Polarization Reversal in Multiferroic $TbMnO_3$ with a Rotating Magnetic Field Direction

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For the memory application of magnetoelectric multiferroics, not only bistability (i.e., ferroelectricity) but also the switching of the polarization direction with some noneverlasting stimulus is necessary. Here, we report a novel method for the electric polarization reversal in $TbMnO_3$ without the application of an electric field or heat. The direction of the magnetic-field-induced polarization along the a axis (P_a) is memorized even in the zero field where P_a is absent. The polarization direction can be reversed by rotating the magnetic-field direction in the ab plane.

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Recent extensive studies of magnetic ferroelectric materials have revealed that electric polarization is considerably modified, flipped, or flopped by the application of a magnetic field [1–10]. Such a cross correlation between magnetic order and ferroelectric polarization can provide the possibility of controlling magnetization with an electric field, or the electric polarization with a magnetic field. However, polarization is recovered after decreasing the magnetic field to zero in most cases, which may be inconvenient for the use of memory. The only exception has been reported for a ferroelectric transverse conical ferrimagnet $CoCr_2O_4$: The electric polarization is flipped by 180 degrees with magnetization reversal by sweeping the magnetic field [4].

Perovskite-$TbMnO_3$ investigated here is a prototypical multiferroic material, which shows the gigantic magnetoelectric (ME) effect [3]. Both large $GdFeO_3$-type and cooperative Jahn-Teller–type distortions accompanied by the e_g orbital order of Mn^{3+} give rise to the competition between nearest-neighbor ferromagnetic and next-nearest-neighbor antiferromagnetic interactions in a MnO_2 sheet normal to the c axis and make the Mn^{3+} ($S = 2$) spin system frustrated [11]. Consequently, $TbMnO_3$ has an incommensurate sinusoidal antiferromagnetic structure with a propagation vector $Q \approx (0\ 0.28\ 1)$ between the antiferromagnetic transition temperature $T_N = 43$ K and the ferroelectric transition temperature $T_C = 28$ K [3,11,12]. The magnetic structure turns into an elliptical cycloid upon T_C [12,13]. The ferroelectric polarization simultaneously appears along the c axis, which can be explained by the inverse effect of the Dyaloshinski-Moriya (DM) interaction [14]. Another striking feature in magnetic ferroelectrics is that the electric polarization is flopped from the c direction to the a direction by a magnetic field applied along the a axis or b axis [3,15]. The microscopic origin of the polarization flop is yet to be solved. The present investigation of magnetoelectric effects with a sweeping magnetic field along various paths can provide us information useful also for understanding the microscopic origin of the polarization flop.

Single crystals of $TbMnO_3$ were grown by a floating zone method in a flow of Ar. The crystals were oriented using Laue x-ray photographs and cut into thin plates with the widest faces perpendicular to a crystallographic principal axis a or c of orthorhombic $Pbnm$ setting. Gold electrodes were sputtered onto the opposite faces of the samples for the measurements of electric polarization P. We obtained the P value by the integration of the pyroelectric or magnetoelectric current, which was measured with an electrometer (KEITHLEY 6517A). Magnetic-field directions were controlled by rotating the sample in a cryostat equipped with a 15 T superconducting magnet. Before each measurement of the magnetic-field direction dependence of P, the sample was cooled from a temperature above 43 K in an electric field of 400 kV/m in a magnetic field along the b axis ($H \parallel b$). The poling electric field was turned off at 9 K before the measurements.

Figure 1(a) shows the magnetic-field dependence of electric polarization along the a axis (P_a) at 9 K for several field directions perpendicular to the c axis. Here, θ denotes the angle between the b axis and the magnetic-field direction (see inset). In the case of $H \parallel b$ ($\theta = 0°$), the polarization flops at 4.6 T, as previously reported [3]. For the magnetic field in a slanted direction with $\theta = 20°$, the transition field considerably increases to 7 T. In the $\theta = 30°$ configuration, no electrical polarization flop is observed up to 14.5 T, whereas the flop manifests itself again for $50° \leq \theta \leq 90°$. P_a shows a large hysteresis between 5 and 10 T in these field directions. We also performed measurements of P_a by changing the magnetic-field direction at various field strengths, as shown in Fig. 1(b). In these measurements, the sample was first cooled down to 9 K in applied electric and magnetic fields along the a and b axes ($\theta = 0°$), respectively, and then the poling electric field was turned off. By rotating a magnetic field of 9 T, P_a vanishes between $\theta = 20°$ and 160°, and P along the c

