Mild Hydrothermal Crystallization of Heavy Rare-Earth Chromite RECrO3 (RE=Er, Tm, Yb, Lu) Perovskites and Magnetic Properties

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ABSTRACT: Crystallization of perovskite structure chromites (ACrO3) in aqueous conditions is difficult owing to the amphoteric nature of the Cr3+ in the alkaline-mediated reactant conditions. This is especially true for the small metal cations at the A-site with large distortion angle of CrO6 octahedral and small Goldschmidt tolerance factors. We performed a progressive dehydration crystallization strategy to synthesize four RECrO3 with the smallest radii of rare-earths (Er, Tm, Yb, Lu) in mild hydrothermal conditions. Profile refinement of the high-resolution powder x-ray diffraction results indicated that slightly longer unit cell parameters of a and c in our samples with a higher distorted angle of CrO6 octahedral units along <010> direction. All of the samples show rounded rectangle plate morphology with uniform distribution of particle sizes. These four RECrO3 crystals can only form in a very narrow mineralization-temperature range *i.e.* 260-280 oC and 4.45-6.24 M of KOH. HRTEM results indicated that the normal crystallographic direction is <001>, and the lattice of steps at the edge of elliptic rounded crystal is consistent with the bulk, which demonstrated single crystalline nature of the as-obtained crystals. Room temperature Raman and FT-IR spectra reveal a continuous symmetry mode-shift dependent on the radii of A-site rare-earth cations. Temperature dependent magnetization curves of RECrO3 show typical antiferromagnetism to paramagnetism transition with Néel temperature of 93, 90, 86 and 83 K for ErCrO3, TmCrO3, YbCrO3 and LuCrO3, respectively. Samples of YbCrO3 and LuCrO3 show clear magnetization reversal and exchange bias phenomena below their Néel points. This paper indicates that the coupling of magnetic exchange in perovskite structure oxides could be tailorable in mild hydrothermal condition, towards for the exploration of new magnetic and other physical properties.

INTRODUCTION

Perovskite structure orthorhombic rare-earth chromites (RECrO3) materials received a lot of attention due to their widely applications as sensors[[1]](#endnote-2), catalysts[[2]](#endnote-3), oxygen ion conductors[[3]](#endnote-4), magnetic refrigeration material[[4]](#endnote-5), interconnect materials for solid oxide fuel cells[[5]](#endnote-6), and multiferroic applications[[6]](#endnote-7), especially, for the heavy rare-earth chromites (RE=Ho, Er, Yb, Lu), which exhibit A-site dependent canted antiferromagnetism and ferroelectric transitions[[7]](#endnote-8). For example, HoCrO3 shows a polar ordering in antiferromagnetic crystal lattice, which is suggested as a new type ferroelectric material with a large spontaneous electric polarization (~ 0.32 µC cm-2 at 10 K)[[8]](#endnote-9). The magnetic and multiferroic behaviours of rare-earth chromites can be generally tailored by doping Fe3+(3d5) and Mn3+(3d4) into the RECrO3 crystal lattice by creating additional ferromagnetic exchange interactions with additional spins and increasing lattice distortion[[9]](#endnote-10),[[10]](#endnote-11), due to the unprecedented partially ordered Fe3+/Mn3+-O-Cr3+ linkages in the new mixed lattice[[11]](#endnote-12),[[12]](#endnote-13). The size and ordering of A-site atoms in RECrO3 determine the crystal lattice distortion by affecting the degree of CrO6 octahedral tilting, which greatly influence the magnetic and polarization behaviours[[13]](#endnote-14),[[14]](#endnote-15). Walton *et al.* have reported an A-site composition dependent magnetic behaviour of LaxSm1-xCrO3 by supercritical hydrothermal method, which shows the continuous decrease of Néel transition temperature (TN) with reduction of the average A-site cation size by increasing the doping level of Sm[[15]](#endnote-16). Heavy rare-earth chromites have shown many interesting physical properties, such as photo-induced magnetic transition in ErCrO3[[16]](#endnote-17), magnetization reversal and exchange-bias in TmCrO3[[17]](#endnote-18),[[18]](#endnote-19), temperature and magnetic field induced magnetization switching and exchange bias in YbCrO3[[19]](#endnote-20),[[20]](#endnote-21), biferroic and magnetodielectric effects of LuCrO3[[21]](#endnote-22),[[22]](#endnote-23). Nonetheless, TmCrO3 is a rarely studied perovskite structure orthochromites with few paper concerns its optical absorption spectrum[[23]](#endnote-24),[[24]](#endnote-25) and magnetic behaviours[[25]](#endnote-26). Magnetic structure of RECrO3 usually show three types of G-type antiferromagnetic configurations with Γ1(AxGyCz), Γ2(FxCyGz), and Γ4(GxAyFz) according to Bertaut notation[[26]](#endnote-27). Heavy rare-earth orthochromites have also been reported to show spontaneous polarization even for the polycrystalline pellets[[27]](#endnote-28). However, there remains a controversy that RECrO3 crystalized into a centrosymmetric *Pbnm* space group, which seems to be impossible to show spontaneous polarization[[28]](#endnote-29). Crystals with small A-site chromites may provide unusual magnetic structure with C-type, rather than the nominal *G*-type structure usually observed in RECrO3 samples with the occurrence of ferromagnetic (FM) nearest-neighbour interaction[[29]](#endnote-30). Therefore, it may provide a fundamental perspective to disclose the effect of the synthetic method on A-site dependent CrO6 distortion and its corresponding physical properties.

