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Periodical polarization reversal modulation in multiferroic $MnWO_4$ under high magnetic fields

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We report polarization reversal periodically controlled by the electric field in multiferroic $MnWO_4$ with a pulsed field up to 52 T. The electric polarization cannot be reversed by successive opposite electric fields in low magnetic fields (< 14 T) at 4.2 K, whereas polarization reversal is directly achieved by two opposite electric fields under high magnetic fields (< 45 T). Interestingly, the polarization curve of rising and falling fields for $H \parallel u$ (magnetic easy axis) is irreversible when the magnetic field is close to 52 T. In this case, the rising and falling polarization curves can be individually reversed by the electric field, and thus require five cycles to recover to the initial condition by the order of the applied electric fields ($+E$, $-E$, $-E$, $+E$, $+E$). In addition, we find that ferroelectric phase IV can be tuned from parallel to antiparallel in relation to ferroelectric phase AF2 by applying a magnetic field approximated to the c axis.

Keywords: polarization reversal, periodical modulation, high magnetic field

PACS: 75.85.+t, 77.80.Fm, 77.22.Ej **DOI:** 10.1088/1674-1056/acca07

1. Introduction

Multiferroic materials in which ferroelectric (FE) and ferromagnetic orders are coupled have attracted extensive research interest because of their application potential in tunable magnetoelectric (ME) devices.[1–3] Of particular interest is a new class of type II multiferroic materials, in which noncollinear magnetic order induces FE polarization and often shows gigantic ME effects.[4] In these materials, the application of a magnetic field can control the FE polarization, and vice versa, i.e., the ME coupling effect. The spin current model or inverse Dzyaloshinskii–Moriya interaction model, $\boldsymbol{P}_{ij\propto} \sim \boldsymbol{e}_{ij} \times (\boldsymbol{S}_i \times \boldsymbol{S}_j)$, is proposed to be the microscopic mechanism for induction of ferroelectricity by magnetic order. A number of multiferroic materials, such as $Ni_3V_2O_8$,[5] $LiCuVO_4$[6] and $TbMnO_3$,[7] have been investigated extensively. In frustrated magnets, many ME phenomena have been observed in multiferroic materials due to the complicated spin structures, such as FE transition, polarization flop and polarization reversal. Indeed, the polarization reversal caused by a magnetic field or chemical doping is still a hot issue[8,9] in most cases of magnetically induced electric polarization. In this paper, we present magnetoelectricity in a frustrated spin system, antiferromagnet $MnWO_4$, with a combination of electric and magnetic fields. We demonstrate that the FE of $MnWO_4$ can be individually reversed by electric and magnetic fields, as well as magnetic field orientation. These results suggest that there exists an exotic ME response in $MnWO_4$, which offers a promising avenue for exploring the ME effect in multiferroics.

$MnWO_4$ is a frustrated spiral magnet, which crystallizes in a monoclinic structure with space group $P2/c$. All Mn^{2+} ($S = 5/2$, $L = 0$) ions form a zigzag chain running along the c axis (see Fig. 1). With decreasing temperature, the spins of Mn^{2+} develop into three antiferromagnetic ordering states, AF3 ($T_{N2} < T < T_{N3}$), AF2 ($T_{N1} < T < T_{N2}$) and AF1 ($T < T_{N1}$).[10] The neutron diffraction results show that AF3 and AF1 phases are collinear spin structures, while AF2 is an incommensurate elliptical spiral phase that breaks spatial-inversion symmetry.[11] Note that the magnetic easy axis, named the u axis, is within the ac plane and deviates from the c axis by 55°,[12] as shown in Fig. 1(b). Consequently, experimental results show that a magnetic field induces two FE phases, AF2 and IV, accompanied by high-field paraelectric states HF and V.[13] Contrary to phase AF2, the sign of IV is spontaneously reversed in a pulsed high magnetic field, and its magnetic structure is still unknown. In the present work,

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we investigate the polarization reversal behaviors of $MnWO_4$ by combining an electric field with a pulsed magnetic field ramped up to 52 T. Experimental results show that the polarization reversal is found to be periodically modulated by the reversing electric field, as well as the strength and orientation of the magnetic field. These results indicate that unique ME characteristics exist in $MnWO_4$, in which the spin chirality is reversed by the electric field.

