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The dependence of magnetic properties on temperature for rare earth $ErCrO_3$ chromites

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Abstract

Multiferroic $ErCrO_3$ was synthesized and the detailed magnetic as well as ferroelectric properties were investigated. The dc magnetization shows that $ErCrO_3$ undergoes a antiferromagnetic ordering at $T_N = 133$ K due to the Cr^{3+}–Cr^{3+} followed by weak ferromagnetic ordering. Around $T_{SR} \approx 22$ K, $ErCrO_3$ exhibits a spin reorientation from Γ_4 to Γ_1. And the stability of the ferromagnetic Γ_4 phase increases with the applied magnetic field increasing. Furthermore, at lower temperature, it shows weak antiferromagnetic ordering of Er^{3+}. We also present the low temperature polarization data for $ErCrO_3$ and find a remarkable decreasing of polarization around $T_N = 133$ K on increasing temperature, this effect might be due to the coupling between magnetic and ferroelectric order parameters, and the magnetic field suppresses the polarization which demonstrates convincingly the strong magnetoelectric (ME) coupling in $ErCrO_3$.

Keywords: C. Magnetic properties; C. Ferroelectric properties; Rare earth chromites; Magnetoelectric effect

1. Introduction

In the past several years, special attention to multiferroics with coexisting ferroelectricity and magnetism as well as magnetoelectric (ME) coupling between them has been paid due to the promising potentials of applications [1–4]. And there is a renewed interest in rare earth ferrites and chromites due to the possible magnetoelectric coupling in these materials [5–7]. The rare earth orthochromites $RCrO_3$ (R = Y, Ho, Er, Yb, Lu), crystallize in a distorted perovskite structure at room temperature [8,9], show extremely rich magnetic properties at low temperatures. Numerous research works have been done such as neutron–diffraction [10], magnetization and susceptibility [10], specific-heat [11], and optical-absorption spectroscopy [12]. Interestingly, it is predicted that below a certain temperature, almost all the RMO_3 (M = transition metal) compounds are supposed to show the magnetoelectric effect due to the lack of the inversion symmetry [12]. The fundamental question about the possibility of ferroelectric ordering in some of the polycrystalline rare earth orthochromite was discussed for the first time by Subba Rao et al. [13]. According to Sahu et al. $RCrO_3$ exhibits multiferroic characteristic [14–16]. Consequently, $ErCrO_3$ is plausibly expected from the multiferroic behavior of the $RCrO_3$ systems. In this paper, we present the results of magnetization and ferroelectricity results for $ErCrO_3$. We also perform the low temperature polarization data for $ErCrO_3$ under different magnetic fields and find a strong magnetoelectric (ME) coupling in $ErCrO_3$.

2. Experimental

$ErCrO_3$ samples were synthesized using the solid state reaction [17]. The crystallinity and microstructure of the samples were checked by X-ray diffraction (XRD) using Cu target (18KW D/max-2500 diffractometer, Cu-$K\alpha$ radiation). The detailed dc magnetization measurements were performed between 2 and 300 K as well as magnetic field vs. magnetization hysteresis measurements on the $ErCrO_3$ using the physical property measurement system (PPMS) from Quantum Design Inc. The M–H loops were collected in a field

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up to ±45 kOe at 15, 50, 100, and 200 K, respectively. The ferroelectricity was probed using the pyroelectric current method (using Keithley 6517), integrated with the PPMS. For probing P, each sample under a poling electric field $E \sim 400$ kV/m and various magnetic fields H (0–9 T) was first cooled down to $T = 2$ K, followed by a sufficiently long time short-circuit procedure. To obtain the T (H)-dependence of P, the pyroelectric current was collected at a 4 K/min T-sweeping rate (0.6 T/min H-sweeping rates).

3. Results and discussion

Fig. 1 shows the XRD θ–2θ spectra of the $ErCrO_3$ samples at room temperature. All reflections can be assigned to the single perovskite structure with *Pbnm* and no detectable impurity phase is available. For identifying possible structural distortion, we perform high-precision Rietveld refining of the XRD data, as shown in Fig. 1. A very small difference between the measured spectra and refined ones is shown. The reliability of the Rietveld refinement is demonstrated by the refinement parameters $Rwp = 9.6\%$ with lattice parameters $a = 5.183$ Å, $b = 5.489$ Å, $c = 7.470$ Å, in good agreement with the previous report [18].

