Influence of parasitic phases on the magnetic properties of BiFeO₃ powders

Sen Zhao, Guping Wang *, Rui Zheng, Yanping Liu

School of Pharmaceutical and Material Engineering, Taizhou University, Taizhou, Zhejiang, 318000, China

*Corresponding author e-mail: gpwang526@sina.com

Abstract: Single phase BiFeO₃ nanoparticles were successfully prepared by sol-gel method. The influence of annealing temperature and precursor drying process on phase purity, microstructures and magnetic properties of BiFeO₃ powders were explored. The precursor was pre-dried at 70 °C for 6 hours and then heated at 100 °C for 12 hours. The single-phase BiFeO₃ powders were successfully obtained by annealing the dried samples at 500 °C for 1 hour. However, powder X-ray diffraction reveals the presence of parasitic phase Bi₂Fe₄O₉ or iron oxide under other preparation conditions. With the increase of annealing temperature, the content of parasitic phase Bi₂Fe₄O₉ increases while the grain size, particle size, morphology and distribution uniformity of BiFeO₃ also change. When the precursor solution was dried directly at 100 °C and then annealed at 500 °C for 1 hour, the parasitic phase of Fe₁.₉₆₆O₂.₉₆₃ appeared. The particles exhibit sphere-like morphology covered with small BiFeO₃ grains. With the increase of drying time, the surface grains changed and the content of parasitic phase Fe₁.₉₆₆O₂.₉₆₃ increased. FTIR and EDS confirm the existence of BiFeO₃. UV-VIS measurements show that the optical band gap of BiFeO₃ nano-powders decrease with the increase of the content of these two parasitic phases. In this paper, effects of these parasitic phases on the magnetic properties of BiFeO₃ have been studied in detail. Results show that the ferromagnetic behavior of the powders could be attributed to the Fe₁.₉₆₆O₂.₉₆₃ parasitic phases. The parasitic phase of Bi₂Fe₄O₉ in the powders does not change the room temperature magnetic properties of BiFeO₃. Both the single phase BiFeO₃ and the Bi₂Fe₄O₉ incorporated powders exhibit bulk antiferromagnetic behavior.

1. Introduction

It is reported that BiFeO₃ has both ferroelectric and ferromagnetic properties and is expected to be used in data storage, magnetic sensors, polymorphic electronic devices and spintronic devices [1]. At the same time, the band gap of BiFeO₃ is small (2.8eV) [2], which is lower than that of the hot photocatalytic material titanium dioxide (3.2eV). Therefore, BiFeO₃ is suitable for photocatalytic applications [3]. Combining the multi-iron characteristics of the former, BiFeO₃ is expected to be applied in the field of commercial femtosecond optical pulse devices [4]. However, there are several common problems in the study of BiFeO₃. Firstly, it is difficult to prepare pure BiFeO₃ due to the volatilization of Bi and the fluctuation of Fe valence. Therefore, it is still a challenge to control the preparation process and conditions of BiFeO₃. Second, the source of room temperature ferromagnetism of BiFeO₃ remains
controversial. Magnetism of BiFeO$_3$ reported by various research groups are different, or even completely opposite. Zhang H [5] reported that Co-doped BiFeO$_3$ have room temperature ferromagnetism. Zahari R M [6] reported that BiFeO$_3$ has room temperature ferromagnetism, and its components contain trace impurity phases Bi$_2$Fe$_4$O$_9$, Bi$_{25}$FeO$_{49}$ or Bi$_{24}$Fe$_2$O$_{39}$. Lotey G S [7] reported that pure BiFeO$_3$ nanoparticles have room temperature ferromagnetism. Lebeugl D [8] reported that the magnetization of BiFeO$_3$ at room temperature is linearly related to the external magnetic field, but the XRD spectra showed that the sample contained trace impurity phase Bi$_{25}$FeO$_{39}$. In the aspect of single pure BiFeO$_3$, the synthesis of single phase BiFeO$_3$ is a big problem because of the narrow temperature stability range of BiFeO$_3$. There are a lot of reports about BiFeO$_3$ synthesis in the scientific filed. We specially concentrate on the reported XRD patterns and find that impurity phases other than BiFeO$_3$, such as Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$FeO$_{49}$ [9]. Liu Y [10] successfully synthesized single-phase BiFeO$_3$ Powder by hydrothermal method, but its magnetic properties were not analyzed. Therefore, the magnetic source of pure BiFeO$_3$ is still controversial.