RECrO3 materials are mainly synthesized based on high-temperature solid-state method above 1000 oC with repeated grindings and sinterings[[30]](#endnote-31). Although there are also numerous synthetic techniques based on solution chemistry reported, such as sol-gel[[31]](#endnote-32), self-propagating synthesis[[32]](#endnote-33), and combustion route[[33]](#endnote-34), all of them involved at least one high-temperature treatment step to obtain the perovskite phase. RECrO3 materials synthesized via these methods are prone to form over-oxidized phase at sample surface, which are overlooked due to the low detectable limit of powder x-ray diffraction for small portion of impurity phase[[34]](#endnote-35). Furthermore, rare-earth chromites can also be synthesized via microwave-assisted method that should be sintering at 1300 oC to obtain high purity products[[35]](#endnote-36). Nanostructures of RECrO3 have been synthesized via a hydrothermal involved ethylene glycol precursor method that should be calcined at 800-1000 oC[[36]](#endnote-37). Single crystals of YbCrO3 have been achieved via flux technique in PbF2-PbO-B2O3 at 1240 oC for 10 days with a slow cooling rate of 3-4 oC/h[[37]](#endnote-38). Although most of perovskite structure chromites could be synthesized with traditional solid state method with repeated mixing and grinding, samples with small A-site ionic sized elements should be synthesized via high-temperature-high-pressure method. For example, ScCrO3 and InCrO3 should be synthesized at a pressure as high as 6 GPa with the temperature of 1500 K[[38]](#endnote-39). Hydrothermal condition provides an effective route to crystallize rare-earth chromites at relative lower reaction temperature. LaCrO3 crystals have been synthesized via hydrothermal method at 400 oC by Yoshimura et al. in 1982[[39]](#endnote-40). Richard I. Walton et al. reported a comprehensive method for hydrothermal syntheses of RECrO3 samples by crystallization of metal hydroxides precursor at 320-380 oC. The crystallites obtained by this method, however, are agglomerated[[40]](#endnote-41). They also demonstrated that hydrothermal method is more effective for the preparation of atomic scale homogeneous distribution of mixed A-site cations than the high-temperature calcination method with the same compositions[[41]](#endnote-42). Recently, Xu et.al. reported a continuous supercritical hydrothermal flow method to synthesize of LaCrO3 nanoparticles[[42]](#endnote-43), which means this family of materials can be produced via a continuous fabrication based on hydrothermal technique. In our laboratory, LaCrO3 micro-crystals have been reported to be synthesized via KOH mineralized hydrothermal method with a temperature of 260 oC[[43]](#endnote-44). We have also prepared a series of micrometer scale single crystal samples of RECrO3 (RE=La, Pr, Nd, Sm, Dy and Ho) by low-temperature hydrothermal method (240-260 oC) with the assistance of concentration-controllable utilization of mineralizer[[44]](#endnote-45),[[45]](#endnote-46). However, the syntheses of perovskite structure chromite single crystals with smaller sized rare-earth occupied at A-site are more challenging in the mild hydrothermal conditions.

In this paper, we report a step-controlled dehydration process for the syntheses of four heavy rare-earth orthorchromite (i.e. ErCrO3, TmCrO3, YbCrO3 and LuCrO3) micro-crystals at mild hydrothermal condition. Samples obtained by this method show a relative longer axis with increased distortion of CrO6 octahedral along <101> directions. The structure, morphology, Raman spectroscopy and magnetic behaviors as a function of temperature and external magnetic field were discussed. Dzyaloshinsky-Moriya antisymmetric exchange interactions are suppressed with lower antiferromagnetic to paramagnetic transition temperatures.

EXPERIMENTAL SECTION

**Chemicals.** Solid chemicals of Er(NO3)3∙6H2O (99.9 %), Tm(NO3)3∙6H2O (99.9 %), Yb(NO3)3∙6H2O (99.9 %), Lu(NO3)3∙6H2O (99.9 %), CrCl3∙6H2O (99.0 %) and KOH (≥ 85.0 %) were purchased from Sinopharm Chemical Reagent Co. Ltd. All of reactant chemicals were used as received without any further purification.

**Sample syntheses.** All of the rare-earth nitrates and CrCl3 solid were dissolved in deionized water (resistance > 18 MΩ) with a concentration of 0.4 M before the synthesis. The four RECrO3 samples were synthesized using our previously reported modified mineralizing process44. For the synthesis of ErCrO3, 5.0 mL 0.4 M CrCl3 solution was firstly dripped into a glass beaker with continuously stirring at room temperature. Then, KOH solid chemical (1.0-2.0 g) was added in the solution. It immediately changed into a viscous green mixture suspended or deposited at the bottom of the beaker. After the heat released from KOH dissolution and the solutions cooled down to room temperature (~5-10 min), 5.0 mL 0.4 M Er(NO3)3 solution was added into the green mixture with continuously magnetic stirring. The green suspension changed into grayish green with the precipitation of rare-earth hydroxides. Another part of KOH (1-3 g) was added accordingly to provide enough mineralizer for the hydroxide mixture dehydration and crystallization into perovskites. Then, the whole mixture was transferred into a Teflon-lined stainless steel autoclave after they released the dissolution heat of KOH (~15-20 min). Crystallization of RECrO3 was carried out under autogenous pressure of the sealed autoclaves at 240-280 oC for several (3-10) days. Then, the autoclaves were cooled down naturally to room temperature and depressurized. Blackish green color crystals were obtained after washing the products with deionized water for several times. The as-prepared samples were dried in an oven at 80 oC for over 2 h. The hydrothermal syntheses of TmCrO3, YbCrO3 and LuCrO3 samples were followed with similar procedures to that for ErCrO3.

