VSM results of the samples are shown in Figures 4 and 5 and Table 1. The results demonstrate that the EG samples have lower coercivity values. It is well known that the magnetic behavior of the nanoparticles assembly varies with the size and morphology of the particles. Also it is strongly affected by interparticle interactions including dipolar coupling and exchange coupling among nanoparticles surface atoms [31].

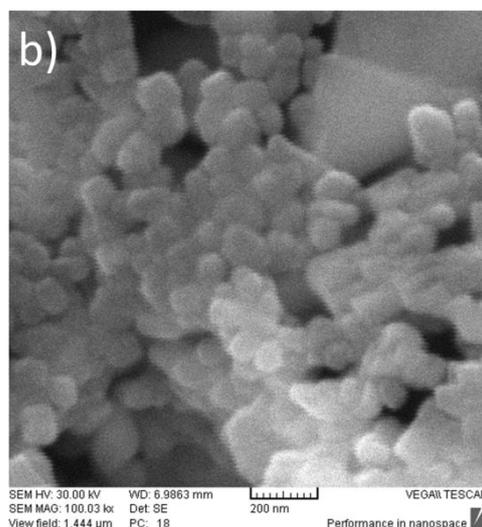
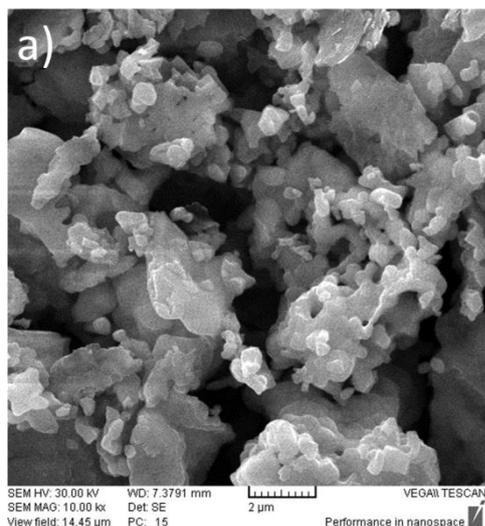


Figure 3. SEM images of the samples a) W and b) EG calcined at 650°C for 2 h.

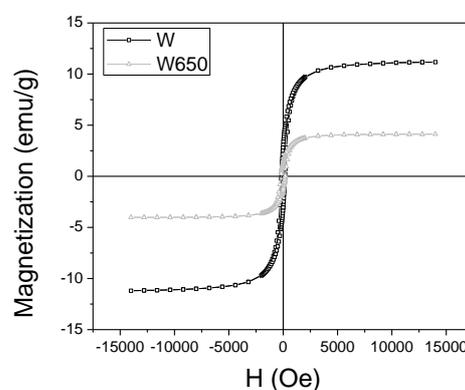


Figure 4. VSM results of the combustion product of sample W and sample W calcined at 650°C for 2 h.

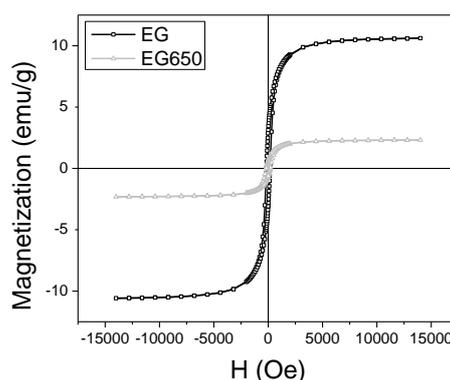


Figure 5. VSM results of the combustion product of sample EG and sample EG calcined at 650°C for 2 h.

Smaller particle size and also presence of smaller amount of Fe₃O₄ phase might be the reason of lower coercivity in the

combustion product of sample EG. The iH_c value of Fe_3O_4 particles with a mean particle size of 100nm is reported to be about 200 Oe [32].

Table1. Magnetic properties of samples W and EG.

