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Abstract

In this work, we report on our studies on the multiferroic properties of two rare earth chromates, GdCrO₃ and YCrO₃. Polycrystalline bulks and thin films have been fabricated using conventional solid state reaction and pulsed laser deposition. Magnetic measurements have revealed that both compounds show weak ferromagnetism below the antiferromagnetic Neel temperature, T_N, of 170 and 140 K for GdCrO₃ and YCrO₃, respectively. However the well-developed ferroelectric polarization electrical field loop was not successfully measured for both samples due to their low resistance. The high conductivity of the samples at room temperature is related to the thermal activation of charge carriers at around 200 K in the samples revealed by temperature dependent dielectric measurement. Capacitance measurement at 77 K within magnetic field of 3000 Oe and zero field for GdCrO₃ bulk sample shows an increase in 58% in capacitance at 400 kHz by a magnetic field.

Keywords

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A novel multiferroic system: Rare earth chromates

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In this work, we report on our studies on the multiferroic properties of two rare earth chromates, GdCrO₃ and YCrO₃. Polycrystalline bulks and thin films have been fabricated using conventional solid state reaction and pulsed laser deposition. Magnetic measurements have revealed that both compounds show weak ferromagnetism below the antiferromagnetic Neel temperature, T_N , of 170 and 140 K for GdCrO₃ and YCrO₃, respectively. However the well-developed ferroelectric polarization electrical field loop was not successfully measured for both samples due to their low resistance. The high conductivity of the samples at room temperature is related to the thermal activation of charge carriers at around 200 K in the samples revealed by temperature dependent dielectric measurement. Capacitance measurement at 77 K within magnetic field of 3000 Oe and zero field for GdCrO₃ bulk sample shows an increase in 58% in capacitance at 400 kHz by a magnetic field. © 2010 American Institute of Physics. [doi:10.1063/1.3360358]

Materials having coupled ferroelectric and magnetic order parameters that result in simultaneous ferroelectricity and ferromagnetism, referred to as the so-called multiferroic or biferroic materials, have attracted a great deal of interest in the ferroelectric, mechatronic, and magnetic communities.^{1,2} Mutual control of the electric and magnetic properties is an attractive possibility, for it adds one more degree of freedom in manipulating the properties of both magnetic and electric materials. So far, only a few single-phase multiferroic materials have been discovered, such as BiFeO₃,^{3,4} BiMnO₃, and rare earth element based REMnO₃ (RE=Y, Tb, Ho, La, and Yb).⁵⁻⁸ The origins of the ferroelectricity in these systems are complicated and are still under debate.⁹ Therefore, it is interesting to find other new materials or systems which could show multiferroic properties. Very recently, YCrO₃ has been reported to be a biferroic material, which shows weak ferromagnetism below 140 K (T_N) and a ferroelectric transition at 473 K, accompanied by a hysteresis loop.¹⁰ It should be noted that most of the rare earth chromates, RECrO₃ (RE=Gd and Y), are typically perovskite-type compounds and crystallize in an orthorhombically distorted perovskite structure. The oxygen polyhedra surrounding the Cr are distorted, and therefore, ferroelectricity is expected in addition to the antiferromagnetic ordering in this system. In this paper, we report on our observations of both ferroelectricity and ferromagnetic properties in GdCrO₃ and make comparisons with the behavior of YCrO₃ compound.

Polycrystalline samples used in this work have been prepared in air by conventional solid state reaction. The starting materials were highly pure powders of Gd₂O₃, Y₂O₃, and Cr₂O₃. These powders were mixed stoichiometrically and well ground, and then pelletized and fired in air at 1300 °C for 24 h. This sintering was repeated 2–3 times to ensure