In this work, BiFeO$_3$ nanoparticles were prepared by a simple sol-gel method. The effects of annealing temperature and precursor drying process on the phase purity of BiFeO$_3$ powder were studied, and the influence of parasitism on the magnetic properties of BiFeO$_3$ powder was studied.

2. Experimental

Using sol-gel method, bismuth (III) nitrate pentahydrate [Bi(NO$_3$)$_3$.5H$_2$O] and ferric nitrate [Fe(NO$_3$)$_3$.9H$_2$O] were used as raw materials, ethylene glycol methyl ether (C$_3$H$_8$O$_2$) was used as solvent, glacial acetic acid (C$_2$H$_4$O$_2$) was used as activator. Bi(NO$_3$)$_3$.5H$_2$O and Fe(NO$_3$)$_3$.9H$_2$O were dissolved in 50 ml methoxyethanol (C$_3$H$_8$O$_2$) and 2 ml glacial acetic acid in the same beaker. The solution was stirred continuously with a magnetic stirrer for 1 hour to obtain a clear orange-red homogeneous precursor solution. The beaker containing the precursor solution was placed in the drying oven, and the temperature was controlled at 70°C. The sols were dried continuously for 6 hours. Then, the oven temperature was adjusted to 100°C, and the dried layered solid samples were obtained for 12 hours. The dried layers were removed from the top layers, and the powder samples were obtained by grinding. The powder samples are divided into three parts and annealed in corundum crucibles at 500, 600 and 700°C for one hour respectively. The heating rate was 10°C/min. After cooling in the furnace, the samples were taken out and grinded again to obtain the final samples, which were marked by S1, S2 and S3 respectively.

For comparative analysis, the precursor was dried directly at 100°C for 4 hours, annealed at 500°C for 1 hour and then cooled in the oven. Thus, the sample S4 was obtained. Similarly, the precursor solution is directly dried at 100°C for 18 hours, annealed at 500°C for 1 hour and then cooled with the furnace, thus, S5 is obtained. The corresponding preparation process of the sample is shown in Table 1.

| samples | Pre-drying temperature /℃ | Pre-drying duration /h | Final drying temperature /℃ | Final drying duration /h | annealing temperature /℃ |
|---------|-----------------------------|------------------------|----------------------------|-------------------------|---------------------------|
| S1      | 70                          | 6                      | 100                        | 12                      | 500                       |
| S2      | 70                          | 6                      | 100                        | 12                      | 600                       |
| S3      | 70                          | 6                      | 100                        | 12                      | 700                       |
| S4      | /                           | /                      | 100                        | 4                       | 500                       |
| S5      | /                           | /                      | 100                        | 18                      | 500                       |

The phase purity and crystal structure of the sample was analyzed by BRUKER D8 ADVANCE X-Ray diffractometer(40KV, 40mA, 0.02°/step). The spectral characteristics of the samples were characterized by Nicolet 5700 Fourier transform infrared spectrometer. The particle size and morphology of the samples were observed and analyzed by S-4800 scanning electron microscope. The optical properties of the samples were tested by U-4100 ultraviolet spectrophotometer. The vibration...
sample magnetometer of PPMS-9T comprehensive physical characteristics testing system was used to determine the magnetic properties of the samples.

