Materials Research Express

PAPER

Enhanced magnetic properties of cobalt-doped bismuth ferrite nanofibers

Sujian You and Bin Zhang

College of Mathematics and Physics, Fujian University of Technology, Fuzhou 350118, People’s Republic of China

1 Authors to whom any correspondence should be addressed.

E-mail: yousujian@vip.163.com and 19901978@fjut.edu.cn

Keywords: ferroelectrics, magnetic materials, electrospinning, bismuth ferrite, cobalt doping, spiral spin structure

Abstract

This study demonstrates the effect of Cobalt substitution on the structure, ferroelectric, and magnetic properties of BiFeO$_3$ (BFO) nanofibers. The BiFe$_{1-x}$Co$_x$O$_3$ ($x=0, 0.05, 0.1$) nanofibers were successfully synthesized by a sol-gel based electrospinning method followed by thermal treatment. The BiFe$_{1-x}$Co$_x$O$_3$ nanofibers prepared under optimized conditions are a polycrystalline fiber that presents a rhombohedral distorted perovskite structure with a little amount impurity phase. Room temperature polarization and magnetization results indicated the multiferroic behavior of the nanofibers. Especially, the remnant magnetization is increased from 0.18 emu g$^{-1}$ to 1.72 emu g$^{-1}$ on increasing amount of Co substitution. The improvement of magnetism can be attributed to the Cobalt doping and size-effect.

1. Introduction

Multiferroic materials, which exhibit ferroelectric, (anti-)ferromagnetic or ferroelastic, etc, have been investigated intensively due to both interesting fundamental physics and practical applications in several technological areas [1–5]. Among the existing multiferroic materials, BiFeO$_3$ (BFO, a high Curie temperature, $T_C$, of about 1103 K and Néel temperature $T_N$ of about 650 K) is of great significance in the research of the origin of multiferroic properties [6, 7].

However, the poor magnetization performance of bulk BFO limits its practical applications [8, 9]. As is known to all, the lone electron pairs of Bi$^{3+}$ lead to the ferroelectric properties of BFO, whereas G-type antiferromagnetic is the result of the ordering of Fe$^{3+}$ spins with a complicated long-period modulation about 62 nm [10, 11]. Therefore, the ferromagnetism can be enhanced by destroying the spiral spin structure. On the one hand, long-period helical structures can be destroyed by size effect on low-dimensional BFO, such as films [1, 12], nanoparticles [2, 13] and nanowires [14, 15]. For example, Wang et al [1] successfully synthesized BFO thin films with a thickness of 50 to 500 nm, compared to the bulk ceramic, the thin films exhibit enhanced magnetism. Park et al [13] synthesized single crystal BFO nanoparticles with a size range from 15 nm to 100 nm by sol-gel method and studied the size-dependent magnetic behavior of BFO nanoparticles. Zhang [14], Jie Wei [16] have successfully prepared BFO nanotubes and nanofibers through AAO templates, and their ferroelectric properties and magnetic properties have been further studied. Xie et al [15] prepared pure BFO nanofibers by the sol-gel electrospinning and studied the ferroelectric and ferromagnetic properties. On the other hand, Chemical substitution of BFO at Bi and Fe sites is also found to cause changes to the lattice and modulated the spin structure of BFO, thereby enhancing magnetic properties [17, 18]. There has been a continuous effort to enhance the magnetoelectric properties of BFO by doping transition metal ions (Co, Mn, Zn, etc) at Fe sites. Among these doping transition metal ions, Cobalt ion doping is proved to be an effective method to increase the magnetism of BFO [19–21]. For example, Xu et al [20] have reported that the BFO doped with 5% Co$^{2+}$ could significantly improve the magnetism of BFO. Its residual magnetization is 0.7 emu g$^{-1}$, and saturation magnetization is about 1.6 emu g$^{-1}$.