2. Experiments

Single crystals of $MnWO_4$ were grown by the flux method and determined by x-ray single-crystal diffraction as described in previous work.[14] A typical single crystal is shown in the inset of Fig. 1(c). The applied magnetic field up to 52 T with a pulse width of 11 ms was generated by a nondestructive pulsed magnet in the Wuhan National High Magnetic Field Center, Huazhong University of Science and Technology. The bias electric field was fixed along the b axis unless otherwise stated, while the magnetic fields were rotated within the ac plane. The direction of the magnetic field is presented as parameter θ, where θ denotes the angle between the magnetic field and the c axis. For the measurement of electric polarization, the sample was cut into a thin plate. We measured the electric polarization with a DC bias electric field of 200 $kV{\cdot}m^{-1}$ provided by a voltage source. Platinum electrodes were sputtered onto the samples and then the platinum wires were attached to the opposite faces of the thin plate. Electric polarization was obtained by integrating the pyroelectric current stimulated by the magnetic field.

3. Results and discussion

Figure 1(c) shows the temperature-dependent magnetic susceptibility χ_a, χ_b and χ_c of $MnWO_4$ single crystal for three crystalline axes. For $H = 0.1$ T, three kinks representing antiferromagnetic ordering with transition temperatures $T_{N3} = 13.7$ K, $T_{N2} = 12.8$ K and $T_{N1} = 6.8$ K are observed when the magnetic field is along the a, b and c axis, respectively. In accordance with the early results, these antiferromagnetic phases were defined as AF3, AF2 and AF1, respectively. In particular, phase AF2 is demonstrated to have an incommensurate magnetic structure, yielding a spontaneous FE state. In addition, the susceptibilities χ_a and χ_c show a drop and χ_b exhibits a rise below T_{N1}, suggesting that the spins of Mn^{2+} are arranged in the ac plane at AF1.[15] This motivates us to explore the evolution of polarization with the application of a magnetic field within the ac plane.