3. Results and discussions

3.1. XRD/FTIR Analysis

Fig. 1 is the XRD spectrum of the samples. It can be seen that all the five samples contain rhombohedral BiFeO$_3$ (PDF: 71-2494, space group: R3c) Except for BiFeO$_3$, no other impurity phases were found in sample S1. The main phase BiFeO$_3$ and Bi$_2$Fe$_4$O$_9$(PDF#:71-2494) impurity phases were found in S2 and S3, while the main phase BiFeO$_3$ and tetragonal magnetite Fe$_{1.966}$O$_{2.963}$ impurity phases were found in S4 and S5. The crystal phase content and main phase BiFeO$_3$ were refined by TOPAS software. In order to study the crystallization performance, the grain size of BiFeO$_3$ (012) crystal plane was calculated by Shelley formula (1).

$$D_{012} = \frac{k\lambda}{\beta \cos \theta}$$

In formula, $D_{012}$ is grain size, correction factor $k=0.9$, the wavelength of CuKa radiation source is 0.154056nm, and $\beta$ is half-width of diffraction angle (FWHM, rad) after deducting instrument broadening. The refinement results and grain size parameters are shown in Table 2.

| samples | Lattice parameters of BiFeO$_3$ | Grain size of BiFeO$_3$ | Phase compotion(wt%) | $\varphi_p$(%) |
|---------|-------------------------------|------------------------|----------------------|----------------|
| S1      | 5.5820254 13.8760244 374.43747 | 43.8 100 0 | BiFeO$_3$ Bi$_2$Fe$_4$O$_9$ Fe$_{1.966}$O$_{2.963}$ | 7.35 |
| S2      | 5.5822853 13.8819497 374.63224 | 45.8 93.35 6.65 | BiFeO$_3$ Bi$_2$Fe$_4$O$_9$ | 12.44 |
| S3      | 5.5839138 13.8820218 374.85281 | 122.9 81.20 18.20 | BiFeO$_3$ Bi$_2$Fe$_4$O$_9$ | 12.71 |
| S4      | 5.5813746 13.8753376 374.33163 | 42.6 95.92 4.08 | BiFeO$_3$ Bi$_2$Fe$_4$O$_9$ | 11.02 |
| S5      | 5.5819453 13.8746121 374.38622 | 42.8 88.09 11.91 | BiFeO$_3$ Bi$_2$Fe$_4$O$_9$ | 9.48 |

It can be seen that a single BiFeO$_3$ phase was successfully obtained by pre-drying the precursor obtained by magnetic stirring at 70°C for 6 hours, then drying at 100°C for 12 hours and annealing at 500°C for 1 hour. With the increase of annealing temperature, the content of the impurity phase Bi$_2$Fe$_4$O$_9$ increased. After annealing at 600°C and 700°C, the content of Bi$_2$Fe$_4$O$_9$ reached 6.65wt% and 18.20wt%, respectively.
respectively. At high annealing temperature, BiFeO$_3$ is easily decomposed into Bi$_3$Fe$_4$O$_9$, which is consistent with the literature [11]. The lattice parameters, cell volume and grain size of BiFeO$_3$ increase with the increase of annealing temperature. Especially, the grain size of S3 annealed at 700 °C increases obviously, which indicates that higher annealing temperature is beneficial to crystal growth of BiFeO$_3$. When the precursor was dried at 100 °C and annealed at 500 °C for 1 hour, the samples with the main phase BiFeO$_3$ and the parasitic phase Fe$_{1.966}$O$_{2.963}$ of tetragonal magnetite were obtained. With the increase of drying time, the content of the parasitic phase Fe$_{1.966}$O$_{2.963}$ increased, and the mass content of the parasitic phase reached 4.08% by drying for 4 hours and 11.91% by drying for 18 hours, respectively. Compared with S4, the grain size of S5 has little change, lattice parameter $a$ and cell volume increase slightly, yet lattice parameter $c$ decreases slightly, which indicates that the $c/a$ axis ratio decreases.