It has been reported that the electrospun BFO nanofibers and the substitution of Co at Fe-site separately indicate an enhancement in the magnetism of BFO. Until now, no one has made an effort to research Cobalt
doped BFO nanofibers. Thus, the doping of Co at BFO nanofibers is expected to dramatically improve its magnetism, this motivates us to explore the influences of Cobalt ion doping concentration on the crystal structure, morphology, ferroelectric, and magnetic properties of the BFO nanofibers.

2. Experimental procedure

2.1. Materials
In this work, bismuth nitrate (Bi(NO$_3$)$_3$·5H$_2$O, Sinopharm Chemical), iron nitrate (Fe(NO$_3$)$_3$·9H$_2$O, Sinopharm Chemical), cobalt nitrate (Co(NO$_3$)$_2$·6H$_2$O, Sinopharm Chemical), acetic acid (CH$_3$COOH, Sinopharm Chemical), acetylacetone (C$_5$H$_8$O$_2$, Kermel), Polyvinylpyrrolidone (PVP, (C$_6$H$_9$NO)_, Mw = 1 300 000, Aladdin) were used for sample treatment and sintering. All the chemical reagents and solvents were of analytical grade without any further purification.

2.2. Precursor solution preparation
BiFe$_{1-x}$Co$_x$O$_3$, (x = 0, 0.05, 0.1) namely, BiFeO$_3$ (BFO), BiFe$_{0.95}$Co$_{0.05}$O$_3$ (BFCO-1), BiFe$_{0.9}$Co$_{0.1}$O$_3$ (BFCO-2) were successfully synthesized by cost-effective sol-gel based electrospinning method. BiFe$_{1-x}$Co$_x$O$_3$ sol-gel solutions were prepared by using bismuth nitrate, iron nitrate, and cobalt nitrate as starting materials, Acetic Acid, and acetylacetone mixed solution as a solvent. The different stoichiometric ratio of those materials was added in the solvent and stirred for 3 h and then added PVP solution, continue stirring for another 10 h to obtain a stable yellow-brown precursor.

2.3. Electrospinning
The viscous solutions thus obtained was drawn into hypodermic syringes, respectively. The electrospinning procedure was shown in figure 1, an optimized high voltage was added to the nozzle, the flow rate was set to 0.1 ml h$^{-1}$, and the distance spacing between the collector and nozzle tip was about 15 cm. When the electrospinning progress was finished, the as-prepared fibers (collected on Al foil) were still placed on the collector with room temperature for 1 h and then dried at 100 °C for 2 h. Based on the analytical results of differential scanning calorimetry and thermogravimetric analysis, the samples were calcined at 300 °C for 4 h, and 650 °C for another 2 h.
2.4. Materials characterizations

The samples were characterized for their thermal properties by TG-DSC system (STA449C, Netzsch GER). The crystalline phases were carried out on x-ray diffraction (XRD) with Cu Kα radiation (λ = 0.154178 nm, Bruker AXS D8 ADVANCE, GER). Scanning electron microscopy (SEM) observations were characterized by using a JSM-6510 system (JPN). The Fourier Transform Infrared Spectra (FTIR) measurements were tested by Fourier transformation infrared miro-spectroscopy (Nicolet 6700, USA). Room temperature polarization versus electric field (P–E loop) measurements were investigated using Precision Premier Workstation’s ferroelectric tester (Radiant Tech Company, USA.) And the magnetic measurement was done on the Physical Properties Measurement System (PPMS-9T, Quantum Design, USA). The chemical oxidation states of the elements in prepared samples were performed using x-ray photoelectron spectroscopy (ESCALAB250Xi, ThermoFisher, UK).

