RAPID COMMUNICATION

Multiferroic properties in terbium orthoferrite*

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Multiferroic properties in a polycrystalline terbium orthoferrite are investigated. Different thermomagnetic behaviors are observed in different magnetic fields, which is attributed to the suppression of the low temperature magnetic phase by an external magnetic field. Further studies reveal that the ferroelectricity originates from the spin configuration below 3.5 K. In addition, the magnetic field control of electric polarization and dielectric constant is observed, which suggests a magnetoelectric effect in $TbFeO_3$. The origin of ferroelectricity in this rare-earth orthoferrite is discussed.

Keywords: multiferroic property, spin reorientation, dielectric property

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1. Introduction

The intrinsic coupling between electric and magnetic orders in multiferroics has inspired intensive interest recently, owing to its potential application in spintronics and magnetic data storage.[1–6] Many theoretical and experimental studies in the field of multiferroics have clarified some microscopic origins of the ferroelectric polarization (P) in phenomena that are found in magnetic materials, such as lone-pair electrons, charge ordering, spin current, exchange striction, and so on.[5,6] In a transition-metal perovskite oxide, it is particularly difficult to simultaneously realize ferroelectric and magnetic orderings, because the electrons occupying the d shells of the transition metal ions prevent the coexistence of the two ferroic orderings.[7] Interestingly, when the crystal contains both a d-ion subsystem and a single rare-earth (Re) subsystem, the magnetic behavior of the system becomes more complicated, showing magnetostriction, spin reorientation, a large magnetocaloric effect, and so on.[8–13] Recently it was realized that the interaction between transition metal and rare-earth spins may also play an important role in multiferroic and magnetoelectric materials.[14–19] For example, the striction through the exchange interaction between the Re^{3+} and Fe^{3+} spins in $GdFeO_3$ and $DyFeO_3$ gives rise to a large P.[17,18] It should be noted that in $GdFeO_3$ the common spin configuration, A type, is responsible for producing a net P, and so is in $DyFeO_3$ (under a magnetic field H above $H_r^{Fe} \sim 2.4$ T). In a relatively high H, the dominant magnetic structure of $GdFeO_3$ is transformed into G type (more exactly, the spin structure of the Fe sites is of the $G_xA_yF_z$ type in Bertaut's notation,[20] and that of the Gd sites is of the G_xA_y type), in which the exchange striction forces from eight nearest-neighbor Fe ions in a cubic cell would be exactly cancelled out.[17] However, if we further consider the orthorhombic unit cell distortion and the ordering of the Gd spins, such a total cancellation is lost. In this case, the strongest pairs of attractive and repulsive forces acting on the Gd ions would point along the c axis and the displacement of every Gd ion should be along the same direction, similar to the A-type magnetic configuration, leading to the generation of P along the c axis.[17] Since the location of the terbium element in the periodic table is between gadolinium and dysprosium elements and the crystal structures of orthoferrite $ReFeO_3$ are similar, it is reasonable to anticipate that terbium orthoferrite would be a single-phase multiferroic or magnetoelectric material.[21,22] As far as we know, there are few reports about its multiferroic properties. In this paper, we prepare a polycrystalline $TbFeO_3$ sample and investigate its magnetic and ferroelectric properties. The P induced by the spin order as well as the manipulation of H on P and dielectric constant ε are observed in this orthoferrite.

2. Experimental setup

A polycrystalline sample of $TbFeO_3$ was prepared by the solid-state reaction method. Stoichiometric amounts of Tb_4O_7 and Fe_2O_3 were thoroughly mixed and calcined at 1273 K in air for 10 h. The resulting mixture was reground and sintered at 1673 K for 24 h in an air atmosphere. The phase purity was checked by powder X-ray diffraction (XRD) with Cu K_α radiation at room temperature. The measured sample was cut into a regular plate with a size of 3 mm × 3 mm × 0.3 mm. The magnetization measurements were performed using a superconducting quantum interference device (SQUID, Quantum Design). For the measurements of the dielectric constant and py-

