Influence of non-isovalent ion substitution at A site on microstructure and magnetic properties of Ba(Ti$_{0.3}$Fe$_{0.7}$)O$_3$ ceramic

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ABSTRACT

The (Ba$_{0.8}$K$_{0.2}$)(Ti$_{0.3}$Fe$_{0.7}$)O$_3$ ceramic was prepared by solid-state reaction, and post-annealed in oxygen ambient. By comparison with Ba(Ti$_{0.3}$Fe$_{0.7}$)O$_3$ made under identical conditions, the effect of non-isovalent A-site substitution of K$^+$ on microstructure and magnetism of as-prepared and annealed Ba(Ti$_{0.3}$Fe$_{0.7}$)O$_3$ samples was investigated using X-ray diffraction, Mössbauer spectroscopy, vibrating sample magnetometer and iodometric titration. It is found that all samples have a single 6H-BaTiO$_3$-type hexagonal perovskite structure without any impurities detected, regardless of A-site K$^+$ substitution or annealing. In the as-prepared state, non-isovalent A-site substitution of K$^+$ induces the variation in Fe occupational site, resulting in the disappearance of room-temperature ferromagnetism. The super-exchange interactions of Fe^{3+} at tetrahedral and octahedral Ti sites determine the paramagnetism of (Ba$_{0.8}$K$_{0.2}$)(Ti$_{0.3}$Fe$_{0.7}$)O$_3$. During the O$_2$ annealing process, the presence of Fe^{4+}, an unusual valence for iron, besides Fe^{3+} is observed, both distributed over octahedral Ti site. By A-site substitution of K$^+$ with a lower valence than Ba^{2+}, the charge compensation mechanism is further enhanced, and thus more Fe^{3+} ions are oxidized to Fe^{4+} in annealed (Ba$_{0.8}$K$_{0.2}$)(Ti$_{0.3}$Fe$_{0.7}$)O$_3$. Consequently, the ferromagnetic Fe^{4+}–O^{2-}–Fe^{4+} super-exchange interactions are strengthened, which leads not only to a paramagnetism–ferromagnetism transition but also to a higher saturation magnetization compared with annealed Ba(Ti$_{0.3}$Fe$_{0.7}$)O$_3$.

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1. Introduction

Achieving ferromagnetic ordering in ferroelectrics through impurity doping has become one of the most promising directions for multiferroic research [1–10]. Multiferroic materials are quite rare in nature, particularly at room temperature and above. In these compounds, electric and magnetic orders coexist, with some couplings between them (the magnetoelectric effect) [11], providing an additional degree of freedom in device design. Therefore, multiferroics have been the subject of intensive investigations due to their potential applications in the emerging field of spintronics [12], data-storage media [13], multiple-state memories [14], etc. Being an important ferroelectric material, BaTiO$_3$ is widely used in capacitors, positive temperature coefficient of resistance thermistors, chemical sensors and piezoelectric devices. Meanwhile, the ABO$_3$-type perovskite structure of BaTiO$_3$ determines its ability to accommodate a wide variety of cations at both the A and B sites, which offers the potential of possessing a very high degree of flexibility on composition, structure and properties. Hence the relevant work on ferromagnetism of BaTiO$_3$ doped with 3d transition metal has been reported theoretically [1] and experimentally [2–5].

So far almost all research on magnetism of doped BaTiO$_3$ has been focused on B-site substitution. In our previous work, room-temperature ferromagnetism was realized in Ba(Ti$_{1-x}$Fe$_x$)O$_3$ ceramics also by partial Fe substitution at the B site [15]. Then the magnetization was remarkably enhanced via subsequent O$_2$ annealing due to the ferromagnetic Fe^{4+}–O^{2-}–Fe^{4+} couplings produced by the presence of Fe^{4+} [16]. Moreover, other transition metals were codoped with Fe at the B site to induce new magnetic exchange mechanisms between ions with different valence states and occupational sites, giving rise to a further improvement of magnetic properties [17]. However, no work referring to A-site substitution has been reported up to now, among research on magnetism of transition-metal-doped BaTiO$_3$ system.