3. Results and discussion

In order to study the thermal behavior of the as-spun nanofibers in detail, the thermogravimetric (TG) weight loss and differential scanning calorimetry (DSC) of BFO sample was recorded in the temperature range from 20 °C to 800 °C, and the TG/DSC curves of the thermal decomposition and combustion was presented in figure 2(a). There is a strong exothermic peak at 286 °C and a weaker exothermic peak at 386 °C, the PVP/BFO decomposed and iodized can be divided into three main steps, To explain those steps, XRD and FTIR were further used to observe the composition and content of samples annealed at different temperatures (100 °C, 200 °C, 300 °C, 400 °C, 500 °C) for 2 h.

Here in our research, at the first or beginning decomposition step (20 °C–150 °C), the as-spun BFO/PVP composite nanofibers are dried in the air, the weight loss on account of the release of adsorbed water and other solvents from BFO/PVP nanofibers in an endothermic reaction (8% mass loss). There is no corresponding peak in the XRD diagrams at 100 °C.

The second decomposition take placed in the temperature range 150 °C–350 °C, where the largest mass loss (50%) occurred. The dramatic mass loss in the TG curve and the very sharp exothermic peak on the DSC curve, indicating the thermal events related to the breakdown of the organic PVP matrix along with the decomposition of Fe and Bi nitrates [22, 23], which were released as CO₂, NO₂, and H₂O. In parallel to gas release, some
amorphous substances are gradually converted to the carbonate phase, as confirmed by XRD, the BiO$_2$CO$_3$ crystalline peaks appear near theta = 28° at 300 °C.

At the third decomposition step in the temperatures range 350 °C–450 °C. In this final decomposition stage, the removal and burning of the carbonized residues of organics along with bismuth oxycarbonate begin to decompose and transform into the BiFeO$_3$ phase. Again, a small peak observed on the DSC curve in this region, indicated the decomposition of carbonate and the formation of the crystalline BFO phase by solid-state reaction. Corresponding in XRD, the peak of which index to BiO$_2$CO$_3$ disappeared, and the peak index to BFO appeared. Finally, the plateau region observed between 450 °C–800 °C. It demonstrates that no residues needed to be further decomposed.

FTIR measurement of BFO nanofibers was also carried out after the annealing process under different temperatures. Wide range spectra (500–4000 cm$^{-1}$) of the samples are presented in figure 2(c) and table in figure 2(d) show the value of different chemical groups’ characteristic absorption peaks obtained from the FTIR. Which verified the perovskite structural formations of BFO. The broad band at 3200–3600 cm$^{-1}$ was corresponding to the symmetric and antisymmetric stretching of the OH group [24]. The absorption peak of C–H at 2927 cm$^{-1}$ and 2853 cm$^{-1}$ correspond to the stretching and bending vibration of CH$_2$ in PVP and Hacac. The absorption peak at 1655 cm$^{-1}$ corresponds to the C=O group in PVP. With the increase of heating temperature, those characteristic peaks decrease gradually. When the temperature reaches 500 °C, the sample does not show any signs of the presence of carbonate (the band around 1655 cm$^{-1}$) and nitrates (the band around 1384 cm$^{-1}$) [25]. Instead, significant absorption peaks near 440 and 560 cm$^{-1}$ are assigned to the stretching and bending vibration of the Fe–O in FeO$_6$ octahedral [26]. The perovskite structure formation can be verified via the Fe–O band in this region [8]. The FTIR results are meeting with the previous thermogravimetric and XRD results. Therefore, in this work, the Optimization of the annealed temperature and time for samples were 650 °C and 2 h respectively.

Figure 3(a) shows the micro-morphology of the image of the uniform 1D as-spun BFO/PVP nanofibers, the mean diameter of the fibers was about 580 nm. After the calcination treatment, the BFO nanofibers (figure 2(b)) maintain a fibrous shape but show reduced and uneven diameter (≈383 nm), the decomposition of PVP from the nanofiber is the reason for the reduction in dimension of annealed fibers. With the increase of Co$^{3+}$ doping amounts, the diameter becomes smaller (the mean diameters of BFCO-1 and BFCO-2 are ≈286 and ≈278 nm respectively), this is owing to appropriate Co$^{3+}$ doping maybe inhibits the growth of BFO grain during the sintering process that is consistent with previous reports [27, 28].

