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# Mossbauer studies of $BiFeO_3$ Mulitiferroic nanoparticles doped with Eu

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## Abstract

This work presents the results of $BiFeO_3$ and $Bi_{0.9}Eu_{0.1}FeO_3$ multiferroic materials, synthesized via a simple solid-phase reaction method. Both of the synthesized materials were in the rhombohedral R3c structure as observed by X-ray diffraction (XRD). The presence of a doublet along with a sextet in Mossbauer spectra indicates an impurity phase ($Bi_2Fe_4O_9$). The presence of $Fe^{2+}$ ions are confirmed from Mossbauer spectroscopy study in the $Bi_{0.9}Eu_{0.1}FeO_3$ sample. And the $Bi_{0.9}Eu_{0.1}FeO_3$ exhibited a slight lattice distortion, observable from the results of XRD and Mossbauer spectra. We can conclude that growing of crystal homogeneity of $Bi_{0.9}Eu_{0.1}FeO_3$ is better than $BiFeO_3$.

**Keywords** Multiferroics · Bismuth ferrite · Mossbauer spectra · Substitution

## 1 Introduction

Multiferroic materials (MF) are substance that simultaneously exhibit two or more types of ferroic order parameters, e.g. ferromagnetism, ferroelectricity and ferroelasticity [1]. Among these materials, $BiFeO_3$ (BFO) is one of the most attractive MF as it owns high Curie temperature ($T_C$~1103 K) and Neel temperature ($T_N$~ 643 K) [2]. Pure BFO can consist of a

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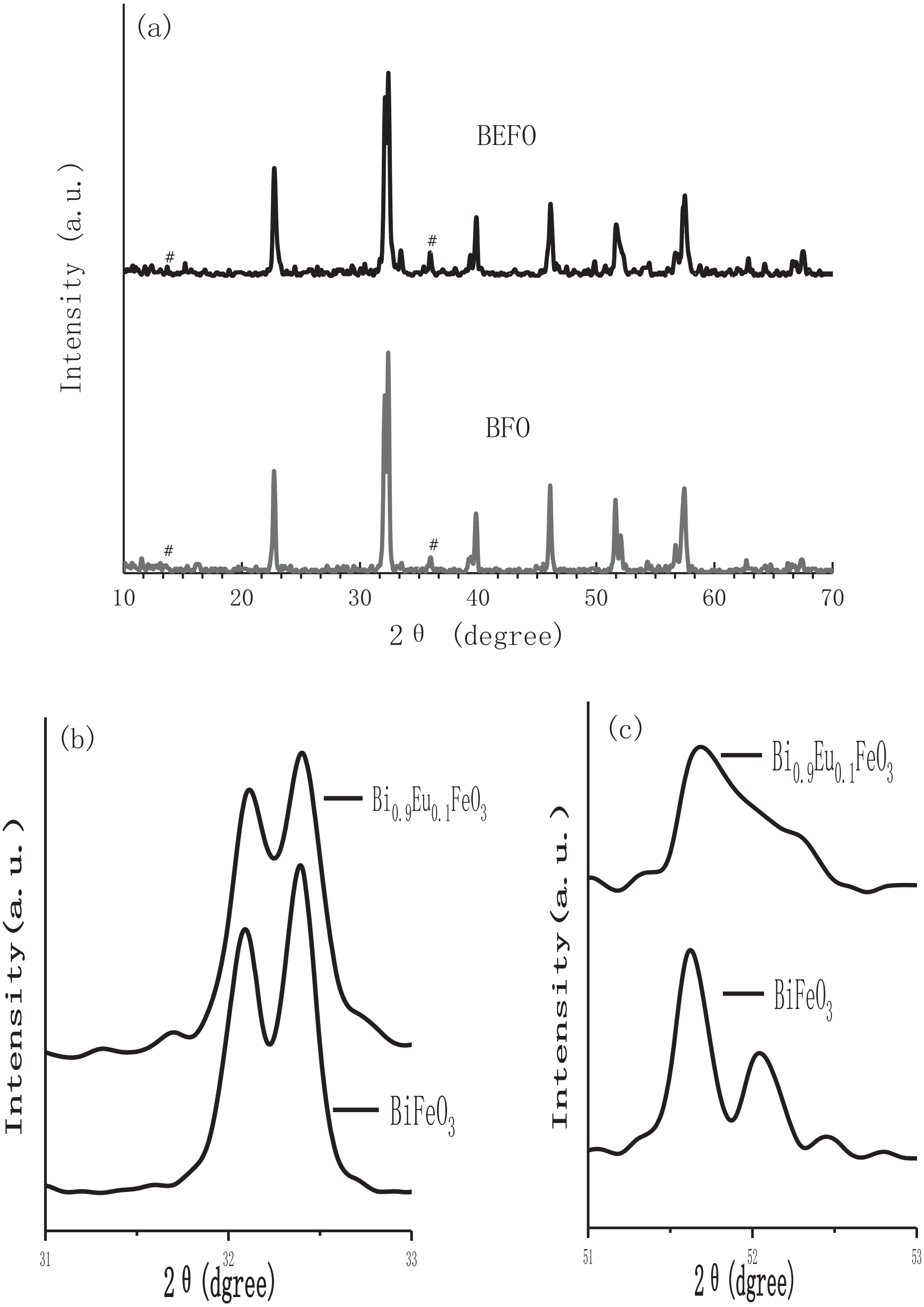

