Role of oxygen vacancies in deciding the high temperature magnetic properties of Ba and Sm substituted BiFeO$_3$ ceramics

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Abstract

A series of Bi$_{1-x}$A$_x$Fe$_2$O$_5$ (A = Ba$^{2+}$, Sm$^{3+}$) compounds have been synthesized in order to reveal the influence of oxygen vacancies on the magnetic behavior of BiFeO$_3$. While the rhombohedral structure is retained for all compositions (0 $<$ x $<$ 0.2), the Ba$^{2+}$ and Sm$^{3+}$ substitution induces different structural disorder, leading to an enhancement in magnetization. Temperature dependence of magnetization between 300 K and 900 K indicates that the increased oxygen vacancy due to Ba$^{2+}$ substitution gradually turns the original antiferromagnetic behavior of BiFeO$_3$ into a ferromagnetic one. In contrast, the antiferromagnetic nature of BiFeO$_3$ is maintained in the whole Sm$^{3+}$ substitution range, in which the concentration of oxygen vacancies is preserved. This result reveals unambiguously that the oxygen vacancies also play a crucial role in deciding the magnetic behavior of BiFeO$_3$. The intrinsic magnetic property of BiFeO$_3$ is originated from not only the Fe$^{3+}$/Fe$^{3-}$ but also the unbalanced Fe$^{3+}$/Fe$^{2+}$ antiferromagnetic superexchange interactions.

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1. Introduction

The multiferroic bismuth ferrite (BFO), which belongs to the perovskite structured (ABO$_3$) family, crystallizes into distorted rhombohedral structures with the space group R3c and turns into antiferromagnetic phase at the Néel temperature ($T_N$) of 643 K while maintaining the ferroelectricity with a ferroelectric transition temperature ($T_C$) of 1103 K [1]. Due to its large magnetic-electric coupling at room temperature, the multiferroic BFO becomes one of the most promising candidates for potential applications in the fields of multiple-state memories, spintronics, magneto-electric sensor devices and so on [2–5], and has attracted extensive research attentions.

However, even though BFO exhibits attractive properties, it also has some sticky issues to confront. Due to the volatilization of Bi$_2$O$_3$ in the sample synthesis process, the impurities of Bi$_2$Fe$_4$O$_9$, Bi$_2$Fe$_5$O$_{10}$, et.al. are commonly existent in BFO [6,7]. Additionally, oxygen vacancies arising from the volatilization are always present in BFO and can compel the Fe$^{3+}$ to change valence state (leading to Fe$^{2+}$) in order to compensate the charge unbalance in BFO [8]. Associated with the impurities and oxygen vacancies, the high leakage current often adversely affects the effective measurements of the ferroelectric and dielectric properties of BFO. On the other hand, the magnetic structure of BFO is related to the complex superexchange interaction between Fe$^{3+}$ ions and forms a cycloidal spiral spin structure with a spin periodicity of 62 nm [1,5]. The antiferromagnetic nature of BFO cancels out the net macroscopic magnetization in BFO [9–13].

Aiming to overcome these difficulties, many efforts have been made and it has been demonstrated that the enhanced magnetization, dielectric constant, ferroelectric polarization and magneto-electric properties of BFO can be realized through nanotechnology and partially substituting the Bi- and/or Fe-sites of BFO with various equivalent/heterovalent cations [13–25]. Moreover, the optical band gap of BFO can be tuned even into the visible region through substituting the Bi-site with alkaline earth metals [13]. Among these works, it is interesting to notice that, apart from the structural distortion-related suppression of spiral spin structure, the present...
of oxygen vacancies is considered to be one possible reason for the enhancement of magnetization in BFO [20–28]. However, the underline physical mechanism of the oxygen vacancies related magnetization enhancement of BFO is still unclear. Additionally, although some interesting magnetic phase transitions are observed in pure and alkaline earth substituted BFO systems at high temperatures (500 K–900 K) [21–25], little attention has been paid to the effect of oxygen vacancies on the high temperature magnetic phase transitions.