Sample Code	Calcination Temperature (°C)	M_s (emu/g)	Coercivity (Oe)
W	-	11.16	169
EG	-	10.55	163.5
W	650	4.12	208
EG	650	2.30	183

Weak ferromagnetism is reported in $Bi_2Fe_4O_9$ nanoparticles. The reported iH_c value for $Bi_2Fe_4O_9$ particles are 130 Oe for the particles with a mean particle size of 300 nm [33]. The coercivity values enhances after calcination of the samples at 650 °C. The reported coercivity value for nanoparticles of $BiFeO_3$ is equal to 185 Oe [14]. The enhanced amount of this phase coexisting with Fe_3O_4 and omission of $Bi_2Fe_4O_9$ might be the reason.

M_s values of the combustion products of the samples are 10.5 and 11.1emu/g in samples EG and W respectively. The reported M_s values for Fe_3O_4 nanoparticles are in the range of 90 to 45 emu/g depending on the particle size and preparation conditions [34]. $BiFe_4O_9$ phase has antiferromagnetic nature [35]. The reported M_s values for $Bi_2Fe_4O_9$ particles are equal to 0.0084 to 0.0054emu/g [33]. The higher amount of Fe_3O_4 phase could be the reason of higher M_s value of sample W. After calcination of the samples at 650°C the M_s values reaches to 4emu/g and 2emu/g. It could be observed that with decreasing of Fe_3O_4 phase M_s values would be reduced. The reported M_s values for nanoparticles of bismuth ferrite with the mean particle size of 32nm and the mean particle size of 26nm are equal to 0.07emu/g and 3.4 emu/g respectively [36, 37]. Therefore it is expected that the reduced amount of Fe_3O_4 phase and formation of higher amount of $BiFeO_3$ reduces the M_s values. This is in

consistence with the obtained results for M_s values of the samples. However as it was explained earlier it should be mentioned that magnetic behavior of the nanoparticles strongly affected by inter particle interactions including dipolar coupling and exchange coupling among the surface atoms of nanoparticles.

4. CONCLUSIONS

Nano particles of bismuth ferrite were synthesized in aqueous and ethylene glycol solvents by sol-gel auto-combustion method. XRD results show that beside bismuth ferrite as the main phase, Bi_2O_3 and Fe_3O_4 phases are present in the combustion product of the samples synthesized in aqueous solvent. In the samples synthesized with ethylene glycol solvent, the sample consists of $BiFeO_3$ as the main phase beside $Bi_2Fe_4O_9$ lateral phase. The amount of present Bi_2O_3 and Fe_3O_4 phases would be reduced in this sample and presence of some amount of $Bi_2O_{2.3}$ phase could be observed. Formation of $Bi_2Fe_4O_9$ and $Bi_2O_{2.3}$ phases could be for the sake of the higher released heat, provided reductive atmosphere and better distribution of the ions in the sol in presence of ethylene glycol. Although calcination of the samples leads to the decrement of the amount of lateral phases but these phases are still present in the sample and single phase bismuth ferrite was not obtained. However the sample synthesized with ethylene glycol has lower amount of lateral phases. SEM micrographs showed refinement of particles and less aggregation using ethylene glycol solvent. This is for the sake of differences in viscosity, dielectric constant and thermal conductivity of water and ethylene glycol. Using ethylene glycol solvent reduces the M_s and iH_c values in the samples. Also M_s values of the samples have been reduced by calcination. M_s value of the sample synthesized with ethylene glycol solvent reaches to 2emu/g which is due to considerable decrement of the

lateral phases and increment of BiFeO₃ phase in the sample.

The authors would like to express their gratitude to the referee for her/his careful reading and helpful comments.

