Magnetoelectric memory effect in the Y-type hexaferrite $BaSrZnMgFe_{12}O_{22}$*

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We report on the magnetic and magnetoelectric properties of the Y-type hexaferrite $BaSrZnMgFe_{12}O_{22}$, which undergoes transitions from a collinear ferrimagnetic phase to a proper screw phase at 310 K and to a longitudinal conical phase at 45 K. Magnetic and electric measurements revealed that the magnetic structure with spiral spin order can be modified by applying a magnetic field, resulting in magnetically controllable electric polarization.It was observed that $BaSrZnMgFe_{12}O_{22}$ exhibits an anomalous magnetoelectric memory effect: the ferroelectric state can be partially recovered from the paraelectric phase with collinear spin structure by reducing magnetic field at 20 K. We ascribe this memory effect to the pinning of multiferroic domain walls, where spin chirality and structure are preserved even in the nonpolar collinear spin state.

Keywords: multiferroic, magnetoelectric effect, memory effect

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1. Introduction

In the past decade, there has been a revival of research on multiferroics materials in which magnetic and ferroelectric orders coexist.[1–5] The discovery of large magnetoelectric (ME) effect in $TbMnO_3$[6] triggered numerous studies of multiferroics showing helical spin orders and led to the discovery of other new spiral multiferroics such as $Ni_3V_2O_8$,[7] $MnWO_4$,[8] and $CoCr_2O_4$.[9] These spiral multiferroics, which exhibit an inherent interplay between magnetic ordering and ferroelectricity, show pronounced ME effects, remarkable changes in electric polarization in response to a magnetic field. The microscope mechanism has been well explained by the spin current model[10] and inverse Dzyaloshinskii–Moriya model.[11] However, the operating temperatures of these multiferroics are too low (below 40 K) to be useful in practical applications.

Recently, some hexaferrites have been found to show magnetically induced electric polarization (P).[12–21] In 2005, it was first found that a Zn_2Y-type hexaferrite $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ shows an relatively high ordering temperature of about 320 K for a proper-screw phase and magnet-field-induced ferroelectricity around 1 T.[12] It was then reported that the critical magnetic field to control spin helix and P became fairly low (1 mT–10 mT) in Mg_2Y-type[13] and Al-doped Zn_2Y-type[14] hexaferrites, resulting in sensitive ME responses and large ME effects. Subsequently, Co_2Z-type hexaferrites were found to show low-field ME effect at room temperature.[16] Shortly afterwards, low-magnetic-field control of electric polarization were successively observed in M-type,[15] U-type,[18] W-type,[22] and Co_2Y-type hexaferrites,[23] and most of them can operate at or near room temperature. Moreover, Co_2Y-type,[23] Co_2Z-type,[24] Al doping Zn_2Y-type,[25] and CoZnY-type[26] hexaferrites also show inverse ME effect (electrical control of magnetization) at room temperature, representing a big step towards technical device applications.

In this paper, we demonstrate a magnetoelectric memory effect in a Y-type hexaferrite $BaSrZnMgFe_{12}O_{22}$ polycrystalline sample. This material possesses a relatively high spiral magnetic transition temperature of 310 K, below which successive metamagnetic transitions driven by magnetic field and resultant magnetically controllable ferroelectricity were observed. Since the ferroelectric polarization of $BaSrZnMgFe_{12}O_{22}$ arises from noncollinear spiral spin structures, the information of ferroelectric domains should be lost in the collinear spin phase. However, an anomalous magnetoelectric memory effect for the direction of electric polarization was observed after poling the sample to the nonpolar ferrimagnetic phase. We ascribe this phenomenon to the pinning effect of magnetic/ferroelectric domain walls by defects and space charge.

