Internal magnetic field effect on magnetoelectricity in orthorhombic RMnO$_3$ crystals

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Available online 7 November 2006

Abstract

We have investigated the role of the $4f$ moment on the magnetoelectric (ME) effect of orthorhombic RMnO$_3$ (R = rare earth ions). In order to clarify the role of the $4f$ moment, we prepared three samples: (Eu, Y)MnO$_3$ without the $4f$ moment, TbMnO$_3$ with the anisotropic $4f$ moment, and (Gd, Y)MnO$_3$ with the isotropic $4f$ moment. The ferroelectric behaviors of these samples are different from each other in a zero magnetic field. (Eu, Y)MnO$_3$ and (Gd, Y)MnO$_3$ show the ferroelectric polarization along the a axis in the ground state, while TbMnO$_3$ shows it along the c axis. Such difference may arise from the influence of the anisotropic Tb^{3+} $4f$ moment. The direction of the ferroelectric polarization of RMnO$_3$ is determined by the internal magnetic field arising from the $4f$ moment.
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A strong correlation between dielectric and magnetic properties, so-called magnetoelectric (ME) effect, has attracted a revived interest. The series of orthorhombic RMnO$_3$ (R = rare earth ions) containing TbMnO$_3$ famous as the "magnetic-field-induced electric polarization flop" [1] is a parent material of the colossal magnetoresistance (CMR) manganite. Recently, the noncollinear transverse spiral antiferromagnetic (AF) order of Mn $3d$ spins is observed between the A-type (EuMnO$_3$) and the E-type (HoMnO$_3$) AF order [2–4]. Such unconventional magnetic order is caused by the competition between the ferromagnetic nearest neighbor (NN) interaction and the AF next NN interaction due to the relatively large orthorhombic distortion. Such noncollinear transverse spiral magnetic structure causes the ferroelectric polarization of RMnO$_3$ [3–6].

In previous work, we have investigated the ME effect in (Eu$_{0.595}$Y$_{0.405}$)MnO$_3$ ((Eu, Y)MnO$_3$) without $4f$ moment [7]. Even if the average ionic radius of R site in (Eu, Y)MnO$_3$ is the same as that of TbMnO$_3$, the direction of the ferroelectric polarization of the ground state of

(Eu, Y)MnO$_3$ is different from that of TbMnO$_3$ in a zero magnetic field: (Eu, Y)MnO$_3$ shows the ferroelectric polarization along the a axis (P_a), while TbMnO$_3$ shows P_c. It is considered that this difference is attributed to the magnetic property of each R ion.

In this paper, we have revealed the role of the rare-earth $4f$ moment on the ME effect of orthorhombic RMnO$_3$. In order to investigate the role of the $4f$ moment, we prepared three samples: (Eu, Y)MnO$_3$ without the $4f$ moment, TbMnO$_3$ with the anisotropic $4f$ moment, and (Gd$_{0.69}$Y$_{0.31}$)MnO$_3$ ((Gd, Y)MnO$_3$) with the isotropic $4f$ moment. The average ionic radius of R site in these samples is fixed to be same as that of TbMnO$_3$.

The compositional ratio of the Eu^{3+} to Y^{3+} ions and that of Gd^{3+} to Y^{3+} were obtained by a calculation based on the Shannon's ionic radius table [8]. The single crystal sample was grown by the floating zone method. We performed X-ray diffraction and rocking curve measurements on the resulting crystal at room temperature, and confirmed that the samples have the orthorhombic *Pbnm* structure without any impurity phases or any phase segregation. All specimens used in this study were cut along the crystallographic principal axes into a rectangular

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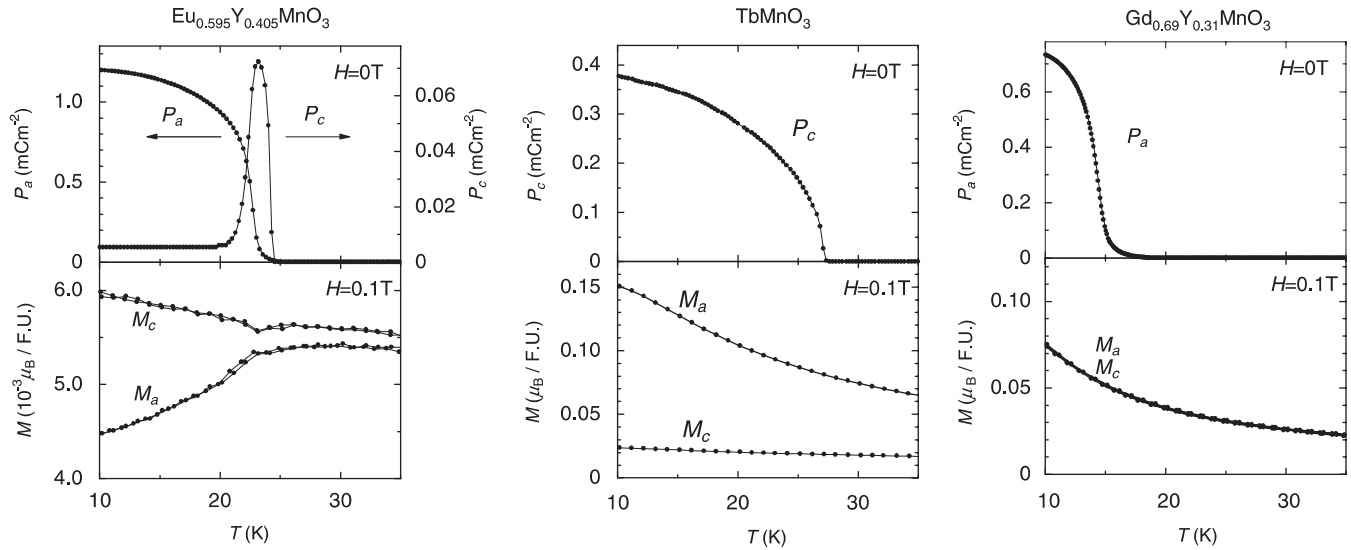E-mail address: n-kohei@sophia.ac.jp (K. Noda).

