Magnetic properties of pure and Fe doped HoCrO_3 thin films fabricated via a solution route

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Abstract

Multiferroic properties of orthorhombically distorted perovskite rare-earth chromites, such as HoCrO_3 , are being investigated extensively in recent years. In the present work, we report on the effect of Fe substitution on the magnetic properties in HoCrO_3 thin films. Thin films of nominal compositions with HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ were fabricated via a solution route on platinized silicon substrates. Structural properties of the films were characterized by X-ray diffraction and Raman spectroscopy. The surface morphology and cross-sections of the films were examined using scanning electron microscopy. Optical band gaps of these films are found to be 3.45 eV and 3.39 eV, respectively. The magnetization measurement shows that the Néel temperatures (where Cr^{3+} orders) for the HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ films are 134 and 148 K, respectively. In a magnetic field of 2 T, the maximum entropy change and relative cooling power, two parameters to evaluate the magnetocaloric properties of a material, were 0.813 J/kg K at 11 K and 21.1 J/kg for HoCrO_3 film, in comparison with 0.748 J/kg K at 15 K and 26.8 J/kg for $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film. To our knowledge, this is the first work exploring the band gap and magnetocaloric properties of rare-earth chromite thin films. These findings should inspire the development of rare-earth chromite thin films for temperature control of nanoscale electronic devices and sensors in the low temperature region (<30 K).

1. Introduction

In the last decade, magnetoelectric multiferroic (ME-MF) materials have attracted considerable attention due to their promising applications in multifunctional devices, such as computer memory, magnetic field sensors, novel spintronic devices, energy harvesting, etc [1–4]. One such system, namely rare-earth chromites (RCrO_3) have been explored widely for their ME-MF properties [5–7]. In some recent reports the magnetocaloric effect (MCE), which is mainly characterized by an isothermal magnetic entropy change (ΔS) achieved by adiabatic tuning of the magnetization, have also been investigated in the RCrO_3 system. Their MCE properties hold promises on their prospective utilization in magnetic refrigeration – a technology which is environmentally friendly that does not use ozone-depleting gases and more energy efficient, as compared to the conventional gas compression refrigeration [8–12]. Currently, there is a great interest in new materials with large MCE. In particular, RCrO_3 compounds show remarkable MCE in the low temperature region (below 30 K) due to rare-earth magnetic transition at low-

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temperatures, complementary to a vast number of alloys (mostly Gd based) and compounds that have been broadly investigated and regarded as applicable in high temperature (near room temperature) magnetic refrigeration [13–15]. For example, in bulk HoCrO_3 powder, Ho^{3+} ordering appears at ~ 10 K, and consequently a large ΔS of ~ 7.2 J/kg K was observed at 7 T and 20 K [9].

For the development of efficient magnetic refrigerators two critical factors are: i) efficient heat exchange between MCE material of a refrigerator and its surroundings (i.e. large ΔS) and ii) use of lower magnetic fields. Thus, it is worthwhile to perturb properties by using reduced dimensions or nano/micro-structuring, i.e., using thin films, ribbons, etc., which may be favorable for heat transport and novel MCE properties due to the high surface to volume ratio [16,17]. Additionally, studies on the MCE properties of thin films have also been driven by the trend of device miniaturization [18–21], on account of their bright prospects in solid-state cooling devices for on-chip cooling and temperature regulation of sensors and micro devices [16,22–24]. A few lanthanum manganite films have been studied to show promising MCE properties near room temperature [22,24,25].

Thin films may show better MCE properties than bulk powder samples, such as larger applicable temperature ranges, better refrigeration capacity, etc. For instance, Miller *et al.* reported that the full width at half maximum of the $\Delta S \sim T$ curve of Gd/W thin film heterostructures had nearly doubled compared to that of bulk Gd metal under the same magnetic field [16]. Likewise, Lampen *et al.* contrasted MCE properties of the bulk polycrystalline, nanocrystalline, and thin film of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and found that the thin film has enhanced refrigerant capacity than its bulk polycrystalline and nanocrystalline counterparts [26]. Further, ΔS were found to be enhanced (to ~ 9 J/kg K at 1 T) at room temperature by exploiting the strain mediated feedback between ferromagnetic $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ film and BaTiO_3 substrate that undergoes structural phase transition [24] as compared to $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film on LaAlO_3 substrate (1 J/kg K at 250 K and at 2 T). Xiong *et al.* synthesized $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ thin films on (001) SrTiO_3 substrate by pulsed laser deposition (PLD), and the ΔS was determined to be 6 J/kg K at 265 K and at 5 T [25]. The above mentioned thin films mostly show large MCE near room temperature that can be useful for domestic and industrial applications. Yet, it is imperative to seek other thin films systems, which exhibit large MCE in the low temperature range, because of the unrelenting pursuit of new materials applicable in space science and liquefaction of hydrogen in the fuel industry [27,28]. One such material system is aforementioned RCrO_3 . In spite of many reports on the MCE properties of RCrO_3 bulk powders [8–12], studies on the MCE properties of their thin film counterparts are still lacking. Additionally, it should be pointed out that current processing techniques (for example physical vapor deposition) of thin films with suitable structural and magnetic properties can be challenging and expensive. Comparatively, a solution method for thin film synthesis is far more economic, facile, and offers easy avenues to control stoichiometry, morphology, etc, and thus can be ideally suited for fast and efficient screening of potential candidate materials for various applications. Accordingly, in this work, we study the structural, magnetic, and MCE properties of HoCrO_3 thin films synthesized by a solution method. By doping Fe at the Cr-site of the HoCrO_3 film, $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ thin films were fabricated, with an aim to increase the Néel temperature and tune its MCE property.

