Single crystal growth of the hexagonal manganites $RMnO_3$ ($R =$ rare earth) by the optical floating-zone method

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Abstract

We report a study on the crystal growth of the hexagonal manganites $RMnO_3$ ($R =$ Y, Lu, Ho, Er, and Tm) by using an optical floating-zone method. It was found that high-quality single crystals of $R =$ Y, Lu, and Ho could be easily grown with essentially the same conditions as those reported in literature, that is, with an atmosphere of normal pressure Ar and oxygen mixture and a growth rate of 2–4 mm/h. However, these conditions were not feasible for growing good crystals of $R =$ Er and Tm. The chemical analysis indicated that it was due to an off-stoichiometric phenomenon in the formed single crystals. We used an effective and simple way to resolve this problem by adjusting the nominal compositions of the polycrystal feed rods to be 1–2% rare-earth excess. The structures and physical properties were characterized by X-ray diffraction, magnetic susceptibility, specific heat, resistivity, and dielectric constant measurements.

Keywords:
A1. Characterization, A2. Floating Zone technique, A2. Single crystal growth, B2. Multiferroic materials
1. Introduction

The hexagonal rare-earth manganites $RMnO_3$ ($R = Y, Lu, Ho, Er, and Tm$) with the space group of $P6_3mc$ have attracted much interest in the past decades because of their multiferroicity [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. In these compounds, each $Mn^{3+}$ ion is surrounded by three in-plane and two apical oxygen ions (a MnO$_5$ bipyramid) and then they form a triangular-lattice layer. Two adjacent layers are separated by a rare-earth layer and the $R^{3+}$ ions are located in two different crystallographic sites, “2a” and “4b” [12, 13]. The $H – T$ phase diagrams of $RMnO_3$ are rather complicated and are strongly dependent on the magnetism of rare-earth ions [6, 8, 14, 15, 16, 17]. Till now, there is still no complete understanding of the low-temperature magnetic structures and their transitions in $RMnO_3$, particularly in HoMnO$_3$ and ErMnO$_3$. For further and deeper studies of the magnetic properties and the mechanism of magnetoelectric coupling effect in $RMnO_3$, high-quality single crystals are very important. The hexagonal $RMnO_3$ single crystals studied in the previous works were grown by using the flux method or the optical floating-zone technique and the latter one seemed to produce better crystals [6, 18, 19, 20, 21, 22]. The crystal growth using the floating-zone technique in these works were all carried out in air at a rate of 2–4 mm/h. The typical size of the obtained crystals was 30–50 mm long with a diameter of 5–6 mm. However, it is not clear whether these conditions have already been optimized.

In this work, we try to optimize the growth conditions of hexagonal $RMnO_3$ single crystals ($R = Y, Lu, Ho, Er, and Tm$) by using the floating-zone method. It was found that very good single crystals of YMnO$_3$, LuMnO$_3$, and HoMnO$_3$ can be obtained by using the reported growth conditions. However, the growths of ErMnO$_3$ and TmMnO$_3$ need some tricks, because the formed single crystals are slightly rare-earth rich and the crystal growths could not be successful with the compositions $R$:$Mn = 1$:$1$ for raw rod. We finally obtained successful growths by modifying the ratio of $R$:$Mn$ in the feed rod. The structures and physical properties of these crystals were characterized by X-ray diffraction (XRD), magnetic susceptibility, specific heat, resistivity, and dielectric constant measurements.
2. Crystal Growth

The polycrystal powders of hexagonal $RMnO_3$ ($R = Y, Lu, Ho, Er, and Tm$) were synthesized by the conventional solid-state reaction. Stoichiometric mixtures of $R_2O_3$ (99.99%) and MnO$_2$ (99.99%) powders were ground together and calcined in air at 1050°C for 24 hours, followed by two more times grinding and calcining to make sure of getting single phase. Then the $RMnO_3$ powders were pressed into $\sim 100$ mm long rods with diameter of $\sim 7$ mm under 30 MPa hydrostatic pressure. The raw rods were sintered at 1250°C for 20 hours in air and used as feed rod and seed rod. The crystal growth was carried out in an optical floating-zone furnace with four 500W halogen lamps and ellipsoidal mirrors (Crystal System Incorporation, Japan).