**Characterizations.** Structures of hydrothermally synthesized RECrO3 crystals were determined by laboratory powder x-ray diffractometer by a Rigaku D/Max 2550V/PC equipment with Cu Kα radiation (λ=1.5406 Å) at 50 kV and 200 mA at room temperature. Diffracted x-ray intensities were collected by a step scanning mode in the angle range of 10 o ≤2θ≤120 o with increment step of 0.02 o and a scanning rate of 1 o/min. All of the collected PXRD patterns were fitted with Rietveld method on GSAS/EXPGUI software. The correction for background was fitted by shifted first-degree Chebyschev polynomial function. The profile shape of the PXRD patterns was fitted with a split pseudo-Voigt function, I(2θ) = x × L(2θ) + (1 − x) × G(2θ) (where L and G are the Lorentzian and Gaussian part, respectively). Diffraction dependent peak width is fitted according to the relation of (FWHM)2 = Utg2θ + Vtgθ + W, where FWHM denotes as the full line width at half maximum. Fitting parameters for the present structural refinements were optimized with the following order until convergence was achieved: background, scale factor, zero point, lattice parameters, peak shape parameters, and fractional coordinates and isotropic displacement parameters of respective atoms. Site occupations for RE, Cr and O are constrained as 1.0 for all of the four PXRD fitting processes. Elemental composition of each as-synthesized RECrO3 sample was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, OPTIMA 3300DV, Perkin Elmer Inc.). In detail, 5-10 mg samples were dissolved in a dense HCl aqueous solution in Teflon-lined autoclaves at 180 °C. The acquired metal cation solutions were then transferred to a 50 mL volumetric flask to form a dilute solution. The solutions were injected into the ICP-AES equipment and the final metal cation concentration was acquired by the comparison with standard elemental concentration. Crystal morphology information of scanning electron microscope (SEM) images were measured with a Helios NanoLab 600I microscope (FEI company) operating at the accelerating voltage of 10 kV and a beam current of 86 pA equipped with characteristic x-ray energy dispersive spectrometer (EDS) detector. The EDS data were collected with an electron accelerating voltage of 20 kV and beam current of 2.7 nA with continuous signal collection for 30 s. The composition was the average value that was finally determined by analyzing at least five crystals for each RECrO3 samples. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and selected area electron diffraction (SAED) images were obtained by using a Talos F200S with the accelerating voltage of 200 kV. Room temperature Raman spectra were collected on a Renishaw via Confocal micro-Raman spectrometer with the excitation wavelength of 532 nm laser at a power of 150 mW. Chemical states of the elements were determined with X-ray photoelectron spectroscope (XPS) equipped with an ultra-high vacuum VG ESCALAB 250 electron spectrometer (Thermo Fisher Scientific Inc.). Before measurement, the binding energy was calibrated with the C 1s peak at 284.7 eV. Peak background of Cr element in the XPS spectra of RECrO3 samples are fitted by Shirley method with 50 cycles of iteration and convergence lower than 0.01. Binding energy peaks were fitted via Powell fitting algorithm with a maximum iteration of 100 and convergence of 0.0001. Pourbaix (E-pH) diagrams for RE-H2O, Cr-H2O and RE-Cr-H2O systems were calculated with HSC Chemistry 6.0 software copyright at Outokumpu Research Oy Antti Roine. Ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectra were measured using a Hitachi U-4100 UV-vis spectrometer in the wavelength range of 200-1200 nm. Fourier transform infrared (FTIR) spectra were measured in the transmission mode by a Bruker Optics-IFS-66 V/S spectrometer in the wavenumber range of 400-1400 cm-1.

**Magnetic property measurements.** Magnetic properties of RECrO3 samples were measured with a superconducting quantum interface device vibrating sample magnetometer (SQUID-VSM, Quantum Design, USA). Samples of 2-10 mg were sealed in a plastic tape enclosed tube that loaded in the magnetic field. Magnetization of samples were measured under field-cooled (FC) and zero-field-cooled (ZFC) condition with the applied field strength of 100 Oe and a temperature range of 2-300 K. Magnetic hysteresis curves for RECrO3 samples at 4, 50, 100 and 300 K were measured in the magnetic field range from -60 kOe to 60 kOe.

RESULTS AND DISCUSSION

**Structure.** Rietveld refinements of powder x-ray diffraction data of hydrothermally synthesized RECrO3 samples have been performed using the GSAS/EXPGUI suite[[46]](#endnote-47). Figure 1 shows the observed, fitted, difference and diffracted peak position plot of RECrO3 samples obtained from Rietveld fittings of PXRD patterns. All of the PXRD patterns were fitted based on a primary phase model of ErCrO3 with an ICSD card No. of 28487, which was solved by low-temperature neutron diffraction technique[[47]](#endnote-48). All of the as-prepared RECrO3 samples are shown to crystalize in a distorted orthorhombic perovskite structure with space group *Pbnm (No. 62)*. All samples are pure phase with sharp peaks and narrow full width at half maximum (FWHM), which indicates that the hydrothermally synthesized RECrO3 crystals are well crystalized. In the fitted PXRD results, the simulated lines match quit well with that of collected diffracted x-ray photon intensities of the data, which indicates a good fitting of the peak positions in each sample. The pink color lines are the difference of fitted and collected diffraction patterns, which are smooth with minimal vibration, indicating the simulated structures are near as that of the real structure of RECrO3 crystals. Inset of Figure 1 shows the enlarged view of the diffraction peaks at high diffraction angle, which also indicated the good fit of the PXRD results.

