Magnetic and dielectric properties of multiferroic Tb$_{0.5}$Eu$_{0.5}$MnO$_3$

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Abstract. The structural, magnetic and dielectric properties of multiferroic compound Tb$_{0.5}$Eu$_{0.5}$MnO$_3$ are reported near the boundary of the multiferroic phase of the Eu-doped Tb$_{1-x}$Eu$_x$MnO$_3$ system. The Mn$^{3+}$ moments order in an incommensurate antiferromagnetic manner below $T_N = 50$ K, followed by a spin canting-like response around 25 K. Below $T_N$, extra hysteresis loops were observed for applied fields $B_a$ around 1-2 T, with decreasing magnetic moment for increasing magnetic fields. The dielectric constant $\varepsilon'$ showed a peak at 28 K, which was attributed to the ferroelectric transition in analogy with the parent compound TbMnO$_3$. Structural analysis indicates the Mn-O$_2$-Mn bond angle within the ab-plane is 145.9$^\circ$ suggesting that there exists a critical angle in the perovskite manganate multiferroic systems.

1. Introduction

Since the discovery of multiferroic behavior in small radius rare-earth RMnO$_3$ compounds, the origin and detailed behaviors of these systems have attracted much interest [1]. Although the ferroelectric transition temperature $T_C$ in these compounds are not high enough for application purposes, the strong electromagnetic coupling and the novel magnetic interaction origin of the ferroelectricity make a new era for research in strongly correlated systems[2]. In addition to the investigations of pure rare earth RMnO$_3$ systems, the substituted compounds Tb$_{1-x}$Gd$_x$MnO$_3$ show a systematic variation from para-electric canted-antiferromagnetism (PECAF) to coexistence of ferroelectricity and antiferromagnetism, know as multiferroic behavior, as the system goes from the Gd to the Tb rich side and the ab-plane Mn-O$_2$-Mn angle decreases [3]. The ferroelectric transition starts to be observed in this Tb-Gd system close to the Gd end at a Mn-O$_2$-Mn angle $\sim$146$^\circ$, or an averaged rare earth ionic radius $\langle r_R \rangle \sim r_{Gd}$. However, the complicated spontaneous polarization re-orientation from a- to c-axis with increasing Tb concentration suggests that the detailed mechanism could be much more complicated [4]. On the other hand, similar phase diagrams were reported for Eu$_{1-x}$Y$_x$MnO$_3$ with multiferroic behavior starting at a similar $\langle r_R \rangle$ value but with very different polarization re-orientation behavior. Moreover, the phase diagrams reported by different groups only agree qualitatively with each other [5,6], which reflects the complicated nature of the interplay between magnetic moments and electric polarizations.

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2. Experimental

Polycrystalline Tb$_{0.5}$Eu$_{0.5}$MnO$_3$ samples were prepared by the solid state reaction method [7]. High-purity oxide ingredient powders were mixed in stoichiometric ratios then calcined at 900°C in air for 30 hours with several intermediate regrindings for homogeneity. After adding 3% wt of polyvinyl alcohol (PVA) to ensure high packing density, the pressed pellets were sintered at 1380°C in flowing Ar atmosphere for 24 hours followed by slow cooling to room temperature. The structure of the sintered compounds were analyzed by Rietveld refinement with a FullPROF program on powder X-ray diffraction patterns collected by a Rigaku Rotaflex 18-kW rotating anode diffractometer with graphite monochromatized Cu-K$_\alpha$ radiation in 2$\theta$ range of 20°-70° [8]. The magnetic measurements were carried out with a Quantum Design 7-T MPMS superconducting quantum interference device (SQUID) magnetometer from 5-300 K. The dielectric permittivity was measured in a parallel-plate capacitor geometry by using an impedance analyzer (Hewlett-Packard, 4194A) with a closed-cycle cryocooler from 13-300 K.

