Effect of Preheating Temperature on Synthesis of Pure BiFeO₃ via Sol–Gel Method

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Abstract. BiFeO₃ (BFO) nanopowder was synthesized in a pure form via a sol-gel method based on glycol gel reaction. Effect of drying and preheating temperature on preventing other phases was studied. Many parameters were studied as calcination temperature and time & stirring temperature as well. The prepared powder was characterized by X-Ray Diffraction of powder (XRD) and Transmission Electron Microscope (TEM). High pure BiFeO₃ was obtained by preheated process at 400 °C for 0.5 h and calcination at 600 °C for 0.5 h without any impurities compared to dry at 110 °C.

Keywords: BiFeO₃, sol-gel, preheating temperature, drying temperature

Introduction

So far, there is a great interest to discover substances that have properties stable in room temperature, which has widespread applications in the manufacturing of devices. Of these, multiferroic materials which defined as substance coupling between two or more of the following property: ferroelectricity, ferromagnetic, ferroelasticity [1]. There are many types of multiferroic materials were studied, but the common issue with them is the ferroic properties are low at room temperature. Consequently, there is difficult to use in many applications. Considerable attention has been paid to BiFeO₃ because it considers the only material has stable multiferroic properties at room temperature [2–4]. Its ferroelectricity cure temperature is 830 °C and the ferromagnetic Neel's temperature is 370 °C [5–7]. BiFeO₃ has been utilized in many applications such as industry of radio, television, microwave and satellite communications, audio-video, digital recording and, as permanent magnets, information storage [8], transducer and magnetoelectric coupling [9, 10]. However, technological application of BiFeO₃ is limited because of forming secondary phases during synthesis, weak magnetic characteristics, lower magnetoelectric coupling coefficients, a large difference in ferroic transition temperatures and high leakage current [11].

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Much research on the synthesis of BiFeO_3 using different methods have been done. Of these, solid-state [12], mechano-chemical [13, 14], solution chemistry methods such as Pechini method [15], precipitation/coprecipitation [16, 17], sol-gel [18–20], alkali metal ions-assisted controllable synthesis hydrothermal method [21–23], sonochemical [24], solution-combustion method [25] and soft chemical method [26]. Most of the mentioned procedures need high-temperature treatments ($>800^\circ\text{C}$) and the appearance of second phases still the major issue of them [27]. To avoid bismuth volatilization and minor phase formation, the development of low-temperature synthesis methods is essential.

The sol-gel method is a very effective method for fabricating a uniform ultrafine porous powder and can also be moved up to accommodate industrial-scale production [28]. There are several techniques for sol-gel method as glycol-gel reaction [29–31], Metal complex [32–35], modified Pechini [36], Polymer complex solution [37–39]. Among them, glycol-gel reaction considers the best because of low chemical used in this reaction and several roles of ethylene glycol [40].

Many researchers used sol-gel method for preparing BFO by studying different parameters for obtaining a pure form. Of these, calcination temperature and time [41–43], precursor type [44], excess amount of Bi^{3+} [45–47], few studies have done on the impact of reaction temperature (stirring temperature) [48] but no one studies the difference of drying and preheats temperature of the resulted gel and its relation to obtaining pure BFO.

The paper provides a comparison study of the impact of different drying temperature on forming a pure form of BiFeO_3 via a sol-gel method based on glycol gel reaction was reported.

Experimental

Materials

Precursors of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, nitric acid and ethylene glycol were of Sigma-Aldrich highly pure grade and used without further purifications.

Methodology

The process of synthesis BiFeO_3 is presented in *Fig 1*. A mixed solution of equimolar (0.2M) of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 50 ml ethylene glycol was prepared. The solution mixture was stirred until completely dissolved and a clear red solution obtained. After dissolving, the mixture was stirred at 80°C until the brown gel was formed. The obtained gel was divided into two parts:

Part I: was dried at 110°C for 48h. The resulted powder was then calcinated from $400\text{--}600^\circ\text{C}$ for different intervals (0.5 h – 3 h).