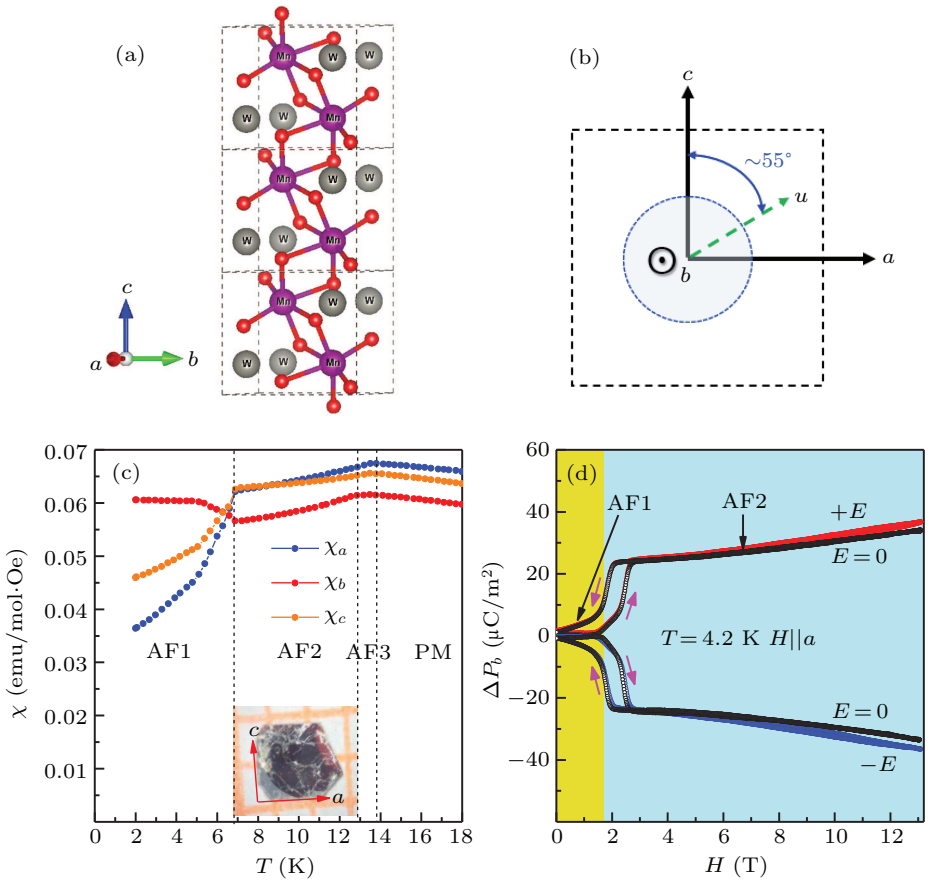


Fig. 1. (a) Crystal structure of $MnWO_4$. Each Mn atom is surrounded by six O (red balls) atoms. The zigzag chains are separated by the W atoms. (b) Schematic diagram of the magnetic easy axis u of $MnWO_4$ viewed along the b axis. (c) The magnetic susceptibility of $MnWO_4$ single crystal with $H = 0.1$ T, where the denotes AF1, AF2, AF3 and PM represent the antiferromagnetic and paramagnetic phases. The inset shows an image of a single crystal of $MnWO_4$ grown by the flux method, and the arrows indicate the crystallographic directions. (d) The field-independence of polarization with different bias fields for $H \parallel a$ at 4.2 K. AF1 and AF2 indicate the nonferroelectric (nonpolarized state) and ferroelectric phases.

Figure 1(d) shows the evolution of the b axis electric polarization tuned by the electric and magnetic fields for $H \parallel a$ ($\theta = 90°$), the value of polarization is calculated from $\Delta P_b \equiv P(H) - P(H = 0)$. Before each measurement, the sample was cooled down from room temperature to 4.2 K (nonpolarized state) under a poling electric field $E = \pm 200$ kV·m^{-1} (labelled as $\pm E$) without a magnetic field. At 4.2 K, a robust change of ΔP_b (~ 20 μC·m^{-2}) is observed in the vicinity of $H = 2$ T with the bias field $+E$, suggesting a transition from a nonpolarized state to the FE AF2 phase. A large hysteresis is observed, which reveals a first-order phase transition. The polarization does not decay in a field of approximately 14 T, coinciding with the observations in early work.[16] Moreover, the magnetic field can render an alternative way to recover the initial polarized state ΔP_b with the removal of the bias field ($E = 0$). As the primitive polar direction is converted to become negative, the opposite direction ΔP_b reproduced by the magnetic field is observed. Those results imply that magnetic field can individually reproduce the FE information from the nonpolarized state, which is known as the ME memory effect. The field-driven polarization is similar to the case of $Ni_3V_2O_8$, in which the FE phase can be reversed by the magnetic field instead of the electric field.[5] Therefore, $MnWO_4$ is a specific material whose polarization reversal by magnetic field deserves to be further studied.

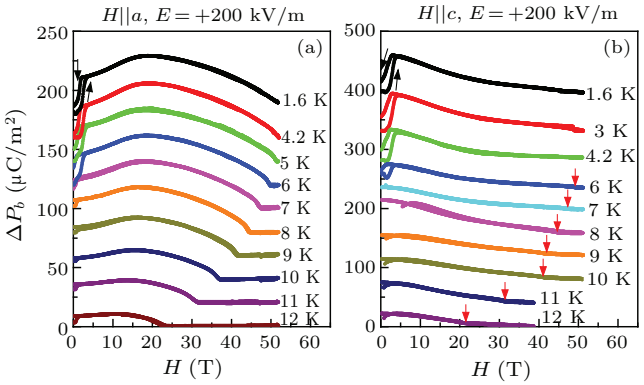


Fig. 2. Polarization ΔP_b measured at different temperatures in a magnetic field applied along the (a) a and (b) c axes, respectively. The bias electric field is equal to $E = +200$ kV·m^{-1}. The red arrows in (b) indicate the transition of polarization.