**Fig. 1** **a** X-ray diffraction patterns of BiFeO3 and $Bi_{0.9}Eu_{0.1}FeO_3$ at room temperature (the “#” peaks correspond to the presence of the impurity $Bi_2Fe_4O_9$), **b** X-ray diffraction pattern in the range of 31–33° and **c** X-ray diffraction pattern in the range of 51–53°

perovskite-like crystal structure distorted in the [111] direction and crystallizes in rhombohedral space group R3c [3]. Although BFO has excellent performance, its application potential has not yet been fully exploited, because there are some issues that hinder its applicability, for instance, the high leakage current, weak ferroelectric behaviour and small remnant polarization [4]. Moreover, the presence of large spatial spin cycloid structure with a period of 62 nm means loss of macroscopic magnetization and suppression of linear magnetoelectric effect. Therefore, breaking the spatially modulated spin structure (SSMS) in $BiFeO_3$ is the key to releasing ferromagnetism and exhibiting magnetoelectric effects [5, 6]. Among numerous methods for enhancing its properties, the most studied one is the ion-doping approach. BFO can be modified by using transition elements, rare earth elements or alkaline earth metal elements to enhance the ferromagnetism and ferroelectricity [6–8]. Eu ions as one of the rare earth elements can be used to replace A-site ($Bi^{3+}$ ions). Doping with Eu ions are expected to suppress the SSMS and improve the leakage current, magnetic and ferroelectric properties of $BiFeO_3$ [5, 9–11].

In the present work, $BiFeO_3$ (BFO) and $Bi_{0.9}Eu_{0.1}FeO_3$ (BEFO) were prepared by using a simple solid-phase reaction method. The as-obtained material was analyzed by XRD and Mossbauer spectrometer to elucidate the Eu-doped structure and composition changes in detail, providing a specific experimental basis for future research and applicability of multiferroic materials.

## 2 Experimental procedure

The specific steps of preparing undoped $BiFeO_3$ and 10% Eu doped with $BiFeO_3$ ($Bi_{0.9}Eu_{0.1}FeO_3$) by a sample solid-phase reaction are as follows. Analytical pure powder of $Bi_2O_3$, $Eu_2O_3$ and $Fe_2O_3$ were used as starting materials. In order to compensate for the strong volatilization of Bi irons, the extra (10 mol%) of $Bi_2O_3$ was incorporated in all samples.

An appropriate proportion of $Bi_2O_3$, $Fe_2O_3$ and $Eu_2O_3$ were weighed, mingled and then ground in a mortar. After a 30-min of the grinding process, the mixtures were calcined at 830 °C for 5 min and cooled at atmospheric temperature. The next step is grinding the compound into fine powder and washing twice with 10% nitric acid solution. The powder was washed with deionized water to remove the residual acid and repeated it for less acid. The last is that the samples were dried in an electric constant temperature drying oven at 150 °C.

The obtained samples were structurally characterized by X-ray diffractometer (XRD). The phase and structural analysis of the X-ray patterns were performed with a program called Jade9.0 that equipped with the ICSD-2010 database and PDF-2007 database. And Mossbauer spectra (MS) were performed at room temperature.