The present paper presents the results of a systemic investigation on the influence of oxygen vacancies on the high temperature magnetic behavior of BFO. The concentration of oxygen vacancies can be modulated through Bi-sites element substitution: the Bi-sites partial substitution with divalent ions increases the concentration of oxygen vacancies [17,23], while the replacement of Bi-sites with rare earth elements will not create extra oxygen vacancies [18,19]. For this purpose, Ba and Sm are adopted in this work to substitute the Bi3+ sites to adjust the number of oxygen vacancies, and high temperature magnetic measurements of Bi1−xAxFeO3 (A = Ba, Sm) compounds have been carried out. It is our intention to clearly reveal the role of oxygen vacancies in deciding the magnetic behavior of BFO through comparing the high temperature magnetic evolutions of Bi1−xAxFeO3 (A = Ba, Sm) compounds, and then to get a comprehensive understanding of the magnetic phase diagram of BFO. Different from the previous studies of Ba and Sm substituted BFO systems [17,18], the main focus of the current work is the role of oxygen vacancies in the magnetic transitions at high temperatures, which has been largely ignored.

2. Experimental details

The facile sol–gel technique was employed to synthesize a series of Bi1−xAxFeO3 (A = Ba, Sm) (0 ≤ x ≤ 0.2) compounds. The stoichiometric amounts of high purity Bi(NO3)3·5H2O, Fe(NO3)3·9H2O, Ba(NO3)2 and Sm(NO3)2·6H2O were mixed and dissolved in equal amount nitric acid with added triple-distilled water. An equal amount of ethylene glycol was added with continuous stirring to the obtained solution. Some glacial acetic acid and citric acid were added into this solution to obtain precursor solution. The solution was heated at 80 °C until a sponge gel was formed, and then heated at 350 °C to obtain xerogel powders. Then the xerogel powders were thoroughly grinded in the agate mortar and pressed into pellets of 13 mm in diameter and about 1 mm in thickness. At the end of the process, the pellets were calcinated at 830 °C for 5 min to get high quality Bi1−xAxFeO3 samples.

The structural and phase composition analyses of the samples were carried out with a Bruker D8 Advance x-ray diffractometer with CuKα radiation in the range of 20°–60° at room temperature. The morphology and particle size distribution were determined using the high-resolution scanning electron microscopic (HRSEM) images. The chemical compositions and valence state of Fe in Bi1−xAxFeO3 samples were determined through X-ray photoelectron spectroscopy (XPS). In order to probe the magnetic evolution, magnetization measurements of the samples were performed using vibrating sample magnetometer (VSM). The magnetization loops were obtained at selected temperatures in the field range between −3T ≤ H ≤ +3T. Meanwhile, the magnetization versus temperature plots were measured at 5 Koe over the temperature range of 300 K–900 K. The antiferromagnet Neél temperature T_N was revealed in the magnetization measurement and was signed by the anomalies in the magnetization signal on the heating cycle.