Infrared spectroscopy can reflect the structure information of materials. For BiFeO$_3$, 418cm$^{-1}$ corresponds to the stretching vibration of Fe-O bond in the octahedral position of FeO$_6$ [12], 443cm$^{-1}$, 450cm$^{-1}$ corresponds to the bending vibration of Fe-O bond in the octahedral position of perovskite structure, and 550cm$^{-1}$ corresponds to the intrinsic stretching vibration of Fe-O bond in the tetrahedral position [13]. From the infrared spectra of Fig.2, it can be seen that S1, S2, S3, S4 and S5 all have absorption peaks at 418 cm$^{-1}$, 443 cm$^{-1}$, 445 cm$^{-1}$, 550 cm$^{-1}$, which are consistent with the literature reports, which confirm the existence of BiFeO$_3$. The absorption peaks of S2 and S3 containing parasitic phase Bi$_2$Fe$_4$O$_9$ are 811 cm$^{-1}$, which correspond to the stretching vibration of FeO$_4$ tetrahedron in octahedral Bi$_2$Fe$_4$O$_9$ [14]. Powder samples S4 and S5 containing parasitic phase Fe$_{1.966}$O$_{2.963}$ contain 845cm$^{-1}$ absorption peaks, which are consistent with those reported in literature [15].

![Fig.2 FTIR patterns of samples](image)

### 3.2. SEM/EDS analysis

Figure 3 shows the SEM morphology of the samples. It can be seen that the BiFeO$_3$ powder of sample S1 shows spherical and uniform shape, and the particle size is 200-300 nm. The particle size of S2 is similar to that of S1. Yet, S3 obviously grows up and leaves small particles with obvious internal voids and irregular shape and the grain size of long strip particle reaches 600 nm, which may be due to the increase of annealing temperature and the increase of ion movement speed and the promotion of grain growth [16]. The sample S4 and S5 aggregate into spherical spheres of approximate size with a diameter of about 1.5 um. The needle-like substance was coated on the surface of sample S4. In order to study the atomic ratio of Bi/Fe, EDS(energy scattering spectra) were carried out for all samples, as shown in
Table 2. EDS scanning of needle-like substance showed that it was consistent with BiFeO₃ substance in atomic ratio, indicating that it was formed by the agglomeration of BiFeO₃ grains. The sphere surface of sample S5 is covered with wormlike particles and its size is about 40 nm, which is consistent with the grain size calculated by XRD Shelly formula. EDS analysis shows that it is in good agreement with BiFeO₃. Table 2 shows that the Bi/Fe atomic ratio on the surface of S1 sample is close to 1, which is consistent with the Bi/Fe atomic ratio (1:1) of single phase BiFeO₃. While the Bi/Fe atomic ratio of S2 is smaller than that of S1. Combining with the previous XRD results, the BiFeO₃/Bi₂Fe₄O₉ content ratio of S1, S2 and S3 samples decreases, while the Bi/Fe atomic ratio of BiFeO₃ is 1, and the Bi/Fe atomic ratio of Bi₂Fe₄O₉ is 0.5, which results in the decrease of Bi/Fe atomic ratio of S1, S2 and S3 samples. With the increase of annealing temperature, Bi is easy to volatilize, resulting in the decrease of Bi/Fe atomic ratio. The Bi/Fe atomic ratios of S4 and S5 are less than 1, which is due to the presence of parasitic phase Fe₁.₉₆₆O₂.₉₆₃, resulting in the increase of Fe content relative to Bi element. The Bi/Fe atomic ratio of S5 is smaller than that of S4, which may be due to the surface composition information detected by EDS, so it is inconsistent with the XRD results.

Table 3. Elemental composition of samples

|         | S1     | S2     | S3     | S4     | S5     |
|---------|--------|--------|--------|--------|--------|
| O       | 13.60  | 14.20  | 14.64  | 11.08  | 21.76  |
| Fe      | 18.19  | 18.70  | 22.85  | 23.15  | 22.84  |
| Bi      | 68.20  | 67.10  | 65.77  | 62.52  | 65.40  |

3.3. optical properties
The optical properties of the samples are evaluated by optical band gap. The optical band gap (band gap) is an important physical property parameter of semiconductor materials. It plays an important role in the transition of electrons and other physical properties. The specific materials can also be qualitatively judged by the optical band gap. The optical band gap can be measured indirectly by coordinate conversion according to the ultraviolet-visible absorption spectrum. BiFeO₃ is a direct band gap semiconductor [17]. The calculation of band gap (Eg) is based on the following relationship:

\[
(ahv)^2 = A(hv - E_g)
\]