**Table 1** Structural parameters calculated from XRD pattern

| Sample | Space group | a(Å) | b(Å) | c(Å) | Volume (Å) | Grain size(nm) | $\sigma_a = \sigma_b$ | $\sigma_c$ | $\sigma_V$ | A for $Bi_2Fe_4O_9$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| $BiFeO_3$ | R3c | 5.5801 | 5.5801 | 13.8486 | 373.44 | 42.8(2) | 0.0041 | 0.0101 | 0.1035 | 7.9(5) |
| $Bi_{0.9}Eu_{0.1}FeO_3$ | R3c | 5.5686 | 5.5686 | 13.8408 | 371.69 | 40.6(4) | 0.0023 | 0.0050 | 0.0409 | 8.3(8) |

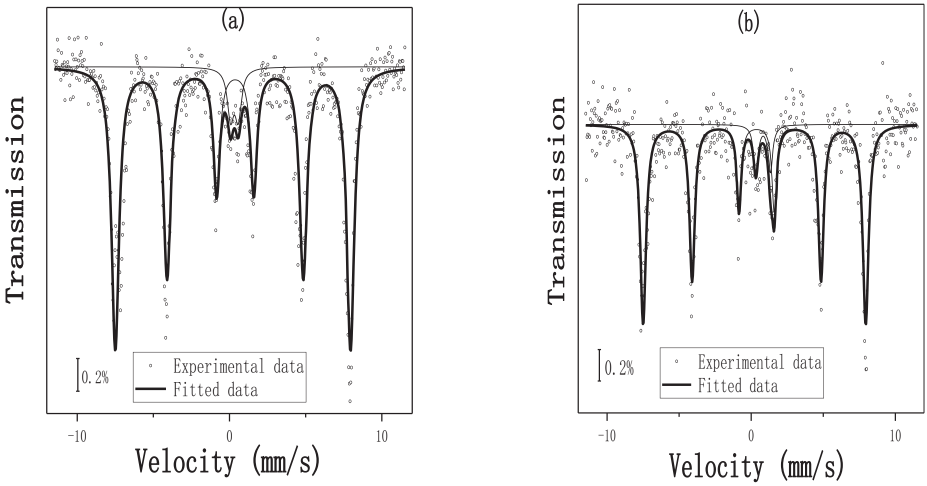

**Fig. 2** $^{57}$Fe Mossbauer spectra in the pure and Eu-substituted $Bi_{1-x}Eu_xFeO_3$ sample: x = (a) 0, (b) 0.1

## 3 Results and discussions

### 3.1 XRD pattern

The X-ray Diffraction (XRD) patterns of $BiFeO_3$ and $Bi_{0.9}Eu_{0.1}FeO_3$ are presented in Fig. 1a. All the peaks were well matched with the PDF (Card No.97–001-5299) and the patterns were indexed to the rhombohedral structure with R3c space group [12]. The secondary phase was identified as $Bi_2Fe_4O_9$(PDF Card No.97–002-0067) and marked by "#" in Fig. 1a. According to the percentage of the area, it can be roughly concluded: there is a small amount (~8%) of $Bi_2Fe_4O_9$ in both of two samples, what can be attributed to the temperature required by our solid-phase reaction method (above 700 °C), where is inevitable to produce impurity phase during the process of synthesizing of $BiFeO_3$ [13]. With Eu doping, the split peaks are merged into one peak in the 2θ range of 31–33° and 51–53° as shown in Fig. 1b-c. This indicates that the Bi ions partially have been replaced successfully with Eu ions. Compared with the $BiFeO_3$ sample, the characteristic diffraction peak of the $Bi_{0.9}Eu_{0.1}FeO_3$ sample shifted marginally to a higher angle, which proved that it maintained the same rhombohedral R3c structure as the $BiFeO_3$ sample, but the doping of Eu ions resulted in the slight lattice distortion in $Bi_{0.9}Eu_{0.1}FeO_3$. The ion radius of $Eu^{3+}$ being 1.07 Å, while the $Bi^{3+}$ is 1.17 Å [14]. The mismatch between the two kinds of ionic radius causes the lattice distortion. In order to explore deeper this phenomenon, we used the Jade9.0 software to analyze the X-ray diffraction patterns. The outcome of measurement and analysis is summarized in Table 1 where the

**Table 2** Hyperfine parameters i.e. isomer shift (IS), quadrupole splitting (QS), internal magnetic field ($H_{int}$) and Area(A)

| Sample | Sub Spectrum | IS (mms$^{-1}$) | QS (mms$^{-1}$) | $H_{int}$ (T) | A (%) |
|---|---|---|---|---|---|
| BFO | Sextet | 0.263 | −0.008 | 472 | 93.6 |
| | Doublet 1 | 0.322 | 0.504 | - | 6.4 |
| BEFO | Sextet | 0.270 | −0.133 | 479 | 91.7 |
| | Doublet 2 | 0.830 | 1.102 | - | 8.3 |

percentage content of $Bi_2Fe_4O_9$ and several crystal structural parameters are listed. The average grain sizes of this compound determined using Scherrer formula. It is observed that average grain size decreases with increasing Eu doping. There is a little difference between $Bi_{0.9}Eu_{0.1}FeO_3$ and $BiFeO_3$ in crystal. However, the smaller lattice parameters and the unit cell volume, consistent with the reported works, possibly because of the smaller ionic radii of $Eu^{3+}$ [15].