We first tried to grow HoMnO$_3$ using the same conditions as those in the literature [22]. The atmosphere for growth was normal-pressure mixture of argon and oxygen with the ratio of 4:1 and the growth rate was 3 mm/h. The feed and seed rods were rotating in opposite directions at 10 and 15 rpm, respectively. After starting growth for only 2 hours, the surface of crystal rod became smooth and two large facets on the opposite sides appeared. This indicated that large and nearly single domain of the crystal could be easily formed in such a short time. Finally, a several-millimeter-long single crystal with shining surface, nice morphology, and long consecutive facets was obtained, as shown in Fig. 1(c). The long facets on the crystal bars were identified to be the hexagonal plane normal to the $c$ axis by using the X-ray Laue back diffraction. YMnO$_3$ and LuMnO$_3$ single crystals with good appearances, as shown in Figs. 1(a) and 1(b), could also be obtained by using the same growth conditions. After trying more, it was found that the growths of these crystals were actually not very sensitive to the growth rate; the rates of 2–4 mm/h gave similar products, which is coincided with the literature. However, the crystal growths are more sensitive to the atmosphere. Other atmospheres like pure oxygen or pure argon were found to be not suitable. In pure oxygen, for example, there were some bubbles in the molten zone and the stable crystal growth was impossible. Small pieces of these as-grown crystals were cut and ground into powders for XRD and the data confirmed the pure and single phase.
addition, the good crystallinity of these crystals were also confirmed by narrow widths of the X-ray rocking curves. For example, the full width at the half maximum (FWHM) of the rocking curve for the (004) Bragg peak is about 0.10–0.14° for these crystals. (The XRD data are not shown here but can refer to those of ErMnO₃, as shown in Fig. 3.)

The main finding of this work is that the growths of ErMnO₃ and TmMnO₃ single crystals are not so simple. It was found that both compounds could not grow in a stable state by using the same process as HoMnO₃, YMnO₃, and LuMnO₃. For example, Figs. 2(a-d) show the photographs which recorded the growth process of ErMnO₃ with a rate of 2 mm/h. At the beginning, the growth looked stable and is very similar to those of HoMnO₃, YMnO₃, and LuMnO₃. After 8 hours, however, some folds appeared on the feed rod. Then the feed rod started to expand with some unmelted solids rolling up on the top edge of the molten zone, which is indicated by a red arrow in Fig. 2(c). With the increase of the unmelted solids, the molten zone became narrower and unstable. The diameter of the single crystals also decreased at the same time, as shown in Fig. 2(d). After 15 hours, the molten zone finally dropped, which was apparently related to the change of viscosity. In addition, small amount of gray powders were found to adhere on the glass shield of the furnace; these were the volatile matters during the growth. All these phenomena were not observable in the growth of HoMnO₃, YMnO₃, and LuMnO₃ crystals. The obtained ErMnO₃ crystal bar has many small cracks inside, indicating a poor crystal quality. It was also found that changing the growth rate or atmosphere could not be helpful for resolving these problems.

We analyzed the chemical constituents of several important parts, A, B, and C shown in Fig. 2(d), by using X-ray fluorescence spectrometry. The measurements were done by using a Sequential X-ray Fluorescence Spectrometer with Rh anode tube (XRF-1800, Shimdzu). The excitation current is 90 mA and the analyzing crystal is LiF₂₀₀. The area illuminated by the incident X-ray beams is 20 mm in diameter. The data were calculated using Fundamental Parameter (FP) method and then the proportion of the rare-earth and Mn elements was obtained. Part A, the unmelted solid on the edge of the feed rod, was found to have a molar ratio of Er:Mn = 0.363:0.637, indicating that much rare-earth element was lost in this part. The molar ratio of Er:Mn in part B was 0.497:0.503 rather than 0.5:0.5. The as-grown
crystal, indicated as part C in Fig. 2(d), had a molar ratio of Er:Mn = 0.508:0.492, which is a bit different from the nominal composition of the raw rod. In addition, the volatile matters on the glass shield were found to be pure Mn oxide and have no Er element. This is reasonable since the rare-earth oxides have boiling points above 2900 °C and are difficult to be volatilized. According to these results and considering the volatilization of Mn element, it is clear that the feed rod of ErMnO$_3$ could not be melted congruently. Instead, the formed ErMnO$_3$ crystal was about 0.8% Er rich. We therefore prepared new polycrystal powder with slightly changing the stoichiometric proportion of Er:Mn to 0.5075:0.4925 and repeated the growth. This time the crystal growth could be stable enough to finish the growth (up to 40 hours), as shown in Figs. 2(e-h). The as-grown ErMnO$_3$ single crystal bar shows very nice appearance and with long consecutive facets on the surface, as shown in Fig. 1(d). The powder XRD of the as-grown crystal confirmed the pure and single phase, as shown in Fig. 3(a). A narrow width of the rocking curve of (300) Bragg peak (FWHM $\approx 0.13\,^{\circ}$), as shown in Fig. 3(b), demonstrated that the ErMnO$_3$ single crystal has good crystallinity.