2. Experimental

To synthesize HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ thin films, firstly stoichiometric ratios of high purity $\text{Ho}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, and CrCl_3 precursors were mixed using acetic acid as solvent to obtain a parent solution. Secondly, a coating solution, obtained by appropriate dilution of the parent solution, was then spin-coated (spin speed of 4000 rpm for 20 seconds) onto $1\text{ cm} \times 1\text{ cm}$ platinized silicon substrates ($\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$), followed by pyrolysis at $600\text{ }^\circ\text{C}$ for 5 minutes. After four consecutive spin-coating and pyrolysis cycles, the films were annealed at $800\text{ }^\circ\text{C}$ in an oxygen environment for 2 hours. An X-ray powder diffractometer (Bruker D5) equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.542\text{ \AA}$) was used to characterize the crystal structure and phase purity of the synthesized thin film samples. Room temperature Raman spectra were measured by a Renishaw 2000 system using a 514 nm Ar-ion laser. Field-emission scanning electron microscopy (FESEM) was utilized to examine the surface morphology and thickness of the films. Room-temperature optical absorbance in the wavelength range of 200-800 nm was recorded using a Shimadzu UV-2450 UV-Vis Spectrometer. Magnetization measurements were carried out using a vibrating sample magnetometer attached to an Evercool Physical Property Measurement System from Quantum Design.

3. Results and Analysis

Figure 1 displays X-ray diffraction (XRD) patterns of the HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ films, in which the (hkl) values of some major peaks were indexed based on JCPDS #77-1035 belonging to an orthorhombic crystal structure with space group $Pbnm$. Since all the peaks in the XRD pattern belonged to either the film or the substrate (marked with asterisk sign), the films are considered to be phase pure within the detection limit of the laboratory XRD. Evidently, the films did not grow in any preferred orientation on platinized silicon substrate, suggesting that they were polycrystalline. Using the Bragg' law and the d -spacing formula for the orthorhombic structure

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}, \quad (1)$$

the lattice parameters for both compositions were calculated using the peak positions of various (hkl) reflections in XRD patterns and are summarized in Table I. The lattice constants of HoCrO_3 film in the present study agree well to those of a HoCrO_3 films prepared by PLD method [29]. The unit cell volumes of HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ films are found to be slightly smaller than their bulk counterparts [9]. Additionally, the unit cell volume of $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film was slightly larger than that of HoCrO_3 film, which can be explained by the difference in the ionic size of Fe^{3+} ($0.645\text{ \AA}$) and Cr^{3+} ($0.615\text{ \AA}$) yielding an increase in lattice constants b and c (see Table I). The orthorhombic strain factor defined as $S=2(b-a)/(b+a)$ [30], which is a measure of the distortions of the unit cell to the cubic structure, was also calculated and are listed in Table I for these films.

Table I. Lattice parameters and the orthorhombic strain factor (S) of HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ films acquired from the experimental XRD data. For comparison, lattice parameters and the

orthorhombic strain factors of the bulk powder and thin film of same composition fabricated via PLD method (as reported in the literature) are also included in the table.

