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Structure and magnetism of BaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ multiferroics

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The effect of Fe dopant content, *x,* on the magnetism of polycrystalline BaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ (BTFO) multiferroic samples was investigated using magnetization measurements in correlation with the crystallographic and local structures. The changes of coercivity and magnetization as functions of *x* are closely related to the variation of oxygen vacancy content, δ, which can be deduced from the Fe oxidation number estimation using Fe *K*-edge x-ray absorption spectroscopy. It is shown that although the samples exhibit ferromagnetic (FM) hysteresis at room temperature, a dominant paramagnetic phase coexisting with the FM phase makes it difficult to identify the FM contribution to the total magnetization. Spin-glass and/or superparamagnetic behavior may be ruled out due to the fact that both zero-field-cooled and field-cooled thermomagnetization curves almost totally overlap together over the whole range of measured temperatures. © *2012 American Institute of Physics.* [doi:10.1063/1.3677778]

It has been known that undoped BaTiO$_3$ (BTO) is a ferroelectric material in both tetragonal and hexagonal polymorphic forms. It is also a band insulator with the bandgap larger than 3 eV.[1] Substituting Ti^{4+} ions with magnetic elements like transition metals (TMs) can stabilize the hexagonal polymorph at room temperature and make the material become magnetic at room temperature.[2] Most of the reports in the literature have revealed that heavily TM-doped BTO materials in the hexagonal form exhibit ferromagnetic (FM) hysteresis loop at room temperature and that they are likely potential candidates for magnetoelectric multifunctional materials, the so-called multiferroics, possessing both ferroelectrics and ferromagnetism simultaneously in a single crystallographic phase.[3–11] Nevertheless, the nature of multiferroicity in TM-doped BTO materials is in general still far from being understood, and an appropriate theoretical model of their room-temperature ferromagnetism has not been emerged yet. Therefore it has not yet been clear which underlying mechanism governs the TM doping effect on the magnetic properties and whether increasing oxygen vacancy and/or TM-doping contents could enhance or degrade the ferromagnetism of the TM-doped BTO materials.

In this paper, we show a situation that BaTi$_{1-x}$Fe$_x$O$_{3-\delta}$ (BTFO) polycrystalline samples do exhibit FM hysteresis at room temperature, while their thermomagnetization curves manifest paramagnetic (PM) behavior, i.e., like the Curie law of temperature dependence. Nevertheless, those thermomagnetization curves measured at low magnetic fields are neither fit to the Langevin function nor to the Brillouin function. This is due to the presence of a PM phase that hinders identifying the FM contribution to the thermomagnetization, while superparamagnetic (SPM) and/or spin-glass (SG) contributions may be ruled out. We also aim to investigate the effect of Fe dopant content on magnetic properties of these samples. The samples were prepared using a solid state reaction method, the detail of which has been presented in our previous paper.[12] The information of crystal and local structures for the samples already reported in this paper is summarized as follows.

X-ray diffraction (XRD) and Raman scattering spectroscopy showed that samples with $x < 0.01$ exhibit a single tetragonal phase (T-BTO) of space group $P4mm$ and that samples with $x > 0.12$ possess a single hexagonal phase (6H-BTO) of space group $P6_3/mmc$. There is a coexistence of both T-BTO and 6H-BTO in the range $0.01 \le x \le 0.12$, where the T-BTO- to -6H-BTO transformation is gradually taken place. Raman spectroscopy can detect the presence of tiny crystallites of 6H-BTO and that of T-BTO, respectively, in samples $x = 0.01$ and $x = 0.12$, which could not detect using XRD method, from the occurrence of the peak at $\sim$630 cm^{-1} for 6H-BTO and the peaks at $\sim$520 cm^{-1} and $\sim$719 cm^{-1} for T-BTO. Most importantly, the estimation of Fe oxidation number (or in other word, Fe valence), which is determined via the Fe *K*-edge of x-ray absorption spectroscopy, shows that the average valence of Fe ions has the values lying between +3 and +4, increases with increasing *x* from 0.01 to 0.12, and then, decreases with increasing *x* further such that the dependence is of a concave parabolic-like function. This means that Fe ions in sample with $x = 0.12$ have the maximum value of the average valence. If we