Figure 2 displays the field dependence of ΔP_b in selected magnetic fields applied along the a and c axes at various temperatures. For H along the a axis, the increase in polarization is extended around 20 T and gradually reduced with increasing field to 52 T at low temperatures. For temperatures $T > T_{N1}$ (~ 6 K), the anomalous jump of polarization disappears. This disappearance is ascribed to the suppression of the nonpolarized state AF1 by the temperature. As the temperature is increased, the boundary of the FE AF2 phase to the high-field paraelectric state V appears in the high-field region and shifts toward a low field, and the magnitude of polarization decays. Above T_{N3} (> 12 K), all the polarizations responding to the magnetic field disappear, indicating that polarization is related to the magnetic order. The effect of magnetic field applied along the c axis ($\theta = 0°$) is distinctly different from that of $H \parallel a$. Except for the nonpolarized state of FE AF2, it is found that the FE AF2 phase is strongly suppressed by the magnetic field, as seen in Fig. 2(b). Similar to observations for $H \parallel a$, the phase transition from the FE AF2 phase to the paraelectric state V is shifted to the low field as temperature increases.

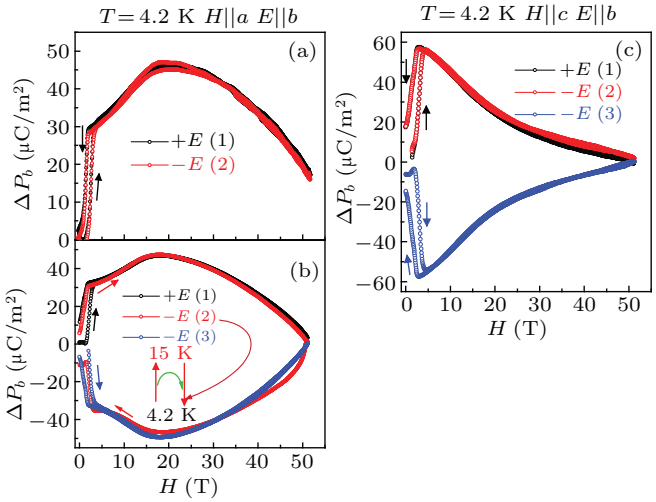


Fig. 3. Field dependence of polarization with different bias electric fields: (a), (b) $H \parallel a$, (c) $H \parallel c$. The inset in (b) shows the temperature raised to 15 K and maintained for several minutes then subsequently lowered to 4.2 K, leading to the polarization between rising and falling fields being irreversible. In addition, the $\pm E$ indicate the magnitude and direction of the bias electric field, and the labels (1)–(3) represent the order of the applied electric field.

Domain switching in $MnWO_4$ has a pronounced character because the polarization can be individually reversed by the magnetic and electric field. For $H \parallel a$, a peak of polarization is observed at around 20 T and rapidly approximates to zero at 52 T (black curve, $+E(1)$), as shown in Fig. 3. Unexpectedly, the sign and magnitude of polarization ΔP_b remain unchanged (red curve, $-E(2)$) when the electric field is reversed. This behavior was ascribed to the ME memory effect, which is exceptional compared with that in traditional ferroelectricity, such as in $BaTiO_3$[17] and $PbZrO_3$.[18] However, once the temperature is lifted to 15 K ($> T_{N3}$) for several minutes and returned to 4.2 K after $+E(2)$ measurement, two opposite electric fields $-E(2)$ and $-E(3)$ can completely reverse the polarization ΔP_b, as shown in Fig. 3(b). Amazingly, an irreversible intermediate state between rising and falling field curves emerges. This result suggests that the high temperature destroyed the history of spins responding to the magnetic field, giving rise to elimination of the ME memory effect. In this case, high temperature is exploited to remove the history process in the multiferroic. For $H \parallel c$, the effect of an external magnetic field on the FE polarization is shown in Fig. 3(c). Firstly, the FE polarization develops a peak at 2.5 T and rapidly reduces to zero (black curve) with electric field

