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Strong room temperature spontaneous exchange bias in BiFeO₃-CoFe₂O₄ nanocomposites



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ABSTRACT

BiFeO₃-CoFe₂O₄ nanocomposites were synthesized by hydrothermal method and an enormous spontaneous exchange bias (3000e) observed during the measurement of our samples in an unmagnetized state without field cooling. The measuring field dependent Hc is monotonic increase, the exchange bias effect decreases as the sweeping range of the measuring field increases. Moreover as the CoFe₂O₄ proportion increases, the exchange bias effect first increases to the maximum and then decreases. This effect suggests that the magnetic unidirectional anisotropy can be set isothermally (room temperature) during the initial magnetization process due to the interface coupling between ferrimagnetic and antiferromagnetic phases in BiFeO₃-CoFe₂O₄ nanocomposites. A possible model proposed to explain the mechanism underlying our experimental results reasonably.

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1. Introduction

Since the exchange bias (EB) discovered by Meiklejohn and Bean in 5 decades ago [1]. Researchers have focused on its fascinating fundamental physics and important applications. Usually EB is induced in a system consisted with ferromagnetic (FM)-antiferromagnetic (AFM) that is cooled with external magnetic field through the Néel temperature (T_N) of the AFM, showing a shift of the hysteresis loop [M(H)] along the applied magnetic field and an increase of the coercivity(Hc) [2–4]. Experimental and theoretical studies show that the EB phenomenon of FM/AFM system is an effect of interfacial magnetic coupling. Nogúes et al. [3] believed that the FM unidirectional anisotropy (UA) in the EB systems could formed by reconfiguring the FM spins at the interface between FM/AFM phases. In addition, reports showed that EB also could be built up in FM-spin glass (SG) [5], AFM-ferrimagnetic(FiM) [6] and FM-FiM [7]. Generally the conventional EB (CEB) effect can be obtained through

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the process of field cooling (FC) [3]. Recently, studies have suggested that the EB could also be realized by depositing the AFM layer onto a saturated FM layer [2,3], ion irradiation in an external magnetic field [8], zero-field cooling (ZFC) with remnant magnetization [9,10]. The above methods all set UA before the hysteresis loop measurement, however, an alternative way to obtain EB by ZFC with an unmagnetized State reported, in which the UA spontaneously set during the hysteresis loop measurement [11–13].

The EB effect that is obtained by ZFC is termed as spontaneous exchange bias (SEB). In SEB, the UA sets spontaneously under the application of the external magnetic field during the first hysteresis loop measuring. SEB have been observed in the Fe/Mn film [14], BiFeO₃-Bi₂Fe₄O₉ composite [13], Nd_{1-x}Sr_xCoO₃ nanoparticles [15], LaFeO₃ nanoparticles [16]. Hossein Ahmadvand et al. [16] observed SEB effect in antiferromagnetic LaFeO₃ nanoparticles synthesized by the sol–gel method, and proposed that the SEB is originated from the coupling between the FM shell and the AFM core of the particles. And the appearance of EB due to the reversal of the AFM spins without the conventional field cooling. Tuhin Maity et al. [13] prepared nanocomposite of core-shell BiFeO₃-Bi₂Fe₄O₉ and found a glassy moment at the interface breaks the symmetry truly spontaneously even before the application of the first measuring field to set the UA in an unmagnetized state.





¹ Yue Huang and Song Li contributed to this work equally, should considered as co-first authors.

However, no matter CEB or SEB, they are usually obtained at low temperature because of the relatively low Néel temperature of AFM. Ali et al. [5] prepared Co/CuMn bilayer and found EB vanished above the temperature of 100 K for selected Cu₅₀Mn₅₀. Ding et al. [17] prepared LSMO/SMO bilayer and EB appears below a blocking temperature $T_{\rm B}$ of about 130 K. If the blocking temperature could be raised to room temperature, and meanwhile the exchange bias effect was sufficiently large, it would be hope of creating a truly practical magnetoelectric device. BiFeO₃(BFO) is a unique singlephase multiferroic material that displays both ferroelectric and antiferromagnetic ordering at room temperature. Its antiferromagnetic Néel temperature of 640 K and ferroelectric Curie temperature of 1100 K. Therefore, BFO is a prime candidate for device integration [18–20]. Martin et al. [18] observed large negative exchange bias and negligible training effect at room temperature in the study on BiFeO₃/SrRuO₃/SrTiO₃/Si(001) epitaxial films, MacManus-Driscoll et al. [21] reported larger exchange bias values with high H_{EB}/H_{C} ratio at room temperature in the study on the self-assembled BiFeO₃-Fe₃O₄ heteroepitaxial nanocomposite films. Furthermore, Electric field controlled magnetization and exchange bias have been achieved at room temperature in BFO related systems due to the magnetoelectric effect, which supplies additional degree of freedom in applications [22,23].