sample homogeneity. The thin film samples used in this work were deposited using a pulsed laser deposition (PLD) system. The excimer laser radiation used was produced by third harmonic generation of a Nd:YAG laser with a wavelength of 355 nm and an intensity of 2–3 J/cm² at a repetition rate of 10 Hz. The deposition was carried out in 100 mtorr dynamic oxygen at temperatures from 650 to 730 °C. A cooling rate of 15 °C/min was used to cool samples to room temperature after deposition. Both GdCrO₃ and YCrO₃ thin films were fabricated by ablating GdCrO₃ and YCrO₃ targets with deposition on Pt/Si substrates. The preferred orientation of the films was realized through controlling the deposition temperature. The phases and structures of the polycrystalline bulks and the films were determined by x-ray diffraction (XRD). A Pt upper electrode with an area of 0.007 85 mm² was deposited on the thin films by magnetron sputtering through a shadow mask. The thickness of the films was obtained through observation of the cross-section of the film under a high resolution scanning electronic microscope. The ferroelectric properties were measured by an aixACCT EASY CHECH 300 system. dc magnetization was determined by a superconducting quantum interference device magnetometer (Quantum Design, Magnetic Properties Measurement System) over a wide range of temperature from 5 to 340 K and in magnetic fields up to 8 T.

Figure 1 presents the XRD patterns of GdCrO₃ and YCrO₃ films deposited on Pt/Si substrates and that of an YCrO₃ bulk polycrystalline sample for comparison. Both films were found to be polycrystalline in nature. The YCrO₃ film with a thickness of 300 nm showed a certain degree of preferred growth along the (001) direction, as the (002) peak is much higher than the other peaks. The GdCrO₃ thin film shows little evidence of any preferred orientation. Figure 2(a) shows the temperature dependence of the magnetization of an YCrO₃ bulk sample for zero-field-cooled (ZFC) and field-cooled (FC) measurements in a field of 2000 Oe. A

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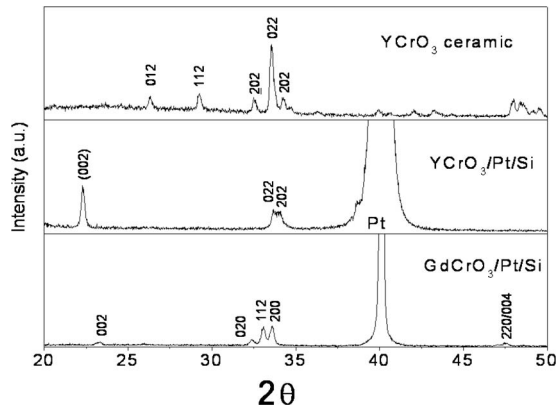


FIG. 1. XRD patterns of YCrO_3 and GdCrO_3 films on Pt/Si substrate.

clear transition, which is believed to be antiferromagnetic, is observed at 151 K for the YCrO_3 bulk. Magnetic hysteresis curves of this sample at 10 K and room temperature are shown in Fig. 2(b). The loop at 10 K for YCrO_3 exhibits ferromagnetic behavior with a large coercive field of 1.3 T. However, the magnetic moments are only 0.02 and $0.06 \mu_B/\text{Cr}$, where μ_B is the Bohr magneton, in zero field and 5 T. This indicates the typical canted antiferromagnetic ordering characteristics in the sample. The inset of Fig. 2(a) shows the temperature dependence of the inverse magnetic susceptibility and its Curie–Weiss law fitting, which gives an effective magnetization, μ_{eff} , of $3.92 \mu_B$, a Weiss temperature of 239 K, and thus a value of $S=3/2$ for Cr^{3+} with a high spin state in YCrO_3 . The film samples exhibit similar features both in their magnetization versus temperature curves and in their magnetic hysteresis loops. A similar weak ferromagnetism is also seen in GdCrO_3 polycrystalline bulks and films [Fig. 3(a)], but with a very small coercive field of a few tens of Oe [Fig. 3(b)]. The Curie–Weiss law fitting of the temperature dependence of the inverse magnetic susceptibility of GdCrO_3 gives a μ_{eff} of $8.16 \mu_B$ and thus a high spin state $S=3/2$ for Cr^{3+} after considering the contribution from both Cr^{3+} and Gd^{3+} , using the formula $\mu_{\text{eff}} = [\mu^2 \text{Cr}^{3+} + \mu^2 \text{Gd}^{3+}]^{1/2}$. It is believed that, for both compounds, below T_N , the net magnetic moment (canted moment) of Cr^{3+} lies parallel to the crystallographic c -axis, leading to the weak ferromagnetic features. The values of the magnetization observed in our samples are almost the same as what has been reported by Yoshii.¹¹