The case of TmMnO$_3$ is very similar to ErMnO$_3$. Based on the X-ray fluorescent spectrometry data, we adjusted the stoichiometric proportion of Tm:Mn to 0.5085:0.4915 and nice single crystals were also obtained, as shown in Fig. 1(e).

The off-stoichiometric growth of ErMnO$_3$ and TmMnO$_3$ single crystals has never been reported in previous literature. However, it is not rare in binary-element systems. As an example, a similar case is growing LiNbO$_3$ crystal from Li$_2$O-Nb$_2$O$_5$ system, in which the congruent melting is located at the molar composition of Li:Nb = 0.486:0.514 [23, 24]. In this case, it crystallizes with an off-stoichiometry of Li$_{0.945}$NbO$_{2.973}$. Another example is the La$_2$O$_3$-Mn$_2$O$_3$ system for growing orthorhombic LaMnO$_3$ [25]. Apparently, in the phase diagrams of the hexagonal ErMnO$_3$ and TmMnO$_3$, the congruent melting points are located at the rare-earth-rich side. Since there would be more Er element crystallized into the single crystal, the percentage of Er element decreased in the molten zone. Thus, the molten zone had to absorb more Er element from the feed rod, inducing the deficiency of Er element in the feed rod. This process could not be continued for a long time when the molten zone was too lack of Er. Modifying the compositions of the feed rods could effectively resolve
this problem. Our results give a more precise understanding about the phase diagrams of hexagonal $R$-Mn-O systems $^{26}$.

The optimized growth conditions for hexagonal $RMnO_3$ are summarized in Table 1. The lattice parameters determined by the powder XRD are also shown in the table and are in good correspondences with the results in previous works. Our crystals have not only good appearances but also good crystallinity, as the XRD and Laue photographs indicated.

3. Magnetic susceptibility and specific heat

The basic physical properties of the obtained hexagonal $RMnO_3$ single crystals were also characterized. DC magnetization and specific heat measurements were done by using a SQUID-VSM (Quantum Design) and a Physical Property Measurement System (PPMS, Quantum Design), respectively. Resistivity was measured by the standard four-probe technique. Dielectric constants were measured by using a precision impedance analyzer (Agilent 4294A).

Fig. 4 shows the temperature dependencies of the magnetic susceptibilities along the $a$ and $c$ axes of YMnO$_3$, HoMnO$_3$, ErMnO$_3$, and TmMnO$_3$. YMnO$_3$ shows much smaller susceptibility than other materials, which means that the rare-earth ions make main contributions in $RMnO_3$. The $\chi_a(T)$ and $\chi_c(T)$ of YMnO$_3$ show clear transitions at 72 K, which is due to the antiferromagnetic (AF) transition of Mn$^{3+}$ moments $^{4, 27}$. For HoMnO$_3$, ErMnO$_3$, and TmMnO$_3$, the AF transitions of Mn$^{3+}$ moments at about 70–90 K can hardly be distinguished from the $\chi(T)$ data, as shown in Figs. 4(b-d). One noticeable transition in the data of these crystals is a weak slope change of $\chi_c(T)$ of HoMnO$_3$ at $\sim$ 40.5 K, which is due to a spin re-orientation of Mn$^{3+}$ sublattice from $P6'_3c'm$ to $P6'_3cm'$. The Ho$^{3+}$ moments form a long-range AF order at about 4.2 K, where the slopes of $\chi_a(T)$ and $\chi_c(T)$ show some rather clear changes. In ErMnO$_3$, the $\chi_c$ shows a quick increase below about 10 K. However, there is no clear indication on $\chi(T)$ curves whether a long-range order is established at temperatures down to 2 K. The Tm$^{3+}$ moments do not show long-range order at temperatures down to 2 K. However, the low-$T$ susceptibilities show deviations from the paramagnetic
behavior below 10 K. These suggest that the magnetic correlations among Tm$^{3+}$ moments are not negligible.