Part II: was preheated at 400°C for 30 min, then calcinated $500\text{--}600^\circ\text{C}$ for 0.5 h.

Nitric acid (10%) was used (when the gel color is started to transfer into green, the acid was added to prevent forming this color) to prevent reduction of Fe^{3+} to Fe^{2+} . Otherwise, electric neutrality required, which lead to a high number of oxygen vacancies [49, 50].

Effect of stirring temperature

Stirring temperature was varied from $20\text{--}80^\circ\text{C}$ after that the gel was dried at 110°C and was calcined at 600°C for 0.5 and 2 h.

Fig. 1. Diagram of the BiFeO₃ synthesis process

Characterization

The structure and phase composition of the synthesized bismuth ferrite powders were investigated using X-ray diffractometer (XRD) BrukerAXSD8 Germany Cu K_α radiation 0.154 and Transmission Electron Microscope (TEM) JEOL (JEM-HR-2100 ELECTRON MICROSCOPE).

Results and discussion

Effect of calcination temperature

no doubt that, temperature affects both the formation and stability of BiFeO₃ nanopowder. This is may because that the elevated temperature leads to the following: i) instability of BiFeO₃ at high temperatures where, BiFeO₃, undergoing a phase transition at about 850 °C [51], ii) it can decompose into Fe₂O₃ and Bi₂O₃, as shown in Eq. (1):

Various heating temperatures were reported by many researchers ranged from 60–140 °C for drying and evaporation of the solvent followed by calcination at varying temperature for forming BiFeO₃ [11, 41, 44, 53–57]. Furthermore, according to previous studies [42, 53], 400 °C was considered as the crystallization temperature of BiFeO₃, oppositely, it decomposed above 600 °C and second phases observed [58, 59]. As a result of that, direct heating

at 400 °C was applied in this work and the maximum calcination temperature was chosen to be 600 °C.

As can be seen, on drying the powder of BFO at 110 °C (Fig. 2 and Table 1), the highest weight percentage of BFO was obtained at calcination temperature 500 °C with 76.9% and crystal size of 71.3 nm and Bi₂O₃ & Bi₂Fe₄O₉, as other phases were formed.

On the other hand, on heating immediately at 400 °C, the XRD (Fig. 3) indicates that sharp and intense peaks of high crystallinity of BiFeO₃ were observed at calcination temperature 600 °C without any second phase formation. The crystal size of BFO determined from XRD at 2θ = 32 was found to be 62.1 nm (Table1).

In comparison between the two parts I, II, Table 1, the overall trend of the increasing temperature on forming BFO the same. As calcination temperature increases the impurity decrease and BFO crystallization raise. Heating gel directly at 400 °C without further drying led to a higher weight percentage of BFO than drying process.

Data obtained in previous studies indicated that, second phases was regarded using sol-gel method for synthesis of BiFeO₃ as follows: Bi₂Fe₄O₉, Bi₃₆Fe₂₄O₅₇ and Bi₂O₃ [60]; Bi₂Fe₄O₉, Bi₂₅FeO₂₉ and Bi₂O₃ [20]; γ-Fe₂O₃ [61], Bi₂Fe₄O₉, Bi₂₅FeO₄₀ [47, 48]; Bi₂Fe₄O₉ [62–64] and Bi₂₅FeO₄₀ [10, 17]. Likewise, Sharma et al. heat at 400 °C for 1 h and calcinated at 700 °C for 2 h, found Bi₂Fe₄O₉ and Bi₂₅FeO₄₀ as a second phase formed with BFO [65]. Zhang et al. use three different temperatures for obtaining a pure form of BFO as follows: 100 °C for solvent evaporation and gel formation, 350 °C for organic removal for 1h, finally calcinated at 550 °C for 2 h [66].