2. Experiments

In experiment, polycrystalline samples with the composition of $BaSrZnMgFe_{12}O_{22}$ were synthesized by conventional solid-state reaction. Stoichiometric proportions of $BaCO_3$, $SrCO_3$, ZnO, MgO, and Fe_2O_3 powders were thoroughly mixed and well ground. Then, the mixed powders were calcined at 940 °C for 10 hours in air. The resulting mixture

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were reground, pressed into pellets, and sintered at 1200 °C for 4 hours in air for two times. Powder x-ray diffraction indicated that the samples are single phase. The magnetic and dielectric properties were performed using a superconducting quantum interference device magnetometer (Quantum Design MPMS-XL). For the measurement of dielectric constant and ME current (I_{ME}), the electrodes were made with silver paste onto the opposite faces of the plate-shaped samples with the dimension of 6.2 mm × 5.54 mm × 0.8 mm. The dielectric response was recorded by a NF ZM2353 LCR meter with an excitation of 1 V. ME current I_{ME} was measured by using an electrometer (Keithley 6517B) and a superconducting magnet (Quantum Design PPMS) with a handmade sample holder. Electric polarization P was obtained by integrating I_{ME} with respect to time.

3. Results and discussion

Figure 1(a) shows temperature dependence of the magnetization for $BaSrZnMgFe_{12}O_{22}$ polycrystalline sample in 0.01 T after zero-field cooling (ZFC) and field cooling (FC). The behaviors of the M–T curves are similar to $Ba_2Mg_2Fe_{12}O_{22}$.[27–29] The ferrimagnetic transition temperature is far above 400 K. With temperature decreasing, $BaSrZnMgFe_{12}O_{22}$ undergoes two magnetic transitions. One is the transition from collinear ferrimagnetic structure to proper screw spin structure at approximately 310 K. The other is the anomaly at 45 K, which is corresponding to the transition from proper screw phase to longitudinal conical phase. As reported in $Ba_2ZnMgFe_{12}O_{22}$ hexaferrite, the nonlinear spiral spin structure was only stabilized below 50 K.[30] While in as-grown composite $BaSrZnMgFe_{12}O_{22}$, the helimagnetic structure can sustain up to above room temperature. This is because the superexchange interaction of Fe–O–Fe bond can be tuned by replacing Ba with Sr owing to different ionic radius between Ba^{2+} and Sr^{2+} ions.[31,32] Furthermore, hexaferrite with the composition $BaSrZn_2Fe_{12}O_{22}$ only shows spiral spin order below rather low temperature (< 10 K).[32,33] Therefore, the high transition temperature of helimagnetic phase of $BaSrZnMgFe_{12}O_{22}$ demonstrates magnetic structures are sensitive to cation distribution, for Zn^{2+} ions preferentially occupy tetrahedral sites while Mg^{2+} ions favor octahedral sites.

Figure 1(b) displays the magnetic field dependence of magnetization at selected temperatures between 30 K and 300 K for $BaSrZnMgFe_{12}O_{22}$. The magnetization curves are similar to those for the helical magnetic phase of several other helimagnetic hexaferrites.[16–20] With magnetic field increasing, the magnetization rises rapidly at low-field region, and then increases gently with two kinks to the saturation magnetization. This stepwise feature of magnetization implies that the magnetic field drives successive metamagnetic transitions into a ferrimagnetic state via a transverse conical spin ordered state.