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roelectric current, gold paste was used for the electrodes. The dielectric response was measured by using an Agilent 4284A LCR meter with an excitation of 1 V. The pyroelectric current was measured with an electrometer (Keithley 6514) and the magnetic-field environment was provided by a physical properties measurement system (PPMS, Quantum Design). Before each measurement, the sample was cooled to 2 K with an applied electric field of 650 kV·m^{-1}. In order to obtain the zero-charge state, the electrodes of the sample capacitor were short-circuited for a long enough time. Then the pyroelectric current was recorded with a heating rate of 3 K/min. The P was obtained by integrating the pyroelectric current with respect to time plus a careful exclusion of other possible contributions, such as the thermally stimulated depolarization current from the detrapped charges.[23]

3. Results and discussion

Figure 1(a) shows the room-temperature XRD pattern of the polycrystalline $TbFeO_3$. All the peaks can be indexed to the orthorhombically distorted perovskite structure with a space group D_{2h}^{16}-*Pbnm*. The crystal structure of our sample is schematically shown in Fig. 1(b), in which each crystal unit cell contains four formula units.[24] As is shown, the Re^{3+} cations occupy a nearly central position in a parallelepiped formed by the Fe^{3+} cations. The Fe^{3+} ions are nearly octahedrally coordinated with six O^{2-} anions. The O^{2-}–O^{2-} axes of the distorted octahedra are tilted alternately, forming a zigzag along the c axis with a tilt angle. Among all the possible magnetic interactions in the rare-earth orthoferrites, the superexchange coupling of Fe^{3+}–O^{2-}–Fe^{3+} between iron magnetic moments is dominant and leads to a non-collinear antiferromagnetic (weak ferromagnetic, which is induced by its staggered spin structure through the Dzyaloshinskii–Moriya interaction) Fe^{3+} sublattice ordering.[8] The direct Fe^{3+}–Fe^{3+} coupling is much weaker, and magnetic Re^{3+}–Fe^{3+} and Re^{3+}–Re^{3+} couplings are of the order of 10^{-2}–10^{-3} in relation to the Fe^{3+}–O^{2-}–Fe^{3+} ones.[24]

Figure 2(a) shows the variation of magnetization as a function of temperature for $TbFeO_3$ under different H. It is obvious that this rare-earth orthoferrite exhibits an interesting thermomagnetic behavior with the change of H, which can be understood through the exchange interaction between two different magnetic sublattices. According to the earlier reports,[16,25–28] below its Néel temperature (T_N(Fe)$\sim$ 650 K), the spins of the Fe^{3+} ions arrange in a canted G-type (G_xF_z mode) antiferromagnetic ordering. Upon cooling in an H of 0.1 T, $TbFeO_3$ undergoes two magnetic transitions driven by Tb^{3+}–Tb^{3+} and Tb^{3+}–Fe^{3+} interactions, respectively.[29] As shown in Fig. 2(a), the magnetization increases with decreasing temperature, and at the Néel temperature of the Tb ions