Fig. 2. Effect of calcination temperature on drying sol-gel method

Table 1. Comparison between the sol-gel method according to calcination temperature after either drying or preheating

Temperature (°C)	Drying on 110 °C for 48 h		Preheating on 400 °C for 0.5 h	
	Wt. (%)	Crystallite Size (nm)	Wt. (%)	Crystallite Size (nm)
400	10.4	47.6	70.9	28.6
500	76.9	71.3	9.2	23.5
600	70.4	71.4	100	62.1

Fig. 3. Effect of calcination temperature, 600 °C, on preheating method of sol–gel

Effect of calcination time

Effect of calcination time was studied on part I (the dried powder of BFO) to improve the purity of BiFeO₃ obtained by this route of sol–gel. This impact was studied within the range of 0.5 h – 3 h. From XRD pattern, *Fig. 4* and *Table 2*, it was clear that 0.5, 1 and 3 h nearly analogous to each other, where the weight percent of BFO were 76.9, 78.4 and 78.4%, respectively. The purity of BFO was found to be time independent. Other studies were found that for sol–gel method, 600 °C calcination temperature with time of 2 h is enough for forming crystals of BiFeO₃ [67–70].

Fig. 4. Effect of calcination time on drying method of sol–gel

Table 2. Effect of calcination temperature and time on drying sol–gel method

Calcination temperature (°C)	Weight percent (%) at different times (h)			
	0.5	1	2	3
400	10.4	72	9.8	33.5
500	76.9	78.4	44.5	78.4
600	70.4	15.4	23.6	31.8

Effect of stirring temperature

The reaction temperature is considered as one of the crucial factors affecting sol and gel formations [71]. The study of the effect of stirring temperature was applied to part I. In comparison, of the results obtained from the effect of calcination temperature for preheating method (600 °C for 0.5 h) and with other researchers like Fukumura et al. [68] (600 °C for

Table 3. Comparison between stirring temperature for samples calcinated for 0.5 and 2 h

Stirring temperature (°C)	BiFeO ₃ 600 °C for 0.5 h		BiFeO ₃ 600 °C for 2 h	
	Crystallite size (nm)	Wt. (%)	Crystallite size (nm)	Wt. (%)
20	78.3	76.7	90.1	83.2
40	110.8	38.7	105.8	96.7
60	97.6	84.3	98.9	82.6
80	109.8	70.4	29.5	23.6

Fig. 5. Effect of stirring temperature on synthesis of BiFeO₃ using drying sol–gel method for 2 h

Fig. 6. Effect of stirring temperature on synthesis of BiFeO₃ using drying sol–gel method for 0.5 h

Table 4. Effect of stirring temperature on sol–gel formation time

Stirring temperature (°C)	Time of sol formation (min)	Time of gel formation (min)
20	21	20
40	2	5
60	9	4
80	9	13

2 h), the effect of stirring temperature was conducted within the range of 20–80 °C at calcination temperature of 600 °C and calcination time of 0.5 h and 2 h in a comparative study.

It was regarded that, there was an improvement in weight percentage of BiFeO₃ on change stirring temperature. From *Table 3* and *Figs 5, 6*, the sharpest, most intense peaks and purity of the multiferroic nano powder were fabricated at stirring temperature of 40 °C for 2 h calcination time with 96.7% weight percent. As well, from *Table 4*, at stirring temperature 40 °C, the time required for forming sol and gel was very small compared with other temperatures. Whereas, Surech and Srinath have studied reaction temperature on the range of 80–400 °C for synthesis BFO through a metal complex reaction sol–gel method and found that, 250 °C reaction temperature give more pure BFO than other studied temperatures [48].

TEM micrographs

Transmission Electron Microscopy (TEM) micrographs of BiFeO₃ *Fig. 7* illustrated that, BFO prepared by drying sol–gel method consists of spherical and rectangular shapes with a particle size of 13.5–24.6 nm. Instead, *Fig. 7c,d*, HR-TEM gave the inter-planer of 0.47 nm of the crystal. For BFO synthesized by preheat sol–gel method, TEM micrographs, *Fig. 8a,b*, exhibit spherical crystals and irregular atomic clusters with particle size ranging from 87.6–179.84 nm. The appearance of agglomerated clusters, as a result of high temperature the sample exposed [72].