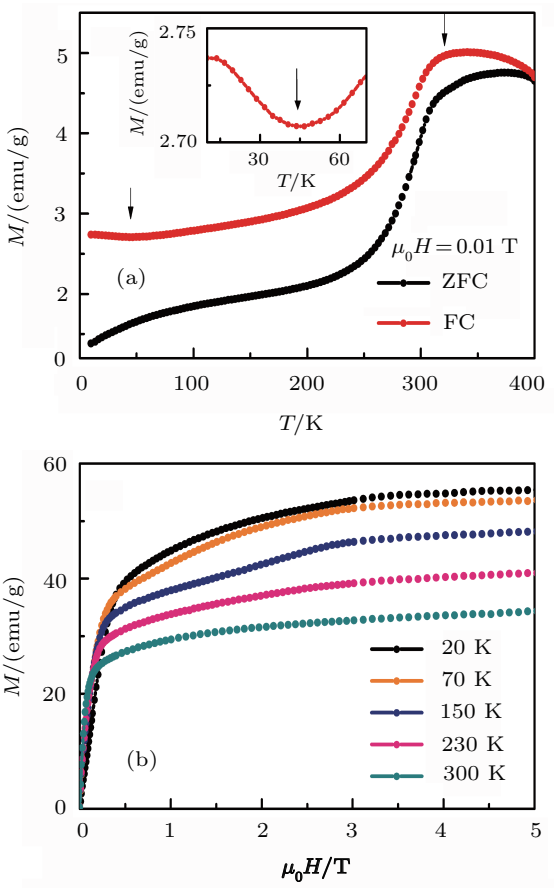


Fig. 1. (color online) Magnetization as a function of temperature under 0.01 T after zero-field cooling (ZFC) and field cooling (FC) processes. The vertical arrows mark the transition temperatures at 45 K and 310 K. (b) Initial magnetization curves measured at selected temperatures.

Even though the proper screw spin state of $BaSrZnMgFe_{12}O_{22}$ can sustain up to 310 K, the ME effect was measureable only below ∼ 100 K due to its low resistivity. Therefore, we show hereafter the low-temperature ME properties for $BaSrZnMgFe_{12}O_{22}$. Figures 2(a) and 2(b) illustrate the magnetic field (H) dependence of magnetization (M), dielectric constant (ε) of $BaSrZnMgFe_{12}O_{22}$ at 20 K. Both of the magnetization and dielectric constant curves show clear hysteresis in low-field region (0 T–0.3 T). M increases in two steps up to the saturation magnetization. As H increases, the magnetization shows a rapid rise from 0 T to ∼ 0.14 T, increases gently from 0.14 T to 3.35 T and then becomes nearly constant above ∼ 3.35 T. These anomalies in M accompany those in the relative dielectric constant ε, as seen in Fig. 2(b). The dielectric constant has one sharp peak at ∼ 0.14 T and the other broad peak around 3 T, which evidence the appearance and vanish of the electric polarization, respectively. The dielectric loss tangent $\tan\delta$ measured at 10 kHz (not shown here) is 10^{-3} and also shows a sharp peak at 0.14 T at 20 K. Moreover, the dielectric constant measured at different frequencies exhibits the same magnetic-field dependence.

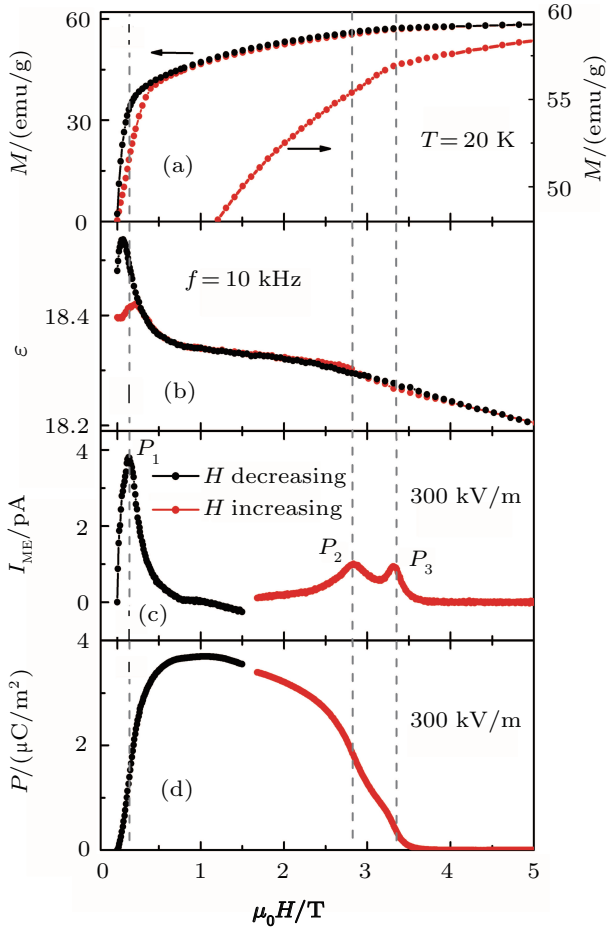


Fig. 2. (color online) Temperature dependence of (a) magnetization, (b) dielectric constant, (c) ME current, and (d) electric polarization at 20 K.

