Magnetic-field-induced ferroelectric polarization flop under pressure in TbMnO$_3$

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Abstract. Magnetoelectric properties of multiferroic TbMnO$_3$ with a cycloidal spiral spin order were investigated as functions of applied pressure and magnetic field. We found that a flop of ferroelectric polarization occurs by applying a magnetic field along the $a$ axis under 2-3 GPa below the Néel temperature of Tb moments. A possible origin of the magnetoelectric transition is discussed based on the observed pressure and magnetic-field profiles of the ferroelectric polarization and the dielectric relaxation. This flop would originate from the 90° rotation of the cycloidal spiral plane from the $bc$ plane to the $ab$ plane.

1. Introduction
A linear magnetoelectric (ME) effect is observed on materials in which both spatial inversion and time reversal symmetries are broken [1]. Recently, new type of multiferroics, in which polar magnetic structures make their lattice distorted through the spin-orbit interaction and induced electric polarization can be controlled by applying a magnetic field, are investigated [2]. This type of multiferroics are expected as realistic candidates for the advanced memory device since their ME effect is often larger than the linear ME effect observed in conventional magnetoelectrics.

TbMnO$_3$ is one of such new type of multiferroics [3]. Below 27 K, Mn moments form a cycloidal spiral magnetic structure with spiral plane parallel to the $bc$ plane in the $Pbnm$ notation. In accordance with the magnetic transition, ferroelectric polarization appears along the $c$ axis. The spiral plane will flop from the $bc$ plane to the $ab$ plane by applying a magnetic field along the $b$ axis. Accompanied by the flop of the spiral plane, the electric polarization also flops from the $c$ to the $a$ axis, which leads to a large ME effect [4, 5]. In this study, we performed high pressure measurements of ME properties in TbMnO$_3$ and found that a ferroelectric polarization flops induced by applying high pressure and magnetic field.

2. Methods
A single crystal of TbMnO$_3$ was prepared by the floating zone method. The grown crystal was cut into plate-shaped specimens with the flat surface perpendicular to the $a$ axis. The typical dimensions of the specimen is $150 \times 150 \times 30 \, \mu$m$^3$. Gold was sputtered to the widest faces of one of the specimens as electrodes. Pressure was applied with a diamond anvil cell (DAC) made of CuBe alloy, applied at room temperature and evaluated by the ruby fluorescence methods [6] at...
3. Results

In Fig. 1(a), temperature $T$ profiles of $\varepsilon'$ collected in 0, 1, 4 and 8 T are displayed. At around 40 K which is the Néel temperature of Mn moments ($T_{N}^{\text{Mn}}$), $\varepsilon'$ shows a sharp increase. At 26 K, $T_{C}$ where the ferroelectric transition occurs due to the $bc$ cycloidal spiral spin order, a small kink structure has been observed in $\varepsilon'$. In this ferroelectric phase, the ferroelectric polarization is along the $c$ axis. Therefore, the observed dielectric anomaly along the $a$ axis is relatively small. At around 6 K which is the Néel temperature of Tb moments ($T_{N}^{\text{Tb}}$), a small drop was observed in magnetic fields lower than 2–3 T, but disappeared in higher magnetic fields. With increasing pressure, the respective transition temperatures were increased monotonically and a
new peak structure developed around $T_{N}^{Tb}$ in magnetic fields lower than 1 T [Figs. 1(b)-(e)]. Above 4 GPa [Fig. 1(d)], the behaviors of $\varepsilon'$ at low temperature is completely different from those obtained below 2.8 GPa (hysteresis behavior, magnetic field dependences, and transition temperature), which indicates the magnetoelectric transition from the cycloidal spiral to the $E$ type antiferromagnetic structure (EAFM) [7, 8]. The obtained data at 0 T are summarized in the pressure-temperature phase diagram shown in Fig. 1(e). The pressure versus magnetic-field phase diagram at 5 K is displayed in Fig. 1(f). The stacked contour map represents the magnitude of the electric polarization along the $a$ axis. At around 2 T and 2.5 GPa, there exists a distinct phase with the electric polarization along $a$. Detailed physical properties of the $P//a$ phase are shown in Fig. 2.

![Figure 2](image)

**Figure 2.** (a) Magnetocapacitance collected at 5 K in various frequencies. (b) Magnetic field dependences of the electric polarization along the $a$ axis collected at 5 K (red) and 7 K (blue). (c) Electric polarization as a function of electric field at 5 K (red) and 7 K (blue) in 2 T. All the data shown here were collected at 2.8 GPa.