2. Experimental methods

In this letter, a series of BFO-CoFe₂O₄ composites were synthesized by hydrothermal method.

2.1. Synthesis of $BiFeO_3$ -CoFe₂O₄ nanocomposites by hydrothermal method

First, iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$ and cobalt nitrate $Co(N-O_3)_2 \cdot 6H_2O$ were dissolved in deionized water by 2:1 M ratio. The pH value of the solution was adjusted to 13 by adding 5 mol/L sodium hydroxide solution with vigorous stirring. After then the solutions were transferred into autoclaves and sealed, and then heated at 160°Cfor 8 h and followed furnace-cooled naturally to room temperature. Gray powders were obtained after filtration. Finally CoFe₂O₄ nanoparticles were obtained after drying at 60 °C for 12 h.

Bismuth nitrate $Bi(NO_3)_3 \cdot 5H_2O$ and iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in deionized water. The pH value of the solution was adjusted to 13 by adding 5 mol/L sodium hydroxide solution. Then the CoFe₂O₄ nanoparticles synthesized previously were added into the above solution and stirred for 10 min. After then the solutions were transferred into autoclaves and sealed, and then heated at 200°Cfor 6 h and followed furnace-cooled naturally to room temperature. The products were washed and then isolated by centrifugation. The final products were obtained after drying at 60 °C for 12 h. To study exchange bias influenced by the constitution of the composites, we synthesized BiFeO₃-CoFe₂O₄ nanocomposites with different stoichiometric proportions as shown in Table 1.

2.2. Characterization of BiFeO₃-CoFe₂O₄ nanocomposites

The crystal structures of the samples investigated by x-ray diffraction (XRD) and the micrographs of the samples studied by

Table 1				
A series of samples with t	heir phase mol	ar ratio.		
Number	D1	D2	D3	

Number	D1	D2	D3	D4	D5
CoFe ₂ O ₄ :BiFeO ₃ (molar ratio)	10:90	15:85	20:80	25:75	30:70

transmission electron microscopy (TEM). The Magnetic properties of the samples measured by Vibrating Sample Magnetometer (VSM).

3. Result and discussion

Fig. 1 shows the XRD patterns of the BiFeO₃-CoFe₂O₄ composites. The XRD pattern of BiFeO₃ shows that there are no obvious impurities. However, There is a hump(around 21°) in composites(D1, D2, D3, D5) corresponds to Bi2Fe4O9(020). According to Fig. S1 and equation. S(1) in supporting information, the added CoFe₂O₄ partly dissolved in solution of the hydrothermal process, which induces in Fe³⁺ concentration increased and then the formation of Bi₂Fe₄O₉ was promoted, therefore, Bi₂Fe₄O₉ impurities appear in this composites(D1, D2, D3, D5). In addition, A weak peak at 48.4° (marked by two red arrows) can be observed in D2 and D3 samples, which can be indexed to BiFeO₃ as compared with the standard XRD pdf card of BiFeO₃. The diffraction peak of CoFe₂O₄ on D1 cannot be observed due to the small content of $CoFe_2O_4$ (the content of $CoFe_2O_4$ is 10%) in this sample. With the increase of CoFe₂O₄ contents in the nanocomposites, the diffraction peaks of CoFe₂O₄ come out with the intensity of the corresponding peak of CoFe₂O₄ gradually increased. Three diffraction peaks of CoFe₂O₄ on sample D5 (the content of CoFe₂O₄ is 30%) were marked.