In the perovskite structure, the replacement of Ti^{4+} by Fe^{3+} implies the formation of one oxygen vacancy for two pentahedral Ti sites or one tetrahedral Ti site [18,19]. Considering the ABO$_3$ structure characteristics, further non-isovalent substitution of an ion, with a lower valance than Ba^{2+}, at the A site of Ba(Ti$_{1-x}$Fe$_x$)O$_3$ will facilitate the formation of oxygen vacancies in order to keep charge balance. Accordingly, the distribution of Fe occupational sites will be changed among octahedral, pentahedral and tetrahedral Ti sites, leading to various magnetic exchange mechanisms and magnetic properties. Furthermore, combining such non-isovalent A-site substitution with O$_2$ annealing can be expected to enable more Fe^{3+} ions to be oxidized to Fe^{4+}. As a result, the ferromagnetic

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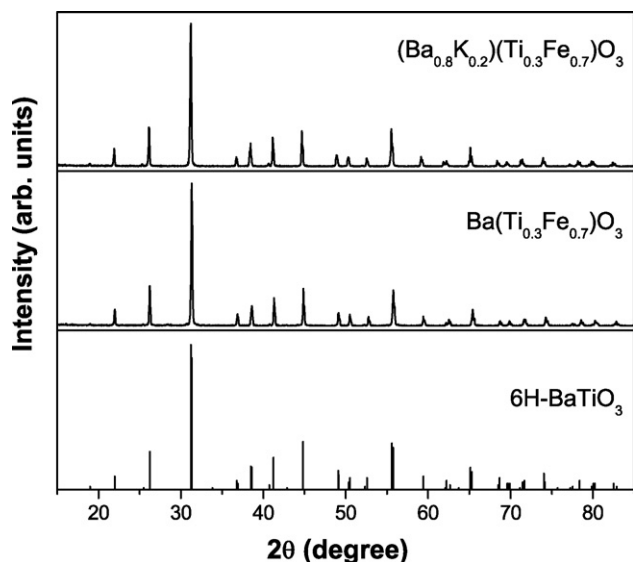 E-mail address: nounou7@163.com (W. Shi).

Fig. 1. XRD patterns of $(Ba_{0.8}K_{0.2})(Ti_{0.3}Fe_{0.7})O_3$ and $Ba(Ti_{0.3}Fe_{0.7})O_3$ ceramics.

$Fe^{4+}-O^{2-}-Fe^{4+}$ couplings will be enhanced, and so will the magnetization. These are the primary work of the present article. Here, K^+ was selected to substitute for the A-site ion, based on its lower valence and almost the same size [20] compared with Ba^{2+}.

2. Experimental

High-purity (above 99.9%) carbonate and oxide powders were used to prepare $(Ba_{0.8}K_{0.2})(Ti_{0.3}Fe_{0.7})O_3$ by conventional ceramic technique. For comparison, $Ba(Ti_{0.3}Fe_{0.7})O_3$ was also synthesized under identical conditions. The doping site of K and Fe ions in $BaTiO_3$ was controlled by stoichiometric proportions of raw materials. Weighed mixtures of chemicals were homogenized by grinding with an agate mortar and pestle for 40 min, and calcined in alumina crucibles at 1000 °C for 36 h. They were then ground, pressed into pellets, and sintered at 1300 °C for 24 h in air followed by a furnace cooling. Each product was divided into two, of which one was post-annealed in oxygen ambient at 1000 °C for 3 h. Thus, the as-prepared and O_2-annealed samples were obtained.

Phase structure was verified by X-ray diffraction (XRD) using a Rigaku D/max 2550 V diffractometer with Cu Kα radiation. ^{57}Fe Mössbauer spectra were recorded in transmission mode on a constant acceleration spectrometer with a ^{57}Co(Pd) source. The velocity scale is calibrated periodically relative to α-Fe foil. Physically realistic fitting to the Mössbauer spectra was proceeded in terms of the sample structure and the ranges of isomer shifts (I.S.) and quadrupole splittings (Q.S.) reported for different Fe valences and occupational sites. Magnetic properties were measured using an HH-15 vibrating sample magnetometer (VSM) at room temperature. The iodometric titration was used to determine the total oxygen vacancy concentration (δ) in our samples. During the titration, the Ti^{4+} ions were deoxidized to Ti^{3+} and Fe^{3+} and Fe^{4+} were deoxidized to Fe^{2+}. Meanwhile the I^- ions were oxidized to I_2. The following reactions occurred:

$$B^{x+} + (x-2.3)I^- = B^{2.3+} + \frac{x-2.3}{2}I_2, \qquad (1)$$

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}, \qquad (2)$$
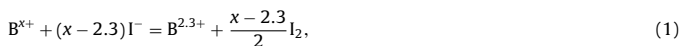
where B^{x+} expressed the B-site ions with the average valence x+ before the titration, and $B^{2.3+}$ expressed the B-site ions with the average valence 2.3+ after deoxidization by I^- ($B^{2.3+} = 0.3Ti^{3+} + 0.7Fe^{2+}$). The titration was carried out in the flowing N_2 gas to prevent the oxidization of I^- ions by air. From Eqs. (1) and (2) and the theorem of charge neutrality, the oxygen vacancy concentration can be calculated based on the amount of $Na_2S_2O_3$ consumed and the amount of sample applied.