ACKNOWLEDGEMENT

REFERENCES

1. Li, M. C., Driscoll, J., Liu, L. H., Zhao, L. C. (2006). "The phase transition and phase stability of magnetoelectric BiFeO₃", *Mater. Sci. Eng. A*, 438–440: 346–349.
2. He, F., Wells, B. O. (2006). "Lattice strain in epitaxial BaTiO₃ thin films", *Appl. Phys. Lett.*, 88: 152908.
3. Karin, M., Rabe, C. H. A. (2007). "Physics of Ferroelectrics, A Modern Perspective", Springer.
4. Eerenstein, W., Mathur, N. D., Scott, J. F. (2006). "Multiferroic and Magnetolectric materials", *Nature*, 442: 759-765.
5. Sharma, S., Singh, V., Kotnala, R. K., Dwivedi, R. K., (2014). "Comparative studies of pure BiFeO₃ prepared by sol-gel versus conventional solid-state-reaction method", *J. Mater. Sci.: Mater. Electron*, 25: 1915-1921.
6. Qi, X., Xu, H. J., Zhang, X. Y., Qi, J. Q. (2012). "Synthesis of Multiferroic BiFeO₃ Powders by Sol-gel Auto-Combustion", *Adv. Mat. Res.*, 412: 99-102.
7. Alamolhoda, S., Mirkazemi, S. M., Benvidi, N., Shahjooyi, T., (2016). "The Effects of Cu and Zn Dopants on Phase Constituents, Magnetic Properties and Microstructure of Nickel Ferrite", *Int. J. Nanosci. Nanotechnol.*, 12: 131-137.
8. Manouchehri, S., Yousefi, M. H., Mozaffari, M., Amighian, J. (2010). "Preparation of Superparamagnetic Co_{0.5}Zn_{0.5}Fe₂O₄ at Room Temperature by Co-precipitation Method and Investigation of Its Physical Properties", *Int. J. Nanosci. Nanotechnol.*, 6: 15-22.
9. Chen, C., Cheng, J., Yu, S., Che, L., Meng, Z. (2006). "Hydrothermal synthesis of perovskite bismuth ferrite crystallites", *J. Cryst. Growth*, 291: 135–139.
10. Shami, M. Y., Awanb, M. S., Anis-ur-Rehmana, M. (2011). "Phase pure synthesis of BiFeO₃ nanopowders using diverse precursor via co-precipitation method", *J. Alloys Compd.*, 509: 10139–10144.
11. Xu, J. H., Ke, H., Jia, D., Wang, W., Zhou, Y. (2009). "Low-temperature synthesis of BiFeO₃ nanopowders via a sol-gel method", *J. Alloys Compd.*, 472: 473–477.
12. Das, N., Majumdar, R., Sen, A., Maiti, H. S. (2007). "Nanosized bismuth ferrite powder prepared through sonochemical and microemulsion techniques", *Mater. Lett.*, 61: 2100–2104.
13. Szafraniak, I., Polomskab, M., Hilczerb, B., Pietraszkoc, A., Kępińskic, L. (2007). "Characterization of BiFeO₃ nanopowder obtained by mechanochemical synthesis", *J. Eur. Ceram. Soc.*, 27: 4399–4402.
14. Godara, S., Sinha, N., Ray, G., Kumar, B., (2014). "Combined structural, electrical, magnetic and optical characterization of bismuth ferrite nanoparticles synthesized by auto-combustion route", *J. Asian Ceram. Soc.*, 2: 416–421.
15. George, M., John, A. M., Naira, S. S., Joy, P.A., Anantharaman, M.R. (2006). "Finite size effects on the structural and magnetic properties of sol-gel synthesized NiFe₂O₄ powders", *J. Magn. Magn. Mater*, 302: 190–195.
16. Sivakumar, P., Ramesh, R., Ramanand, A., Ponnusamy, S., Muthamizhchelvan, C. (2012). "Synthesis, studies and growth mechanism of ferromagnetic NiFe₂O₄ nanosheet", *Appl. Surf. Sci.*, 258: 6648– 6652.
17. Carvalho, T. T., Tavares, P. B., (2008). "Synthesis and thermodynamic stability of multiferroic BiFeO₃", *Mater. Lett.*, 62: 3984-3986.
18. Bao, L. Qi, X., Ni, B., Zhang, M., Mei, R. (2016). "BiFeO₃ Powders Synthesized by Different Sol-gel Methods", *Key Eng. Mater.*, 697: 84-88.
19. Dhanalakshmi, B. et al. (2016). "Effects of Mn doping on structural, dielectric and multiferroic properties of BiFeO₃ nanoceramics", *J. Alloys Compd.*, 676: 193-201.
20. Su, H. L., Xie, Y., Li, B., Liu, X. M., Qian, Y. T. (1999). "A novel one-step solvothermal route to nanocrystalline Sn₄P₃", *J. Solid State Chem.*, 146: 110-113.
21. Yin, S., Shinozaki, M., Sato, T. (2007). "Synthesis and characterization of wire-like and near-spherical Eu₂O₃-doped Y₂O₃ phosphors by solvothermal reaction", *J. Lumin.*, 126: 427–433.
22. Rahaman, M. N. (2003). "Ceramic Processing and Sintering", Marcel Dekker, New York.
23. Yu, Z., Wen, W., Dechang, J., Feng, Y. (2002). "Synthesis of SrBi₂Ta₂O₉ nanocrystalline powder by a modified sol-gel process using bismuth subnitrate as bismuth source", *Mater. Chem. Phys.*, 77: 60–64.
24. Pillai, V., Shah, D. O. (1996). "Synthesis of high-coercivity cobalt ferrite particles using water-in-oil microemulsions", *J. Magn. Magn. Mater*, 163: 243-248.
25. Jain, S. R., Adiga, K. C., PaiVernecker, V. R. (1981). "A new approach to thermochemical calculations of condensed fuel-oxidizer mixtures", *Combust. Flame*, 40: 71-79.

