

Effects of Mn Doping on Structural and Magnetic Properties of Multiferroic BiFeO₃ Nanograins Made by Sol-gel Method

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BiFeO₃ is a multiferroic material that attracts attentions of many research groups due to its potential as being ferroelectric and ferromagnetic above room temperature. We have prepared both undoped- and Mn-doped BiFeO₃ by sol-gel auto-ignition method. Doping of Mn has resulted in decreasing grain size from 60 to 32 nm. X-ray diffraction data show that the samples are pure and single-phase. Infrared measurements on BiFeO₃ and Mn-doped BiFeO₃ revealed intrinsic stretching vibrations of tetrahedral sites of Fe³⁺-O and of octahedral Bi³⁺-O as well. On the other hand, as the Mn concentration increases, the magnetic moment of BiFeO₃ increases. It gives some suggestions in manipulating structural and magnetic properties of BiFeO₃ by doping Mn.

Keywords : nanocrystalline, multiferroics, structural properties, magnetic properties

1. Introduction

Materials which exhibit both magnetic and electrical ordering have attracted great interest in the past few years, partly because of their technological potential. Besides a range of possible device applications, the science of these materials is truly fascinating. Multiferroics are materials with coexistence of magnetic and ferroelectric ordering in a certain temperature range. This implies that they possess spontaneous magnetization which can be reoriented by an applied magnetic field, spontaneous polarization which can be reoriented by an applied electric field and spontaneous deformation which can be reoriented by an applied stress [1-5].

Despite the possible coexistence of ferroelectricity and magnetism, a pronounced interplay between these properties has rarely been observed. This has prevented the realization of multiferroic devices offering such functionality. Typical multiferroics belong to the group of the perovskite transition metal oxides, which include rare-earth manganites and ferrites (*e.g.* TbMnO₃, HoMn₂O₅, LuFe₂O₄). Other examples are the bismuth alloys BiFeO₃ and BiMnO₃ and non-oxides such as BaNiF₄ and spinel chalcogenides, *e.g.* ZnCr₂Se₄. Besides scientific interest in their physical properties, multiferroics have potential for

applications as actuators, switches, magnetic field sensors or new types of electronic memory devices.

BiFeO₃ is unique amongst various magnetoelectric multiferroics, as its ferroelectric and magnetic transition temperatures are well above the room temperature. This raises the possibility of developing potential devices based on magnetoelectric coupling operating at the room temperature. As a result, BiFeO₃ has received tremendous attention over the last few decades and the last couple of years have witnessed several new results on this compound in pure and solid solution forms. L. Hongri *et al.* [6] synthesized Ti doped BiFeO₃ and J. H. Xu *et al.* [7] synthesized low temperature BiFeO₃ using sol-gel method. Our main objective of this paper is to achieve nanoscaled BiFeO₃ and BiFe_{0.8}Mn_{0.2}O₃ powders by sol-gel method and to see the effect of Mn concentration on both structural and magnetic properties. The sol-gel auto-ignition method is used to speed up the synthesis of complex materials. It is a simple process, which offers a significant saving in time and energy consumption over the traditional methods. This method is employed to obtain improved powder characteristics, more homogeneity and narrow grain size distribution, thereby influencing structural and magnetic properties.

2. Experimental

Nanocrystalline powders of BiFeO₃ and BiFe_{0.8}Mn_{0.2}O₃

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were prepared by sol-gel auto-ignition method [8]. The A.R Grade citric acid (C₆H₈O₇·H₂O), bismuth nitrate (Bi(NO₃)₃·5H₂O), manganese nitrate (Mn(NO₃)₃·4H₂O), ferric nitrate (Fe(NO₃)₃·9H₂O) (≥99%) were used as starting materials. The entire synthesis process is described elsewhere [8]. The as-prepared powder of the sample were heat treated at 500 °C.

The X-ray diffraction of the ferrite powders was carried out by using a Philips PW 1820 powder diffractometer with CuKα graphite-monochromated radiation, operating at 40 kV and 30 mA, with solar slits and divergent and receiving slits of 0.2 mm. The diffracted intensity was registered in the angular range 8° ≤ 2θ ≤ 80°, with a step size of 0.02° (2θ). The standard Scherrer formula $D = 0.9\lambda/B\cos\theta$ was applied for the calculation of average grain size D . Here, B is full width at half maximum (FWHM) difference in profile widths of broadened ferrite peaks and standard peaks. The structural changes with annealing temperature are observed by ABB Bomem MB 102 infrared spectrometer equipped with CsI optics and DTGS detector. The samples were mixed with KBr and made in the form of pellets and IR transmission was recorded at 4 cm⁻¹ resolution (10 consecutive scans were averaged for each spectrum), giving the spectra in the 250-4000 cm⁻¹ range. For our study we have chosen the range from 300-1000 cm⁻¹. The micrographs of all samples were taken on FEI Quanta FEG 200 High Resolution Scanning Electron Microscope.