3. Results and discussions

The structural characterization of the sintered Tb$_{0.5}$Eu$_{0.5}$MnO$_3$ sample by powder x-ray diffraction is shown in Figure 1, which can be well indexed by an orthorhombic structure with space group $Pbnm$ (No. 62) indicating high purity of the sample. The obtained lattice constants $a = 0.53200(2)\ nm$, $b = 0.58556(2)\ nm$, $c = 0.74237(3)\ nm$ and unit cell volume $V = 0.23126(1)\ nm^3$ is in good agreement with the expected values extrapolated from the reported stoichiometric TbMnO$_3$ and EuMnO$_3$ compounds indicating high sample quality with no, or at least low, vacancies due to off-stoichiometry of oxygen content [7,9].

The refined atomic positions (atom sites of $Pbnm$ is shown in the parenthesis) of orthorhombic Tb$_{0.5}$Eu$_{0.5}$MnO$_3$ are listed in Table 1. The deduced MnO$_6$ octahedra in the perovskite structure elongates along and rotates 13.6° about the c-axis then tilts 17.5° away from c-axis resulting a buckled Mn-O network in the ab-plane with an Mn-O2-Mn angle of 145.9°. The large deviation of the Mn-O2-Mn angle from ideal 180° thus frustrates the magnetic exchange interactions between the Mn moments, which order incommensurately below the Néel temperature $T_N$. 

![Figure 1. The x-ray diffraction data (open circles), Rietveld refinement and the deviation from data (black and blue lines respectively) of Tb$_{0.5}$Eu$_{0.5}$MnO$_3$. The vertical bars represent allowed reflections of the $Pbnm$ structure.](Image)
Table 1. Refined atomic positions (atom sites denoted in the parenthesis) of orthorhombic Tb$_{0.5}$Eu$_{0.5}$MnO$_3$ with space group $Pbnm$ and lattice constants $a = 0.53200(2)$ nm, $b = 0.58556(2)$ nm, $c = 0.74237(3)$ nm.

| Atom    | x       | y       | z       | $B_{iso}$ | occupation |
|---------|---------|---------|---------|-----------|------------|
| Tb/Eu (4c) | -0.0176(2) | 0.0795(2) | 1/4 | 0.9(2) | 0.5/0.5 |
| Mn (4b)  | 1/2     | 0       | 0       | 0.5(3)   | 1          |
| O1 (4c)  | 0.102(1) | 0.462(1) | 1/4 | 0.8(9)   | 1          |
| O2 (8d)  | 0.715(1) | 0.334(1) | 0.0497(8) | 0.3(7) | 1 |

$R_p = 9.18\%$, $R_{wp} = 10.7\%$, $R_{exp} = 2.96\%$, $R_{Bragg} = 5.23\%$

Figure 2a shows the zero-field-cooled (ZFC) and field-cooled (FC) molar magnetic susceptibility $\chi_m(T)$ and $1/\chi_m$ for Tb$_{0.5}$Eu$_{0.5}$MnO$_3$. At elevated temperatures, the susceptibility follows a Curie-Weiss (CW) law as clearly revealed by the linear $1/\chi_m$ with an effective paramagnetic moment $\mu_{eff} = 8.70 \mu_B$, which is attributed mainly to paramagnetic Tb$^{3+}$ and Mn$^{3+}$ moments with minor contributions from Eu$^{3+}$ low-lying multiplets excitations at these temperatures. Since the sample orders antiferromagnetically with an incommensurate magnetic moment arrangement below $T_N$, there is no clear peak or inflection point of the $\chi_m(T)$ curve at $T_N$. Since $\chi_m(T > 60 \text{ K})$ follows a Curie-Weiss law, the deviation point was used to determine the Néel temperature as in the literature [10]. The obtained $T_N = 50$ K is similar to the reported values for EuMnO$_3$ and TbMnO$_3$ and similar to doped systems (e.g., Eu$_{1-x}$Y$_x$MnO$_3$ and Tb$_{1-x}$Gd$_x$MnO$_3$) [4,5]. As the temperature is lowered further, ZFC and FC curves of $\chi_m(T)$ deviate at an irreversibility point $T_{irr} = 38$ K followed by canted-antiferromagnetic-like (CAF-like) behavior below $T_{CAF} = 25$ K, which is the peak for ZFC and the inflection point for FC curves. No trace of Tb$^{3+}$ ordering was observed in the temperature range investigated.