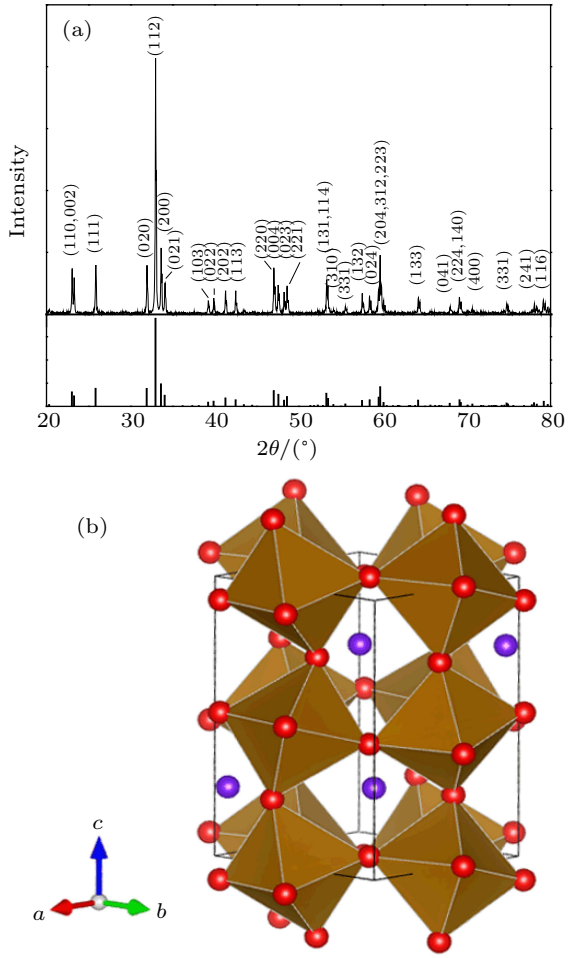


Fig. 1. (color online) (a) The room-temperature X-ray diffraction spectrum of $TbFeO_3$. The spectrum at the bottom is the standard XRD pattern of bulk $TbFeO_3$ with JCPDS No. 74-1477. (b) Sketch of the orthorhombically distorted perovskite structure of $TbFeO_3$. The Fe^{3+} cations locate in the centers of the oxygen octahedra.

(T_N(Tb)$\sim$ 8.5 K), this orthoferrite undergoes the first magnetic transition: the occurrence of the ordered spins in the Tb^{3+} ions and the spin rotation of the Fe^{3+} ions in the ac plane.[25] Below 8.5 K, the spin configurations of this intermediate-temperature (IT) magnetic phase are f_xc_y and G_zF_x for Tb^{3+} and Fe^{3+} spins, respectively, in which the two magnetic sublattices are coupled by anisotropic exchange forces.[26] As the temperature decreases further, the magnetization first increases and then decreases, showing a maximum at 3.5 K, which corresponds to the second magnetic transition.[25] During this process, the spins of Tb^{3+} and Fe^{3+} undergo the re-orientation transition to a low-temperature (LT) phase, in which the Fe^{3+} spins rotate back to their higher temperature G_xF_z mode while the Tb^{3+} spins order antiferromagnetically in the a_xg_y mode. In this magnetic structure, the Tb^{3+}–Tb^{3+} exchange is negligible and the two magnetic sublattices are decoupled.[26] It is worth noting that the peak around 3.5 K becomes more and more flat with increasing H, suggesting the weak ferromagnetic LT phase is suppressed by high H. Figure 2(b) shows the magnetic hysteresis loops (M–H) of $TbFeO_3$ at different temperatures. It is obvious that the M–H loop at 2 K is different

from that at 4 K, which can be ascribed to the spin reorientation transition induced by the external H. In the LT magnetic phase, when an applied H is parallel to the a axis of single-crystal $TbFeO_3$, the angular phase $G_xF_zG_zF_x$ is induced in the Fe^{3+} subsystem while the spin configuration of Tb^{3+} is unchanged. When the field is above 0.2 T, the magnetic structures of the Fe^{3+} and Tb^{3+} sublattices are described by the representation $G_zF_xf_xc_y$, being the same as the spin structures of the IT phase.[8,16] In the case of our polycrystalline sample, as shown in Fig. 2(b), a metamagnetic transition is observed above 0.2 T, which can be attributed to the spin reorientation transition of $TbFeO_3$.