Figure 2(c) depicts the magnetic field dependence of ME current ($I_{\rm ME}$) at 20 K. Before each measurement, an electric field (300 kV/m) was applied at zero magnetic field. Then, the magnetic field, perpendicular to the electric field, was set to 1.5 T. These steps poled the sample into the magnetic-field-driven ferroelectric phase. After the poling process, electric field was removed and then $I_{\rm ME}$ was measured by sweeping $\mu_0 H$ up and down at a rate of 8 mT/s. As $\mu_0 H$ decreases from 1.5 T to 0 T, the $I_{\rm ME}$ has a sharp peak P_1 around 0.14 T. During H increasing sweep, two peaks appear around 2.8 T (P_2) and 3.35 T (P_3), respectively. The electric polarization was obtained from the integration of the ME current by time, as shown in Fig. 2(d). As $\mu_0 H$ increasing from 0 T, the electric polarization grows rapidly and reaches a maximum (3.7 μC/cm^2) at $\sim$ 1 T. Then, the H-induced P decays slowly. As H further increasing, P descends fast around 2.8 T and disappears above $\sim$ 3.35 T. The maximum of ME coefficient $\alpha_{\rm ME} = {\rm d}P/{\rm d}H$ of this sample is $\sim$ 17.3 ps/m at 20 K. Because of the longitudinal-conical spin ground state for $BaSrZnMgFe_{12}O_{22}$, no spontaneous polarization appears at zero magnetic fields, according to the spin-current and the inverse Dzyaloshinskii–Moriya models. When applying moderate magnetic fields, the longitudinal conical spin phase can be driven into the transverse conical spin structure with the cycloidal component, and resulting in net polarization. With magnetic fields increasing, the cone angle and the modulation period of the transverse conical spin structure are varied, which lead to changes in magnitude of electric polarization P. As the magnetic field further increases, the system becomes ferrimagnetic and therefore the electric polarization vanishes. In this nonpolar ferrimagnetic state, the information of ferroelectric domains should be lost, as the ferroelectric polarization originates from noncollinear spin structures. However, when $\mu_0 H$ swept back from 13 T to 0 T, we have also detected the signal of ME current, which indicates changes in electric polarization. There may be a memory effect.

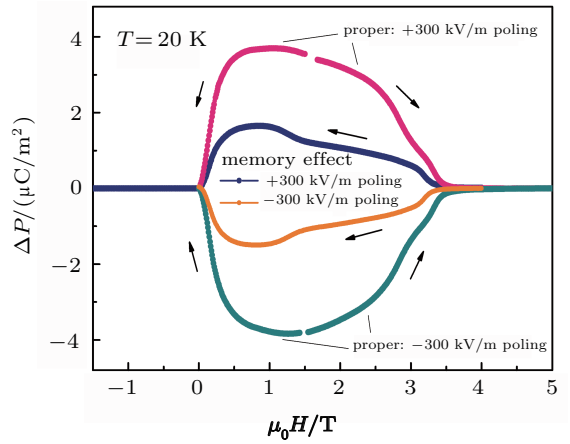


Fig. 3. (color online) Magnetic field profiles of electric polarization at 20 K. For the P–H data labeled as "proper ±300 kV/m poling", electric field were applied at 0 T and then removed at $\mu_0 H = 1.5$ T. While for the P–H data labeled as "memory effect", electric field was switched off after sweeping H up to 4 T. After these procedures, magnetoelectric current was measured during H increasing or decreasing sweeps.

In order to verify whether the memory effect exists or not, following experiments with two kinds of poling procedures were carried out. The two sets of P–H data are shown in Fig. 3. For the P–H data labeled as "proper ± 300 kV/m poling", we performed a proper ME poling procedure in which the poling electric fields were applied at 0 T (paraelectric state) and then switched off at $\mu_0 H = 1.5$ T (ferroelectric state). After the poling procedure, the measurements were carried out during H increasing and decreasing sweeps. As shown in Fig. 3, P only appears between 0 T and 3.35 T, and the sign of P can be changed by altering that of poling electric field. These results suggest that the sample shows ferroelectricity only in the spin spiral phase. It is noteworthy that no electric polarization is observed when H reversed. For the P–H data labeled as "memory effect" in Fig. 3, the specimen was poled differently. An electric field of 300 kV/m was first applied at 0 T, and then sweeping $\mu_0 H$ up to 4 T (nonpolar ferrimagnetic state). After poling, the electric field was removed and then ME current $I_{\rm ME}$ was recorded during H decreasing process. If the phase above