C:\Users\Yuan_Long\Desktop\ErCrO3-Rietveld.tifC:\Users\Yuan_Long\Desktop\TmCrO3-Rietveld.tifC:\Users\Yuan_Long\Desktop\Rietveld Fitting of YbCrO3.tifC:\Users\Yuan_Long\Desktop\LuCrO3 Rietveld Fitting.tif

Figure 1. Room temperature powder x-ray diffraction (PXRD) results of hydrothermally synthesized RECrO3 crystals with the Rietveld refinement (a) ErCrO3, (b) TmCrO3, (c) YbCrO3 and (d) LuCrO3, respectively. All peaks can be well indexed in orthorhombic *Pbnm*. Observed (Χ), calculated (red line), background (blue line) and difference (pink line) profiles are shown. The Bragg reflection peak positions are marked with vertical green bars.

The unit cell parameters and refinement results are listed in Table 1. Lattice parameters of a, b, c and unit cell volume for RECrO3 are linearly reduced in the sequence of Er, Tm, Yb, Lu, which is in accordance with the ionic radii reduction40. Besides, the tolerance factor of them is reduced from 0.8680 to 0.8572, which is far from ideal *Pm3m* perovskite structure. With the contraction of unit cell of RECrO3 due to the getting smaller of A-site rare-earth cations, the formula weight and theoretical density of the samples are getting increased accordingly. The octahedral tilt angles of hydrothermally synthesized RECrO3 could be calculated based on the lattice parameters with the notation of φ[010], θ[101] and Φ, that describe the tilting along <010>, <101> and “three-fold axes” for a, b, c in respect to primitive *Pm3m* ABX3 perovskite unit-cell, respectively[[48]](#endnote-49). The tilt angle of φ[010] show a near value of 20.2-20.6 o for the four RECrO3 samples, while θ[101] increases from 10.69 o to 11.94 o. These two rotation effects are compromised in the evolution of Φ, from 22.98 o to 23.69 o. According to these tilting angle calculation, the distortion degree of CrO6 octahedral units increased linearly with the reducing the radii of A-site rare-earth cations in the sequence of Er, Tm, Yb and Lu. The distortion of θ is near as that of previous report, while the value of φ is much larger than their values[[49]](#endnote-50), which indicates that a larger distortion of CrO6 octahedral is achieved in mild hydrothermally synthesized RECrO3 samples. Results of atomic site-occupancy for the as-synthesized RECrO3 samples are listed in Table S1-S4, respectively. The oxidation states of RE, Cr and O are assumed as +3, +3 and -2, respectively. The crystallographic sites of RE, Cr and O are in consistent with that of ErCrO3 according to the ICSD-2848747.

Table 1. Structure parameters and octahedral tilt angles (φ[010], θ[101]) of Rietveld refinement of mild hydrothermal synthesized RECrO3 with RE= Er, Tm, Yb, and Lu, respectively.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | ErCrO3 | TmCrO3 | YbCrO3 | LuCrO3 |
| symmetry | orthorhombic | orthorhombic | orthorhombic | orthorhombic |
| space group | *Pbnm*(62) | *Pbnm*(62) | *Pbnm*(62) | *Pbnm*(62) |
| tolerance factor ***a*** | 0.8680 | 0.8644 | 0.8608 | 0.8572 |
| a/Å | 5.2321(3) | 5.2155(2) | 5.1999(2) | 5.1856(3) |
| b/Å | 5.5845(3) | 5.5583(2) | 5.5418(2) | 5.5403(3) |
| c/Å | 7.5301(4) | 7.5102(3) | 7.4966(3) | 7.4957(3) |
| Vol./Å3 | 220.02(3) | 217.72(2) | 216.03(2) | 215.35(2) |
| formula weight | 267.25 g/mol | 268.93 g/mol | 273.03 g/mol | 274.96 g/mol |
| Z | 4 | 4 | 4 | 4 |
| calculated density | 8.0675 g/cm3 | 8.2041 g/cm3 | 8.3943 g/cm3 | 8.4801 g/cm3 |
| Rp | 0.09 | 0.06 | 0.08 | 0.10 |
| wRp | 0.11 | 0.07 | 0.11 | 0.13 |
| reduced χ2 | 1.276 | 1.352 | 1.747 | 2.421 |
| φ[010]*b* | 20.46 o | 20.23 o | 20.23 o | 20.61 o |
| θ[101]*c* | 10.69 o | 10.85 o | 11.20 o | 11.94 o |
| Φ*d* | 22.98 o | 22.85 o | 23.01 o | 23.69 o |

***a*** The tolerance factor t = (rRE + rO)/√2(rCr + rO), where rRE, rO and rCr are the ionic radii of RE3+, O2-, and Cr3+, respectively. *b* The tilt angle of φ[010] is determined from the lattice parameters with the relation of φ[010]=arccos(a/b). *c* The tilt angle of θ[101] is determined from the lattice parameters with the relation of θ[101]=arccos(√2a/c). *d* The distortion of perovskite structure that described by three-fold axes of Φ is defined as Φ=arccos(√2a2/bc), in which cosΦ=cosφ\*cosθ. Numbers in the bracket for structure parameters are the standard deviations calculated via Rietveld method.