26. Hu, H., Mo, M., Yang, B., Zhang, X., Li, Q., Yu, W., Qian, Y. (2003). "Solvothermal synthesis of Sb₂S₃ nanowires on a large scale", *J. Cryst. Growth*, 258: 106–112.
27. Lide, D. R. (2002-2003). "CRC Handbook of Chemistry and Physics", 83rd ed, CRC Press, USA.
28. Smallwood, I. M. (1996). "Handbook of organic solvent properties", Edward Arnold, New York.
29. Choi, J. Y., Kim, D. K. (1999). "Preparation of monodisperse and spherical powders by heating of alcohol-aqueous salt solutions", *J. Sol-Gel Sci. Technol.*, 15: 231–241.
30. Qin, B., Guo, Y., Pan, D., Sun, C., Wang, X., Duan, H. (2016). "Size-controlled synthesis of BiFeO₃ nanoparticles by a facile and stable sol-gel method", *J. Mater. Sci.: Mater. Electron*, DOI 10.1007/s10854-016-5186-x.
31. Xiang, J., Zhou, G., Shen, X., Chu, Y., Guo, Y. (2012). "Effect of Bi₂O₃ addition on structure and magnetic properties of Ni_{0.5}Zn_{0.5}Fe₂O₄ nanofibers", *J. Sol-Gel Sci. Technol.*, 62:186–192.
32. Araj, S., Amin, N., Anderson, E. E., (1991). "Magnetic coercivity of Fe₃O₄ particle systems", *J. Appl. Phys.*, 69: 5122
33. Zhang, M. Yang, H., Xian, T., Wei, Z. Q., Jiang, J. L., Feng, Y. C., Liu, X. Q. (2011). "Polyacrylamide gel synthesis and photocatalytic performance of Bi₂Fe₄O₉ nanoparticles", *J. Alloys Compd.*, 509:809–812.
34. Caruntu, D., Caruntu, G., O'Connor, C. J., (2007). "Magnetic properties of variable-sized Fe₃O₄ nanoparticles synthesized from non-aqueous homogeneous solutions of polyols", *J. Phys. D: Appl. Phys.*, 40: 5801–5809.
35. Lin, Y., Kang, P., Yang, H. Liu, M., (2015). "Preparation and magnetic properties of Bi₂Fe₄O₉/CoFe₂O₄ composite powders", *J. Mater. Sci.: Mater. Electron*, 26: 1102-1106.
36. Kumar, A., Rai, R. C., Podraza, N. J., Denev, S., Ramirez, M., Chu, Y., Martin, L. W, Ihlefeld, J., Heeg, T., Schubert, J., Schlom, D. G., Orenstein, J., Ramesh, R., Collins, R. W., Musfeldt, J. L., Gopalan, V. (2008). "Linear and nonlinear optical properties of BiFeO₃", *Appl. Phys. Lett.*, 92: 121915.
37. Yanga, J. Li, X., Zhou, J., Tang, Y., Zhang, Y., Li, Y. (2011). "Factors controlling pure-phase magnetic BiFeO₃ powders synthesized by solution combustion synthesis", *J. alloys compd.*, 509: 9271-9277.