3. Results and Discussions

Fig. 1 represents the XRD patterns of the powders calcined at 500 °C. The pure perovskite BiFeO₃ can be obtained by the rapid sintering at 500 °C with citric acid

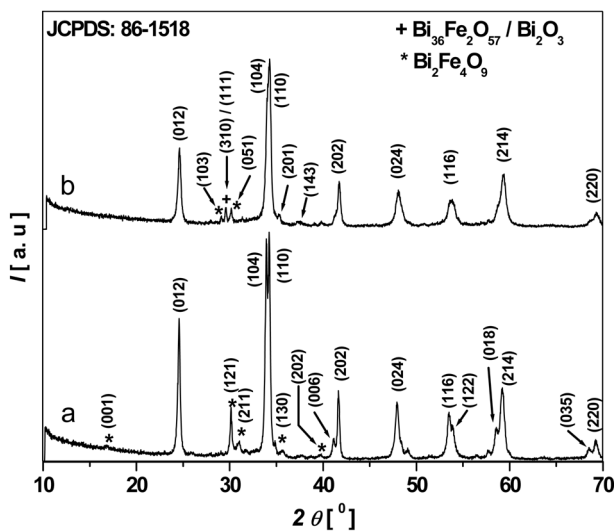


Fig. 1. XRD patterns of (a) BiFeO₃ and (b) BiFe_{0.8}Mn_{0.2}O₃.

as chelating agent (shown in Fig. 1(a)). All the reflection peaks can be readily indexed to the pure rhombohedrally distorted perovskite structure of BiFeO₃ (BFO R-phase) with lattice parameters of $a = b = 5.5781 \text{ \AA}$ and $c = 13.867 \text{ \AA}$ [space group: R3c (161)], which are in good agreement with the reported data (JCPDS no.: 86-1518) and with those of pure BiFeO₃ prepared by sol-gel and solid state reaction [9, 10]. Besides the formation of BiFeO₃ (R-phase), small amount of non-perovskite phases, such as Bi₂Fe₄O₉ (JCPDS no.: 25-0090), Bi₃₆Fe₂O₅₇ (JCPDS no.: 86-1518) and Bi₂O₃ (JCPDS no.: 77-0374) appear unavoidably (as shown in Fig. 1(a)). It can be explained that during auto ignition process the excess of carbonaceous materials inevitably give rise to the formation of impurity phases [11-13]. The grain size obtained for pure BiFeO₃ is around 60 nm. With the substitution of Mn ions in BiFeO₃, the grain size reduced to 32 nm. The reduction of grain size in the case of BiFe_{0.8}Mn_{0.2}O₃ (BFMO) may be due to the variation in the concentration of chemical solution and thus during auto-ignition process the reaction temperature was found to be low compared to BiFeO₃. W. S. Kim *et al.* [14] also observed similar kind of behavior in the reduction of particle size with doing Co and Ti for BiFeO₃ ceramics.

The phase formation of BiFeO₃ and BiFe_{0.8}Mn_{0.2}O₃ by XRD is further supported by infrared analysis (IR). The IR spectra of BiFeO₃ and BiFe_{0.8}Mn_{0.2}O₃ exhibit features similar to that of other spinel compounds [15]. As seen in Fig. 2, they gave rise to two main absorption envelopes, consisting of metal-oxygen stretching bands ν_1 and ν_2 , in the range 750-500 cm⁻¹ and 500-250 cm⁻¹, respectively. In the spectrum of BiFeO₃, the ν_1 bands are assigned to intrinsic stretching vibrations of tetrahedral sites consisting of Fe³⁺-O, while ν_2 envelope corresponds to stretching

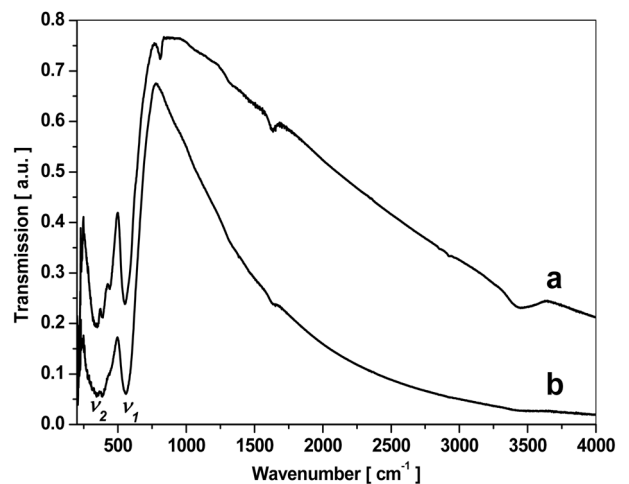


Fig. 2. FTIR absorption spectra of (a) BiFeO₃ and (b) BiFe_{0.8}Mn_{0.2}O₃.