To observe the structure of samples in detail, transmission electron microscopy (TEM) study have been done on D1, D3 and D5 samples and the morphologies of the corresponding samples are shown in Fig. 2(a), (b) and (c). Fig. 2 suggests that CoFe₂O₄ and BiFeO₃ grains are mixed. Compared with Fig. 2(a)-(c), one can see that the average grain size is gradually increased as the content of CoFe₂O₄ gradually increased. This result could be understood in view of that the added CoFe₂O₄ partly dissolved and induces in the alkalinity of the solution increased, which promoted the growth of the BiFeO₃ particles. Such deduction is supported by the reaction time dependent grain size of the products shown in Fig. S1, reaction dynamic equation S(1) and the corresponding analyze in detail[see the supporting information]. Fig. 2(d) is the high resolution TEM (HRTEM) image of D3 sample. Two distinctive crystal lattice stripe images observed and the space distances has been calibrated and indexed. The interplanar distance of 0.387 nm is corresponded to the (101) planes of BFO and 0.256 nm corresponded to the (311) planes of CoFe₂O₄, and Fast Fourier transform (FFT) of the corresponding regions shown in the inert to Fig. 2(D) and confirmed the



Fig. 1. The XRD patterns of BiFeO₃-CoFe₂O₄ composites with different stoichiometric proportions.



Fig. 2. TEM image of sample D1(a), D3(b), D5(c) and HRTEM image of sample D3(d), the insets are FFT of specific area.

selected regions are BiFeO₃ and CoFe₂O₄ grains, respectively. Such results further suggested the sample are BiFeO₃ and CoFe₂O₄ nanoparticles inter-embedded composites. Furthermore, TEM results suggest that the average grain size of BFO is larger than that of CFO, and most of the grain size of CFO is in range of 20–30 nm. Considering the magnetic property of CFO, the nanoscale CFO could be in the states of parameters or super-parameters, thus, the globe magnetic behavior of CFO could be spin-glassy.

Room temperature applied magnetic field dependent magnetization of samples D1-D5 were measured and the hysteresis loops of the corresponding samples are shown in Fig. 3(a), the swept filed is in range of ± 1.5 kOe and the inert to Fig. 3(a) is the enlarged M-H loops of samples D1-D5 with the applied magnetic field in range of $\pm 2000e$. Fig. 3(a) indicates that with the increase of the content of CoFe₂O₄ in the studied samples, the magnetization at 1.5 T applied field and the coercivity Hc of the corresponding samples gradually increased. The insert to Fig. 3(a) indicates that the M-H loops of the samples are shifted both in horizontal and vertical, this result suggests that there is exchange bias effect in these samples, the largest shift of the M-H loop observed on D3 (the content of



Fig. 3. (a) Room temperature M-H loops of samples D1-D5, the swept filed is in range of \pm 1.5 kOe, and the insert is the enlarged M-H loops near zero applied magnetic field. (b) Hysteresis loops of sample D3 under different measurement magnetic field at room temperature, the inert is applied measurement filed dependent Hc of D3.



Fig. 4. (a) Exchange bias and (b) vertical magnetization shift of group D under different measurement magnetic field.

CoFe₂O₄ is 20%) sample.

To explore the exchange bias effect in the studied samples, the M-H loops of all the samples were measured with the swept external applied magnetic field in range of ± 2 , ± 2.5 , ± 4 kOe at room temperature, respectively. Here, the M-H loops measured under different applied field of sample D3 were shown in Fig. 3(b), and the insert to Fig. 3(b) is the applied filed dependent Hc of sample D3.

Fig. 3(b) reveals that obvious exchange bias effect can be observed as the hysteresis loop shifts both to the negative field and positive magnetization. The horizontal shift along the field axis is defined as the exchange-bias field H_E and the vertical shift is defined as the magnetization shift M_E. Fig. 3(b) clearly shows that H_E and M_E reduced with the measurement magnetic field increased. The inert to Fig. 3(b) demonstrates that the coercivity Hc of this sample is gradually increased as the applied measurement field increased. Compared with conventional EB [16], the EB effect observed in Fig. 3 is SEB. Usually the EB effect of BFO-based system can be observed at room temperature is under field cooling from higher temperature(700 K) [21] or growing films with applied field [18], but few studies about EB effect of unmagnetized State. The similar phenomenon that EB effect reduces with increasing measure field also observed in perovskite cobaltite La_{1-x}Sr_xCoO₃ [24].