Fig. 7. TEM morphology of (a) BFO prepared with drying sol-gel method for 1 h calcination at 500 °C (c) and (d) HR-TEM image

Fig. 8. TEM morphology of BFO prepared with preheating sol-gel method for 0.5 h calcination at 600 °C

Conclusion

BFO synthesized using a sol-gel method with two different drying temperatures results indicated that variation on drying temperature (110 or 400 °C) led to a variation on purity, morphology and crystal size of the final product. In comparison, between the two temperatures, drying on 110 °C, 96% BFO was formed with crystal size 105.8 nm at calcination temperature 600 °C for 2 h with 40 °C stirring temperature. On the other hand, extra phase was observed with BFO nanopowder. In contrast, for preheating on 400 °C, pure BFO nanopowder without any secondary phases resulted with crystal size 62.1 nm and some irregular morphology.

References

- [1] Muneeswaran M., Jegatheesan P., Gopiraman M., Kim I., Giridharan N. V. (2013) Structural, optical, and multiferroic properties of single phased BiFeO₃. *Applied Physics A* **114**(3) 853–859.
- [2] Catalan G., Scott J. F. (2009) Physics and applications of bismuth ferrite. *Advanced Materials* **21**(24) 2463–2485.
- [3] Sando D., Yang Y., Bousquet E., Carretero C., Garcia V., Fusil S., Dolfi D., Barthelemy A., Ghosez P., Bel-laiche L., Bibes M. (2016) Large elasto-optic effect and reversible electrochromism in multiferroic BiFeO₃. *Nature Communication* **7** 10718–10724.
- [4] Fu C., Huo M., Cai W., Deng X. (2012) Preparation of bismuth ferrite nanopowders at different calcination temperatures. *Journal of Ceramic Processing Research* **13**(5) 561–564.
- [5] Neaton J. B., Ederer C., Waghmare U. V., Spaldin N. A., Rabe K. M. (2005) First-principles study of spontaneous polarization in multiferroic BiFeO₃. *Physical Review B* **71**(1) 014113.
- [6] Freitas V. F., Dias G. S., Protzek O. A., Montanher D. Z., Catellani I. B., Silva D. M., Cotica L. F., dos Santos I. A. (2013) Structural phase relations in perovskite-structured BiFeO₃-Based multiferroic compounds. *Journal of Advanced Ceramics* **2**(2) 103–111.
- [7] Lennox R. C., Taylor D. D., Vera Stimpson L. J., Stenning G. B., Jura M., Price M. C., Rodriguez E. E., Arnold D. C. (2015) PZT-like structural phase transitions in the BiFeO₃-KNbO₃ solid solution. *Dalton Trans* **44**(23) 10608–10613.
- [8] Kuo C. Y., Hu Z., Yang J. C., Liao S. C., Huang Y. L., Vasudevan R. K., Okatan M. B., Jesse S., Kalinin S. V., Li L., Liu H. J., Lai C. H., Pi T. W., Agrestini S., Chen K., Ohresser P., Tanaka A., Tjeng L. H., Chu Y. H. (2016) Single-domain multiferroic BiFeO₃ films. *Nat Commun* **7** 10718.
- [9] Zhong Z., Ishiwara H. (2009) Variation of leakage current mechanisms by ion substitution in BiFeO₃. *Thin Films, Applied Physics Letters* **95**(11) 112902–112904.
- [10] Kuang D. H., Zhang Y. L., Tang P., Yang S. H. (2014) Effect of annealing temperatures on the structure and leakage mechanisms of BiFeO₃ thin films prepared by the sol-gel method. *J Sol-Gel Sci Technol* **73**(2) 410–416.