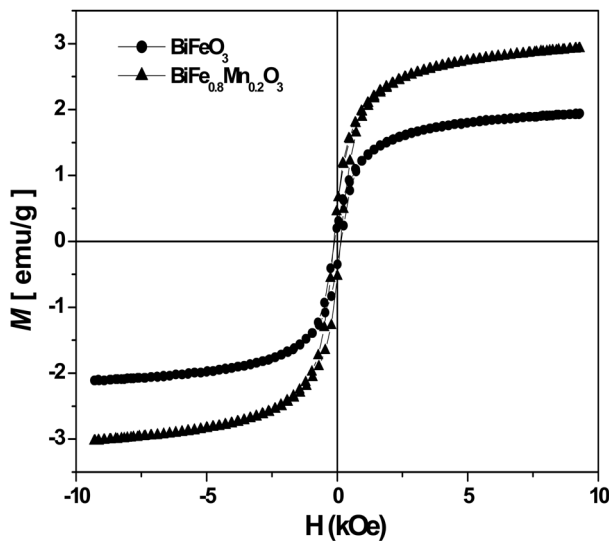


Fig. 3. M-H curves for BiFeO_3 and $\text{BiFe}_{0.8}\text{Mn}_{0.2}\text{O}_3$ at 300 K.

vibrations of octahedral $\text{Bi}^{3+}\text{-O}$ sites. Spectrum of $\text{BiFe}_{0.8}\text{Mn}_{0.2}\text{O}_3$ is somewhat simpler than that of BiFeO_3 . It consists of one ν_1 band, which corresponds to tetrahedral $\text{Fe}^{3+}\text{-O}$ and $\text{Mn}^{2+}\text{-O}$ stretchings, while ν_2 envelope consists of two bands, corresponding to octahedral $\text{Bi}^{3+}\text{-O}$ stretchings. Hermet *et al.* [16] have interpreted the infrared spectrum of BiFeO_3 using first principle approach based on density functional theory. They proved that theoretical data can be directly used for the interpretation of experimental data. According to this interpretation, we conclude that lattice dynamics is significantly different in $\text{BiFe}_{0.8}\text{Mn}_{0.2}\text{O}_3$, giving rise to simpler spectrum.

Fig. 3 shows the magnetization curve of the BiFeO_3 and $\text{BiFe}_{0.8}\text{Mn}_{0.2}\text{O}_3$ nanograins measured at 300 K with an applied field of 10 kOe. A typical magnetic hysteresis loop was observed, indicating that the BiFeO_3 nanograins show a weak ferromagnetic order at room temperature, which is quite different from the linear M-H relationship observed in the bulk BiFeO_3 [17, 18]. The similar ferromagnetic phenomenon was also observed in BiFeO_3 films [19], nanotubes [17] and nanocrystallites [20]. The origin of the weak magnetic property in our sample may be attributed to the size confinement effect of the nanostructures. It is clearly shown that spontaneous moment at a room temperature increased with Mn substitution for Fe.

Fig. 4(a) also exhibits R-Phase in BiFeO_3 . It is clear that the BiFeO_3 R-phase grains exhibits a uniform feature with approximately 50-60 nm in size, which is smaller than the obtained size of 200 nm from by sol-gel method [9]. The grain size measured from XRD is very well in