Parameter	HoCrO ₃ (solution)	HoCr _{0.7} Fe _{0.3} O ₃ (solution)	HoCrO ₃ (bulk) [9]	HoCr _{0.7} Fe _{0.3} O ₃ (bulk) [9]	HoCrO ₃ (PLD) [29]
<i>a</i> (Å)	5.273	5.238	5.248	5.259	5.24
<i>b</i> (Å)	5.460	5.479	5.525	5.540	5.57
<i>c</i> (Å)	7.519	7.660	7.545	7.564	7.48
<i>V</i> (Å ³)	216.48	219.83	218.79	220.38	218.32
<i>S</i>	0.03485	0.04498	0.05142	0.05204	0.06105

Since the thin films are deposited on the Pt layer of the platinized silicon substrates, which has cubic crystal structure ($a_s=3.97$ Å), there is a lattice mismatch between the sample and substrate, resulting in strain at the film-substrate interface defined by [31]:

$$\eta = (a_s - a_f)/a_s, \quad (2)$$

where a_f is the pseudocubic lattice parameter of the film, calculated by $a_f = \sqrt{(a^2 + b^2)/2}$. The values of η are 4.40% and 4.53% for HoCrO₃ and HoCr_{0.7}Fe_{0.3}O₃ film, respectively, indicative of slight tensile strain that gives rise to stress in the films and is used later in the discussion of the ordering temperature of Cr³⁺ ions. The SEM images of the surface {Figure 2(a-b)} and cross-sections {Figure 2(c-d)} of the films revealed that the films were dense with no apparent pores or cracks. The thicknesses of the HoCrO₃ and HoCr_{0.7}Fe_{0.3}O₃ films were determined to be ~286 nm and ~217 nm, respectively.

To further confirm the phase purity of the samples, room temperature Raman spectra were recorded and are shown in Figure 3. The Raman modes assigned according to the report of Weber *et al.*[32] in the present thin films are consistent with those of HoCrO₃ and HoCr_{0.7}Fe_{0.3}O₃ bulk powders [9], despite of some slight shifts in wave numbers as listed in Table II. In addition, the intensity of A_g(2) mode is higher than that of B_{2g}(1) mode in the HoCrO₃ and HoCr_{0.7}Fe_{0.3}O₃ films, while the relative intensity of these two modes are opposite in their bulk counterpart [9] that might be attributed to the difference in the lattice constants between the film and bulk powder [32].

Table II. Position of the Raman modes in HoCrO₃ and HoCr_{0.7}Fe_{0.3}O₃ films, in comparison with those observed in HoCrO₃ and HoCr_{0.7}Fe_{0.3}O₃ bulk powder from Ref.[9].

Sample	A _g (2)	B _{2g} (1)	B _{1g} (1)	A _g (3)	B _{2g} (2)	A _g (4)	B _{1g} (2)	A _g (5)	B _{2g} (3)	B _{3g} (3)
HoCrO ₃ film (this work)	141.9	164.8	263.0	275.2	316.9	344.6	404.8	422.0	493.6	566.3
HoCrO ₃ bulk [9]	141.8	163.0	261.1	275.1	316.8	342.7	403.0	420.1	493.5	564.5
HoCr _{0.7} Fe _{0.3} O ₃ film (this work)	140.3	163.2	-	271.9	313.6	341.3	-	420.4	488.7	553.3
HoCr _{0.7} Fe _{0.3} O ₃	139.3	160.5	-	269.1	309.1	336.8	-	417.7	492.8	548.7

bulk [9]										
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In single phase magnetoelectric multiferroic materials, the band gap plays an important role as the leakage currents or insulating behavior depends on it [33]. Therefore, it is essential to measure their energy band gaps, in order to strengthen their potential applications in devices. The room-temperature optical absorbance of the HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ films was measured and is plotted in Figure 4. To calculate the band gap (E_g), Tauc's equation was used [34,35]

$$\alpha h\nu = (h\nu - E_g)^{1/2} \quad (3)$$

where α is the optical absorption coefficient and $h\nu$ is the photon energy. The E_g values were acquired by extrapolating the linear region of the absorption curve to the energy axis as shown in Figure 4. HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ films are both found to be insulating with E_g of 3.45 eV and 3.39 eV, respectively, which are slightly larger than those of the experimental HoCrO_3 bulk (3.26 eV) [36] and the theoretically obtained values for bulk HoCrO_3 (3.1 eV) or bulk $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ (2.7 eV) [9]. This may be interpreted as an effect of the surface strain in the present films. In $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$, the width of the available unoccupied d -orbitals of the Fe^{3+} at the conduction band reduces, which can lead to the shift of the conduction band minima to higher energies. As a result, E_g in $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ increases as compared to that in HoCrO_3 .