**Crystallization mechanism.** According to Pourbaix diagrams of Cr3+ and Er3+, pH-dependent stable species for Cr-H2O system are Cr3+, Cr(OH)3, Cr(OH)4- from pH=0-14 (Figure S1), respectively, at room temperature atmosphere pressure, which is amphoteric character of Cr3+ as illustrated in Scheme 1. When the temperature raised to 260 oC, the region of Cr(OH)3 expands from pH=1.1-5.1, while Cr(OH)4- transforms into HCrO4- and CrO42- when the pH>7.0 and 9.0, respectively (Figure S2). This result indicated that high concentration of KOH mineralizer is unfeasible for crystallization of solid phases of chromium oxides from aqueous solutions. Stable species of RE-H2O system are RE3+ and RE(OH)3. The transition pH-value is dependent on the radius of RE3+ and the temperature of the system. For example, Er(OH)3 forms at pH>5.0 with the system temperature of 25 oC (Figure S3), while it could be stable at pH>1.8 at 260 oC (Figure S4). The transition point from RE3+ to RE(OH)3 is pH=6.9, 6.2 and 5.0 for La3+ (Figure S5), Sm3+ (Figure S6) and Er3+ (Figure S3), respectively, which indicates that the difficulty of dehydration for the hydrated RE3+ is decreased with reducing the radii of them. Crystallization of perovskite structure RECrO3 needs simultaneous dehydration of RE3+ and Cr3+ in aqueous solution. According to the E-pH diagram of Cr-La-H2O (Figure S7 and S8), perovskite phase is stable in the field of pH=2.1-8.8 at 260 oC and satiated pressure of water (46.28 bar). If more concentration of KOH was provided, the final products will be CrO42- and La(OH)3. The existence of ErCrO3 could not be predicted by HSC Chemistry 6.0 software due to the inexistence of thermodynamic data for this compound. However, it clearly predicts the existence of ErO2- anions (Figure S9), which will crystalized into ErO(OH) as illustrated in Table 2.

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Scheme 1. The relationship of the aqueous species of Cr(III) and final hydrothermal crystallization product.

Crystallization of perovskite structure heavy rare-earth orthorhombic chromites via hydrothermal method follows a two-step process: (i) formation of mixed double metal hydroxide precursors; (ii) dehydration of the hydroxide precursor for nucleation and propagation for crystal growth by similar polymerization procedure. PXRD of the double metal hydroxide precursor is shown in Figure S10, which is consistent with that of layered rare-earth hydroxide nitrates[[50]](#endnote-51). The most critical factors that determine the formation of perovskite phase heavy-rare-earth chromites in hydrothermal condition are the controllable dehydration processes of mineralizer concentration, reaction temperature and duration for crystal growth. Figure S11 illustrate the effect of the sequence for the addition of reactants on the dehydration process of precursor with the corresponding experiment listed in Table S5. If the Er(NO3)3 was added firstly followed by KOH, the precursor in dehydration process is crystalline ErO(OH) (Figure S11 (a)). The further addition of CrCl3 makes barely no change of the precursor due to the formation of Cr(OH)4- according to E-pH diagram. However, the pre-formation of Cr(OH)4- makes the Er-hydroxide precursor poorer crystallinity, which means a mixed double metal hydroxide precursor formed instead. Directly adding Er(NO3)3 and CrCl3 with single step mineralization makes a Er(OH)CrO4, which is impossible for crystallization of perovskite phase (Figure S11 (b)). Therefore, because of the amphoteric property of Cr3+ in aqueous solutions[[51]](#endnote-52), the KOH mineralizer should be added into the reaction by two steps: the first part of KOH for precipitation of Cr3+ and the second part for providing enough mineralizer concentration for polymerization induced nucleation of perovskite phase. If the whole KOH added in the first step, a mixture of rare-earth hydroxides and amorphous chromium hydroxides is the final product even after the same hydrothermal synthetic processes. The addition of whole mineralizer in the last part makes the formation of layered rare-earth hydroxides crystallite mixed with chromium-oxygen clusters with bright green color in the suspended solutions. A sufficient concentration of KOH should be kept to ensure the Cr-species in proper form for hydrothermal polymerization in the dehydration process of mixed rare-earth and chromium precursors. Pure phase RECrO3 (RE=Er, Tm, Yb, Lu) single crystal samples should be synthesized with a temperature over 260 oC for up to 7 days, which indicates that the dehydration crystallization of heavy-rare-earth chromites should be more dependent on increasing the hydrothermal reaction temperature, rather than providing higher concentration mineralizer. Although the mineralizer addition follows the mild hydrothermal syntheses of RECrO3 with RE=La, Pr, Nd, Sm, Dy and Ho in our previous work44,45, no pure phase perovskite products could be obtained up to 240 oC for over 7 days. The as-synthesized SEM graphs and phases of the hydrothermal products for RECrO3 crystals are shown in Figure S12-S15 and S16-17, respectively. We also tried to synthesize the RECrO3 samples via traditional hydrothermal method at the same reaction temperature for mixed rare-earth and chromium hydroxide precursors. However, only poorly crystalized REO(OH) phases were obtained (Figure S18).