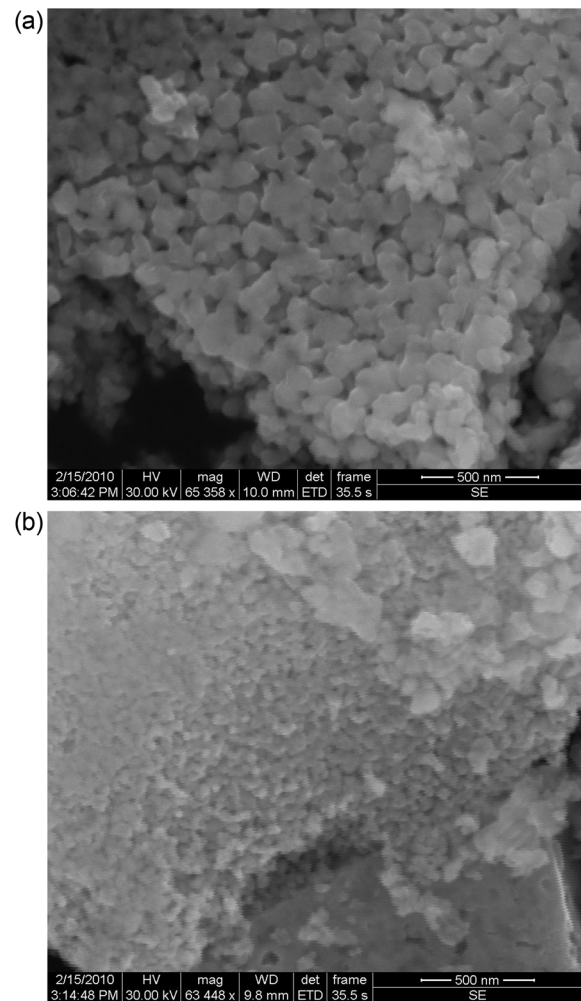


Fig. 4. SEM images of (a) R-phase BiFeO_3 and (b) $\text{BiFe}_{0.8}\text{Mn}_{0.2}\text{O}_3$.

agreement with our SEM data. It demonstrates that the sol-gel auto-ignition process is a good method for preparing nanoscale BFO grains with uniform features. Fig. 4(b) shows the SEM image of $\text{BiFe}_{0.8}\text{Mn}_{0.2}\text{O}_3$. The morphology of the powder is seen to be uniform with narrow grain size compared to pure BiFeO_3 . The Mn substitution decreased the grain size resulting in the several nano-grain-sized nanostructures.

4. Conclusions

Both undoped and Mn-doped BiFeO_3 were prepared by sol-gel auto-ignition method. Doping of Mn ions reduced the grain size from 60 to 32 nm. The magnetic moment of BiFeO_3 increased with the substitution of Mn concentration. Infrared measurements of BiFeO_3 and Mn-doped BiFeO_3 revealed intrinsic stretching vibrations of tetrahedral sites of $\text{Fe}^{3+}\text{-O}$ and of octahedral $\text{Bi}^{3+}\text{-O}$.

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References

- [1] C. N. R. Rao and C. R. J. Serrao, *J. Mater. Chem.* **17**, 4931 (2007).
- [2] R. Ramesh and N. A. Spaldin, *Nat. Mater.* **6**, 21 (2007).
- [3] W. Eerenstein, N. D. Mathur, and J. F. Scott, *Nature* **442**, 759 (2006).
- [4] S. W. Cheong and M. Mostovoy, *Nat. Mater.* **6**, 13 (2007).
- [5] A. Singh, V. Pandey, R. K. Kotnala, and D. Pandey, *Phys. Rev. Lett.* **101**, 247602 (2008).
- [6] L. Hongria, L. Zuli, L. Xiaolu, and Y. Kailun, *Physica B* **400**, 252 (2007).
- [7] J. H. Xu, H. Ke, D. C. Jia, and W. W. Y. Zhou, *J. Alloy. Compd.* **472**, 473 (2009).
- [8] A. T. Raghavender, D. Pajic, K. Zadro, T. Milekovic, P. V. Rao, K. M. Jadhav and D. Ravinder. *J. Magn. Magn. Mater.* **1**, 316 (2007).
- [9] J. H. Kim, S. U. Kim, and W. J. Kim, *Mater. Lett.* **59**, 4006 (2005).
- [10] M. M. Kumar, V. R. Palkar, K. Srinivas, and S. V. Suryanarayana, *Appl. Phys. Lett.* **76**, 276 (2000).
- [11] X. Wang, Y. Zhang, and Z. Wu, *Mater. Lett.* **64**, 486 (2010).
- [12] S. Ghosh, S. Dasgupta, S. Sen, and H. S. Maiti, *J. Am. Ceram. Soc.* **88**, 1349 (2005).
- [13] S. Ghosh, S. Dasgupta, A. Sen, and H. S. Maiti, *Mater. Res. Bull.* **40**, 2073 (2005).
- [14] W. S. Kim, Y. K. Jun, K. H. Kim, and S. H. Hong, *J. Magn. Magn. Mater.* **321**, 3262 (2009).
- [15] A. T. Raghavender, K. Zadro, D. Pajic, Z. Skoko, and N. Biliskov, *Mater. Lett.* **64**, 1144 (2010).
- [16] P. Hermet, M. Goffinet, J. Kreisel, and P. Ghosez, *Phys. Rev. B* **75**, 220102(R), 2007.
- [17] C. Chen, J. Cheng, S. Yu, L. Che, and Z. J. Meng, *J. Cryst. Growth* **291**, 135 (2006).
- [18] S. T. Zhang, M. H. Lu, D. Wu, Y. F. Chen, and N. B. Ming, *Appl. Phys. Lett.* **87**, 262907 (2005).
- [19] Y. Wang, Q. Jiang, H. He, and C. W. Nan. *Appl. Phys. Lett.* **88**, 142503 (2006).
- [20] Y. Wang *et al.* *J. Am. Ceram. Soc.* **90**, 2615 (2007).