Fig. 2 describes the curves of the magnetic data taken at 100 Oe. The magnetizations show the Curie–Weiss-like behavior above about 135 K. The Curie constant derived from the magnetization data is 10.57 μ_B, closely related to the calculated value, 10.33 μ_B. And the Weiss temperature obtained is antiferromagnetic (AFM), −35 K. Further cooling to 133 K, a step change appears, which attributes to the AFM ordering of the Cr^{3+} spins, the typical behavior in the Γ_4 state [19], and then the moment increase monotonously to a peak around 22 K. The sudden decrease in magnetization below $T_{SR} \approx 22$ K (apparently higher than 9.3 K [10]), undergoing a

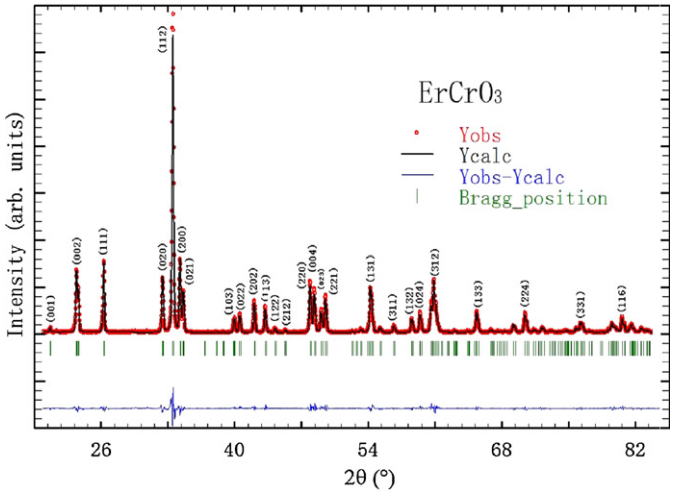

Fig. 1. X-ray diffraction patterns of $ErCrO_3$ powder at room temperature. (red dot, measured, and black line, using Rietveld structural refinement, respectively). The difference (blue line, difference) between the measured and Rietveld refined spectra for the sample, is plotted for clarity. The short vertical solid lines are guides for the eyes for the corresponding Bragg position. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

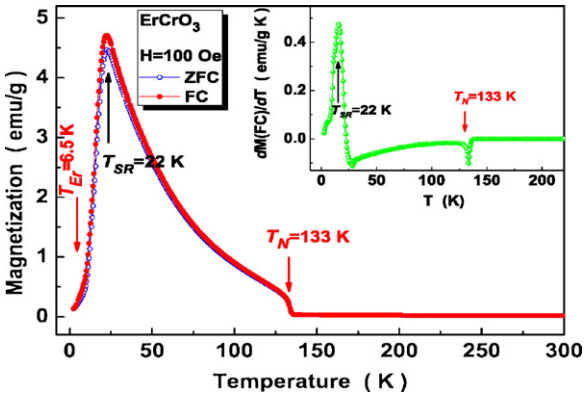

Fig. 2. Thermal magnetization curves for experimental $ErCrO_3$ under $H = 100$ Oe. *The inset*: the differential coefficient $dM(FC)/dT$ vs. T. The vertical arrows point the temperature of magnetic transitions.

spin reorientation from Γ_4 to Γ_1 [20], the system gradually transforms into AFM and the magnetization drops sharply. While $T \leq 6.5$ K, the magnetization decrease slowly, caused by the rare earth Er^{3+} spin ordering in AFM arrangement, $T_{Er} = 6.5$ K (Er ions ordered at about 4.3 K by neutron diffraction Ref. [20]) (Fig. 2). Thus, in the low temperature, Er^{3+}–Er^{3+} interactions must be considered.

As we know, in $RCrO_3$, the Cr^{3+} ions take trivalent state with $3d^3$ electronic configuration, sit in the octahedral geometry CrO_6 surrounded by six O^{2-} ions that leads to the splitting of $3d^3$ orbital into t_{2g} and e_g [21]. The t_{2g} orbital is half filled and the e_g ones is completely empty. The unfilled e_g orbital hybridizes with the $2p$ orbital of O^{2-} where two Cr^{3+} ions interact via O^{2-} ion in 180° position. On the other hand, each Cr^{3+} ion has eight R^{3+} nearest neighbors, the interaction between Cr^{3+} and R^{3+} ions via O^{2-} at 90° position which is weaker and dominates at lower temperatures only. The R^{3+}–R^{3+} superexchange interaction is still one order of magnitude weaker than the superexchange interaction between R^{3+} and Cr^{3+} and appears below 10 K. Due to the Dzialoshinski–Moriya type antisymmetric exchange interaction [22] of Cr^{3+}–Cr^{3+} ions which plays a very important role here, the Cr–O–Cr bond angle slightly deviates from 180°, resulting in residual electronic spin originating from imperfect superexchange interaction and show that $ErCrO_3$ is a canted FM (CAFM) below $T_N = 133$ K with a weak ferromagnetic (FM) component. These canted moments of Cr^{3+} induce an overall internal magnetic field at the Er^{3+} sites, which in turn changes the orientation of Er^{3+} spins in the direction of this induced field.