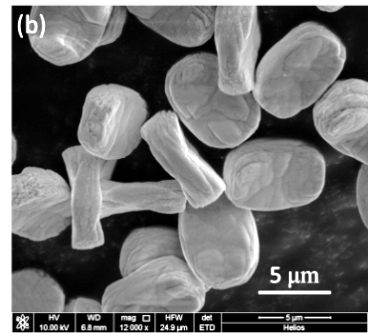
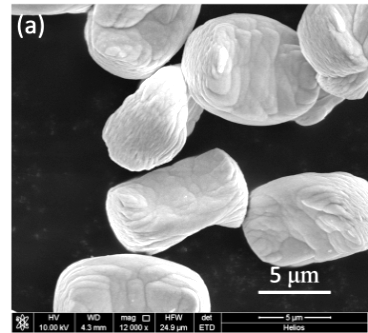
Both of the first (i.e. precipitation of Cr3+ species) and second (i.e. the overall mineralizer concentration) steps of KOH addition are important for hydrothermal syntheses of RECrO3 crystals. The synthesis of ErCrO3 was taken as an example to illustrate the effect of amount and adding sequence of KOH on the final products of hydrothermal reactions (Table 2). If the first step KOH amount is lower than 1.0 g, no enough chromium hydroxide precursors formed for polymerization of perovksite. If the first step KOH amount is over than 2.0 g, the Cr-species changed into Cr(OH)4- that solved rather than formed as solid hydroxide precursors for crystallization. However, 2.0 g KOH is not enough for the nucleation and propagation of RECrO3 at 260 oC. The second part of KOH should be added to provide enough OH- environments for crystallization. If the second part of KOH is lower than 1.5 g, RE(OH)3 is the main by-product.

Table 2. Hydrothermal synthetic condition and the resulted products for crystallization of ErCrO3.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Sample | KOH (g) ***a*** | Alkalinity (M) *b* | Duration (day) *c* | Temperature  (oC) *d* | Products *e* |
| ErCrO3 | 2.0+1.0 | 5.35 | 7 | 240 | Er(OH)3+ErCrO3 |
| 2.0+2.0 | 7.13 | 7 | 240 | Er(OH)3+ErCrO3 |
| 2.0+3.0 | 8.91 | 7 | 240 | ErO(OH)+Er(OH)3+ErCrO3 |
| >2.0+4.0 | >10.69 | 7 | 240 | ErO(OH)+ErCrO3 |
| 1.5+(1.0-2.0) | 4.45-6.24 | 7 | 260-280 | ErCrO3 |

***a*** Mineralizer amount (first + second step) added in the reactant precursor solutions. *b* Mineralizer concentration. *c* Hydrothermal reaction time for crystallization. *d* Hydrothermal reaction temperature for each condition. *e* Phase composition resulted from each synthesis experiment.

**Morphology and composition.** Crystal morphologies of the hydrothermally synthesized heavy rare-earth chromite series of RECrO3 samples are shown in Figure 2 and S19. All of the as-synthesized four crystals have regular shape and uniform particle size. All of the samples show clear rounded rectangular plate shape with stacked layers along the longest axis of the crystals, while it seems compact view along the shortest axis. The morphology at the fringe of ErCrO3 and TmCrO3 crystals is similar to that of YbFe0.5Cr0.5O3 and LuFe0.5Cr0.5O39, which has not occurred in YbCrO3. The average length and width for each RECrO3 crystals are 9.3 and 6.4 μm, 6.9 and 5.2 μm, 5.6 and 4.3 μm, 5.5 and 3.1 μm for ErCrO3, TmCrO3, YbCrO3 and LuCrO3, respectively. Particle sizes of the as-synthesized RECrO3 crystals are getting reduced from Er to Lu accordingly. Particle size distribution for the as-synthesized four samples indicate that hydrothermal method is an effective method for preparation of high quality micrometer sized single crystals of rare-earth chromites with uniform crystal shape and size distribution. Crystal morphology of rare-earth chromites are getting from cubic to plate-like shape from LaCrO3 to LuCrO3 in mild hydrothermal condition44,45. In fact, only LaCrO3 and its A- or B-site doped analogues crystalizes as cubic morphology[[52]](#endnote-53), the plate-like characteristics is getting obvious from PrCrO3 and SmCrO3 (part of the cubic-like shape) to NdCrO3-LuCrO3 (totally plate shape).



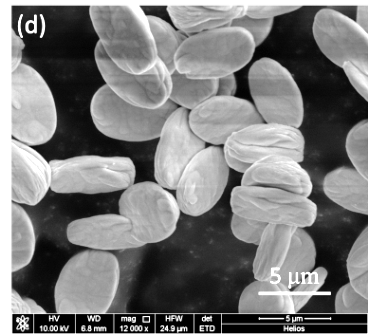
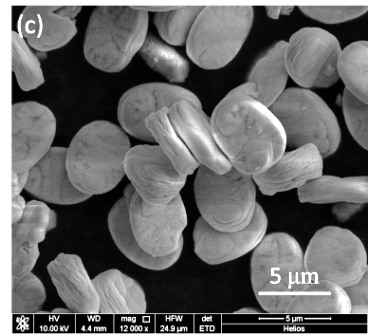


Figure 2. SEM images of mild hydrothermally synthesized samples (a) ErCrO3, (b) TmCrO3, (c) YbCrO3 and (d) LuCrO3, respectively.