$+E(1)$. Unlike $H \parallel a$, polarization along the c axis rapidly decays when magnetic field exceeds 2 T, which reveals the strong anisotropy of polarization in $MnWO_4$. In parallel with $H \parallel a$, almost no change in polarization is observed if the electric field is reversed only once (red curve, $-E(2)$), and polarization reversal can be directly realized upon reversing the electric field for the second time (blue curve, $-E(3)$). In this case, realization of polarization reversal by the bias electric field requires two steps. Note that the ferroelectricity in $MnWO_4$ is ascribed to spin chirality, and the direction of polarization depends on the chiral vector.[16] These results show the reentrant FE AF2 phase driven by $-E(2)$ is different from that observed in $+E(1)$, which means that the chirality of spin is changed by the electric field.

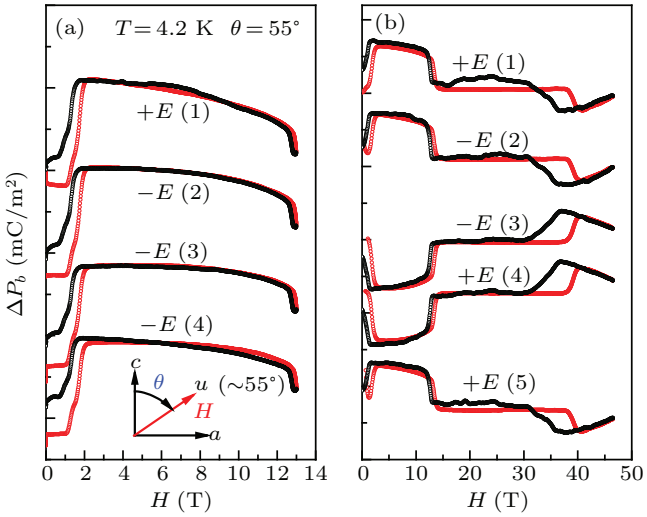


Fig. 4. Electric field modulates the polarization reversal in different magnetic fields: (a) 13 T, (b) 48 T. The red curves represent the polarization process with rising field, while the black curves indicate the falling field. The $\theta = 55°$ shown in the inset is the tilted angle from the magnetic easy axis to the c axis. $\pm E(1)$ to $\pm E(5)$ denote the direction and order of the applied bias electric field.

In order to further explore the polarization reversal, we apply a magnetic field along the magnetic easy axis u, stated as $\theta = 55°$. Figure 4 shows the polarization reversal controlled by combining the magnetic and electric fields for $\theta = 55°$; the selected temperature is 4.2 K. Before each measurement, the sample is subjected to an electric field. At low magnetic fields ($H < 5$ T), the FE AF2 phase robustly emerges at 2 T and shows a maximum value of ~ 60 μC·m^{-2}. For magnetic fields above 13 T, the polarization of this FE phase is quickly suppressed because of the alignment of spins driven by the magnetic field,[19] as shown in Fig. 4(a). These experimental data are basically consistent with the corresponding results in previous works.[13,14] However, the electric field is reversed several times, and we found that the polarization ΔP_b remains unchanged for all the measurements. By contrast, when a magnetic field is swept up to 48 T, the paraelectric phase HF and FE phase IV emerge at 14 T and 38 T, respectively. Meanwhile, a second first-order phase transition from HF to IV is observed. Most remarkably, the FE phases IV and AF2 maintain opposite directions in each field circle. In this case, the application of two consecutive opposite bias electric fields, $-E(2)$ and $-E(3)$, related to the first measurement can trigger the spontaneous change in the direction of polarization. After that, the polarized state of $MnWO_4$ can be recovered by using a positive electric field two times, marked as $+E(4)$ and $+E(5)$. Therefore, reversal of polarized states with just an electric field is demonstrated.