- [11] Bhushan B., Wang Z., Tol J. V., Dalal N. S., Basumallick A., Vasanthacharya N. Y., Kumar S., Das D., Viehland D. D. (2012) Tailoring the magnetic and optical characteristics of nanocrystalline BiFeO₃ by Ce doping. *Journal of the American Ceramic Society* **95**(6) 1985–1992.
- [12] Singh V., Sharma S., Kumar M. M., Kotnala R. K., Dwivedi R. K. (2014) Structural transition, magnetic and optical properties of Pr and Ti Co-doped BiFeO₃ ceramics. *Journal of Magnetism and Magnetic Materials* **349** 264–267.
- [13] Fischer P., Polomska M., Sosnowska I., Szymanski M. (1980) Temperature dependence of the crystal and magnetic structures of BiFeO₃. *Journal of Physics C: Solid State Physics* **13**(10) 1931–1940.
- [14] Szafraniak I., Potomska M., Hilezer B. (2007) Characterization of BiFeO₃ nanopowder obtained by mechanochemical synthesis. *Journal of the European Ceramic Society* **27** 4399–4402.
- [15] Selbach S. M., Tybell T., Einarsrud M., Grande T. (2007) Size-dependent properties of multiferroic BiFeO₃ nanoparticles. *Chem Mater* **19** 6478–6484.
- [16] Muneeswaran M., Jegatheesan P., Gopiraman M., Kim I.-S., Giridharan N. V. (2013) Structural, optical, and multiferroic properties of single phased BiFeO₃. *Applied Physics A* **114**(3) 853–859.
- [17] Mubarak T. H., Azhdar B., Hassan K. H., Kareem C. H. (2014) Effect of Temperature on structural and electrical properties of bismuth ferrite nanoparticles prepared by sol gel method. *International Journal of Innovative Research in Science, Engineering and Technology* **3**(10) 17034–17041.
- [18] Eerenstein W., Mathur N. D., Scott J. F. (2006) Multiferroic and magnetoelectric materials. *Nature* **442**(7104) 759–65.
- [19] Wang J., Wei Y., Zhang J., Ji L., Huang Y., Chen Z. (2014) Synthesis of pure-phase BiFeO₃ nanopowder by nitric acid-assisted gel. *Materials Letters* **124** 242–244.
- [20] Srinivas V., Raghavender A. T., Kumar K. V. (2016) Structural and magnetic properties of Mn doped BiFeO₃ nanomaterials. *Physics Research International* **2016** 1–5.
- [21] Tabares-Munoz C., Rivera J., Bezinges A., Monnier A., Schmid H. (1985) Measurement of the quadratic magnetoelectric effect on single crystalline BiFeO₃. *Japanese Journal of Applied Physics* **24**(S2) 1051.
- [22] Chen C., Cheng J., Yu S., Che L., Meng Z. (2006) Hydrothermal synthesis of perovskite bismuth ferrite crystallites. *Journal of Crystal Growth* **291**(1) 135–139.
- [23] Suzuki K., Tokudome Y., Tsudad H., Masahide T. (2016) Morphology control of BiFeO₃ aggregates via hydrothermal synthesis. *Applied Crystallography* **49** 168–174.
- [24] Das S., Rana S., Mursalin S., Rana P., Sen A. (2015) Sonochemically prepared nanosized BiFeO₃ as novel SO₂ sensor. *Sensors and Actuators B: Chemical* **218** 122–127.