Fig. 1. Temperature dependence of the ferroelectric polarization (upper) and magnetization (lower) of the $(Eu, Y)MnO_3$ (left panel), $TbMnO_3$ (center panel), and $(Gd, Y)MnO_3$ (right panel).

shape by means of X-ray back-reflection Laue technique. The measurement of the temperature dependence of the spontaneous ferroelectric polarization was carried out in a temperature-controllable cryostat. The spontaneous electric polarization was obtained by the accumulation of a pyroelectric current. The magnetization was measured using a commercial apparatus (Quantum Design, PPMS).

At first, we focus on $(Eu, Y)MnO_3$ without $4f$ moment. In a zero magnetic field, this compound shows two distinct ferroelectric phases with P_a ($T \leqslant 23\,K$) and P_c ($23\,K \leqslant T \leqslant 25\,K$) (see Fig. 1 left panel). The magnitude of the magnetization is about $10^{-4} \sim 10^{-3}\,\mu_B/F.U.$ in $H = 0.1\,T$. The behavior of magnetization is directly reflecting the behavior of the Mn $3d$ spins, because this compound is free from $4f$ moment. In previous work, we have demonstrated the ferroelectric polarization switching between P_a and P_c by application of the magnetic field: for example, the P_a changes to the P_c by the application of the magnetic field parallel to the a axis (H_a^{ext}) [7]. This switching behavior is caused by the flop of the transverse spiral AF plane of Mn $3d$ spins, which can be explained in terms of the inverse Dzyaloshinskii–Moriya interaction [6].

In the case of $TbMnO_3$, the dielectric and magnetic properties are different from those of $(Eu, Y)MnO_3$, although the average ionic radius of R site is the same (see Fig. 1 center panel). $TbMnO_3$ shows only P_c in a zero magnetic field. The magnitude of the magnetization is about $10^1 \sim 10^2$ times as large as that of $4f$-moment free $(Eu, Y)MnO_3$, because of the influence of the Tb^{3+} $4f$ moment. Introducing the $4f$ moment enhances the magnitude of the magnetization along the a axis (M_a) compared with the other axes. This result suggests that the $4f$ moment of $TbMnO_3$ is anisotropic, and the internal magnetic field due to the $4f$ moment seems to be parallel to the a axis

(H_a^{int}). In the case of $4f$-moment free $(Eu, Y)MnO_3$, the ground state has P_a, and the direction of the ferroelectric polarization is changed from the a axis to the c axis by the application of H_a^{ext}, as mentioned above. Therefore, in $TbMnO_3$, P_c is stabilized by the application of H_a^{int}, like the case of $4f$-moment free $(Eu, Y)MnO_3$ in H_a^{ext}. Hence, the difference of the direction of the ferroelectric polarization between $4f$-moment free $(Eu, Y)MnO_3$ and anisotropic $4f$-moment $TbMnO_3$ can be understood from the scenario that H_a^{int} acts as H_a^{ext}.

In the case of $(Gd, Y)MnO_3$, the P_a only appears in a zero magnetic field (see Fig. 1 right panel). The magnitude of the magnetization is nearly the same as that of $TbMnO_3$. However, in this compound, no significant difference is observed between the temperature dependence of M_a and M_c, in contrast to the case of $TbMnO_3$. Therefore, the $4f$ moment of this compound is isotropic. As a result, the effective internal magnetic field does not exist. Consequently, the direction of the ferroelectric polarization of this compound is the same as that of $4f$-moment free $(Eu, Y)MnO_3$.

From these results, we conclude that, in $RMnO_3$ crystals, the Mn $3d$ spins are indispensable for realizing the ferroelectric polarization, while the $4f$ moment is not. The magnetic easy axis of the $4f$ moment determines the direction of the ferroelectric polarization through the channel of the internal magnetic field, even in a zero external magnetic field. The results obtained in this experiment should provide an improved understanding of the mechanism of the magnetoelectric effect in $RMnO_3$ crystals.

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