HRTEM of the as-synthesized crystals shows the lattice of ErCrO3 with crossed {020} and {110} plane (Figure 3 (a)). The d*hkl* for these planes were measured with DigitalMicrograph software according to the profile of the white-to-bright contrast value of the integration of each line along the circled profile region. Crystallographic zone axis of the two planes is determined based on Weiss Zone Law: *h*u+*k*v+*l*w=0, which is <001> direction in the as-synthesized samples (Figure 3 (b)). The dihedral angle between (020) and (110) plane is 45 o in HRTEM result, which is in agreement with that in the crystal structure graph plotted according to the file of ICSD-28487. No clear HRTEM and SAED pattern could be provided due to the thickness of the crystal is much larger than 100 nm, which is unfeasible to make electrons transmitting across the crystal, even at the edge. According to SEM in Figure 2, steps mainly shown at the short side of the elliptic shape rounded crystals, especially at the corner (in reference to rectangular shape). An enlarged TEM graph was taken to show the detailed morphology at this position (Figure 3 (c)). Although it seems to be stacked plates at here, HRTEM graph in Figure 3 (d) clearly shows the same orientation of the surface step with the bulk at the edge of the crystal, with the continuous fringe of extended {110} planes. SAED pattern show clear diffraction dots rather than circles (Figure S20), which is a sign of single crystal rather than polycrystalline for the as-synthesized sample.

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Figure 3. HRTEM results of hydrothermally-synthesized ErCrO3 crystal with rounded shape. (a) HRTEM graph at the edge of crystal with {020} (yellow) and {110} (red) crystal planes that crossed with an angle of 45 o, inset of (a) is the crystal structure of ErCrO3; (b) crystallographic directions of perovskite chromite crystal; (c) morphology of the edge of the as-synthesized crystal and (d) HRTEM of the surface step and edge of the sample.

Sample composition of the as-synthesized RECrO3 samples were determined by EDS and ICP-AES techniques. Relative EDS data show that the elemental ratio of the crystals is close to RE: Cr: O= 1: 1: 3 (Figure S21), which is the ideal perovskite structural composition, that is in agreement with ICP-AES results (Table 3). There are clearly no detectable peaks of K-element, which demonstrates that no K-doping in the as-synthesized samples. According to Bravais–Friedel–Donnay–Harker theory, the most stable crystallographic facets for RECrO3 are {020} and {101} facets, which are usually preserved in KOH mineralized hydrothermally synthesized products[[53]](#endnote-54). The final morphology and particle size are dependent on the growing speed along each preferential direction and nucleation concentration at the beginning of the crystallization process. In regard of the increasing distortion of CrO6 octahedral units along <010>, <101> directions according to the values of φ[010], θ[101] evolution from La to Lu, the crystal morphology of RECrO3 of Er, Tm, Yb and Lu changes from cubic (LaCrO3 and PrCrO3) to smooth parallelepiped plate (Nd-HoCrO3) and finally intersected twin crystal plate shapes. The distortion of CrO6 octahedral affects the propagation of unit cell along this two crystallographic directions in spite of the most stable facets are {020} and {101} based on the crystal structure of RECrO3, which not only the reason of absence of acute surface, but also increased the difficulty for the synthesize heavy rare-earth chromites under mild condition.

Table 3. Composition information of RECrO3 determined from ICP-AES and EDS analysis

|  |  |  |  |
| --- | --- | --- | --- |
| Samples | ICP results (RE:Cr) |  | EDS results (RE:Cr) |
| ErCrO3 | 1.00:1 |  | 0.99:1 |
| TmCrO3 | 0.97:1 |  | 0.98:1 |
| YbCrO3 | 0.99:1 |  | 1.03:1 |
| LuCrO3 | 1.01:1 |  | 1.03:1 |

**Valance states.** Chemical bond distance, Cr-O-Cr bond angle and bond valance sum results of Cr and RE for each RECrO3 sample are listed in Table 4. Average length of Cr-O bonds in RECrO3 is getting decreased from 2.0051 to 1.9913, which is in agreement with that of the unit cell parameter evolution due to the size reduction of A-site cations. Method of bond valence sum calculation is an effective route in gaining chemical insight into Cr with varied coordinated number and type of ligands in establishing the oxidation states of Cr in solid state compounds[[54]](#endnote-55). The calculation of BVS mainly takes the first coordination sphere anions into consideration. The oxidation states of Cr in RECrO3 are estimated as 2.819, 2.856, 2,882 and 2.918 for ErCrO3, TmCrO3, YbCrO3 and LuCrO3, respectively. These results are linearly increased for the oxidation state of Cr with decreasing the radius of rare-earth at A-site, which is in consistent with the reduction of unit cell volumes that may result in the reduction of chemical bonds between Cr-O atoms. The average bond length of Cr-O reduces from 2.0051 to 1.9913 Å for the RECrO3 from Er to Lu, which is in accordance with the increasing of BVS states of Cr in the distorted perovskite lattice. The BVS for all the four RECrO3 samples are slightly lower than the ideal oxidation states of +3 valance state of Cr in perovskite structure oxides, which may be resulted from the contribution of the next-nearest neighbour of O that was omitted for BVS calculation. Valance states for RE in the resulted refinement information are also slightly variant from ideal +3, which may be resulted the underestimation of the more scattered contribution of the remote negatively-charged coordinated O from neighbour unit cell.