- [25] Fruth V., Mitoseriu L., Berger D., Lanculescu A., Matei C., Preda S., Zaharescu M. (2007) Preparation and characterization of BiFeO₃ ceramic. *Progress in Solid State Chemistry* **35** 193–202.
- [26] Ghosh S., Dasgupta S., Sen A., Maiti H. S. (2005) Low-temperature synthesis of nanosized bismuth ferrite by soft chemical route. *J Am Ceram Soc* **88**(5) 1349–1352.
- [27] Silva J., Reyes A., Esparza H., Camacho H., Fuentes L. (2011) BiFeO₃: A review on synthesis, doping and crystal structure. *Integrated Ferroelectrics* **126**(1) 47–59.
- [28] Safi R. and Shokrollahi H. (2012) Physics, chemistry and synthesis methods of nanostructured bismuth ferrite (BiFeO₃) as a ferroelectro-magnetic material. *Progress in Solid State Chemistry* **40**(1–2) 6–15.
- [29] Babooram K., Ye Z. (2006) New soft chemical routes to ferroelectric SrBi₂Ta₂O₉. *Chemistry of Materials* **18**(2) 532–540.
- [30] Park T., Papaefthymiou G. C., Viescas A. J., Moodenbaugh A. R., Wong S. S. (2007) Size-dependent magnetic properties of single-crystalline multiferroic BiFeO₃ nanoparticles. *Nano Letters* **7**(3) 766–772.
- [31] Liu T., Xu Y., Feng S., Zhao J. (2011) A facile route to the synthesis of BiFeO₃ at low temperature. *Journal of the American Ceramic Society* **94**(9) 3060–3063.
- [32] Matsumoto K., Yamaguchi K., Fujii T., Ueno A. (1991) Preparation of bismuth-substituted yttrium iron garnet powders by the citrate gel process. *Journal of Applied Physics* **69**(8) 5918–5920.
- [33] Suastiyanti D., Ismojo (2016) FTIR spectrum of BiFeO₃ ceramic produced by sol-gel method based on variation of sinter and calcination treatment. *The International Journal of Engineering and Science* **5**(5) 114–117.
- [34] Suastiyanti D., Wijaya M. (2016) Synthesis of BiFeO₃ nanoparticle and single phase by sol-gel process for multiferroic material. *ARPJ Journal of Engineering and Applied Sciences* **11**(2) 901–905.
- [35] Waghmare S. D., Jadhav V. V., Gore S. K., Yoon S., Ambade S. B., Lokhande B. J., Mane R. S., Han S. (2012) Efficient gas sensitivity in mixed bismuth ferrite micro (cubes) and nano (plates) structures. *Materials Research Bulletin* **47**(12) 4169–4173.
- [36] Kirillov S. A., Romanova I. V., Farbut I. A. (2006) Synthesis of mixed oxides using polybasic carboxylic hydroxy-and amino-acid routes. *Problems and Prospects* **229** 495–504.
- [37] Gulgun M. A., Nguyen M. H., Kriven W. M. (1999) Polymerized Organic-Inorganic Synthesis of Mixed Oxides. *Journal of the American Ceramic Society* **82**(3) 556–560.
- [38] Liu T., Xu Y., Zhao J. (2010) Low-Temperature Synthesis of BiFeO₃ via PVA Sol-Gel Route. *Journal of the American Ceramic Society* **93**(11) 3637–3641.