Figure 4 shows the room temperature P-E loops measured at different applied voltages for a Pt/ GdCrO_3 /Pt thin

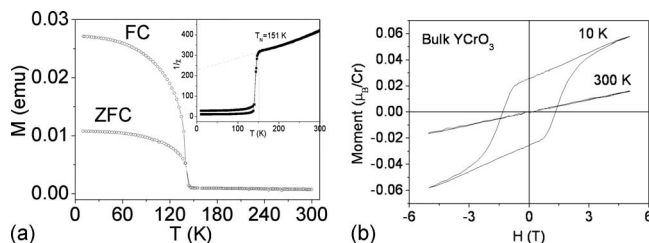


FIG. 2. (a) FC and ZFC magnetization vs temperature of the bulk YCrO_3 sample; inset is the temperature dependence of the inverse magnetic susceptibility with a Curie–Weiss law fitting. (b) Magnetization-magnetic field (M-H) hysteresis loop of bulk YCrO_3 sample measured at 10 and 300 K.

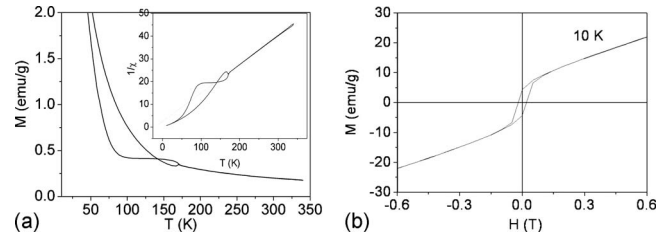


FIG. 3. (a) FC and ZFC magnetization vs temperature of the bulk GdCrO_3 sample; inset is the temperature dependence of the inverse magnetic susceptibility with a Curie–Weiss law fitting. (b) Magnetization-magnetic field (M-H) hysteresis loop of bulk GdCrO_3 sample measured at 10 K.

film capacitor. The rounded loops indicate a significant contribution from leakage current even at a low electrical field, which hindered the successful observation of saturated polarization. Similarly, no well-developed P-E hysteresis loop is observed for both YCrO_3 bulk samples and Pt/ YCrO_3 /Pt thin film capacitor sample due to very serious current leakage problem (figures are not shown).

Dielectric properties measurements of a GdCrO_3 bulk sample indicated that it has a dielectric constant of 10, a dielectric loss, $\tan \delta$, of 0.7%, and high resistivity below around 200 K at a frequency of 3 kHz (shown in Fig. 5). However the sample experiences a strong thermal excitation of charge carriers, for example, oxygen vacancies, starting from around 170 K, which transforms the material from a good insulator to a semiconductor. The thermal activation of localized charge carriers also cause increase in the dielectric constant, due to the formation of the dipoles consisting delocalized charge carriers and their shielding opposite charges, and accompanied energy absorption shown by $\tan \delta$. The activation energy of the charge carriers was obtained as 1.06 eV through liner fitting of $\log \rho \sim 1/T$ plot, which falls with energy band gap of 1.4 eV,^{12,13} which indicates that energy levels of the charge carriers fall within the valence band and bottom of conduction band. The observed thermal activation of the charge carried serious hinder the measurement of the ferroelectric polarization at room temperature. It is believed that similar mechanism contributes to the low resistance of YCrO_3 sample. To study the magnetoelectrical coupling effect in GdCrO_3 film sample, which capacitance was measured at 77 K within 3000 Oe magnetic field in comparison to zero field. An enhancement of 58% in capacitance at 400k Hz by magnetic field was observed (shown in Fig. 6).