Thermal variation of the magnetization (M) data of HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ films on the zero-field cooling (ZFC) mode and field cooling (FC) mode was measured using a magnetic field of 0.05 T and are plotted in Figure 5(a), 5(b). Note that the data for M has contributions from both the film and the substrate in each case. For both films, bifurcation between the ZFC and FC modes occurs below a certain temperature – the ordering temperature of Cr^{3+} ions (T_N^{Cr}) resulting from a weak G-type antiferromagnetic ordering [37], which can be best determined by plotting the temperature dependent $d(\chi T)/dT$ [38]. As shown in the insets of Figure 5(a), 5(b), from the peak positions of the $d(\chi T)/dT$ vs. T curve, values of T_N^{Cr} are determined to be 135 K and 150 K for the HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ films, respectively [9]. Evidently, T_N^{Cr} of HoCrO_3 film increases by iron doping at the Ho-site, which is similar to that observed in bulk Fe doped HoCrO_3 [9]. Nevertheless, T_N^{Cr} of the thin films are slightly lower than those of their bulk counterparts (140 K for HoCrO_3 and 174 K for $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$) [29,39], possibly arising due to the tensile strain in the films as a result of the aforementioned lattice mismatch between the film and substrate. This is consistent with the report by Ghosh *et al.*, where T_N^{Cr} of HoCrO_3 film with tensile strain was around 130 K, lower than 140 K for HoCrO_3 bulk sample [29]. It should also be noted that The maximum values of magnetization of the HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ films on the FC mode are 70.85 emu/cc (or 8.64 emu/g) and 66.75 emu/cc (or 8.14 emu/g) at 5 K, lower than their bulk counterpart (30.8 emu/g and 20.9 emu/g), which can be attributed to the surface disorder of the films. Note that the density of HoCrO_3 $\sim 8.2 \text{ g/cm}^3$ was used in the unit conversion from emu/cc to emu/g [40].

The field dependent magnetization hysteresis loops (M vs. H) of HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ films at 5 K, 80 K, 150 K, and 180 K are presented in Figure 6. It should be noted that the magnetization data had contributions both from the film and the diamagnetic platinized

silicon substrate. For removing the contributions from the substrate, the M vs. H data of substrate was also measured as plotted in the inset of Figure 6(a) and it was subtracted from the film + substrate data before converting the magnetization values in terms of emu/cc or emu/g as shown in Figure 6(a). Like their bulk counterparts [9], HoCrO₃ and HoCr_{0.7}Fe_{0.3}O₃ films show canted antiferromagnetic behavior at low temperature (5 K) and paramagnetic behavior at 150 K and 180 K, respectively that are above their respective T_N^{Cr} . This change is due to the superposition of a weak canted antiferromagnetic component of the Cr³⁺ or Fe³⁺ ions and a strong paramagnetic component of the Ho³⁺ ions. At temperature of 5 K and field of 2 T, HoCrO₃ film shows larger magnetization 198.4 emu/cc (or ~24.2 emu/g) than the HoCr_{0.7}Fe_{0.3}O₃ film 182.0 emu/cc (or ~22.2 emu/g). This difference is used in the ensuing discussion of their MCE properties. In contrast, the bulk counterparts exhibit larger magnetization ~50 emu/g under the same conditions. Generally, the magnetic hysteresis is an important factor to evaluate the potential of a material for magnetic refrigeration [41], which is mainly characterized by a coercive field (H_C) and a remnant magnetization (M_R). The H_C and M_R values were determined to be 0.1429 T and 0.1391 T, and 79.1 emu/cc (or ~9.65 emu/g) and 74.3 emu/cc (or ~9.06 emu/g) for HoCrO₃ and HoCr_{0.7}Fe_{0.3}O₃ films, respectively. In comparison, H_C values for their bulk counterparts are 0.2003 T and 0.2133 T, respectively [9]. The difference in magnetic hysteresis between the bulk powder and the films could be understood by the variation in magnetic domain structures, sample shapes, microscopic defects, etc [42]. Evidently, HoCrO₃ film has slightly larger magnetic hysteresis than HoCr_{0.7}Fe_{0.3}O₃ film, which is also discussed further in the following comparison of their MCE properties.

To investigate the MCE property of the films, the isothermal magnetization curves with magnetic field applied up to 2 T were measured and are depicted in Figure 7. Slope of the curves changes considerably near 0.3 T, suggesting weak ferromagnetic properties for the HoCr_{1-x}Fe_xO₃ system, which is similar to the rare-earth manganite system [43]. The MCE behavior of HoCrO₃ and HoCr_{0.7}Fe_{0.3}O₃ films can be extracted from the isothermal magnetization curves and are evaluated by the magnetic entropy change (ΔS) [41]

$$\Delta S(T, H) = \int_0^H \left(\frac{\partial M(T, H)}{\partial T} \right)_H dH; \quad (4)$$