- [39] Jayakumar O. D., Achary S. N., Girija K. G., Tyagi A. K., Sudakar C., Lawes G., Naik R., Nisar J., Peng X., Ahuja R. (2010) Theoretical and Experimental Evidence of Enhanced Ferromagnetism in Ba and Mn Co-substituted BiFeO₃. *Applied Physics Letters* **96**(3) 032903.
- [40] Niederberger M. (2007) Nonaqueous Sol-Gel Routes to Metal Oxide Nanoparticles. *Acc Chem Res* **40** 793–800.
- [41] 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. *Journal of Materials Science: Materials in Electronics* **25**(4) 1915–1921.
- [42] Xu J., Ke H., Jia D., Wang W., Zhou Y. (2009) Low-Temperature Synthesis of Pure-phase BiFeO₃ Nanopowder by Nitric Acid-assisted Gel. *Journal of Alloys and Compounds* **472** 473–477.
- [43] Hu Y., Fei L., Zhang Y., Yuan J., Wang Y., Gu H. (2011) Synthesis of Bismuth Ferrite Nanoparticles via a Wet Chemical Route at Low Temperature. *Journal of Nanomaterials* **6** 1–6.
- [44] Hardy A., Gielis S., Ru H. V. D., D'Haen J., Van Bael M.K., Mullens J. (2009) Effects of Precursor Chemistry and Thermal Treatment Conditions on Obtaining Phase Pure Bismuth Ferrite from Aqueous Gel Precursors. *Journal of the European Ceramic Society* **29** 3007–3013.
- [45] Do D., Kim J. W., Kim S. S., Kim W. (2010) Effects of Bi Content on the Ferroelectric Properties of BiFeO₃ Thin Films. *Journal of the Korean Physical Society* **57**(6) 1875–1878.
- [46] Sharma S., Saravanan P., Pandey O. P., Vinod V. T. P., Cernik M., Sharma P. (2016) Magnetic behaviour of sol-gel driven BiFeO₃ thin films with different grain size distribution. *Journal of Magnetism and Magnetic Materials* **401** 180–187.
- [47] Wang D., Wang M., Liu F., Cui Y., Zhao Q., Sun H., Jin H., Cao M. (2015) Sol-gel synthesis of Nd-doped BiFeO₃ multiferroic and its characterization. *Ceramics International* **41**(7) 8768–8772.
- [48] Suresh P., Srinath S. (2015) Effect of synthesis route on the multiferroic properties of BiFeO₃: A comparative study between solid state and sol-gel methods. *Journal of Alloys and Compounds* **649** 843–850.
- [49] Palkar V. R., Pinto R. (2002) BiFeO₃ thin films: Novel effects. *PRAMANA – Journal of Physics* **58** 1003–1008.
- [50] Wang Y. P., Zhou L., Zhang M. F., Chen X. Y., Liu J. M., Liu Z. G. (2004) Room-temperature saturated ferroelectric polarization in BiFeO₃ ceramics synthesized by rapid liquid phase sintering. *Applied Physics Letters* **84**(10) 1731–1733.
- [51] Morozov M. I., Lomanova N. A., Gusarov V. V. (2003) Specific features of BiFeO₃ formation in a mixture of bismuth(III) and iron(III) oxides. *Russian Journal of General Chemistry* **73**(11) 1772–1776.
- [52] Christensen M. J. (2014) On the effect of A to B stoichiometry variation on conductivity and phase purity in 0.8BiFeO₃-0.2Bi_{0.5}K_{0.5}TiO₃: Development of lead-free ferroelectric. *Department of Materials Science and Engineering, Norwegian University of Science and Technology* 1–67.
- [53] Suresha P. H., Ramanian, Radhakrishna M. C., Angadi B., Devaraj J. T. (2012) Characterisation of BiFeO₃ synthesised by microcontroller based thermogravimetric analyser. *Indian Journal of Engineering & Materials Sciences* **19** 196–198.
- [54] Rusevova K., Kofertein R., Rosell M., Richnow H. H., Kopinke F., Georgi A. (2014) LaFeO₃ and BiFeO₃ perovskites as nanocatalysts for contaminant degradation in heterogeneous fenton-like reactions. *Chemical Engineering Journal* **239** 322–331.
- [55] Humayun M., Zada A., Li Z., Xie M., Zhang X., Qu Y., Raziq F., Jing L. (2016) Enhanced visible-light activities of porous BiFeO₃ by coupling with nanocrystalline TiO₂ and mechanism. *Applied Catalysis B: Environmental* **180** 219–226.
- [56] Srivastav S. K., Gajbhiye N. S. (2012) Low temperature synthesis, structural, optical and magnetic properties of bismuth ferrite nanoparticles. *J Am Ceram Soc* **95**(11) 3678–3682.
- [57] Wang T., Song S. H., Wang M., Li J. Q., Ravi M. (2016) Effect of annealing atmosphere on the structural and electrical properties of bifeo₃ multiferroic ceramics prepared by sol-gel and spark plasma sintering techniques. *Ceramics International* **42**(6) 7328–7335.
- [58] Lebeugle D., Colson D., Forget A., Viret M., Bonville P., Marucco J.-F., Fusil S. (2007) Room temperature coexistence of large electric polarization and magnetic order in BiFeO₃ single crystals. *Physical Review B* **76** 024116–024124.
- [59] Fedulov S. A., Venevtsev Y. N., Zhdanov G. S., Smazhevskaya E. G. (1961) High temperature X-ray and thermographic studies of bismuth ferrite. *Kristallografiya* **6** 795.
- [60] Kim J. K., Kim S. S., Kim W. (2005) Sol-gel synthesis and properties of multiferroic BiFeO₃. *Materials Letters* **59**(29–30) 4006–4009.
- [61] Sharma S., Saravanan P., Pandey O. P., Vinod V. T. P., Cernik M., Sharma P. (2016) Magnetic behaviour of sol-gel driven bifeo₃ thin films with different grain size distribution. *Journal of Magnetism and Magnetic Materials* **401** 180–187.
- [62] Peng L., Deng H., Tian J., Ren Q., Peng C., Huang Z., Yang P., Chu J. (2013) Influence of Co doping on structural, optical and magnetic properties of BiFeO₃ films deposited on quartz substrates by sol-gel method. *Applied Surface Science* **268** 146–150.