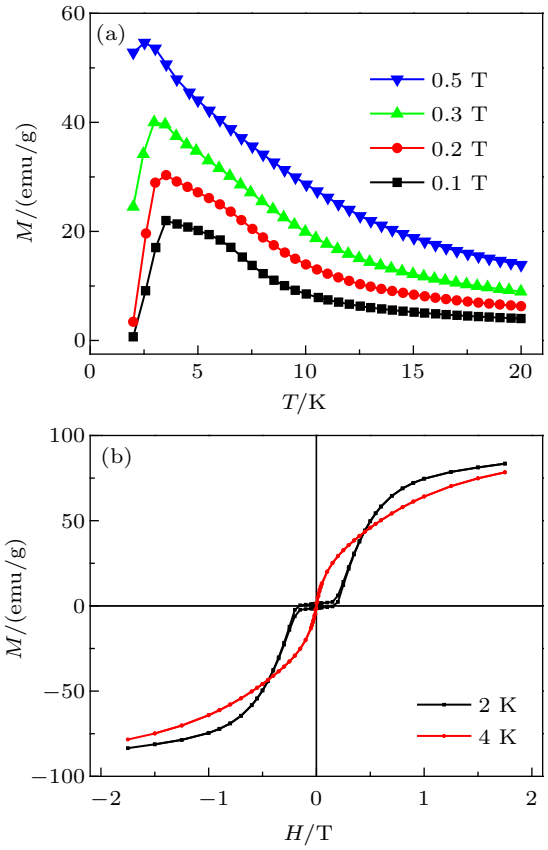


Fig. 2. (color online) (a) The temperature dependence of magnetization under various magnetic fields. (b) The magnetic hysteresis loops of $TbFeO_3$ at 2 K and 4 K.

Figure 3 shows the temperature dependence of P for $TbFeO_3$ in selected H after magnetoelectric cooling down to 2 K. It is obvious that this orthoferrite shows spontaneous P under zero H, suggesting the ferroelectricity of the ground state. The onset temperature of P is around 3.5 K, which is consistent with the spin reorientation transition temperature of the LT phase, suggesting an intrinsic coupling between the magnetic and ferroelectric orders. By applying H, an obvious decrease in P is observed, indicating the effect of H on P. Such a magnetoelectric effect can be seen more clearly in the inset of Fig. 3, which shows the H dependence of P at 2 K. For comparison, the magnetic initial curve at 2 K is also plotted. As shown in the inset of Fig. 3, P decreases abruptly above 0.2 T, which corresponds to the metamagnetic transition from the LT phase to the IT phase, suggesting that the P of $TbFeO_3$ is induced by the LT magnetic phase. Similar results are also observed in other orthoferrites, such as $GdFeO_3$ and $DyFeO_3$, in which the anomaly of P is ascribed to the spin reorientation.[17,18]

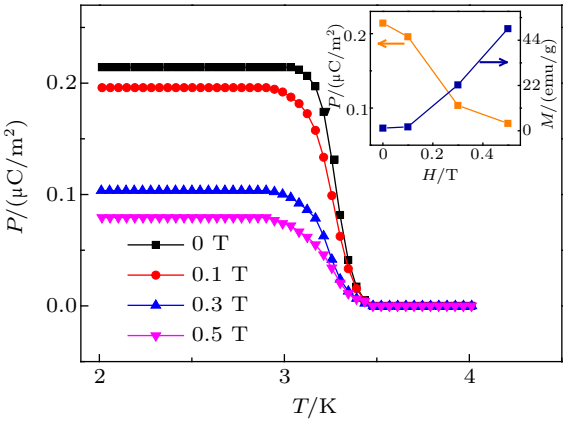


Fig. 3. (color online) The temperature dependence of ferroelectric polarization under various magnetic fields. The inset shows the polarization (left-ordinate) and magnetization (right-ordinate) versus the magnetic field at 2 K.

It is known that an anomaly in ε may indicate a sudden change of P.[15] To investigate the magnetoelectric coupling in $TbFeO_3$ further, we also measured the temperature dependence of ε in $TbFeO_3$ under different H. As shown in Fig. 4, ε shows a peak at around 3.5 K, which is consistent with the onset temperature of P. With increasing H, the dielectric peak of $TbFeO_3$ becomes more and more gentle. The similar temperature dependences of M (Fig. 2(a)), P (Fig. 3), and ε (Fig. 4) further demonstrate the magnetoelectric coupling in $TbFeO_3$.