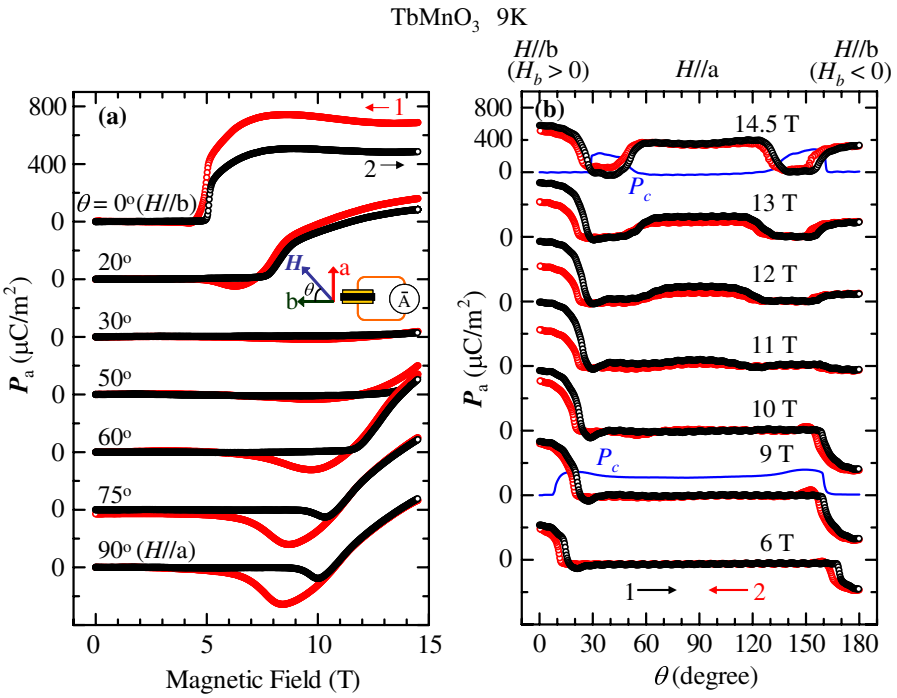

FIG. 1 (color online). Magnetic-field dependence of electric polarization at 9 K. (a) Magnetic-field dependence of P_a at various field directions. (b) Change in electric polarization with magnetic-field rotation for various magnetic fields. θ denotes the magnetic-field direction, as shown in the inset of (a). P_a is shown by circles, and P_c by thin solid lines.

axis (P_c) appears instead, as indicated by a a thin solid line. As θ exceeds 160°, $TbMnO_3$ reenters into the $P \parallel a$ phase. Here, note that P_a appears in the opposite direction to the initial state. A similar behavior is observed in magnetic fields between 6 and 10 T. On the other hand, in magnetic fields higher than 12 T, P_a appears not only for the field direction near the $\theta = 0°$ and $\theta = 180°$ but also around $\theta = 90°$ ($H \parallel a$). In such cases, the sign of P_a in the reentrant $P \parallel a$ phases does not change from the initial state.

A magnetoelectric phase diagram in $TbMnO_3$ at 9 K for magnetic fields applied normal to the c axis is shown in Fig. 2(a). It is noteworthy that the $P \parallel c$ phase intervenes between the $P \parallel a$ phases (yellow regions). This phase diagram is not explained only in terms of the magnetic-field response of Mn spins, which have the easy axis in the b direction. Therefore, we should take account of the magnetic-field response of Tb moments. $TbMnO_3$ shows a metamagnetic transition and a change in magnetic modulation wave number simultaneously with the electric polarization flop by the application of a magnetic field along the a axis or b axis [15–17]. In the polarization flopped $P \parallel a$ phase, Mn and Tb moments are rearranged with $Q = (0\ 1/4\ 1)$. Quezel *et al.* have reported that each Tb moment in $TbMnO_3$ behaves as an Ising spin [18], as shown in Fig. 2(b). Half of Tb moments are canted by $+57°$ and the other half by $-57°$ from the b axis toward the a axis, respectively. The field directions with which the $P \parallel c$ phase remains up to 14.5 T are approximately perpendicular to an Ising direction [Fig. 2(a), red line]. Generally speaking, antiferromagnetic ordering is robust against the magnetic fields applied perpendicular to the magnetic moments. Rearrangement of Tb moments possibly requires a higher magnetic field in these directions. This phase diagram indicates an important role of Tb moments in the magnetic-field-induced electric polarization flop.