The magnetic relaxation behavior of the $ErCrO_3$ sample was also probed in different temperature ranges (Fig. 3). The curves were measured at $H = 100$ Oe just after the sample was cooled from paramagnetic state at 160 K to the desired temperature at zero magnetic fields. The magnetizations at all temperature change slightly, e.g., 0.5% during 6000s at $T = 30$ K (the inset of Fig. 3), and coincide with the M_{ZFC} vs. T curve at $H = 100$ Oe in Fig. 2. Then we can get a conclusion that, with the temperature decreasing, the magnetization exhibits an AFM-like transition around $T_N = 133$ K and a spin reorientation from Γ_4 to Γ_1 at $T_{SR} = 22$ K.

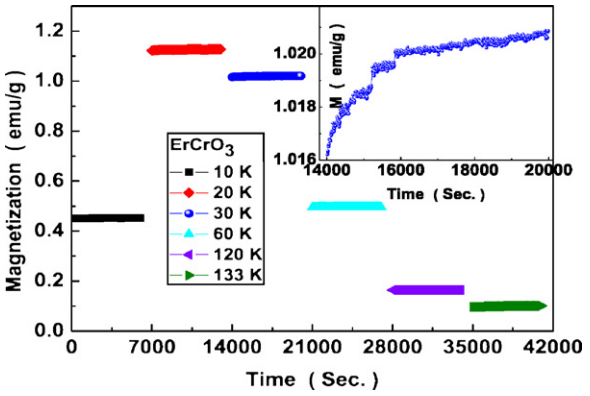

Fig. 3. Magnetization plotted as a function of time at different temperatures. The curves were measured at $H = 100$ Oe after the sample was cooled from 160 K to the desired temperature at zero magnetic fields. The inset in panel shows the detailed measurements at 30 K.

An additional fact is that $ErCrO_3$ does exhibit significant magnetization response to external magnetic field. Fig. 4 presents some representative M–H loops at selected temperatures. When $T < 133$ K, there exhibits a noticeable hysteresis and no perfect saturation is established up to $H = 4.5$ kOe (inset in Fig. 2(a)). While, the small hysteresis at 15 K and a large increase in magnetization in the range of 0–0.2 Tesla indicates that the Γ_1 state coexists with the Γ_4 state below T_{SR}. This corresponds to the recovery of the Γ_4 state induced by the applied fields. Furthermore, the magnetization M increases linearly in the region of larger magnetic field. This kind of magnetization loop and its linear change at high field is also attributed to the coexistence of FM and CAFM state. Therefore, the high-field part of the $M(H)$ evolution can be represented as $M(H) = \chi_{AF}H + \sigma_s$, where $\chi_{AF}H$ is the AFM contribution and σ_s is the saturation magnetization of the weak FM [23]. The σ_s are obtained by the extrapolation of the linear part of M–H curve to zero. In addition, the FM contribution for $ErCrO_3$ can be, thus, obtained as shown in Fig. 2(b), (c), and (d) for the different temperatures 15, 50, 100 K by subtracting the AFM contribution from the total magnetization respectively. Obviously, the values of σ_s decreases monotonously while the value of the coercivity H_c and the residual magnetization M_r increase in a monotonic way, e.g., the saturation magnetization $\sigma_s = 17.4$ emu/g, the coercivity $H_c = 0.017$ Tesla and the residual magnetization $M_r = 1.78$ emu/g at $T = 15$ K, $\sigma_s = 1.6$ emu/g, $H_c = 0.034$ Tesla and $M_r = 0.91$ emu/g at $T = 100$ K, respectively. At $T \geq 200$ K, the M–H loop shows almost a straight line indicating an absence of any FM ordering, as expected for a paramagnetic material.