In the formula, \( h \) is Planck constant, \( v \) is photon frequency, \( A \) is material constant (\( \sim 1 \)), and \( a \) is absorption coefficient. By extrapolating the intersection of linear part extension line and abscissa, the
Intersection point is $E_g$. As shown in Figure 4, the optical band gaps of S1, S2, S3, S4 and S5 are 2.04 eV, 1.99 eV, 1.95 eV, 1.98 eV and 1.96 eV, respectively. The measured $E_g$ of single-phase BiFeO$_3$ is consistent with the $E_g$ value of BiFeO$_3$ reported by Francis P N [18] and the band gap of BiFeO$_3$ is attributed to the transfer of valence band electrons from $O^{2-}$ to Fe $3d$ ($O^{2-} \rightarrow Fe^{3+}$). The room temperature band gap of the parasitic phase Bi$_2$Fe$_4$O$_9$ is 1.5 eV [19], and that of the parasitic phase Fe$_2$O$_3$ is 1.96-2.09 eV [20], which is slightly smaller than that of BiFeO$_3$ (~2.8 eV). Therefore, the optical band gap of S2, S3 containing the parasitic phase Bi$_2$Fe$_4$O$_9$ and S4, S5 containing the parasitic phase Fe$_{1.966}$O$_{2.963}$ are smaller than that of the samples S1 only containing the single BiFeO$_3$. The optical band gap of pure BiFeO$_3$ is smaller than that of bulk materials, which is attributed to the nano-size effect of particles [21]. From the point of view of photocatalysis, combined with the above analysis, it is shown that by adjusting the crystalline phase composition and particle size of the material through annealing temperature and precursor drying, the bandwidth can be reduced to absorb more visible light to produce electron-hole pairs, which can improve the photocatalytic ability [22]. This is one of the important applications of this energy band engineering technology. The existence and content changes of BiFeO$_3$, Bi$_2$Fe$_4$O$_9$ and Fe$_{1.966}$O$_{2.963}$ are indirectly confirmed by the above optical band gap changes, XRD and FTIR analysis.

Fig. 4 (ahv)$^2$-E curve of samples (Inset: UV-VIS spectrum)

3.4. Magnetic analysis

The magnetic properties of BiFeO$_3$ are related to many factors. Hasan M [23] reports that the magnetic properties of BiFeO$_3$ increase with the decrease of particle size. Dhir G [24] reports that the magnetic properties of BiFeO$_3$ decrease with the increase of grain size.
Theoretically, there are several reasons for the magnetic enhancement of BiFeO$_3$: firstly, the uncompensated spin between magnetic lattices [25]. Secondly, the spin cycloid structure of BiFeO$_3$ is suppressed by reducing the particle size and lattice distortion. Thirdly, the crystal structure of BiFeO$_3$ is transformed from rhombus to tetragonal [26]. Fig. 5 shows the room temperature M-H hysteresis loop of the sample. As can be seen from the figure, the M-H curves of S1, S2 and S3 show a linear relationship without any spin magnetization, indicating the intrinsic antiferromagnetism (AFM) [27], which is attributed to the space-modulated spin structure [28]. The linear slope of the M-H curves of S1, S2 and S3 decreases in turn, indicating that the magnetization of the samples decreases under the same applied magnetic field. This is because BiFeO$_3$ itself is a combination of weak ferromagnetism and antiferromagnetism, and Bi$_2$Fe$_4$O$_9$ is a diamagnetic material [29]. In addition, the particle size of S1, S2 and S3 increases in turn, which weakens the effect of inhibiting the spin cycloid structure of BiFeO$_3$. Therefore, with the increase of Bi$_2$Fe$_4$O$_9$ impurity phase content, the magnetization intensity decreases slightly under the same external magnetic field, and there is no spin magnetization. While the M-H curve of both S4 and S5 containing parasitic phase deviate from the linear relationship shows the ”S” shape, which indicates the hysteresis effect, that is, the transformation from antiferromagnetism to weak ferromagnetism. With the increase of parasitic phase Fe$_{1.966}$O$_{2.963}$ content, the ferromagnetism of the samples increased obviously. When the applied magnetic field reaches 6000Oe, the magnetization of S4 is 0.34359emu/g, however, that of S5 reaches 0.50633emu/g. According to the preparation of samples and the analysis of the microstructure of BiFeO$_3$: (1) There is no doping and no non-compensatory spin between magnetic lattices; (2) The grain size and particle size of S4 and S5 are similar, so it is not due to inhibiting the spin cycloid structure of BiFeO$_3$; (3) XRD spectra showed that all samples BiFeO$_3$ and BiFeO$_3$ were rhombic crystals with no change in crystal structure. From the above analysis, it can be seen that with the increase of Fe$_{1.966}$O$_{2.963}$ parasitic phase content, both remanence and coercivity of the sample increase. The presence of remanence but not fully saturated hysteresis loop indicates a small FM contribution, accompanied by the contribution of AFM [31].
In order to better understand the ferromagnetic ordering of FM, Arritt plot ($M^2$-H/M) [32] based on Weiss molecular field theory, is used to analyze all Arrot in the high field with linear function, and the Y value extrapolated from Y intercept is considered as Ms (saturated magnetization). As shown in Fig. 6, the Y intercepts of S4 and S5 are negative, indicating that FM has a small contribution to order, i.e., weak ferromagnetism. The drift of Y intercept implies that the contribution of FM order increases, therefore, the increase of S5 intercept relative to S4 intercept is attributed to the greater contribution of FM order. On the contrary, the antiferromagnetic order of S4 contributes greatly, and the samples are the result of ferromagnetic and antiferromagnetic compositions.