3. Results and discussion

The room temperature X-ray diffraction (XRD) patterns of Bi1−xAxFeO3 (A = Ba, Sm) (0 ≤ x ≤ 0.2) samples are displayed in Fig. 1, which reveal the polycrystalline nature of all the specimens. Different from the previous literature on the heterovalent substituted BFO samples [15,18,21], no structural phase transition has been observed up to 20% Ba or Sm substituting. All the reflection peaks were indexed to the distorted perovskite structure with rhombohedral lattice type and R3c space group. Some traces of secondary phases Bi25FeO40 (less than 5%) were also observed in the XRD patterns. Aforementioned, the occurrence of this impurity phase is due to the Bi2O3 volatilization during heat treatment. Analysis of XRD patterns of Bi1−xAxFeO3 (A = Ba, Sm) (0 ≤ x ≤ 0.2) samples reveals that, due to the ionic radius difference among Bi3+ (R_{Bi} = 1.03 Å), Ba2+ (R_{Ba} = 1.35 Å) and Sm3+ (R_{Sm} = 0.958 Å) [30], the substitution of Bi3+ with Ba2+ and Sm3+ results in different structural distortion: the volume of the unit cell expands with increase the Ba2+ content while contracts when the Sm3+ substitution increase. This is evidenced by the different shift in the peak positions of the XRD pattern of Bi1−xAxFeO3 compounds, as shown in the inset of Fig. 1(a) and (b). Here, no matter the Bi3+ is substituted by Ba2+ or Sm3+, the resultant structural distortion would lead to modulations in lattice parameters, Fe–O–Fe bond angles and bond lengths of BFO [15,18,23,24]. Since the complex substitution change interaction between Fe2+ ions is sensitive to the Fe–O–Fe bond angles of BFO, the Ba2+ and Sm3+ substitution induced structural distortion certainly will affect the magnetic behavior of BFO.

The surface morphology and particle distribution of typical Bi0.8A0.2FeO3 (A = Ba, Sm) compounds were investigated using scanning electron microscopy (SEM) and are shown in Fig. 2. The images show that the grains are roughly rectangular for Bi0.8A0.2FeO3 (A = Ba, Sm) samples and are nonuniformly distributed over the entire surface with certain degree of porosity.

In order to identify the element, chemical shift, and oxidation state of Fe of the pure and Ba/Sm substituted BFO samples, detailed X-ray Photoelectron Spectroscopy (XPS) analysis was performed. The XPS survey spectra of the pure BFO and selected Bi0.8A0.2FeO3 (A = Ba, Sm) compounds are displayed in Fig. 3. As one can see that, the Bi, Fe, and O elements are generally present in the three samples, while the substituted Ba (Sm) element is only identified in Bi0.8Ba0.2FeO3 (Bi0.8Sm0.2FeO3) compound. As to the unexpected element C, it is well known that, the C 1s peak is taken as a reference for the calibration of the binding energy values. So, the XPS results further confirm the chemical compositions of the pure BFO and Bi0.8A0.2FeO3 (A = Ba, Sm) compounds.

For pure BFO, it is widely considered that the Fe ions are a combination of Fe3+/Fe2+ states [8]. In order to evaluate the oxidation state of Fe, and to explore whether the substitution of Bi with Ba/Sm has an effect on the oxidation state of Fe, the narrow Fe 2p line in the XPS spectra for Bi1−xAxFeO3 (A = Ba, Sm) (0 ≤ x ≤ 0.2) compounds are presented in Fig. 4(a). Based on the spectra of BFO, the Fe 2p core level splits into two peaks of Fe2p3/2 and Fe2p1/2. The asymmetric Fe 2p3/2 peak can be further separated into two independent peaks centered at 709.9 eV and 711 eV, as shown in Fig. 4(b). Generally, the binding energy values of 709 eV and 711 eV are considered to correspond to the oxidation states of Fe2+ and Fe3+ [31–34], respectively. So, the asymmetric shape of Fe 2p3/2 peak indicates the combination of Fe3+ and Fe2+ oxidation states in BFO. By calculating the percentage area under the peak obtained from fitting the Fe 2p3/2 spectrum, the concentration of Fe3+ is estimated to be 12% in pure BFO. As to the substituted Bi1−xAxFeO3 (A = Ba, Sm) compounds, the substitution of Bi with Ba/Sm leads to a change in the binding energy value of Fe 2p3/2 when compared to pure BFO, as shown in Fig. 4(a). By fitting the Fe 2p3/2 spectrum of Bi1−xAxFeO3 (A = Ba, Sm) compounds, it has been found that the percentage of Fe2+ is...
existence of Fe2⁺