Fig. 5 shows the magnetization curves of YMnO$_3$, HoMnO$_3$, ErMnO$_3$, and TmMnO$_3$ at 2 K with the magnetic field applied along the $a$ and $c$ axes. The $M(H)$ curves of YMnO$_3$ show no field-induced transition but only a linear behavior up to 7 T. Moreover, the magnetization at 7 T is very small, which is far from the theoretical value ($4 \mu_B$) of free Mn$^{3+}$ ions. This is because the Mn$^{3+}$ ions have formed a 120° AF arrangement in the $ab$ plane at 72 K [4, 27], and 7 T is too low to polarize the Mn$^{3+}$ moments. The behaviors for the other three compounds with magnetic Ho$^{3+}$, Tm$^{3+}$, and Er$^{3+}$ ions are more complicated.

For TmMnO$_3$, the magnetization curves show strong anisotropy. The magnetization in the $a$-axis field is much smaller than that in the $c$-axis field, which is supportive to a strong Ising-anisotropy of the Tm$^{3+}$ on 4$b$ sites [6, 28]. The $M(H)$ curve along the $a$ axis is close to a linear function up to 7 T except for a small curvature at low fields, which is mainly the paramagnetic response of the 2$a$ moments. In contrast, a clear transition is shown at 3.5 T in the $M(H)$ curve for $H \parallel c$, which is coincided with a field-induced transition of Mn$^{3+}$ magnetic structure from $P6_3'c'm$ to $P6_3c'm'$ [6]. This is directly related to a spin-flop transition of the 4$b$ moments. The slower increase of magnetization above this field is likely the paramagnetic contribution from the 2$a$ moments.

For ErMnO$_3$, the earlier studies suggested that at low temperatures Er$^{3+}$ moments at the 2$a$ and 4$b$ sites could form respective long-range AF order with the easy axis along the $c$ direction [6]. As shown in Fig. 5(c), the magnetization for $H \parallel a$ is much larger than that for $H \parallel c$, and it just shows a simple spin polarization process up to 7 T with the magnitude of 7.4 $\mu_B$ per formula. This seems to be in contradictory with the proposed Ising anisotropy of Er$^{3+}$ moments. The $M(H)$ curve for $H \parallel c$ is consistent with the data in previous literature [7] and shows two transitions at 0.01 and 0.85 T, which are related to the magnetic transitions from the so-called FIM$_1$ state (multi-domain of $\Gamma^{Er}_{2}$) to FIM$_2$ state (single domain of $\Gamma^{Er}_{2}$) then to the ferromagnetic state.

The case of HoMnO$_3$ is somewhat similar to ErMnO$_3$ in the regard that the magnetization for $H \parallel a$ is much larger than that for $H \parallel c$ and it shows a simple spin polarization process
with the magnitude of 7.8 $\mu_B$ per formula at 7 T. This is also in contradictory with the proposed Ising anisotropy of Ho$^{3+}$ moments. The magnetization curve is more complicated in the $c$-axis field. It shows two step-like transitions at 0.85 and 2.5 T, respectively, which are in good correspondence with the field-induced transitions proposed from the earlier dielectric and heat transport measurements [6, 10, 29]. If Ho$^{3+}$ ions have weak spin anisotropy, these two transitions could be spin flops of Ho$^{3+}$ moments at the 2$a$ and 4$b$ sites, associated with the spin re-orientations of Mn$^{3+}$ spin structures. There would be another transition at higher field above 7 T, which is due to the polarization of Ho$^{3+}$ spins [6, 10]. Actually, Kim et al. have indeed observed a third transition of $M(H)$ curve at about 6.5 T in HoMnO$_3$ thin film. The lower transition field might be due to the difference between bulk and film samples [30].

Low-temperature specific heat data of $RMnO_3$ ($R = Y, Ho, Er,$ and $Tm$) crystals are shown in Fig. 6. They all show a transition at the temperatures ranging from 69 to 87 K, which are attributed to the AF order of Mn$^{3+}$ moments. Below 20 K, as shown in the inset to Fig. 6, there is no transition down to 2 K for YMnO$_3$ and LuMnO$_3$, since both Y$^{3+}$ and Lu$^{3+}$ are nonmagnetic. For TmMnO$_3$, there is a hump-like feature at about 4–16 K, which is related to the development of short-range correlation of Tm$^{3+}$ moments [9]. HoMnO$_3$ shows a peak at about 4.5 K, indicating the long-range AF order of Ho$^{3+}$ moments. For ErMnO$_3$, there are a small peak at 2 K and a broader peak at 3.2 K, which indicate the transition from the AF state to the FIM$_1$ state and the short-range correlation of Er$^{3+}$ moments at the 2$a$ sites, respectively [7].