- [63] Sarkar K., Mukherjee S., Mukherjee S., Mitra M. K. (2014) Synthesis, characterization and studies on optical, dielectric and magnetic properties of undoped and cobalt doped nanocrystalline bismuth ferrite. *Journal of The Institution of Engineers (India): Series D* **95**(2) 135–143.
- [64] Ibrahim E. M. M., Farghal G., Khalaf M. M., El-Lateef H. M. A. (2017) Effect of calcination temperature on magnetic and electrical properties of BiFeO₃ nanoparticles prepared by sol-gel method. *Journal of Nanotechnology & Advanced Materials* **5**(1) 33–39.
- [65] Sharma N., Kumar S., Mall A. K., Gupta R., Garg A. (2017) Sr and Mn Co-doped sol-gel derived BiFeO₃ ceramics with enhanced magnetism and reduced leakage current. *Materials Research Express* **4**(1) 015702.
- [66] Zhang C., Li Y., Chu M., Rong N., Xiao P. (2016) Hydrogen-treated BiFeO₃ nanoparticles with enhanced photoelectrochemical performance. *RSC Advances* **6** 24760–24767.
- [67] Kim J. K., S.S. Kim, W. Kim (2005) Sol-gel synthesis and properties of multiferroic BiFeO₃. *Materials Letters* **59** 4006–4009.
- [68] Fukumura H., Matsui S., Tonari N., Nakamura T., Hasuike N., Nishio K., Isshiki T., Harima H. (2009) Synthesis and characterization of Mn-doped BiFeO₃ nanoparticles. *Acta Physica Polonica A* **116** 47–50.
- [69] Deng J., Banerjee S., Mohapatra S. K., Smith Y. R., Misra M. (2011) Bismuth iron oxide nanoparticles as photocatalyst for solar hydrogen generation from water. *Journal of Fundamentals of Renewable Energy and Applications* **1** 1–10.
- [70] Fu C., Huo M., Cai W., Deng X. (2012) Preparation of bismuth ferrite nanopowders at different calcination temperatures. *Journal of Ceramic Processing Research* **13**(5) 561–564.
- [71] Twej W. A. A. (2009) Temperature influence on the gelation process of tetraethylorthosilicate using sol-gel technique. *Iraqi Journal of Science* **50**(1) 43–49.
- [72] Zhang C., Li Y., Chu M., Rong N., Xiao P., Zhang Y. (2016) Hydrogen-treated BiFeO₃ nanoparticles with enhanced photoelectrochemical performance. *RSC Advances* **4** 24760–24767.