4. Conclusion

Single phase BiFeO$_3$ powder was successfully prepared by sol-gel method. The effects of drying conditions of precursors and annealing temperature on the phase purity of BiFeO$_3$ were studied by powder X-ray diffraction. The results show that pure BiFeO$_3$ can be successfully prepared by pre-drying the precursor solution at 70$^\circ$C for 6 hours, then drying at 100$^\circ$C for 12 hours and annealing at 500$^\circ$C for 1 hour. The parasitic phase Bi$_2$Fe$_4$O$_9$ appears at annealing temperature higher than 500 $^\circ$C, while the parasitic phase Fe$_{1.966}$O$_{2.963}$ appears when the precursor is dried at 100 $^\circ$C without pre-drying and annealed at 500 for 1 hour. These two types of parasitism have certain effects on the particle size, magnetic properties and optical properties of BiFeO$_3$. Compared with single phase BiFeO$_3$, BiFeO$_3$ containing parasitic phase Bi$_2$Fe$_4$O$_9$ exhibits an increase in particle size, but a decrease in particle distribution uniformity and magnetization under the same applied magnetic filed. Therefore, the parasitic phase Bi$_2$Fe$_4$O$_9$ does not fundamentally change the bulk antiferromagnetic behavior of BiFeO$_3$. However, BiFeO$_3$ powder samples containing parasitic phase Fe$_{1.966}$O$_{2.963}$ show obvious external ferromagnetic behavior and aggregat into large spheres with worm-like particles coated on the surface of the spheres. The optical band gaps of BiFeO$_3$ nano-powders decrease with the increase of the content of these two parasitic phases.

Acknowledgements

This work is supported in part by Provincial College Students Science and Technology Innovation Program and New Miao Talents Program (2018RA36007), National Natural Science Foundation of China(51802211), Material Science& Engineering of Zhejiang Province First-class Discipline(Taizhou University), and Chemical Engineering &Technology of Zhejiang Province First-class Discipline (Taizhou University).
References

[1] Gomez-Iriarte G A., Labre C, Oliveira L A S D, Sinnecker J P. Pure phase BiFeO3 thin films sputtered over Si: A new route towards high magnetization [J], Journal of Magnetism and Magnetic Materials, 2018, 460(15):83.