Figure 4 shows the XRD patterns of BFO, BFCO-1, and BFCO-2 nanofibers. All the main peaks are well following standard data (JCPDS card#20-0169). It was found that the phase structure and crystal structure of these one-dimensional nanostructures were rhombohedral distorted perovskite (ABO$_3$) structure and spatial R3c. The strong and sharp diffraction peaks indicated good crystallinity of the samples in the patterns of the nanofibers. A small quantity of the impurity phase that identified as Bi$_2$Fe$_3$O$_9$ [15] and Bi$_{25}$Fe$_{40}$O$_{74}$ [29] were also detected, which could be the metastable phase come from the BFO-based materials synthesis process [17, 30]. The views of the XRD patterns (2θ from 31.5° to 33.5°) was enlarged in the figure 4 (bottom). Compared to the
pure BFO nanofibers, it can be observed that the two major peaks, assigned to (104) and (110) planes, have slightly shifted towards higher diffraction angle values with the increasing of Cobalt concentration. This result is differing from other element doping samples (such as Y3+ [31], Zn2+ and Ti4+ [17], La3+ [32]), which two major peaks are moving towards to the higher angle side and having merge trends with the doping element increasing [33]. It can be used a variation of Goldschmidt tolerance factor to explain as follow [17]:

\[
t = \frac{(r_{\text{Bi}^{3+}} + r_{\text{O}^{2-}})}{\sqrt{2 \left[ (1 - x) r_{\text{Fe}^{3+}} + x r_{\text{Co}^{3+}} + r_{\text{O}^{2-}} \right]}}
\]

where \(r_{\text{Bi}^{3+}}, r_{\text{O}^{2-}}, r_{\text{Fe}^{3+}}, \text{and } r_{\text{Co}^{3+}}\) assigned to the radius of the Bi3+, O2−, Fe3+ and Co3+ ions, respectively. The value of \(t\) is equal to one for the ideal perovskite structure. As the ionic radius of Co3+ (0.650 Å) is similar to the ionic radius of Fe3+ (0.645 Å) ions, the \(t\) value is expected to be slightly changed with the concentration of Co3+ doping. On the contrary, as the radius of Y3+ (0.890 Å) etc. is larger than Fe3+, the Y-doping would decrease the value of \(t\). The small \(t\) means compresive strain acting on the lattice, which leads to the distortion. Therefore, differ from other elements doping, Co3+ has little effect on the lattice structure.

Polarization versus electric field (P–E loop) measurement of the BFO and BFCO-2 samples at room temperature are presented in figure 5. Because the sintered samples are brittle, it is difficult to add an electric field along the axis of BFO nanowires directly. The obtained nanofibers were ground and then pressed into cylindrical sheets with a diameter of 5 mm and a height of 0.5 mm by isostatic pressing. Then both sides of the sample deposited Pt point electrodes by magnetron sputtering. The area of the electrode is 0.25 mm². The pure BFO sample displays a well-defined hysteresis loop, indicating the good ferroelectric nature of the nanofiber. Meanwhile, the same measurement on the BFCO-2 sample shows a decrease in ferroelectricity property (the value of \(P_r\) from 1.25 to 1.07 μC cm⁻²), this is due to the bonding of Fe3+ ion to six O2− has two different bond lengths, the doping of Co element in BFO results in a decrease in the differentiation of two lengths, lead to the homogenizing of the Fe–O bonds in the octahedral. Therefore, cobalt element doped BFO nanofibers should have less polarity compared to pure samples in nature [34].