The magnetic hysteresis loops $M(B_a)$ of Tb$_{0.5}$Eu$_{0.5}$MnO$_3$ in the temperature range 5-30 K are shown in Figure 2b. At $T = 5$ K, a saturation behavior of $M(B_a)$ is observed with a saturation moment $\sim 1.9 \mu_B$ per formula. This is far smaller than the expected saturation

![Figure 2](image1.png)

Figure 2. (a) Temperature dependence of the molar magnetic susceptibility $\chi_m(T)$ and its inverse, $1/\chi_m$, for Tb$_{0.5}$Eu$_{0.5}$MnO$_3$ with an applied field $B_a = 1$ kG. (b) The magnetic hysteresis $M(B_a)$ for temperature between 5 to 30 K. The inset is a closer look at the extra loop at $T = 20$ K. Thin arrows label the loop direction, where the start and end of the loop are indicated by vertical arrows.
moment calculated from the ionic contributions, which suggests further transitions induced at higher applied field. In addition, meta-magnetic loops were observed at 1-2 T. The inset of Figure 2b is a closer look at the loop at T = 20 K. As B_a increases, unlike general metamagnetic behavior, the magnetic moment M(B_a) experienced an abrupt decrease of ~0.1 \(\mu_B\) around B_a = 1.6 T and an abrupt increase of ~0.06 \(\mu_B\) with descending B_a at 0.95 T. Since the change of the magnetic moment tends to increase the magnetic potential energy -M \(\cdot\) B_a, which is in contrast to general moment changes, it is believed to be accompanied by other transitions that lower the total energy even further. These extra loops were not reported previously probably due to the small change in moment and typical large applied field increment in this field regime. Since it is important to clarify the effect of inhomogeneous field of the SQUID magnetometer on these loops further investigations by other means are planned and in progress.

Figure 3 shows the low-temperature dependence of the real part dielectric constant \(\varepsilon'(T)\) of Tb_{0.5}Eu_{0.5}MnO_3 at frequencies of 10 kHz to 1 MHz. The observed \(\varepsilon'(T)\) is slightly frequency dependent, which is attributed to the capacitance contributed from the grain boundaries of the polycrystalline sample. A small peak in \(\varepsilon'\) can be observed at 28 K. Since the peak position is frequency-independent and can be systematically traced with different Eu doping to TbMnO_3, we attributed this to the ferroelectric (FE) transition temperature \(T_C\) [11]. Comparing the anomaly peak strength with TbMnO_3 and the similar doping systems, Tb_{1-x}Gd_xMnO_3 and Eu_{1-x}Y_xMnO_3, we conclude that Tb_{0.5}Eu_{0.5}MnO_3 is close to the multiferroic boundary. The observation of CAF-like behavior below \(T_{CAF} < T_C\) and no second \(\varepsilon'\) peak suggest possible coexistence of the FE and CAF phases. On the other hand, the Mn-O2-Mn angle is very close to the reported value in Tb-Gd system, indicating that there is a critical angle for the appearance of multiferroic behavior in the perovskite manganate compounds.

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Figure 3. Temperature-dependence of the real part of the dielectric constant \(\varepsilon'(T)\) of Tb_{0.5}Eu_{0.5}MnO_3 at frequencies from 10 kHz to 1 MHz. The dielectric anomaly near T = 28 K is marked and attributed to the ferroelectric transition temperature \(T_C\).