Given the detailed magnetic properties, we need to check the ferroelectricity and the ME coupling between the ferroelectricity and magnetism of $ErCrO_3$ by the response of P to H. The P vs. T curves under different magnetic fields ($H = 0$, 5 T) is plotted in Fig. 5. It is observed that the P decreases rapidly around 133 K with the temperature increasing. This anomaly can be identified as the CAFM ordering of the Cr^{3+}ions and a clear indications of the ME coupling. The underlying physics is straightforward by considering the fact that the AFM order with the proper spin chirality can be further stabilized by the established ferroelectric order via their coupling. Furthermore, it is obvious that the magnetic field H suppresses significantly the low-T polarization. These results demonstrate convincingly the strong ME coupling in $ErCrO_3$.

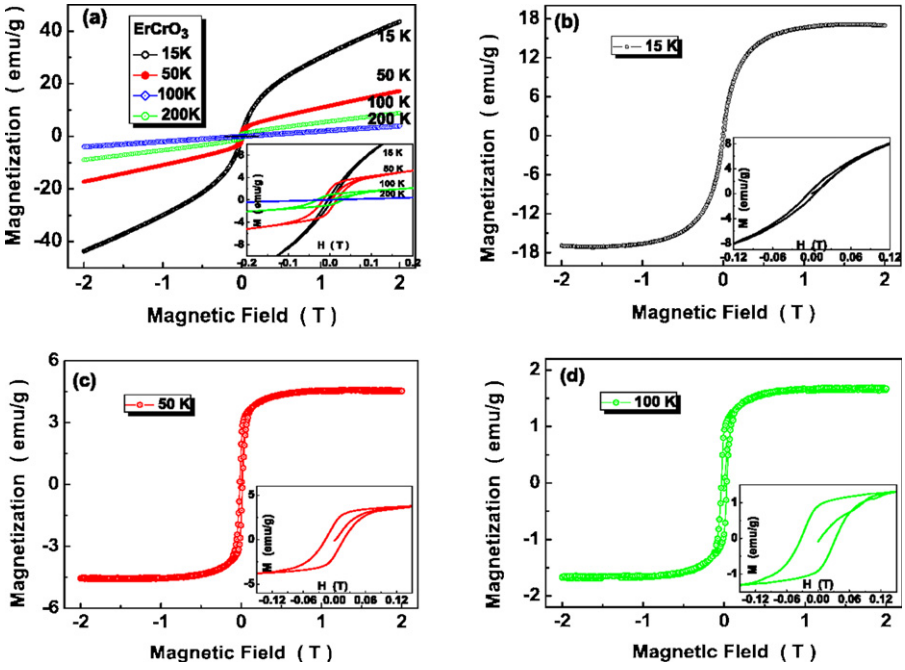

Fig. 4. (a) M–H curves at various temperatures of $ErCrO_3$. (b), (c), and (d) The FM contribution vs. magnetic field H at 15, 50, and 100 K, respectively. The insets are the extended views of each hysteresis loop.

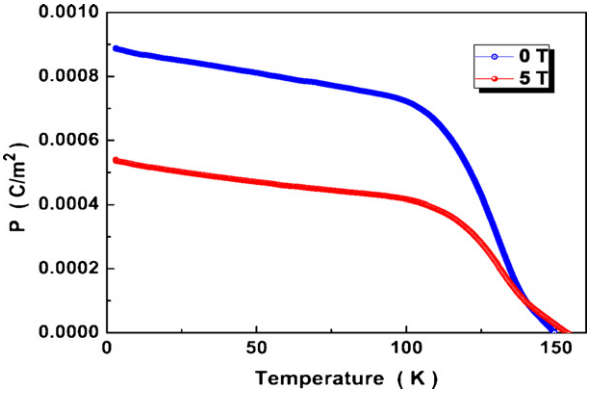

Fig. 5. Temperature dependence of electric polarization P in the selected magnetic field ($H = 0$, 5 T) for $ErCrO_3$.

4. Conclusion

The investigation of the magnetic and ferroelectric properties in the disordered perovskite $ErCrO_3$ exhibits anomalous behavior. At $T_N = 133$ K, the Cr^{3+} spins ordered AFM with a weak FM. Around $T_{SR} = 22$ K, $ErCrO_3$ undergoes a field- and temperature-induced spin reorientation from Γ_4 to Γ_1. Furthermore, the stability of the FM Γ_4 phase increases with increasing applied field. While $T \leq 6.5$ K, the dc magnetization decrease slowly, maybe caused by the rare earth Er^{3+} spin ordering in AFM arrangement. The curves of P vs. T exhibit a clear indications of the ME coupling and the magnetic field suppresses significantly the low-T polarization, indicating forcefully the strong ME coupling in $ErCrO_3$, a possible candidate for multiferroic materials.

Acknowledgments

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