Fig. 7 shows the temperature dependencies of the $c$-axis resistivity of $RMnO_3$ ($R = Y, Ho, Er,$ and Tm) single crystals. It can be seen that the resistivity values of these manganites are very large and increase with lowering temperature roughly in an exponential way, indicating good insulating behaviors [22].

Low-temperature dielectric constants along the $c$-axis and at 50 kHz of $RMnO_3$ ($R = Y, Ho, Er,$ and Tm) single crystals are shown in Fig. 8. The main features are the slope changes of data at about 70–80 K and the lower-temperature cusps. It has been known that they are related to the Néel transitions of Mn$^{3+}$ moments and some spin re-orientations of Mn$^{3+}$ ions, respectively [6, 22, 31, 32, 33, 34].
Apparently, these magnetic, specific heat, and electric data are essentially in good agreement with most of the previous reports. This means that our single crystals are comparable to those from other groups. One may note that the off-stoichiometric compositions of ErMnO$_3$ and TmMnO$_3$ in principle should affect the low-temperature physical properties, since about 1% rare-earth ions occupy the Mn$^{3+}$ sites. In the common measurements, such effect seems to be not yet detected. It calls for further investigations on the relationship between the microstructure and the magnetic properties of the hexagonal rare-earth manganites.

4. CONCLUSIONS

High-quality single crystals of the hexagonal $RMnO_3$ ($R = Y, \text{Lu, Ho, Er, and Tm}$) were grown by the optical floating-zone method. YMnO$_3$, LuMnO$_3$, and HoMnO$_3$ single crystals could be grown very easily. However, ErMnO$_3$ and TmMnO$_3$ single crystals showed some difficulty in growth process. Chemical analysis indicated that it was due to the off-stoichiometric compositions of these two single crystals. The problem was resolved by modifying the nominal compositions of the polycrystal feed rod. The structure and crystallinity of obtained crystals were characterized by X-ray diffraction and Laue photographs. The low-temperature magnetization, specific heat, resistivity, and dielectric constant were measured to characterize the basic physical properties.

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Figure 1: (Color online) Photographs of $R\text{MnO}_3$ ($R = Y, Lu, Ho, Er,$ and Tm) single crystals.

Figure 2: (Color online) The photographs recording the growth process of ErMnO$_3$ single crystals. (a-d) The composition of the feed rod is ErMnO$_3$ and growth rate is 2 mm/h. The red arrows indicate three different areas A, B, and C, which are the unmelted solids on the feed rod, the molten zone, and the crystal, respectively. The molten zone was finally dropped after about 15 hours. (e-h) The composition of the feed rod is Er$_{1.015}$Mn$_{0.985}$O$_3$. The growth rate is also 2 mm/h. The growth was very stable up to 40 hours when it was finished.

Figure 3: (a) X-ray diffraction of powders ground from a piece of ErMnO$_3$ single crystal. (b-c) X-ray diffraction pattern of (h00) plane and the rocking curve of (300) peak.

Figure 4: (Color online) Magnetic susceptibilities of (a) YMnO$_3$, (b) HoMnO$_3$, (c) ErMnO$_3$, and (d) TmMnO$_3$ single crystals measured with 0.1 T magnetic field applied along the $a$ or $c$ axis. The arrows indicate the weak changes in the slope of $\chi(T)$ curves. Among them, the slope change in panel (b) is due to a spin-reorientation of Mn$^{3+}$ sublattice ($T_{SR}$), while those in other panels are due to the AF transition of Mn$^{3+}$ moments ($T_N$).

Figure 5: (Color online) Magnetization curves of (a) YMnO$_3$, (b) HoMnO$_3$, (c) ErMnO$_3$, and (d) TmMnO$_3$ single crystals at 2 K with the magnetic field applied along the $a$ or $c$ axis.

Figure 6: (Color online) Temperature dependencies of specific heat of $R\text{MnO}_3$ ($R = Y,$ Lu, Ho, Er, and Tm) single crystals.

Figure 7: (Color online) Temperature dependencies of the $c$-axis resistivity of $R\text{MnO}_3$ ($R = Y,$ Ho, Er, and Tm) single crystals.