### 3.2 Mossbauer study

$^{57}Fe$ Mossbauer spectroscopy is one of the most useful investigation methods to study the hyperfine magnetic behavior and oxidation state of the iron atoms. The Mossbauer spectra of BFO and BEFO samples matched well with the superposition of a sextet and a doublet, shown in Fig. 2(a) and Fig. 2(b), respectively [16]. In order to obtain a clearer comparison of the results, we collected the Mossbauer spectral parameters of BFO and BEFO samples in Table 2. The numerical value of isomer shift (I.S.) shows the valence of iron atoms. The value of I.S., corresponding to $Fe^{2+}$ is 0.6–1.7 mm/s, while is 0.05–0.5 mm/s for $Fe^{3+}$, and − 0.15-0.05 mm/s in the case of $Fe^{4+}$ [14]. According to the measured Mossbauer spectra at room temperature, we can figure out that the isomer shifts of sextet and doublet1 in BFO is 0.263 mm/s and 0.322 mm/s, respectively, which showed only the existence of $Fe^{3+}$ in BFO sample. But the isomer shift of Doublet2 is 0.830 mm/s (higher than 0.6 mm/s), proving that there are $Fe^{2+}$ ions in BFEO, which could be attributed to the generation of oxygen vacancy [17]. The Doublet 1 is assigned to a small fraction of paramagnetic impure phase of $Bi_2Fe_4O_9$. The Doublet2 with higher quadrupole splitting value (1.102 mm/s) arises due to smaller particles having superparamagnetic relaxation [18]. A small increment (~2%) in impurity phase was detected by Mossbauer spectroscopy. This is consistent with the results obtained by X-ray diffraction pattern as well. With the introduction of Eu in the material, the quadrupole splitting (Q.S.) of $BiFeO_3$ sample changed from −0.008 mm/s to −0.133 mm/s, suggesting the added Eu disturbed the lattice structure of $BiFeO_3$ samples and induced the change in the lattice parameters. [15] With the doping of Eu, the value of $H_{int}$ has been increased slightly, from 472 kOe to 479 kOe, which is due to the growing of crystal homogeneity of BFEO is better than BFO [19].

## 4 Conclusion

$Bi_{1-x}Eu_xFeO_3$ ($x = 0, 0.10$) multiferroic nanoparticles were successfully prepared by a simple solid-phase reaction, also obtaining a small amount of $Bi_2Fe_4O_9$ as "impurity" in the both samples. With the doping of Eu, a small rise in the impurity phase was detected by Mossbauer spectroscopy. A slightly distorted rhombohedral perovskite structure has been observed from XRD and Mossbauer spectroscopy, being caused by the different ionic radius of $Bi^{3+}$ and $Eu^{3+}$. The Mossbauer study found that only $Fe^{3+}$ exists in BFO sample, where in BEFO the introduction of oxygen vacancy produces mixed valence states of irons: $Fe^{2+}$ and $Fe^{3+}$. Compared with $BiFeO_3$, the $H_{int}$ value of $Bi_{0.9}Eu_{0.1}FeO_3$ has been increased slightly, from 472 kOe to 479 kOe, due to the better growing of crystal homogeneity of $Bi_{0.9}Eu_{0.1}FeO_3$.