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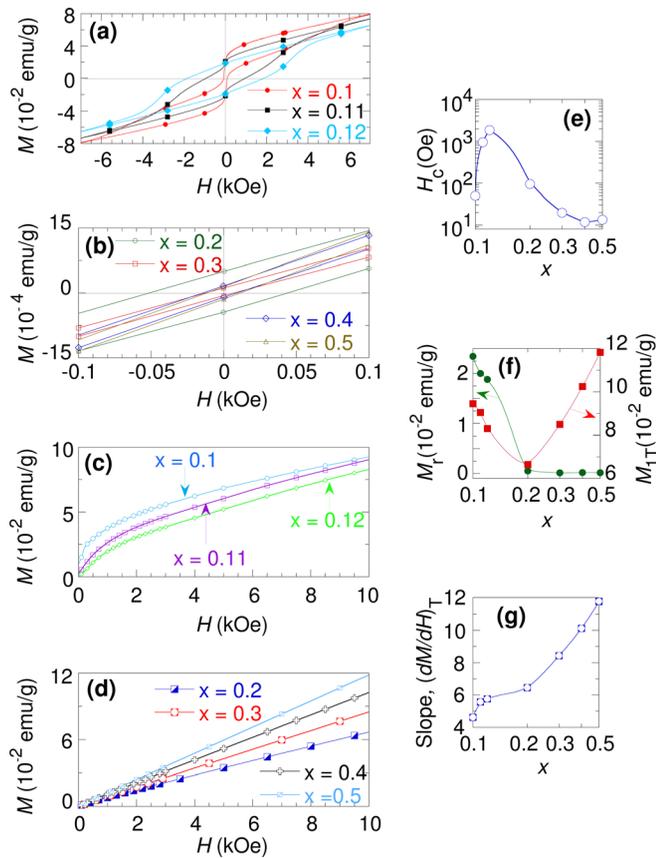c)Electronic mail: honglv@ims.vast.ac.vn.

FIG. 1. (Color online) Data of magnetization measurements at room temperature for BTFO samples. Panels (a) and (b) are magnetic hysteresis loops; panels (c) and (d) are initial magnetization curves. Panels (e) to (g), respectively, show the magnetic coercivity (H_c), remanent magnetization (M_r), magnetization at 10 kOe (M_{1T}), and the slope of the linear part of the initial magnetization curves at high magnetic fields [$(dM/dH)_T$] as functions of x.
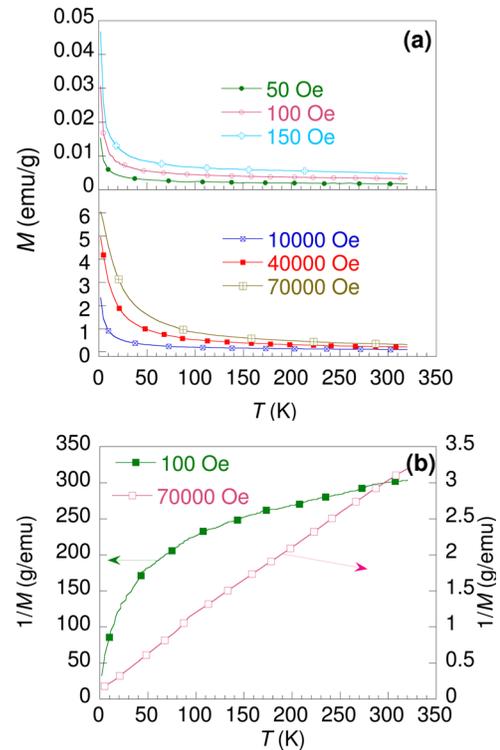

FIG. 2. (Color online) Theromagnetization curves after being field-cooled from 320 K in various magnetic fields in the range 50 Oe to 70 000 Oe (a) and the inverse of thermomagnetizations as functions of temperature in cooling fields of 100 Oe and 70 000 Oe (b).

assume that Ti ions are all in the form Ti^{4+}, and the oxygen vacancy content, per chemical formula, is denoted by δ, as in the BTFO chemical formula $BaTi_{1-x}Fe_xO_{3-\delta}$, then δ is, in turn, a convex parabolic-like function of x, which is minimized at $x = 0.12$. This variation is crucial in that it can be employed to interpret the dependence of magnetic coercivity on Fe dopant content as shown in Fig. 1(e). Having in mind the knowledge of crystal and local structures of the samples, we are now going to present their magnetic properties from magnetization measurements shown in Figs. 1 and 2.

Figure 1 presents the data of magnetization measurements carried out on a PPMS 6000 system at room temperature. As one can see in Figs. 1(a) and 1(b), all of measured samples exhibit ferromagnetic hysteresis. The dependence of the magnetic coercivity, H_c, on Fe dopant content, x, is shown in Fig. 1(e), which is also a concave function. When increasing x, H_c increases dramatically to the maximum of 1858.3 Oe at $x = 0.12$ and then gradually decreases to the values of two orders of magnitude lesser than the maximum for $x \geq 0.4$. This magnetic "softening" or ferromagnetic weakening phenomenon due to Fe doping could be understood in correlation with the variation of oxygen vacancy content, δ, with respect to x as aforementioned. It is known that, in the hexagonal lattice, Fe ions substitute for Ti^{4+} ions in their sites of the face-sharing Ti_2O_9 octahedra.[13,14] In

addition, the oxygen deficiency is necessary to stabilize the hexagonal phase at room temperature. According to our estimation of Fe oxidation number, Fe ions that are substituted into these Ti_2O_9 octahedral units can exist in both Fe^{3+} and Fe^{4+} forms and give rise to the oxygen vacancy by removing one or even two O(1) ions from the $Ba(1)O(1)_3$ layers between the octahedron pairs of the $Ti(Fe)_2O_9$ units in the hexagonal lattice of BTFO samples. The removal of oxygen ion in the $Ba(1)O(1)_3$ layers obviously results in the variation in the surrounding oxygen coordination of Fe ions, and hence the crystal field, from octahedral to pentahedral, or even to tetrahedral symmetry.[15,16] Consequently, the strength of the magnetocrystalline anisotropy acting on local Fe magnetic moments, which governs the magnetic coercivity, will be closely related to the content of oxygen vacancies. Therefore the variation of the magnetic coercivity is directly related to the change of the magnetocrystalline anisotropy due to the presence of oxygen vacancies, the content of which is varied with respect to x. That is, the lower magnetic coercivity corresponds to the higher content of oxygen vacancies and, hence, to the weaker magnetocrystalline anisotropy.