Next, we focus on the manipulation of the direction of P_a. As shown in Fig. 1, the sign of P_a is maintained

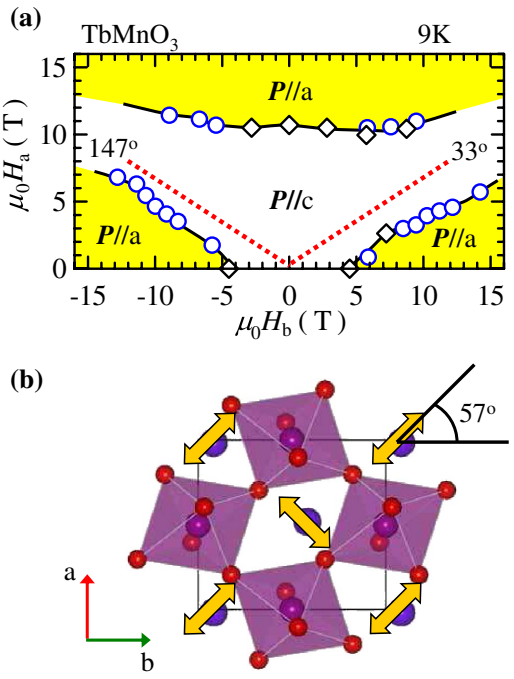

FIG. 2 (color online). (a) Magnetoelectric phase diagram of the magnetic-field direction in the a-b plane of $TbMnO_3$. Vertical and horizontal axes indicate magnetic-field components of $H \parallel a$ and $H \parallel b$, respectively. (b) Schematic drawing of crystal structure of $TbMnO_3$ projected on the (0 0 1) plane. Thick arrows are the Ising directions of Tb moments.

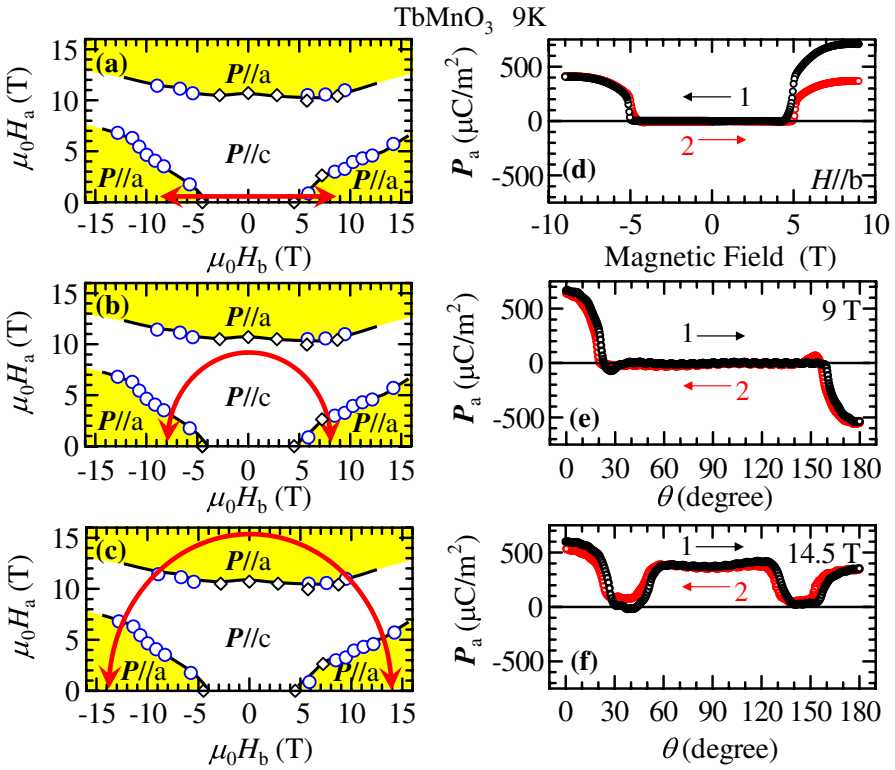

FIG. 3 (color online). Changes in electrical polarization with sweeping magnetic field along several paths at 9 K. (a),(d) With sweeping magnetic field along the b axis. (b),(e) With rotating magnetic field at 9 T, and (c),(f) at 14.5 T.