The magnetization hysteresis curves (M–H) for BFO nanofibers with various Co doping concentrations measured at room temperature with a magnetic field of 20 kOe are presented in figure 6(a). Compared to the bulk BFO ceramic, the nanofibers exhibit enhanced magnetization values (The bulk BFO do not exhibit
magnetism due to G-type ordering [35], the improved magnetization originates from associated size-dependent magnetic behavior [13]. Meanwhile, the Co doping effectively enhanced the magnetism of BFO, the values of remanent magnetization (Mr) are 0.18, 0.96, 1.72 emu g$^{-1}$, and saturation magnetization (Ms) is 0.86, 2.32, 3.98 emu g$^{-1}$, and coercive force (Hc) are 150, 1146, 1288 Oe for BFO, BFCO-1, and BFCO-2, respectively. The Mr values of BFCO-2 has a remarkable enhanced, nearly ten times as much as that in pure nano fibers. According to the previous XRD results, the nano fibers are rhombohedral distorted perovskite (ABO$_3$) structure with no secondary magnetic phases. Therefore, it can be assumed that the magnetization enhanced due to the addition of cobalt. If the iron of BFO is substituted by the added cobalt at the B-site, the differences of the magnetic moment between Co$^{3+}$ ($\sim$4 $\mu B$) and Fe$^{3+}$ ($\sim$5 $\mu B$) might be attributed to suppress the G-type antiferromagnetic spin structure of BFO [36]. Total spontaneous magnetization increased due to the breaks of the antiferromagnetic spin structure of Fe$^{3+}$. Therefore, When Co atoms start to substitute Fe atoms, and the total magnetic moment increases with the increase of cobalt content. Further, to understand the origin of the magnetism of the nanofibers, different elements’ chemical oxidation state in samples were studied using x-ray photoelectron spectroscopy technique and the corresponding spectra are presented in figure 6(b). A scan of three samples’ Fe 2p line is presented in figures 6(c)–(e). The position of Fe 2p is expected to be at 711 eV for Fe$^{3+}$ and 709.5 eV for Fe$^{2+}$. The peak fitting analysis demonstrates that both Fe$^{2+}$ and Fe$^{3+}$ coexist in undoped BFO and Co doping BFO nanofibers. That is inevitable because the sintering process takes place in the air, which would cause the valence fluctuate of Fe ions. The amount of Fe$^{3+}$ ions gradually decreases with the increasing

**Figure 5.** Polarization versus electric field, P-E loop of BFO and BFCO-2 at room temperature.

**Figure 6.** (a) Magnetization hysteresis (M–H) curves of undoped and Co-doped BFO nanofibers measured in a magnetic field of 20 kOe at room temperature, (bottom) the magnified patterns in a magnetic field of 5 kOe, (inset) Photographs of BFO and BFCO-2 with a magnet. XPS spectra of samples: (b) survey spectra. The Fe 2p3/2 state contains the contributions from the Fe$^{2+}$ and Fe$^{3+}$ ion states: (c) BFO, (d) BFCO-1, (e) BFCO-2.
amount of Co substitution. The ion Fe$^{3+}$, Fe$^{2+}$, and Co$^{3+}$ would lead to a minor distortion of local structure and possible have a double exchange interaction through oxygen between 2$^{+}$ and 3$^{+}$ ions [12]. This factor may cause enhanced magnetic behavior in the cobalt doped-BFO nanofibers.

### 4. Conclusions

In summary, the cobalt doped BFO nanofibers were successfully prepared by sol-gel based electrospinning methods. The XRD patterns confirmed the R3C structure of BFO nanofiber and doped-BFO nanofibers. With the Co doping amount increasing, the magnetic properties are enhanced gradually, the maximum remanent magnetization was approximately 1.72 emu g$^{-1}$ (0.18 emu g$^{-1}$ for pure BFO nanofiber) at a cobalt content of 10 at%, apparently higher than the Cobalt doped BFO in the previous literature with the same doping level(Mr = 0.7 emu g$^{-1}$ [20]). The improvement of magnetism can be attributed to the Cobalt doping and size-effect. The implication of the Cobalt doping BFO nanofibers has great application potential in multifunctional nano-devices.