and negligible residual magnetization are observed for BFO. As for the Bi1₋ₓAxFeO3 compounds, thin hysteresis loops are measured over the magnetic properties of BFO, allowing a weak ferromagnetic ordering in Bi1₋ₓAxFeO3 compounds [7,13,36]. Moreover, related with the increased oxygen vacancies, the enhanced Fe3⁺−O²⁻−Fe2⁺ superexchange interactions are considered to be another important factor for the enhancement of BFO in the Bi1₋ₓAxFeO3 system [20–23]. In the Bi1₋ₓSmxFeO3 system, due to the ionic sizes of Sm³⁺ is smaller than that of Bi³⁺, the introduction of Sm³⁺ in BFO will shorten the Sm−O and Fe−O distances, which will enhance the exchange interaction between Sm³⁺−Sm³⁺ and Fe³⁺−Sm³⁺ and then lead to the increase of the magnetization [18,19].

In order to investigate the high temperature magnetic phase transition and reveal the intrinsic magnetic interaction of BFO, the temperature dependence of magnetization (M-T) was measured in the temperature range 300 K–900 K at a field of 5 kOe for all the samples. The results are shown in Fig. 6. Since the BFO is considered to be antiferromagnetic below T_N=643 K, the magnetization increases with increasing temperature up to 643 K, where a distinct peak appears indicating the antiferromagnetic phase transition. For the Bi1₋ₓAxFeO3 compounds, it is interesting to observe that, even though both Ba²⁺ and Sm³⁺ substitution result in the enhancement of magnetization, the original antiferromagnetic behavior of BFO gradually turns into ferromagnetic behavior with increasing Ba²⁺ concentration but maintains antiferromagnetic feature in the whole Sm³⁺ substitution range, as evidenced from the magnetic-
temperature curves of Bi$_{1-x}$Ba$_x$FeO$_3$ compounds given in Fig. 6(a) and (b).

Since the structural distortion exists commonly in both Bi$_{1-x}$Ba$_x$FeO$_3$ and Bi$_{1-x}$Sm$_x$FeO$_3$ compounds, so the different concentration of oxygen vacancies should be a critical factor responsible for the different high temperature magnetic evolution of these two systems. As mentioned above, the Fe$^{3+}$ commonly exists in BFO. The increased Ba$^{2+}$ concentration produces more Fe$^{2+}$ ions which consequently enhance the uncompensated Fe$^{3+}$-$O^{2-}$-Fe$^{2+}$ antiferromagnetic superexchange interaction, competing with the initial Fe$^{3+}$-$O^{2-}$-Fe$^{3+}$ antiferromagnetic superexchange interaction and eventually resulting in the ferromagnetic behavior of the high-level Ba$^{2+}$ substituted compounds. As to the Bi$_{1-x}$Sm$_x$FeO$_3$ samples, because Sm$^{3+}$ is in the same oxidation state as that of Bi$^{3+}$, the concentration of oxygen vacancies remains essentially unchanged with Sm substitution. Therefore, only relatively small enhancement of magnetization is achieved in the Bi$_{1-x}$Sm$_x$FeO$_3$ ($0 \leq x \leq 0.2$) samples below $T_N \approx 643$ K, leaving the antiferromagnetic order Fe$^{3+}$-$O^{2-}$-Fe$^{3+}$ to be persevered as the dominant interaction. And this small magnetization enhancement may be originated from the structural distortion related spin canting and the Sm$^{3+}$-Sm$^{3+}$ and Sm$^{3+}$-Fe$^{3+}$ exchange interaction [18,19,37,38].