Figure 8: (Color online) Temperature dependencies of the dielectric constant along the $c$ axis and at 50 kHz of $R\text{MnO}_3$ ($R = Y,$ Ho, Er, and Tm) single crystals. The arrows show the slope changes of data or lower-temperature cusps; the former ones are related to the Néel transitions of Mn$^{3+}$ moments while the latter ones are related to some spin re-orientations of Mn$^{3+}$ ions.
Fig. 1

a. YMnO$_3$

b. LuMnO$_3$

c. HoMnO$_3$

d. ErMnO$_3$

e. TmMnO$_3$
Fig. 2

ErMnO$_3$

5 hours  8 hours  12 hours  15 hours

Er$_{1.015}$Mn$_{0.985}$O$_3$

5 hours  15 hours  20 hours  30 hours
Fig. 3

Intensity (kCPS)

0 10 20 30 40 50 60 70

0 10 20 30 40 50 60 70

0 10 20 30

0 10 20 30 40

0.13°

θ (deg)

2θ (deg)

ErMnO$_3$

(002) (102) (004) (111) (110)

(008) (221) (220) (215) (212) (106) (115) (010)

(004) (114) (204) (116) (214) (302) (014) (012)

(003) (113) (111) (110) (102) (101) (100) (009) (008) (006) (004) (003) (002) (001) (000)

Intensity (kCPS)
Table 1: Optimized growth conditions for different rare-earth hexagonal manganites. The lattice parameters are obtained from the powder X-ray diffraction of single crystals.

|         | a (Å)   | c (Å)   | Stoichiometry (R:Mn) of feed rod | Growth rate (mm/h) | Atmosphere            |
|---------|---------|---------|----------------------------------|---------------------|-----------------------|
| YMnO$_3$ | 6.139(4)| 11.426(1)| 1:1                              | 2–4                 | 1 atm Ar+O$_2$(4:1)    |
| HoMnO$_3$ | 6.138(6)| 11.426(6)| 1:1                              | 2–4                 | 1 atm Ar+O$_2$(4:1)    |
| ErMnO$_3$ | 6.106(4)| 11.432(7)| 1.015:0.985                      | 2                   | 1 atm Ar+O$_2$(4:1)    |
| TmMnO$_3$ | 6.082(7)| 11.391(6)| 1.017:0.983                      | 2                   | 1 atm Ar+O$_2$(4:1)    |
| LuMnO$_3$ | 6.040(8)| 11.395(1)| 1:1                              | 2–4                 | 1 atm Ar+O$_2$(4:1)    |
Fig. 4

(a) $\chi$ (emu/mol) vs. $T$ for YMnO$_3$ with $H \parallel a$ and $H \parallel c$. The magnetic phase transition temperatures are indicated by $T_N$. 

(b) $\chi$ (emu/mol) vs. $T$ for HoMnO$_3$ with $H \parallel c$. The magnetic phase transition temperature is indicated by $T_{SR}$. The data is multiplied by 2. 

(c) $\chi$ (emu/mol) vs. $T$ for ErMnO$_3$. The magnetic phase transition temperature is indicated by $T_N$. The data is multiplied by 3. 

(d) $\chi$ (emu/mol) vs. $T$ for TmMnO$_3$. The magnetic phase transition temperature is indicated by $T_N$. 

**Symbols and Notations:**
- $\chi$: magnetic susceptibility (emu/mol)
- $T$: temperature (K)
- $T_N$: magnetic transition temperature
- $T_{SR}$: spin reorientation temperature
- $H$: magnetic field
- $a$, $c$: crystallographic axes
Fig. 5

(a) $Y\text{MnO}_3$

(b) $\text{HoMnO}_3$

(c) $\text{ErMnO}_3$

(d) $\text{TmMnO}_3$

$M (\mu_B/\text{f.u.})$ vs. $H (T)$ for different compounds at $T = 2 \text{ K}$.

- Red squares and blue circles represent $H \parallel a$ and $H \parallel c$, respectively.
Fig. 6
Fig. 7

\[ \rho_c (\Omega \text{ cm}) \]

[T (K)]

- YMnO\(_3\)
- HoMnO\(_3\)
- ErMnO\(_3\)
- TmMnO\(_3\)
Fig. 8

(a) $\varepsilon_c$ vs. $T$ for $\text{YMnO}_3$ at 50 kHz.

(b) $\varepsilon_c$ vs. $T$ for $\text{HoMnO}_3$.

(c) $\varepsilon_c$ vs. $T$ for $\text{ErMnO}_3$.

(d) $\varepsilon_c$ vs. $T$ for $\text{TmMnO}_3$. 

$T$ (K)