Fig. 4 shows the variation of H_E and M_E on D1-D5 samples under different measuring fields. It is clearly seen that both the H_E and M_E decrease with the increase of the measurement field, indicating that the exchange bias effect decreases as the measurement field increases. The maximum H_E of about 3000e under 1.5 KOe measurement field was observed on sample D3, i.e. small applied field induces a relatively large spontaneous exchange bias effect at room temperature. Compared with different samples, Fig. 4 suggests that D1 shows almost no exchange bias effect, D3 has the largest H_E and M_E under all the measured applied field, while the H_E in D4 is smaller than that in D3 but larger than that in D5. The M_E in D1-D5 has similar behavior with that of H_F in the corresponding samples. According to the TEM results in Fig. 2, when the content of CoFe₂O₄ increases, average grain size of CoFe₂O₄ and BiFeO₃ increases. Such a result induce in two effects, one is the increase of magnetism of CoFe₂O₄ and another is the decrease of the interface density. These two of these factors have a contrary contribution to exchange bias, the increase in magnetic property will enhance exchange bias effect but the decrease of interface density between CoFe₂O₄ and BiFeO₃, therefore, has negative effect on enhancing exchange bias. Thus, the observed SEB can be explained in view of the competition between the increase in gain size of CoFe₂O₄ and the decrease of interfaces between CoFe₂O₄ and BiFeO₃. When the content of CoFe₂O₄ is low, the magnetization of sample is low, so weak SEB was observed in sample D1. With the increase of the CoFe₂O₄ content in the samples, the average magnetization of CoFe₂O₄ increased while the density of interfaces between CoFe₂O₄ and BiFeO₃ reduced a little, in this case, the globe effect of the increase of the CoFe₂O₄ content in the studied samples has positive effect on the enhancement in SEB just observed in Sample D3. As the content of CoFe₂O₄ in the studied samples further increases, the reducing of the density of the interfaces between CoFe₂O₄ and BiFeO₃ has dominated contribution to the SEB, thus the SEB effect reduced as observed in sample D5. In this way, the result in Fig. 4 is reasonable explained.

As known, the appearance of EB needs the spin coupling near the interface between FiM/AFM systems. As suggested in Fig. 2, our samples are nanoparticles in which, FiM $CoFe_2O_4$ and AFM BiFeO₃ are inter-embedded. Thus, the understanding of EB effect in our samples, the interface spin coupling between $CoFe_2O_4$ and BiFeO₃ should be considered. On view of energy, Zeeman energy and anisotropy energy of the FiM clusters E_{ZF} and E_{FiM} , the anisotropy



Fig. 5. (a) Simplified schematic diagrams of the FiM domains embedded in an AFM single domain under external magnetic field. (The white arrows represent that the spins direction of FiM domains) (b) FiM and AFM spin interaction at the interface. (The dotted red rectangle represents the establishment of UA). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

energy of the AFM EAF, and the exchange energy at the FiM/AFM interface Eint compete due to spin coupling and contribute to the formation of the SEB. Therefore, when the effective Zeeman energy E_{Zeff} ($E_{Zeff} = E_{ZF} - E_{FiM}$) is smaller than E_{int} , the E_{Zeff} is too weak to overcome the interfacial energy barrier. In this case, parts of FiM spins will stay frozen state, and keep the original orientation as the applied magnetic field reverses, such a state will induce a vertical magnetization shift, namely, M_E [24]. As $E_{Zeff} > E_{int}$, FiM spins can rotate with applied magnetic field, and build up a coupling between the AFM. In this case, FiM spins at the interface induces an additional torque spins, which will lead to EB effect [3]. Meanwhile, the structural defects or grain size distribution or surface coarse cause the AFM anisotropy has local variations. For the low AFM anisotropy case, the spins in the AFM can be dragged by the spins in the FiM, and results in its coercivity enhancement (without loop shift). In general, both effects can be observed simultaneously [2].