[2] Clark S J, Robertson J. Band gap and schottky barrier heights of multiferroic BiFeO3 [J], Applied Physics Letters, 2007, 90: 132903.

[3] Gao T, Chen Z, Zhu Y X, Niu F, Huan Q L, QiN L S, Sun X G, Huang Y X. Synthesis of BiFeO3 nanoparticles for the visible-light induced photocatalytic property [J], Materials Research Bulletin, 2014, 59(11): 6.

[4] Maleki H. Photocatalytic activity enhancement by addition of lanthanum into the BiFeO3 structure and the effect of synthesis method [J], Journal of Materials Science: Materials in Electronics, 2018, 29(14): 11862.

[5] Zhang H, Long W J, Chen Y Q, Guo D J. Effects of deposition temperature on phase purity, orientation, microstructure and property of cobalt substituted bismuth ferrite thin films [J], Journal of Materials Science: Materials in Electronics, 2012, 23:2157.

[6] Zahari R M, Shaari A H, Abbas Z, Baqiah H, Chen S K, Lim K P, Awang Kechik M M. Simple preparation and characterization of bismuth ferrites nanoparticles by the thermal treatment method [J]. Journal of Materials Science Electronic, 2017, 28: 17932.

[7] Lotey G S, Verma. Structural, magnetic, and electrical properties of Gd-doped BiFeO3 nanoparticles with reduced particle size [J], Journal of Nanoparticles Research, 2012, 14:742

[8] Lebeugle D, Colson D, Forget A, Viret M, Bonville P, Marucco J F, Stephane Fusil S. Room temperature coexistence of large electric polarization and magnetic order in BiFeO3 single crystals [J], Physical Review B, 2007, 76(2): 877.

[9] Sharma S, Singh V, Kotnala R K, Dwivedi R K. Comparative studies of pure BiFeO3 prepared by sol-gel versus conventional solid-state-reaction method [J], Journal Materials Science:Materials in Electronics, 2014, 25(4): 1915.

[10] Liu Y, Zuo R Z. Tunable morphology and optical absorption of bismuth ferrite synthesized by sol-gel-hydrothermal method [J], Journal Materials Science:Materials in Electronics, 2012, 23: 2276.

[11] Nguyen H P, Gyawali G, Jo Y H, Kim T H, Lee S W. Effect of heat treatment on ultrasonic synthesized bismuth ferrites: an effective visible light-driven photocatalyst [J], Research on Chemical Intermediates, 2017, 43: 5113.

[12] Sumathi S, Lakshmi Priya V. Structural, magnetic,electrical and catalytic activity of copper and bismuth co-substituted cobalt ferrite nanoparticles [J], Journal Materials Science:Materials in Electronics, 2017, 28: 2795.

[13] Pandey R, Panda C, Kumar P, Kar M. Phase diagram of Sm and Mn co-doped bismuth ferrite based on crystal structure and magnetic properties [J], Journal of Sol-Gel Science Technology, 2018, 85(1): 166.

[14] Murshed M M, Nenert G, Burianek M, Robben L, Muhlberg M, Schneider H, Fischer R X, M.Gesing T G. Temperature dependent structural studies of mullite-type Bi2Fe4O9 [J], Journal of Solid State Chemistry, 2013, 197: 370.

[15] Liu T. Low-Temperature Synthesis of BiFeO3 via PVA Sol–Gel Route [J], Journal of America Ceramic Society., 2010, 93 [11] 3637.

[16] Abid A, Hassan M, Hussain S S, Riaz S, Naseem S. Temperature-Dependent Phase Formation, Surface Morphological and Magnetic Studies of Bismuth Iron Oxide Grown by Co-precipitation Method [J],Journal Superconductivity and Novel, 2017, 30: 2549.

[17] Sarkar K, Mukherjee S, Mukherjee S, Mitra M K. Synthesis, Characterization and Studies on Optical, Dielectric and Magnetic Properties of undoped and Cobalt doped Nanocrystalline Bismuth Ferrite [J], Journal of the Institution of Engineers(India): Series D, 2014, 95(2):135.