3. Results and discussion

3.1. Effect of A-site K^+ substitution on microstructure and magnetic properties of as-prepared $Ba(Ti_{0.3}Fe_{0.7})O_3$

Fig. 1 shows the XRD patterns for $Ba(Ti_{0.3}Fe_{0.7})O_3$ samples with and without A-site K^+ substitution. The XRD data indicate no structural difference between two samples. All sharp diffraction peaks can be indexed to pure 6H-$BaTiO_3$ phase (JCPDS No. 34-0129). No

evidence for any secondary phases such as K/Fe clusters or K/Fe oxides is found. Both samples are of single phase, crystallizing in a hexagonal perovskite structure. The K and Fe ions seem to have been incorporated into $BaTiO_3$ host lattice, replacing Ba^{2+} at the A site or Ti^{4+} at the B site. It is seen that the K^+ substitution at the A site of $Ba(Ti_{0.3}Fe_{0.7})O_3$ does not change phase composition or crystal structure.

Fig. 2 presents the magnetization versus magnetic field (M–H) curves for $Ba(Ti_{0.3}Fe_{0.7})O_3$ samples with and without A-site K^+ substitution. Room-temperature ferromagnetism is exhibited in $Ba(Ti_{0.3}Fe_{0.7})O_3$, indicated by a distinct hysteresis loop. A linear paramagnetic behavior superimposed upon hysteresis is also observed, originating from paramagnetic regions contained in the sample due to nearly isolated Fe ions, e.g., where the local Fe concentration is the lowest. Similar occurrences have been reported in other composition $Ba(Ti_{1-x}Fe_x)O_3$ [4,15,16] and $Ba(Ti_{0.65}M_{0.05}Fe_{0.3})O_3$ (M = Cr, Mn, Ni) ceramics [17]. The contributions from ferromagnetic and paramagnetic phases are separated according to the following equation:

$$M_T(H) = \frac{2M_S}{\pi}\tan^{-1}\left[\frac{H \pm H_C}{H_C}\tan\left(\frac{\pi S}{2}\right)\right]$$
$$+ N_g\mu\left[\mathrm{ctnh}\left(\frac{\mu H}{KT}\right) - \left(\frac{\mu H}{KT}\right)^{-1}\right], \qquad (3)$$

where the first term is the usual function used to represent a ferromagnetic hysteresis curve, the second term is the usual expression for a paramagnetic component, M_S and $N_g\mu$ are the saturation magnetization of the ferromagnetic and paramagnetic parts, H_C is the coercivity, S is the squareness of the ferromagnetic loop, i.e., the ratio of the remanent magnetization, M_R, to M_S, and μ is the average moment [21,22]. It can be concluded from Fig. 2 that the saturation magnetization (M_S) of the ferromagnetic phase is about 0.0018 μ_B/Fe. On the contrary, paramagnetism is shown in $(Ba_{0.8}K_{0.2})(Ti_{0.3}Fe_{0.7})O_3$ at room temperature. The transition from ferromagnetism into paramagnetism suggests an obvious variation in magnetic exchange mechanism induced by A-site substitution of K^+.

In order to further investigate micro-configuration for clarifying the origin of magnetism, the valence state and occupational site of magnetic Fe ions were analyzed by Mössbauer spectroscopy, based on its high sensitivity to the Fe-atom surroundings. The Möss-
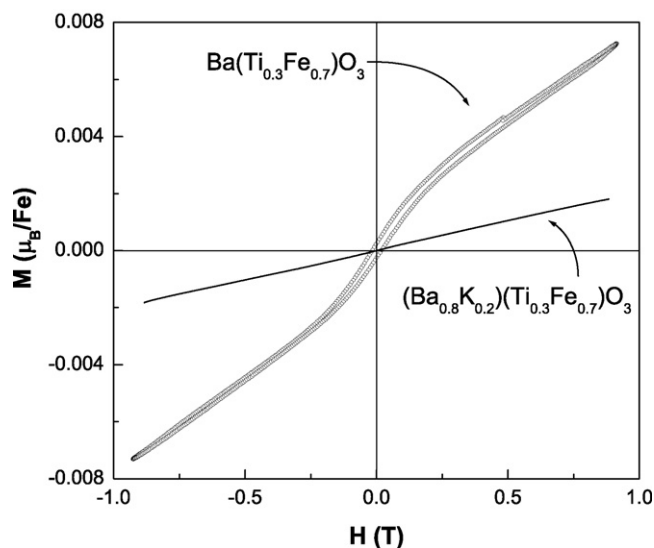

Fig. 2. Room-temperature M–H curves of $(Ba_{0.8}K_{0.2})(Ti_{0.3}Fe_{0.7})O_3$ and $Ba(Ti_{0.3}Fe_{0.7})O_3$ ceramics.