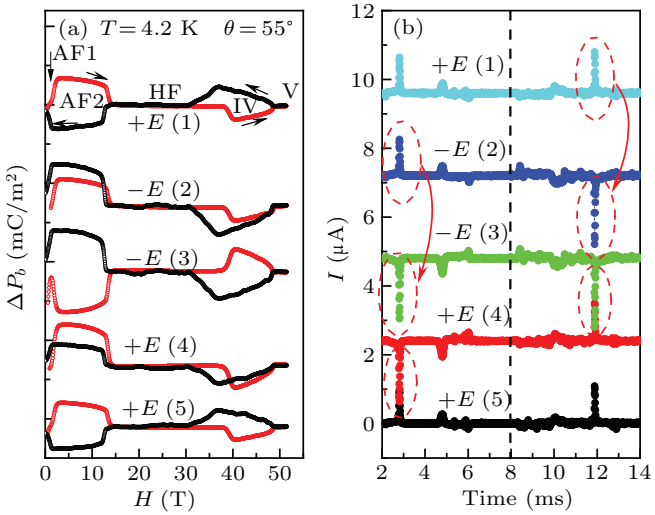


Fig. 5. The electric polarization and the corresponding pyroelectric current reversed by the different bias electric fields: (a) electric polarization, (b) pyroelectric current. Here, the pyroelectric current is as a function of pulse time, and the rising and falling field currents are separated by the vertical broken line. In addition, AF1 is a nonpolarized state and AF2 and IV are ferroelectric states, while HF (high-field paraelectric state) and V are paraelectric phases.

In order to further explore the occurrence of polarization reversal, a relatively high magnetic field is applied to the sample. Figure 5 shows the electric polarization and corresponding pyroelectric current induced by the magnetic field up to 52 T. Prior to the electrical measurements, a bias electric field is applied to the sample. When the magnetic field exceeds 52 T, another paraelectric state, V, is observed at 48 T, as shown in Fig. 5(a). Interestingly, the polarizations in rising (red curve) and falling (black curve) fields are reversed. Thus, the trace of polarization forms a transformed '∞' loop in a magnetic field cycle. Under a negative electric field $-E(2)$, it is seen that the polarization in a falling field is completely reversed, whereas that in a rising field is not affected by the field. Repeating this process by using $-E(3)$, the signs of polarization and the corresponding pyroelectric current are changed with respect to a falling field. This can be evidenced by the change in the peak for pyroelectric current, which is a function of time as shown in Fig. 5(b). In Fig. 5(b), it is seen that the currents in rising and falling fields are separated and individually reversed by the electric field. Hence, the electric field completely reverses the polarization curve in comparison with

the initial state. Similar behavior is observed when the electric field is switched to a positive direction: the polarization recovers to the initial state in two steps. The symmetry of current changing with time reflects the polarization modulated by the reversed electric field, as shown in Fig. 5(b). These results show that polarization reversal in combination with electric and magnetic fields is a unique characteristic of $MnWO_4$ in high fields. This behavior appears to be observed in similar systems such as $Ni_3V_2O_8$, where the FE state can be manipulated by reversing the electric field. In $Ni_3V_2O_8$, the high-field FE phase is directly reversed by the negative electric field, and the reversal of the low-field phase is realized in the second time field. However, the two FE phases in $MnWO_4$ can be simultaneously reversed without an intermediate state. The evolution of polarization measured at different temperatures in $H \parallel u$ has been described in the literature in detail.[14]