[18] Francis P N, Dhanuskodi S, Jayalakshmy M S, Muneeswaran M, Philip J, Giridharan N V. Optical limiting and magnetoelectric coupling in multiferroic BiFeO3 Nanoparticles [J], Materials
[19] Wang T T, Deng H M, Shen P, Hong J, Yue F Y, Zhu L Q, Yang P X, Chu J H. The synthesis and microstructural, optical, magnetic characterizations of m 0 0-oriented epitaxial Bi2Fe4O9 thin film by pulsed laser deposition [J], Materials Letters, 2017, 204(1):81.

[20] Huang LiHong, Chen Yungui. Successful hydrothermal synthesis of α-Fe2O3 hexagonal micro-platelets and its application in Li-Ion battery [J], Rare Metal Materials and Engineering, 2013, 4(10): 2014.

[21] Wang X, Lin Y, Zhang Z C, Bian J Y. Photocatalytic activities of multiferroic bismuth ferrite nanoparticles prepared by glycol-based sol–gel process [J], Journal of Sol-Gel Science Technology, 2011, 60:1

[22] Ihlefeld J F, Podraza N, Liu Z K, Rai R C. Optical Band gap of BiFeO3 Grown by Molecular-Beam Epitaxy [J], Applied Physics Letters, 2008, 92(14): 9208.

[23] Haison M, Hakim M A, Basith M A, Ahmmad B, Zubair M A, Hussain A, Isalam M F. Size dependent magnetic and electrical properties of Ba-doped nanocrystalline BiFeO3 [J], Aip Advances, 2016,6(3) :035314.

[24] Dhir G, Lotey G S, Uniyal P, Verma N K. Size-dependent magnetic and dielectric properties of Tb-doped BiFeO3 nanoparticles [J], Journal of Materials Science: Materials in Electronics,2013,24(11):4386.

[25] Qian F Z, Jiang J Z, Guo S Z, Jiang D M, Zhang W G. Multiferroic Properties of Bi1–xDyxFeO3 Nanoparticles [J], Journal of Applied Physics, 2009,106:084312.

[26] Guo R, Fang L, Dong W, Zheng F, Shen M. Enhanced Photocatalytic Activity and Ferromagnetism in Gd Doped BiFeO3 Nanoparticles [J], The Journal of Physics Chemistry C, 2010, 114: 21390.

[27] Chen L S, Zheng L R, He Y H, Zhang J, Mao Z Q, Chen X. The local distortion and electronic behavior in Mn doped BiFeO3 [J], Journal of Alloys and Compounds, 2015,633:216.

[28] Pillai S, Bhuwa D, Shripathi T, Shelke V. Synthesis of single phase bismuth ferrite compound by reliable one-step method [J], Journal of Materials Science: Materials in Electronics, 2013, 24: 2950.

[29] Kumarc P, Kar M. Effect of Structural Transition on Magnetic and Dielectric Properties of La and Mn co-substituted BiFeO3 Ceramics [J],Material Chemistry and Physics, 2014,148(3): 968.

[30] Hu B, Wang J F, Zhang J,Gu Z B, Zhang S T. Synthesis, structures and properties of single phase BiFeO3 and Bi2Fe4O9 powders by hydrothermal method [J], Journal of Materials Science: Materials in Electronics, 2015,26(9): 6887.

[31] Bea H, Bibes M, Fusil S, Wyczisk F, Forget A, Lebugle D, Colson D, Viret M. Influence of parasitic phase on the properties of BiFeO3 epitaxial thin films [J], Applied Physics Letters, 2005, 87(7): 072508.

[32] Zhang H, Liu W F, Wu P, Wang S Y, Liu G Y, Rao H G. Unusual magnetic behaviors and electrical properties of Nd-doped BiFeO3 nanoparticles calcined at different temperature [J],Journal of Nanoparticle Research, 2014, 16(1): 2205.

[33] Pandey R, Panda C, Kamar P, Kar M. Phase diagram of Sm and Mn coded bismuth ferrite based on crystal structure and magnetic properties [J], Journal of Sol-Gel Science Technology, 2018, 85(1):166.