On further analyzing these M-T curves, it has been found that in these Ba$^{2+}$ substituted samples, the antiferromagnetic phase transition peak becomes smaller when the Ba$^{2+}$ concentration is increased, implying the dominant role of Fe$^{3+}$-$O^{2-}$-Fe$^{3+}$ is gradually replaced by the uncompensated Fe$^{3+}$-$O^{2-}$-Fe$^{2+}$ antiferromagnetic superexchange interaction. Furthermore, the Fe$^{3+}$-$O^{2-}$-Fe$^{3+}$ can only be maintained below $T_N \approx 643$ K, while the uncompensated Fe$^{3+}$-$O^{2-}$-Fe$^{2+}$ antiferromagnetic order can exist up to a much higher temperature ($T \approx 778$ K), indicating a much stronger superexchange interaction. In order to verify this high temperature ferromagnetic-like phase transition in Bi$_{1-x}$Ba$_x$FeO$_3$ (0.1 $< x < 0.2$), M-H loops of Bi$_{0.8}$Ba$_{0.2}$FeO$_3$ sample at selected temperatures are measured and are displayed in Fig. 7. As one can see that, the well defined hysteresis loop can still be detected at $T = 700$ K, and the remnant magnetization gradually decreases with increasing temperature. These results provide direct evidence for the existence of a ferromagnetic-like phase transition at high temperature. Although these hysteresis loops of Bi$_{0.8}$Ba$_{0.2}$FeO$_3$ sample are weak, it is clear that the ferromagnetic-like transition arises from the uncompensated Fe$^{3+}$-$O^{2-}$-Fe$^{2+}$ antiferromagnetic superexchange interaction and the magnetization, which depends on the difference between Fe$^{3+}$ and Fe$^{2+}$, is relatively small.

Finally, based on the analysis of high temperature magnetic behaviors of Bi$_{1-x}$A$_x$FeO$_3$ ($A = \text{Ba, Sm}$) ($0 \leq x \leq 0.2$) compounds, we are able to roughly establish the relationship between the magnetic superexchange interaction and the concentration of oxygen vacancies of BFO, as shown in Fig. 8. According to this graph, with
increasing oxygen vacancies, the dominated magnetic structure of $\text{Bi}_{1-x}\text{A}_x\text{FeO}_3$ changes from cycloidal spiral spin structure into the ferrimagnetic order, resulting in the obvious enhancement of magnetization. It is worth nothing to mention that, since the oxygen vacancies always exist in BFO, the formation of uncompensated $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{2+}$ antiferromagnetic superexchange interaction is reasonable. Then, we can infer that the general magnetic structure of BFO should be the coexistence of cycloidal spiral spin structure and unbalanced antiferromagnetic spin structure. So, even though the present of oxygen vacancies increases the leakage current and makes the measurement of ferroelectric property more difficult, they are important for the magnetic properties of BFO. Proper adjusting the concentration of oxygen vacancies, it is possible to effectively enhance the magnetization of BFO.
4. Conclusions

In summary, we have investigated the high temperature magnetic behavior of a series $\text{Bi}_1-x\text{A}_x\text{FeO}_3$ ($A = \text{Ba}, \text{Sm}$) ($0 \leq x \leq 0.2$) compounds in detail. The XRD analysis of $\text{Bi}_1-x\text{A}_x\text{FeO}_3$ confirms the rhombohedral space group of R3c and the structural distortion with $\text{Ba}^{2+}/\text{Sm}^{3+}$ substitution. Mainly due to the structural distortion and the increased concentration of oxygen vacancies, obvious enhancement of magnetization has been observed in $\text{Ba}^{2+}$ and $\text{Sm}^{3+}$ substituted compounds. Interestingly, the original antiferromagnetic behavior of BFO, which is maintained in all $\text{Sm}^{3+}$ substituted samples, alters into a ferromagnetic one with increasing $\text{Ba}^{2+}$ concentration. The XPS narrow scan of the Fe 2p spectra reveals the increased concentration of oxygen vacancies due to the substitution of $\text{Ba}^{2+}$ result in the increased percentage of $\text{Fe}^{3+}$, and consequently the ferromagnetic behavior in $\text{Bi}_1-x\text{Ba}_x\text{FeO}_3$ samples. So, we conclude that the oxygen vacancies also play an important role in deciding the magnetic behavior of BFO ceramic.

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References