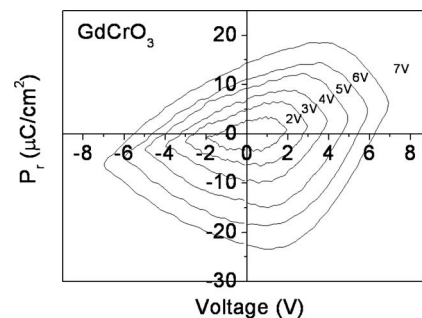


FIG. 4. (a) Polarization-electric field hysteresis loops of GdCrO_3 film capacitor.

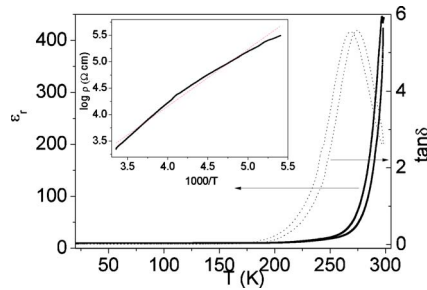


FIG. 5. (Color online) Temperature dependence of dielectric constant, dielectric loss, of GdCrO₃ bulk sample at a frequency of 3 kHz, and linear fitting of $\log \rho \sim 1000/T$ (inset).

Through the determination of the detailed structure by first-principles band structure calculations, a noncentrosymmetric monoclinic structure with space group $P2_1$, rather than $P2_1/n$, which is centrosymmetric, has been found to be responsible for the presence of the ferroelectricity in YCrO₃.¹⁰ It is believed that the structural distortion of the parent cubic perovskite structure leads to the ferroelectric structure. Antiferrodistortive type structural instabilities have been suggested to dominate the polarization in YCrO₃.¹⁰ GdCrO₃ has a distorted orthorhombic perovskite structure with space group $Pbnm$ at room temperature and a canted antiferromagnetic ordering of localized Cr³⁺ moments. Its magnetic structure is expected to have a G-type configuration. An antisymmetric exchange interaction or a pseudodipolar interaction between Gd³⁺ and Cr³⁺ produces an effective magnetic field at the Gd³⁺ site whose direction is opposite to that of the canted Cr³⁺ moment. This type of extra magnetic moment contributed by the Gd³⁺ would enhance the degree of noncentrosymmetric distortion in the crystal lattice compared to that in YCrO₃. This would cause GdCrO₃ to show a larger electric polarization than YCrO₃. Further study on the origins of the ferroelectricity in GdCrO₃ is much needed.

Although ambiguous ferroelectricity is observed in both GdCrO₃ and YCrO₃ compounds, magnetocapacitance effect was measured in GdCrO₃, making them novel potential multiferroic materials from the viewpoint of both fundamental research and the potential for practical applications, both compounds show significant conductivity at room temperature. It is believed that the ferroelectricity will be better demonstrated below the temperature where the change in resistance occurs.

In summary, we report on the observation of both ferroelectricity and weak ferromagnetism in GdCrO₃ and YCrO₃

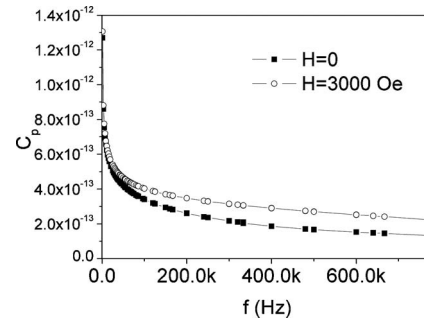


FIG. 6. Magnetocapacitance effect in GdCrO₃ film at 77 K, measured without magnetic field and under 3000 Oe field.

polycrystalline bulks and thin films fabricated using conventional solid state reaction and PLD. Both compounds show a weak ferromagnetism below the antiferromagnetic Neel temperature, T_N , of 170 K and 151 K for GdCrO₃ and YCrO₃, respectively, and show ambiguous ferroelectricity at room temperature, and magnetocapacitance effect. However the large conductivity at room temperature, caused by thermal activation of charge carriers, seriously limits the ferroelectric performance.

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