unchanged after successive polarization-flop transitions with the sweeping magnetic field along some paths, whereas it is reversed along some other paths. Figure 3 demonstrates typical three cases. When a magnetic field is swept along the b axis, P_a always appears in the same direction as the initial poling direction, as shown in Figs. 3(a) and 3(d). Note that no poling electric field is applied in the sweeping run. P_a is 750 μC/m^2 right after cooling in a poling field E_{pol} of 400 kV/m in 9 T. With a sweeping magnetic field from 9 to -9 T, P_a is quenched and P_c appears between 4.5 and -4.5 T. At -9 T, P_a does not reach the initial value but decays to 400 μC/m^2 without the reversal of direction. After the following sweep from -9 to 9 T, P_a does not decay any further. This result indicates that this compound has a nonvolatile memory in the zero field, which can be read as the magnetoelectric current direction ($+a$ or $-a$) when a magnetic field is applied along the b axis. A similar memory effect is also observed by magnetic-field sweeping in a constant direction for $\theta \leq 20°$ and $50° \leq \theta$, as shown in Fig. 1(a). These results imply that the sign of P_a in the magnetic-field-induced $P \parallel a$ phase is memorized even in the $P \parallel c$ phase in an unidentified way. P_a also keeps the sign with the magnetic-field rotation at 14.5 T, as shown in Figs. 3(c) and 3(f). In contrast, after changing the magnetic-field direction by 180° at 9 T, P_a orients in the opposite direction to the initial state [see Figs. 3(b) and 3(e)]. We also performed a similar measurement with the negatively poled initial state ($E_{\mathrm{pol}} = -400$ kV/m). The polarization is reversed to positive after a 180° rotation of a 9 T magnetic field. This magnetic-field-induced polarization reversal is applicable to the rewrite of the memory.

The mechanism of the history-dependent memory and reversal of the P_a direction in $TbMnO_3$ is an open question at the present stage. Both P_c in the zero field and P_a in strong fields are believed to originate from the particular orderings of Mn moments. In the $P \parallel c$ phase, the helicity of the cycloidal order of Mn^{3+} with a spiral plane normal to the a axis determines the polarization direction [19]. It

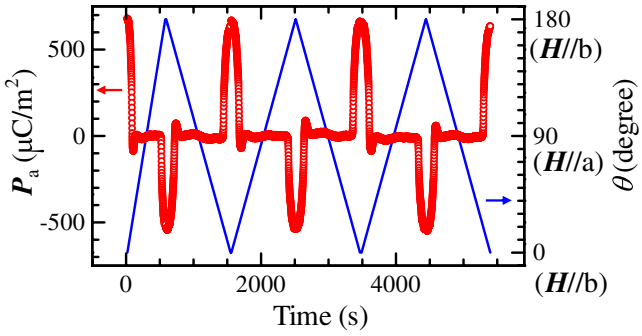

FIG. 4 (color online). Repeatable reversal of electric polarization direction by a rotating magnetic field of 9 T around the c axis. Electric polarization (circles, left side) and magnetic-field direction (thin solid line, right side) are plotted as a function of time.

seems unlikely that the cycloid order of Mn spins in the $P \parallel c$ phase directly memorizes the last P_a direction. Tb moments would instead play an important role for the memory effect. Although Tb moments themselves do not contribute to the polarization in the $P \parallel c$ phase [19], Tb and Mn moments align with the same modulation vector (0 1/4 1) in the $P \parallel a$ phase [16,17]. Therefore, one can expect that some attributes of the long-wavelength arrangement of Tb moments such as helicity and/or phase may correlate to whether the polarization P_a is positive or negative. Upon the polarization-flop transition, the $P \parallel a$ and $P \parallel c$ phases should coexist separated by domain walls because of the first-order nature of the transition. Since the arrangement of Tb moments is different between two phases, Ising-like Tb moments at domain walls align in some particular way, which depends also on the magnetic-field direction. Tb moments in the $P \parallel c$ phase, which are not directly coupled to Mn spins, could memorize the polarization direction of the last $P \parallel a$ phase. It is also likely that the arrangement of Tb moments is modified by magnetic-field sweeping, which can result in the sign reversal of P_a at the next polarization flop.

The discovered polarization switching with the rotating magnetic-field direction is reversible and repeatable. Electric polarization is completely reversed by rotating the magnetic-field direction between 0° and 180° without any noticeable decay in its magnitude, as shown in Fig. 4. Such reproducible polarization flip with the rotating field direction is a new feature of multiferroic $TbMnO_3$. This kind of polarization manipulation by a sweeping magnetic field possibly contributes to the invention of developing a novel rewritable memory device.

In summary, we have discovered electric polarization reversal by the rotating magnetic-field direction in multiferroic $TbMnO_3$. A field-angle dependent ME phase diagram shows an important role of Tb $4f$ moments in the electric polarization flop. The arrangement of Tb moments is modified by magnetic-field sweeping. Mn spin configuration is changed under the influence of the f-d interaction. Consequently, the sign of electric polarization is reversed or memorized.

The sample rotator was made by the Machine Shop, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan. The measurements of P in magnetic fields up to 14.5 T were performed at the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University, Japan. This study was supported in part by grant-in-aid for COE Research and Scientific Research (No. 16076207, No. 19052001) from MEXT, Japan.

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