and the relative cooling power (RCP) is usually calculated by

$$RCP = - \int |\Delta S| dT. \quad (5)$$

Figures 8(a)-(b) show the dependence of ΔS on temperature under the magnetic field ranging from 0.2 to 2 T. As the field increases, the parameter ΔS rises according to Eq. 4, since larger magnetic field induces larger magnetization. At a certain field, ΔS of HoCrO₃ film goes up with temperature from 5 K to 11 K, and then decreases thereafter. Although ΔS for HoCr_{0.7}Fe_{0.3}O₃ film exhibits similar behavior, its maximum is at ~15 K. At 2 T, the maximum ΔS for HoCrO₃ and HoCr_{0.7}Fe_{0.3}O₃ films are 0.813 J/kg K and 0.748 J/kg K, respectively, which are smaller than their bulk counterparts (1.92 J/kg K and 1.23 J/kg K at 2 T, respectively). This might be attributed to the smaller magnetization value, which could be due to surface disorder of the films. Likewise, Miller *et al.* reported that ΔS of Gd/W thin film has a maximum ~3.4 J/kg K at about 284 K, which is one third of that of the bulk Gd sample [16]. Consistent with their bulk

counterparts, the HoCrO_3 film has larger ΔS than the $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film, which can be explained by its relatively larger magnetization as mentioned above.

The RCP values of HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ films from 0.2 to 2 T are presented in Figure 8(c)-(d). At 2 T, the RCP values in the refrigeration cycle (5-100 K) are 21.1 J/kg and 26.8 J/kg for HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film, respectively. In spite of a smaller ΔS value, $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film has a larger RCP value than HoCrO_3 film, because the RCP value is the integration of ΔS over temperature (see Eq. 5), and the $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film exhibits a wider $\Delta S \sim T$ curve, resulting in larger integration results. Additionally, $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film shows smaller magnetic hysteresis, yielding less energy loss in the thermal process and thus larger cooling power [41]. Similarly, in the report of Lampen *et al.*, $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ thin film shows smaller ΔS , but larger RCP value than its bulk counterpart due to evident broadening of the $\Delta S \sim T$ curve in the thin film [26]. Moreover, ΔS of HoCrO_3 bulk sample (7.2 J/kg K) is smaller than that of HoMnO_3 (12.5 J/kg K), while its RCP value (408 J/kg) is larger than that of HoMnO_3 (312 J/kg).

4. Conclusion

For the first time, the magnetocaloric properties of rare-earth chromite (RCrO_3) thin films, is studied here, evaluating their prospective applications in magnetic refrigeration in the low temperature region (< 30 K). Thin films with nominal composition of HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ were prepared on platinized silicon substrate by a solution method. Structural characterizations using XRD and Raman spectroscopy showed that the facile and economic solution method resulted in phase pure polycrystalline samples. The magnetic measurement demonstrates that the Néel temperatures for the HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ films are 134 and 148 K, respectively. In a magnetic field of 2 T, the maximum entropy change and relative cooling power for HoCrO_3 and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ films are 0.813 J/kg K at 11 K and 0.748 J/kg K at 15 K, 21.1 J/kg and 26.8 J/kg, respectively. Further efforts are needed to study the effect of strain on the MCE properties of these thin films, which hold promise for magnetic refrigeration in low temperature region (< 30 K).

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Figure 1. Room temperature X-ray diffraction patterns for HoCrO_3 film (a) and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ films (b). Peaks marked by * are from the platinized silicon substrate.

Figure 2. SEM images of surface area of HoCrO_3 film (a) and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film (b); and cross-section of HoCrO_3 film (c) and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film (d).

Figure 3. Room temperature Raman spectra for HoCrO_3 film (a) and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film (b).

Figure 4. Absorption spectra of HoCrO_3 film (a) and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film (b).

Figure 5. Thermal variation of magnetization data (M) of the HoCrO_3 film (a) and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film (b) on the zero-field cooling (ZFC) mode and field cooling (FC) mode measured at 0.05 T. The insets display the derivative of the product of temperature and susceptibility with respect to temperature ($d(\chi T)/dT$), in order to reveal the Cr^{3+} ordering temperature.

Figure 6. Field dependent isothermal magnetization data at 5 K, 80 K, and 150 K (180 K) of HoCrO_3 film (a) and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film (b). Inset of (a) shows the magnetization data of the substrate measured at 5 K, 80 K, 150 K, and 300 K.

Figure 7. Isothermal magnetization curves (in first quadrant) at many temperatures (5–80 K) for HoCrO_3 film (a) and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film (b).

Figure 8. The temperature dependent entropy change (ΔS) of HoCrO_3 film (a) and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film (b), and the temperature dependent relative cooling power (RCP) of HoCrO_3 film (c) and $\text{HoCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ film (d).