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## References

1. Agrawal, S., Jawad, A., Ashraf, S.S.Z., Naqvi, A.H.: Structural, optical, dielectric and magnetic properties of Cu doped BiFeO3nanoparticles synthesized by sol gel method. Mater. Focus. **3**, 60–66 (2014)
2. Wang, J.Y., Wei, Y.W., Zhang, J.J., Ji, L.D., Huang, Y.X., Chen, Z.: Synthesis of pure-phase BiFeO3nanopowder by nitric acid-assisted gel. Mater. Lett. **124**, 242–244 (2014)
3. Lazenka, V., Jochum, J.K., Lorenz, M., Modarresi, H., Gunnlaugsson, H.P., Grundmann, M., Bael, M.J.V., Temst, K., Vantomme, A.: Interface induced out-of-plane magnetic anisotropy in magnetoelectric BiFeO3-BaTiO3 superlattices. Appl. Phys. Lett. **110**, 092902 (2017)
4. Sharma, J., Bhat, B.H., Kumar, A., Kumar, S., Kaur, T., Want, B., Srivastava, A.K.: Magnetic and dielectric properties of Ce-Co substituted BiFeO3 multiferroics. Mater. Res. Express. **4**, 036104 (2017)
5. Jiang, Z.M., Peng, A.G., Liu, M., Liu, G.Q., Zhang, G.: The structure and magnetic properties of Eu-doped BiFeO3 prepared by a solid-phase sintering method. Mod. Phys. Lett. B. **33**, 1950094 (2019)
6. Fki, H., Koubaa, M., Sicard, L., Cheikhrouhou-Koubaa, W., Cheikhrouhou, A., Ammar-Merah, S.: Influence of Y doping on structural, vibrational, optical and magnetic properties of BiFeO3ceramics prepared by Mechanical Activation. Ceram. Int. **43**, 4139–4150 (2017)
7. Hussain, S., Hasanain, S.K., Jaffari, G.H., Ali, N.Z., Siddique, M., Shah, S.I.: Correlation between structure, oxygen content and the multiferroic properties of Sr doped BiFeO3. J. Alloys Compd. **622**, 8–16 (2015)
8. Puhan, A., Bhushan, B., Rout, D., Nayak, A.K., Priyam, A.: Structural and optical properties of Ba,Cr Co-doped BiFeO3Multiferroic nanoparticles. AIP Conf. Proc. **1832**, 050108 (2017)
9. Chakrabarti, K., Das, K., Sarkar, B., Ghosh, S., De, S.K., Sinha, G., Lahtinen, J.: Enhanced magnetic and dielectric properties of Eu and Co co-doped BiFeO3 nanoparticles. Appl. Phys. Lett. **101**, 042401 (2012)
10. Zhang, X.Q., Sui, Y., Wang, X., Wang, Y.J., Wang, Z.: Effect of Eu substitution on the crystal structure and multiferroic properties of BiFeO3. J. Alloys Compd. **507**, 157–161 (2010)
11. Dai, H.Y., Chen, Z.P., Xue, R.Z., Li, T., Liu, H.Z., Wang, Y.Q.: Structure and multiferroic properties of Eu-substituted BiFeO3 ceramics. Appl. Phys. A Mater. Sci. Process. **111**, 907–912 (2013)
12. Uniyal, P., Yadav, K.L.: Room temperature multiferroic properties of Eu doped BiFeO3. J. Appl. Phys. **105**, 07D914 (2009)
13. Prihor, F., Ianculescu, A., Mitoseriu, L., Postolache, P., Curecheriu, L., Dragan, N., Crisan, D.: Functional Properties of the (1- x)BiFeO3—xBaTiO3 Solid Solutions. Ferroelectrics. **391**, 76–82 (2009)
14. Sati, P.C., Kumar, M., Chhoker, S., Jewariya, M.: Influence of Eu substitution on structural, magnetic, optical and dielectric properties of BiFeO3multiferroic ceramics. Ceram. Int. **41**, 2389 (2015)
15. Tamilselvan, A., Balakumar, S., Sakar, M., Chiranjib, N., Murugavel, P., Kumar, K. S., Dalton T.: Role of oxygen vacancy and Fe–O–Fe bond angle in compositional, magnetic, and dielectric relaxation on Eu-substituted BiFeO3 nanoparticles. **43**, 5731 (2014)
16. Jartych, E., Lisinska-Czekaj, A., Oleszak, D., Czekaj, D.: Mater Comparative X-ray diffraction and Mossbauer spectroscopy studies of BiFeO3 ceramics prepared by conventional solid-state reaction and mechanical activation. Mater. Sci. Pol. **31**, 211–220 (2013)
17. Dai, H.Y., Xue, R.Z., Chen, Z.P., Li, T., Chen, J., Xiang, H.W.: Effect of Eu, Ti co-doping on the structural and multiferroic properties of BiFeO3 ceramics. Ceram. Int. **40**, 15617–15622 (2014)
18. Das, A., Bandyopadhyay, S., Chatterjee, S., Das, D.: Magnetoelectric and hyperfine properties of x(CoFe2O4)-(1-x)(BiFeO3) (x=0.2-0.4) nanocomposites. AIP Conf. Proc. **1665**, 050046 (2015)
19. Raevski, I.P., Kubrin, S.P., Pushkarev, A.V., Olekhnovich, N.M., Radyush, Y.V., Titov, V.V., Malitskaya, M.A., Raevskaya, S.I., Chen, H.: The effect of Cr substitution for Fe on the structure and magnetic properties. Ferroelectrics. **525**, 1–10 (2018)