Furthermore, from the magnetization curves presented in Fig. 1 one may argue that the magnetic hysteresis is not necessary due only to the presence of any ferromagnetic phase(s) but also to the SPM and/or SG behavior(s), which is/are usually the case(s) for diluted magnetic semiconductor such as Mn-doped II-VI compounds.[17] Nevertheless, we could rule out the possibility of SPM and/or SG presence here because of the fact that the field- cooled thermomagnetization curves, shown in Fig. 2(a), are almost merged together with the zero-

field-cooled (ZFC) ones (not shown here) in the whole range of measured temperatures, and there is no signal for characteristic blocking and/or freezing temperature(s), typically manifested by the maxima of the ZFC curves, that can be observed. On the other hand, one can note that there does have a PM phase coexisting with a FM phase and dominantly contributing to the magnetization. This can be seen clearly from the linear part of the initial magnetization curves at high magnetic fields, which is mainly due to the PM contribution, for all samples. The linear part even spans to very low magnetic fields for samples with $x \geq 0.2$ as shown in Fig. 1(d). As a result, it is difficult to understand the variation of the total magnetization with respect to x as shown in Fig. 1(f). Therefore, to separate the FM contribution to the total magnetization and to know how it is varied with x, the remanent magnetization, M_r, is a good quantity. This is because the PM contribution to the total magnetization is vanished at zero magnetic field. In this way, we can determine the values of M_r from the magnetic hysteresis loops in Figs. 1(a) and 1(b) and plot them with respect to x as in Fig. 1(f). As clearly seen, M_r decreases monotonically with x and sharply drops its value about two order of magnitude for $x \geq 0.2$. We may expect that FM magnetization at nonzero magnetic fields is also followed a dependency on x similar to that of the M_r quantity. Interestingly, this degradation of ferromagnetism of BTFO polycrystalline materials, when increasing Fe dopant content, was also observed in a recent work of Lin *et al.*,[8] and they demonstrated that ferromagnetism was enhanced substantially when reducing the oxygen vacancy content by means of annealing BTFO samples in enriched oxygen environments.[9]

In contrast, we can understand the PM contribution to the total magnetization by the following assumptions: (i) the total magnetization at high magnetic fields can be expressed as the sum of FM and PM contributions $M(H, T) = M_{FM}(T, H) + (C_{PM}/T) \times H$, where H, T, and C_{PM} are the magnetic field, the temperature, and the Curie constant of the PM phase, respectively; (ii) the FM contribution to the total magnetization is saturated at high magnetic fields so that $M_{FM}(T, H)$ is independent of magnetic field, i.e., $M_{FM}(T)$. In terms of these assumptions, it is clearly that the total magnetization is a linear function of the magnetic field. If we define the slope of this straight line as $(dM/dH)_T$, then $(dM/dH)_T = C_{PM}/T$, which is exactly the PM susceptibility at temperature T (here $T = 300$ K). These assumptions may be applied for all temperatures and for high magnetic fields but not for low magnetic fields. This can be seen in Fig. 2(b) where the magnetization is inversely proportional to temperature, i.e., obeying the Curie law, for the high field only. Interestingly, as seen in Fig. 1(g), the PM susceptibility increases with increasing x and, we can infer, so does the PM contribution to the total magnetization. Finally, if combining together this variation of the slope $(dM/dH)_T$ with that of M_r with x, the interpretation for the convex-function dependence of the total magnetization at 1 T, M_{1T}, on x as shown in Fig. 1(f) is now straightforward.

In conclusion, our experimental analysis shows that increasing Fe dopant content higher than 0.12 results in a degradation of the ferromagnetism but enhances substantially the contribution to the total magnetization of an unexpected para-

magnetic phase. The dependence of magnetic coercivity on Fe dopant content could be understood in terms of the variation of oxygen content. The degradation of the ferromagnetism with increasing Fe dopant content implies that the exchange interactions between local Fe moments are not only the direct FM exchange but also include other kinds of exchange interactions such as the super exchange, the indirect exchange, and even the double-exchange interactions due to the presence of mixed valent Fe^{3+}/Fe^{4+} pairs. Isolated Fe magnetic moments or the spins of free electrons or polarons that are excited thermally from the donor levels in the forbidden band may be responsible for the PM phase, which increase in density with increasing oxygen vacancy content. The reduction of the PM phase and enhancement of the FM phase can be done by annealing the BTFO polycrystalline samples in oxygen-rich environments as reported in the work of Lin *et al.*[9]

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