3.35 T were truly paraelectric, the ceramic would not memorize the information of ferroelectric domains and the polarity of the poling electric field after this poling procedure. However, as shown in Fig. 3, the crystal retains its original polarity of the poling electric field or the electric polarization in spiral spin state. This is a memory effect. The maximum of obtained electric polarization P is about 1.6 μC/m^2, smaller than that measured after proper ME poling procedure. A plausible explanation is magnetic/ferroelectric domain walls were partially pinning by defects. Therefore, the spin chirality and direction of P are memorized within the frozen domain walls even at paraelectric state.

If the sample was initially cooled down to 20 K under electric field (300 kV/m) and then poled the system in the proper ME poling process as stated above, the ME current could be detected with H sweeping from positive to negative. The electric polarization was integrated ME current by time. As shown in Fig. 4, the magnitude of P reaches to 6 μC/cm^2, bigger than that of zero-electric-filed cooling procedure (3.7 μC/cm^2). It is worth to note that the electric polarization does not vanish when H reduced to zero, different from zero-electric-field cooling procedure (as shown in Fig. 3). Moreover, a finite P was observed when H reverses, but the maximum of P is reduced to 2.5 μC/cm^2. With H further sweeping between ±4 T, the P–H curve shows a large hysteresis loop having a symmetrical shape, as depicted in Fig. 4. These results indicate that electric-field cooling is helpful to memorize the information of ferroelectric domain, which may attribute to the pinning of multiferroic domain walls by space charge. Therefore, the spin chirality and structure of much more frozen domain walls are memorized, so that P appears to be conserved when H reversed, in response to frozen domain-wall motion. To understand the microcosmic mechanism of this unique memory effect, further experimental and analysis should be carried out.

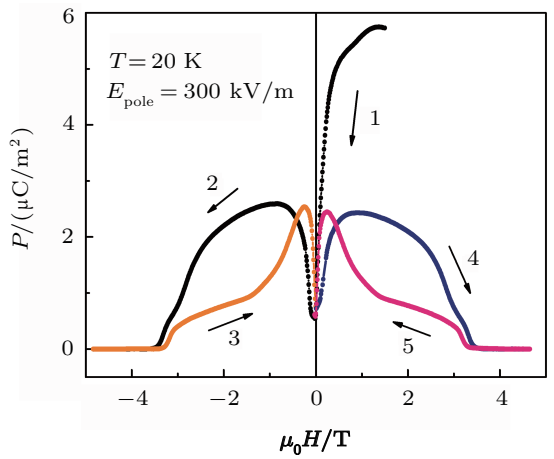


Fig. 4. (color online) P–H curves measured at zero electric field after the following poling procedure: cooled the sample with electric field (300 kV/m) down to 20 K and then swept $\mu_0 H$ from 0 T to 1.5 T.

4. Conclusion

In summary, $BaSrZnMgFe_{12}O_{22}$ possesses a relatively high spiral magnetic transition temperature (∼ 310 K), below which successive magnetic-field-driven metamagnetic transitions occur. Magnetoelectric measurements have shown that magnetic field can control electric polarization, related to evolution in magnetic structures. Because the sample is not insulating enough to sustain the ferroelectric polarization, ME effects can only be measured below ∼ 100 K. An anomalous magnetoelectric memory effect that the ferroelectric state can be partially reproduced from the paraelectric collinear spin phase by reducing magnetic field was observed. The frozen domain-wall motion is responsible to this memory effect. Furthermore, after electric-field cooling, magnetically controllable polarization can be preserved when magnetic field reverses, due to the pinning of multiferroic domain walls by defects and space charge.We expect that similar memory effects could happen in other multiferroic hexaferrites. Especially, in highly insulating hexaferrites with a high spiral transition temperature, one may observe the memory effect even at room temperature.

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