Our data also show that polarization responds to magnetic field in a special direction. Figure 6 shows polarization controlled by the electric field with a tilted angle of $\theta = 70^\circ$ at 4.2 K. At low fields ($H < 48$ T), it is obvious that a new high-field FE phase, +IV, is observed in $+E(1)$ as well as the FE AF2 and PE HF phases. In this case, the FE phases AF2 and IV become parallel to each other rather than antiparallel. Note that the change of sign of FE phase IV originates from the magnetic field rather than the electric field, implying that magnetic anisotropy is an alternative way to manipulate the polarized state in $MnWO_4$. Associated with the ME memory, no change of polarization is observed for the first opposite electric field $-E(2)$. For the second negative electric field $-E(3)$ the polarization curves in rising and falling fields are completely reversed. The above process can be returned to the initial state by applying positive electric fields twice ($+E(4)$, $+E(5)$). Thus, the polarized state can return to the original configuration with periodically reversed electric fields $+E(1)$, $-E(2)$, $-E(3)$, $+E(4)$, $+E(5)$. The high-field paraelectric state V emerges at a high field (~ 52 T), as shown in Fig. 6(b). Compared with that in $H \parallel u$, the process of polarization becomes reversible with a large hysteresis in a relatively high field. The discrepancy between $\theta = 70^\circ$ and $\theta = 55^\circ$ indicates that the polarization information in the two directions is different. On the other hand, the direction of polarization can be reversed and recovered by the negative and positive fields, respectively. Therefore, the rising and falling field curves can be individually tuned by the electric field in both directions. These experimental phenomena were first observed in $MnWO_4$ with a high magnetic field. No similar cases have been found in other compounds, such as magnetic-induced FE $TbMnO_3$[20] and $CuCr_2O_4$.[21]

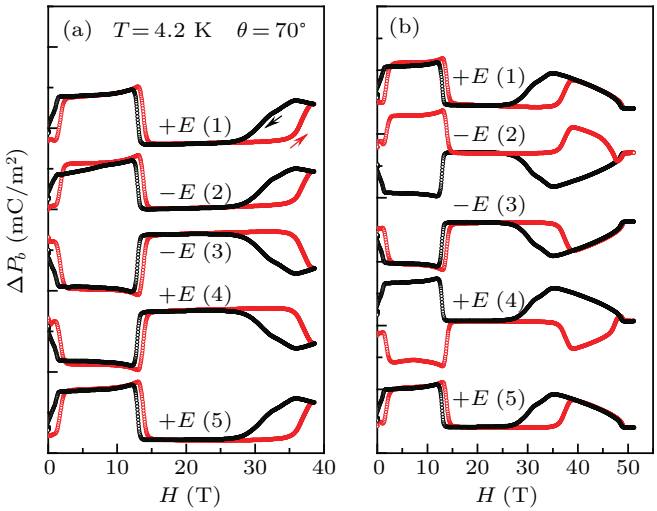


Fig. 6. The magnetic field dependence of polarization with a circularly changing bias electric field: (a) 38 T, (b) 52 T.

According to the above results, it is found that the field-induced FE polarization in $MnWO_4$ is strongly sensitive to the orientation of the magnetic field. Two FE phases AF2 and IV merge into a single phase in a certain magnetic field direction; detailed evolution of the polarization is described in the literature.[14] Here, we suppose that the value of polarization is approximately equal to the sum of two parts, P_1 ($H < 14$ T) and P_2 ($H > 14$ T), where P_1 is considered a result of the FE AF2 phase[22] and P_2 relates to the FE IV phase, as shown in Figs. 7(a) and 7(b). Hence, the strength of polarization ΔP_b can be phenomenologically expressed by $\Delta P_b \equiv P_1 + P_2$ below the transition temperature. The total polarization for $H \parallel a$ can be written as the sum of P_1 and P_2. In contrast to $H \parallel a$, the polarization for $H \parallel c$ is shown as $\Delta P_b \equiv P_1 - P_2$ due to the direction of change of P_2. In this case the emergence of the paraelectric HF in the *ac* plane could be explained as the result of competition between P_1 and P_2. In addition, the sign of FE phase IV is susceptible when the angle θ exceeds 55°, as depicted in the early literature.[14] Regarding the polarization reversal, it can be realized by magnetic field,[23] electric field[24] or chemical doping, such as Co^{2+} doping in $MnWO_4$.[22] These results imply that the unusual ME effect in $MnWO_4$ is attributed to the spin arrangements driven by magnetic field, as has been discussed in previous work.[14] Therefore, if we suppose that the critical fields of FE transition triggered by magnetic field are marked by H_{c1}, H_{c2}, H_{c3} and H_{c4}, as shown in Figs. 7(a) and 7(b), in the field range of H_{c1}–H_{c2} it is seen that the FE phase AF2 remains unchanged when the angle θ is varied from 55° to 70°. However, the contrasting result for FE IV phase reversal by magnetic field is observed in fields H_{c3}–H_{c4}. This result implies that the spin chirality in FE phase IV is distinguished from that in FE phase AF2. Indeed, the spiral spin structure of phase IV analogous to AF2 has been demonstrated by time-resolved neutron Laue diffraction.[19] Combined with the results for the *a* and *c* axes,