The reasons for the exchange bias effect changing with the measuring field in sample D3 are as follows. As the measuring field increases, the effective Zeeman energy of FiM clusters increases [11,24], as a consequence the proportion of the FiM spins staying 'frozen' reduces which will cause M_E decreases. Meanwhile the FiM clusters grow up with increasing applied magnetic field [11,25]. As the increment of the size of the FiM clusters, the relative proportion of the AFM to the FiM clusters significantly decreases. The small portion of the AFM spins cannot pin the huge moments of the FM region. Consequently, EB effect weakened (i.e. H_F decreases). This effect is similar to the FM/AFM bilayer system where the EB disappears as the AFM layer thickness less than a critical value and $H_{\rm F}$ is approximately inversely proportional to the FM layer thicknes $s(HE \propto 1/t_{FM})$ [2,3]. The coercivity Hc increases with the measuring field increases which shows more AFM spins can rotate with increasing measuring field [2]. The Zeeman energy of AFM spins (which is proportional to the magnitude of magnetic field) is larger than the exchange energy of FM-AFM at the interface (E_{int}) and their anisotropy energy (E_{AF}) , the applied field will align these AFM spins along the direction of external field [11]. The rotated AFM spins can't pin the FiM spins, so it will lead to the decrease in H_F with increasing measuring filed and usually accompanied by an increase in the coercivity Hc [16].

Fig. 5 is the schematic diagram of a possible model to explain our experimental results. The Curie temperature of CoFe₂O₄ is 793 K and Néel temperature of BiFeO3 is 643 K [26], at room temperature CoFe₂O₄ is ferrimagnetic and BiFeO₃ is antiferromagnetic. Duo to the structural defects or grain size distribution [2] and the random field from frozen SG spin moments [13,16], it will induce a variation in the anisotropy of the AFM. Respect to the principal easy axes of AFM grains, the AFM grains may be fully hysteretic, nonhysteretic or partially hysteretic with applied field. The partially hysteretic AFM grains set the UA, in a direction opposite to the applied field, it shows in Fig. 5(b). The spins of AFM pin the FiM spins as 'pin effect' at the interface of FiM/AFM. When the direction of magnetic field reversed and if the magnetic field is relatively low, a part of FiM spins will still keep the initial direction of magnetic field, and this will show up as a vertical magnetization shift. Other FiM spins can rotate when the direction of magnetic field reversed by overcoming the 'pin effect' at the interface, and this will lead to EB effect. The 'pin effect' occurs under conditions of rotatable FiM spins and non-rotatable AFM spins with applied field reversed. AFM spins fail to reverse with the magnetic field due to the spins cannot overcome higher anisotropic energy barrier [27]. The 'pin effect' made the inversion of FiM spins at interface needs more addition energy. For the low AFM anisotropy case, the AFM spins can be dragged by the spins in the FiM, so spins of AFM and FiM can reverse together when the applied field reverses. This will cause coercivity enhancement.



Fig. 6. Hysteresis loops of $CoFe_2O_4$ nanoparticles under different measurement magnetic field, and the insert to Fig. 6 is then M-H loops of BiFeO₃ performed under different external fields.

To make sure that the EB is originated from BiFeO₃-CoFe₂O₄ composites, VSM test was done on CoFe₂O₄ and BiFeO₃ nanoparticles at room temperature. From Fig. 6, there are hysteresis loops in CoFeO₄ nanoparticles under different applied magnetic field, but there are no shift of hysteresis loops. The BiFeO₃ nanoparticles have no hysteresis loop and the magnetic field dependence of magnetization curve is a straight line due to the antiferromagnetic of BiFeO₃ as shown in the insert to Fig. 6. From Fig. 6, it is reasonable to conclude that the observed exchange bias shown in Fig. 4 is induced by the coupling between FiM CoFe₂O₄ and AFM BiFeO₃.

4. Conclusion

In summary, we report an enormous and tunable spontaneous exchange bias of 300 Oe at room temperature in nanocomposites of BiFeO₃-CoFe₂O₄. In sample D1(CoFe₂O₄:BiFeO₃ = 1:9) we cannot observe the exchange bias effect but the other samples do. In sample D3 it can be observed the maximum H_E (3000e). Considering the SEB is significant influenced by the ratio of CoFe₂O₄ and BiFeO₃, we propose the phase interface plays an important role in exchange bias. The measuring field dependent Hc is monotonic increase, the exchange bias effect decreases as the sweeping range of the measuring field increases. Moreover as the CoFe₂O₄ proportion increases, the exchange bias effect first increases to the maximum and then decreases. This phenomenon is attributed to unidirectional anisotropy formed during the initial magnetization process at room temperature.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jallcom.2018.05.125.

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