The magnetocapacitance collected at 2.8 GPa and 5 K is shown in Fig. 2(a). The data taken at various frequencies are displayed. At around 1 and 3 T, a small shoulder structure at 1 T and a clear peak structure at 2 T developed in $\varepsilon'$ measured at low frequencies. Around the same magnetic field region the electric polarization along the $a$ axis appeared. In turn, the electric polarization flops from $c$ to $a$ occurred only below $T_{N}^{Tb}$ driven by a magnetic field along the $a$ axis. The presence of finite electric polarization below $T_{N}^{Tb}$ at around 2 T is evidenced by polarization-electric field curves displayed in Fig. 2(c). The magnitude of the spontaneous polarization is 700 $\mu$C/m$^2$ and the coercive field is 1 MV/m. The magnitude is also the same with the spontaneous polarization along the $c$ axis while the coercive field is relatively smaller than that along the $c$ axis (8 MV/m at 10 K, 2.7 GPa). It can be considered that the difference of the coercive fields is derived from the difference of $T_C$. Since $T_C$ is far above 10 K in the case of $P$ along $c$, the ferroelectric domains would start to freeze. Another remarkable feature seen in Fig. 2 is the large frequency dependences of $\varepsilon'$. Further details of dispersive behavior in the $P//a$ phase is shown in Fig. 3.
The temperature profiles of $\varepsilon'$ measured at several frequencies are shown in Fig. 3(a). The data are taken at 2.8 GPa and 2 T. As seen in Fig. 3(a), the dielectric constant strongly depends on the frequency only around $T_{N}^{Tb}$. The relaxation time $\tau$ is estimated by the Cole-Cole plot at the respective temperatures. The temperature dependence of $\tau$ is displayed in Fig. 3(b). Since the gradient of $\tau$ in semi-log plot varies below and above $T_{N}^{Tb}$, two distinct activation energies can be obtained from the fit to the Arrhenius relation ($i.e.$, $\tau=\tau_0\exp(\Delta E/k_BT)$). $\Delta E/k_B$ is 36.7 K above $T_{N}^{Tb}$ and 57.3 K below $T_{N}^{Tb}$ respectively.

4. Discussion

At first, let us summarize experimental results. As seen in Fig.1(f), a new ferroelectric phase develops at around 2-3 GPa and 1-3 T below $T_{N}^{Tb}$. The ferroelectric phase exhibits a spontaneous polarization along the $a$ axis, which is distinct from that along $c$ at ambient pressure. At the small region in the $P$-$H$-$T$ phase diagram, concretely below $T_{N}^{Tb}$, 2-3 GPa and 1-3 T, the ferroelectric phase in which the polarization is along the $a$ axis has developed [Fig.1(f)]. Remarkable features of this new ferroelectric phase are that (1) the magnitude of ferroelectric polarization is almost the same as that in the ambient-pressure ferroelectric phase, (2) the polarization flop has occurred with applying $H$ along not $b$ but $a$ below $T_{N}^{Tb}$, and (3) the dielectric constant strongly depends on the measured frequency at around the phase transition. Since the magnitude of the electric polarization is the same as that at ambient pressure, the ferroelectricity would originate from a cycloidal spiral spin order and the spiral plane is on the $ab$ plane referring to the configuration predicted by Katsura et al. [9]. The transition corresponding to the magnetic-field-induced electric polarization flop from $c$ to $a$ has been well investigated well in DyMnO$_3$ [10, 11]. By applying a magnetic field along $b$ below $T_{C}$, the $bc$ spiral transform into the $ab$ spiral, and remarkable dielectric relaxation is observed in DyMnO$_3$. Though similar dielectric relaxation was observed in the present study on pressurized TbMnO$_3$, the triggered magnetic field is along the $a$ axis and the transition occurs only below $T_{N}^{Tb}$ unlike in DyMnO$_3$. At ambient pressure, Tb moments show a metamagnetic transition at 2 T below $T_{N}^{Tb}$. Since the flop of $P$ has been observed only below $T_{N}^{Tb}$, the metamagnetic transition should influence the polarization flop transition. However the effect of the magnetic ordering of Tb moments on the relaxation time $\tau$, which is characteristic time scale of the motion of the spiral domain has been observed clearly [Fig. 3(b)]. It might be the consequence of the stabilization of the domain of $P$ along the $\pm a$ direction due to the polarization-flop phase transition.
5. Summary

Pressure effects of the magnetoelectric response were examined on multiferroic TbMnO$_3$ showing three successive phase transitions by using a diamond anvil cell. All of the three transitions, i.e., the sinusoidal ordering of Mn moments $T_{\text{Mn}}^N$, the cycloidal spin ordering of Mn moments (ferroelectric transition) $T_C$, and the antiferromagnetic ordering of Tb moments $T_{\text{Tb}}^N$, shift toward higher temperature with applying pressure. Furthermore the magnetic-field effect on the ferroelectric properties below $T_{\text{Tb}}^N$ varies sensitively with applying pressure. At around 3 GPa and below $T_{\text{Tb}}^N$, it was revealed that the electric polarization flows from the $c$ to the $a$ axis by applying a magnetic field along the $a$ axis. Accordingly, distinct dielectric relaxation is observed and the relaxation time is affected by the magnetic transition of the Tb moments. The spin spiral flop from the $bc$ to the $ab$ spiral accompanied with the metamagnetic transition of Tb moments is discussed as a possible origin of the electric polarization flop.

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