### Acknowledgments

This work was supported by the Research Foundation of Education Bureau of Fujian Province, China (Grant No. JAT170394, No. JAT170395), PhD research startup foundation of Fujian University of Technology (No. GY-Z160137).

### ORCID iDs

Sujian You @ https://orcid.org/0000-0001-6356-3431
Bin Zhang @ https://orcid.org/0000-0002-5698-1499

### References

[1] Wang J et al 2003 Science 299 1719–22
[2] Carranza-Celis D et al 2019 Sci. Rep. -UK 9 3182
[3] Spaldin N A and Ramesh R 2019 Nat. Mater. 18 203–12
[4] Fiebig M et al 2016 Nature Reviews Materials 1 16046
[5] You H et al 2019 Angewandte Chemie. 58 11779–84
[6] Jia T et al 2018 Applied Physics Reviews 5 021102
[7] Yin L and Mi W 2020 Nanoscale 12 477–523
[8] Das R et al 2016 Journal of Magnetism and Magnetic Materials 401 129–37
[9] Tabares-Munoz C et al 1985 Jpn. J. Appl. Phys. 24 1051
[10] Sobhan M et al 2015 Epl-Europhys. Lett. 111 18005
[11] Ming L and Ziyao Z ed 2019 Integrated Multiferroic Heterostructures and Applications (New York: Wiley) 3 51–119 https://www.wiley.com/en-cn/Integrated-Multiferroic-Heterostructures-and-Applications-p-9785527803699#content-section Integrated Multiferroic Heterostructures and Applications Integrated Multiferroic Heterostructures and Applications Integrated Multiferroic Heterostructures and Applications Integrated Multiferroic Heterostructures and Applications Integrated Multiferroic Heterostructures and Applications

[12] Wang Y et al 2006 Appl. Phys. Lett. 88 142503
[13] Park T J et al 2007 Nano Lett. 7 766–72
[14] Zhang X Y et al 2005 Appl. Phys. Lett. 87 143102
[15] Xie S H et al 2008 Appl. Phys. Lett. 93 222904
[16] Wei J et al 2008 Scripta. Mater. 58 45–48
[17] Zhu J H et al 2018 Ceram. Int. 44 9215–20
[18] Wang B et al 2012 Ceram. Int. 38 6643–9
[19] Wang Y et al 2008 Mater. Lett. 62 3806–8
[20] Xu Q et al 2009 Applied Physics Letters 95 112510
[21] Yang K et al 2010 Journal of Applied Physics 107 124109
[22] Ponhan W and Maensiri S 2009 Solid State Sciences 11 479–84
[23] Szilagyi I M et al 2011 Journal of Thermal Analysis & Calorimetry 105 73
[24] Gabbasova Z V et al 2010 Physics Letters A 38 7 14849–1
[25] Zaleskii A V et al 2003 Physics of the Solid State 45 141–5
[26] Rao C N R et al 1970 Applied Spectroscopy 24 436–43
[27] Yang R et al 2018 Ceramics International 44 14032–5
[28] Feng Y N et al 2013 Journal of Applied Physics 113 146101
[29] Marzouki A et al 2017 Acta. Mater. 145 316–21
[30] Ren J et al 2018 Journal of Alloys & Compounds 766 50925838818324502
[31] Fang-Cheng L U et al 2017 Ceramics International 43 16101–6
[32] Lin Y H et al 2007 Applied Physics Letters 90 172507
[33] Arya G S et al 2013 Mater. Lett. 93 341–4
[34] Ray J et al 2015 J. Alloy Compd. 628 32–8
[35] Kumar M M et al 2012 Journal of Magnetism & Magnetic Materials 388 203–12
[36] Naganuma H et al 2008 J. Appl. Phys. 103 07E314