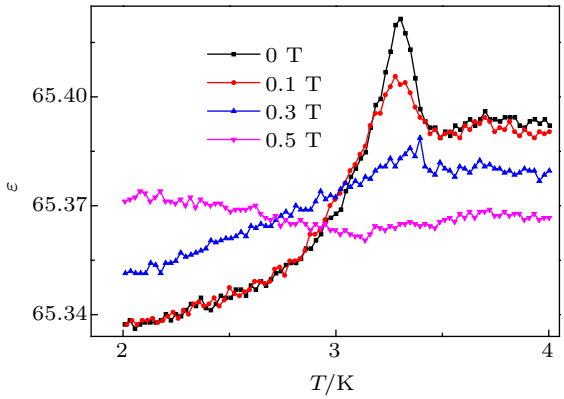


Fig. 4. (color online) The variation of dielectric constant of $TbFeO_3$ at selected magnetic fields of 0 T, 0.1 T, 0.3 T, and 0.5 T as a function of temperature between 2 K and 4 K.

However, the ferroelectricity of $TbFeO_3$ cannot be understood by the exchange striction model, which is considered as the microscopic origin of some multiferroic rare-earth

orthoferrites.[17,18,30] Below 3.5 K, the magnetic configurations for Tb and Fe moments are a_xg_y and G_xF_z, respectively. Here the interaction energy is given by

$$E_{int} = \sum_{\langle i,j \rangle} j_{ij} \langle S_i^{(\mathrm{d})} \cdot S_j^{(\mathrm{f})} \rangle, \quad (1)$$

where j_{ij} is the exchange integral between the Fe spin on the i-th site $S_i^{\langle \mathrm{d} \rangle}$ and the Tb spin on the j-th site $S_j^{\langle \mathrm{f} \rangle}$. According to Eq. (1), we should only consider the x components of the A-type magnetic configuration of Tb^{3+} and the G type of Fe^{3+}. By using the exchange striction model, we find that there are four different microscopic P vectors with antiparallel alignment per crystal unit cell, unlike $GdFeO_3$ and $DyFeO_3$.[17,18] In that case, the total P would be exactly cancelled out, which results in zero net P.

In the LT phase of $TbFeO_3$, the terbium sublattice orders with a_xg_y while the iron sublattice rotates back to its higher temperature order with G_xF_z. The Tb and the Fe magnetic sublattices are described by nonpolar point groups mmm' and $m'm'm$, respectively. The point symmetries of these two magnetic sublattices differ by mirror-plane symmetry and inversion center, giving the point group $2'2'2$, which is also nonpolar. Based on the point group symmetry, the proposed magnetic structures of $TbFeO_3$ cannot give rise to the observed ferroelectric polarization either.

There are two possibilities to circumvent the constraint of the $2'2'2$ symmetry. a) In the actual orthorhombic unit cell of $TbFeO_3$, a tiny degree of off-centering distortion may exist in the oxygen octahedron [FeO_6] and break the symmetry of space group $Pbnm$. A similar distortion has been considered to explain the ferroelectric and piezoelectric nature of $SmFeO_3$.[31] b) Below 3.5 K, a fine magnetic structure may exist in $TbFeO_3$, which does not belong to the $2'2'2$ symmetry. Moreover, the investigation of the crystal structure and the magnetic structure of $TbFeO_3$ should be further performed to determine the origin of the electric polarization.

4. Conclusion

In conclusion, the magnetic and ferroelectric properties are studied in terbium orthoferrite. This perovskite undergoes two magnetic transitions at 3.5 K and 8.5 K, which are driven by Tb^{3+}–Tb^{3+} and Tb^{3+}–Fe^{3+} interactions, respectively. With the H above 0.2 T, $TbFeO_3$ shows a metamagnetic transition from the LT to IT magnetic phase at 2 K. The onset temperature of P is consistent with the magnetic transition temperature, suggesting the spin origin of the ferroelectricity. Moreover, the effect of H on P and the dielectric constant is observed in this rare-earth orthoferrite, indicating a magnetoelectric effect. As for the mechanism of ferroelectricity, we argue that if the spin structure cannot produce a net P, the ferroelectricity may be achieved in $TbFeO_3$ by further considering the distortion of the crystal structure or the fine magnetic structure.

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