we construct a schematic diagram in which the spin chirality is determined by the magnetic field and angle θ, as displayed in Fig. 7(c). In this figure, the FE phases AF2 and IV exhibit different polarization directions, and the chirality of IV is altered in certain areas. Thus, we observe that the polarization of $MnWO_4$ is strongly dependent on the magnetic field, the electric field and the magnetic field orientation. Utilizing the polarized states periodically tuned by electric field and FE phase IV modulated by anisotropy in $MnWO_4$ may help us to design a device controlled by those factors. In addition, the mechanism of the polarized states periodically tuned by electric field and FE phase IV spontaneously reversed by magnetic field is exotic. These experimental phenomena first observed in multiferroic $MnWO_4$ have not been found elsewhere. This novel behavior supplies a promising avenue in the search for field-modulated polarization reversal in other multiferroic crystals.

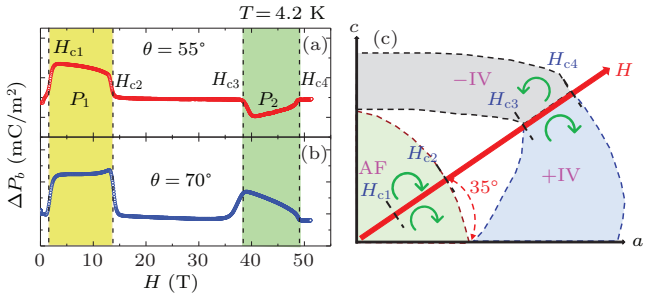


Fig. 7. Schematic diagram of spin chirality of the polarization direction determined by the strength and direction of magnetic field. (a), (b) The measured polarization in a rising field for the angles $\theta = 55°$ and $70°$ at 4.2 K, respectively. H_{c1}–H_{c4} show the critical fields of polarization transition. (c) The change of spin chirality by rotating a magnetic field within the *ac* plane. The green curved arrows indicate the spin chirality. Due to the sign of polarization, two different ferroelectric phases, −IV and +IV, are defined.

4. Conclusions

In summary, the ME effect in $MnWO_4$ has been studied with the magnetic field rotated in the *ac* plane. The field-induced electric polarization shows strong anisotropy in dependence on field angle. Polarization reversal can be directly realized by the electric field in two steps without intermediate states when the magnetic field is applied along the *a* and *c* axes, and high temperature can remove the ME memory. For angles $\theta = 55°$ or $70°$, the polarization is reversed or recovered by a two-step inversed electric field, accompanied with reversal of rising or falling curves. Moreover, the sign of phase IV for $\theta = 70°$ is distinct from that observed at $\theta = 55°$, indicating that they are two different states. The discrepancy can be exploited to save information by changing the direction of the magnetic field. These experimental results show that polarization in $MnWO_4$ can be modulated by temperature, anisotropy, magnetic and electric fields. Finally, the reversed behaviors of $MnWO_4$ provide us with a concept for designing a ME device to save or extract information, in combination with variations in anisotropy, electric field and magnetic field.

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