Table 4. Selected bond lengths, bond angles and bond valence sums for RECrO3. *a*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | ErCrO3 | TmCrO3 | YbCrO3 | LuCrO3 |
| Bond length (Å) | |  |  |  |
| RE-O(1) | 2.3228×1 | 2.3204×1 | 2.2836×1 | 2.2571×1 |
| 2.1808×1 | 2.1236×1 | 2.1346×1 | 2.1652×1 |
| 3.1920×1 | 3.2350×1 | 3.2257×1 | 3.1849×1 |
| 3.4769×1 | 3.4734×1 | 3.5025×1 | 3.4993×1 |
| RE-O(2) | 2.4905×2 | 2.4548×2 | 2.4409×2 | 2.3947×2 |
| 2.2709×2 | 2.2888×2 | 2.2729×2 | 2.2719×2 |
| 2.6044×2 | 2.6220×2 | 2.6249×2 | 2.6634×2 |
| 3.6083×2 | 3.5560×2 | 3.5554×2 | 3.5644×2 |
| Cr-O(1) | 1.9957×2 | 2.0067×2 | 2.0077×2 | 1.9929×2 |
| Cr-O(2) | 2.0505×2 | 1.9976×2 | 2.0073×2 | 2.0152×2 |
| 1.9690×2 | 1.9920×2 | 1.9721×2 | 1.9657×2 |
| Average Cr-O | 2.0051 | 1.9988 | 1.9957 | 1.9913 |
| Selected bond angles (deg) | |  |  |  |
| Cr-O(1)-Cr | 141.21 | 138.67 | 137.97 | 140.20 |
| Cr-O(2)-Cr | 144.32 | 145.59 | 145.43 | 144.77 |
| Bond valence sums (BVS) | |  |  |  |
| RE | 2.903 | 3.094 | 2.890 | 2.965 |
| Cr | 2.819 | 2.856 | 2.882 | 2.918 |

***a*** , , N is the coordination number, B= 0.37, R0(Er3+) = 2.010, R0(Tm3+) = 2.000, R0(Yb3+)=1.985, R0(Lu3+)=1.971, and R0(Cr3+) = 1.724[[55]](#endnote-56).

XPS emission spectra for the as-synthesized RECrO3 samples were collected at room temperature as shown in Figure 4. Binding energy values of Cr in RECrO3 are consistent with those from National Institute of Standards and Technology (NIST) database of the peak positions and spin-orbit doublet separations[[56]](#endnote-57). All spectra are fitted by assumption of only one chemical environment of Cr in each RECrO3 and the fitted curves show in good agreement with the experimental results with minimum difference between the measured counts and simulated results. The core-level XPS Cr2p spectra show two spin-orbit split peaks of 2p1/2 and 2p3/2 delineated with the fitted red and blue curves. Peaks of Cr2p1/2 and 2p3/2 are located at 586.68 and 576.78 eV, 586.35 and 576.45 eV, 586.75 and 576.85 eV, 586.41 and 576.56 eV for ErCrO3, TmCrO3, YbCrO3 and LuCrO3, respectively. The slightly variance of the peaks of binding energies for different A-site RECrO3 may be resulted from the average bond length changed with coordination environment of CrO6 octahedral in these orthochromites. The doublet separation of ~9.90 eV for all of the as-prepared four RECrO3 samples suggests that the oxidation state of Cr is +3[[57]](#endnote-58), which is in agreement with that of calculated BVS results in Table 4.

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C:\Users\Yuan_Long\Desktop\YbCrO3-Cr-XPS.tifC:\Users\Yuan_Long\Desktop\LuCrO3-Cr-XPS.tif

Figure 4. Binding energy of Cr in mild hydrothermally synthesized samples of (a) ErCrO3, (b) TmCrO3, (c) YbCrO3 and (d) LuCrO3, respectively.

**Vibration modes**. Raman spectroscopy is a sensitive technique to characterize the derivations of real perovskite structure compounds from the ideal cubic perovskite (Pm-3m), due to no Raman active modes in the ideal phase[[58]](#endnote-59). Theoretically, 24 Raman active modes (7Ag+5B1g+7B2g+5B3g) are expected from the Γ point of Brillouin zone in orthogonal perovskite chromites[[59]](#endnote-60),[[60]](#endnote-61), which results from 5 sets of vibration: (i) two symmetric (Ag+B1g), (ii) four antisymmetric octahedral stretching modes (2B2g+2B3g), (iii) four bending modes (Ag+2B2g+B3g) and (iv) six rotation or tilt modes of the octahedral (2Ag+B1g+2B2g+B3g), (v) eight A-site vibration modes (3Ag+3B1g+B2g+B3g) [[61]](#endnote-62),[[62]](#endnote-63). Besides, there are other twenty-five optical modes and three acoustic modes Raman inactive in this space group. However, no report has observed all of the vibration modes in experimental patterns. The orthorhombic *Pbnm* structure RECrO3 is formed by an antiphase tilt of the adjacent of corner-shared CrO6 octahedra in respect to the ideal *Pmm* perovskite structure with a Glazer’s notation of a-b+a-[[63]](#endnote-64). The Raman spectra of YbCrO3 and LuCrO3 have been reported in the literature40,49 whereas spectra of ErCrO3 and TmCrO3 are not known. Figure 4 shows room-temperature Raman spectra of mild hydrothermally prepared micro-crystals of RECrO3 samples. The quality of Raman spectra of mild hydrothermally synthesized RECrO3 crystals is much better than that of previously reported spectra of high-temperature hydrothermally synthesized samples40, which may due to their samples show agglomerated morphology rather than single crystals as that of in our samples. The peaks are assigned with nominated Raman modes for all of the four samples according to the assignment of LuCrO3 in reference49, which indicate a consistency in each crystal. Totally 12 modes (4Ag+2B1g+3B2g+3B3g) could be discriminated from the spectra as shown in Figure 5. Peaks of B3g(1), Ag(2) and B2g(1) for the four RECrO3 samples are nearly located at the same frequency, which are pertinent to the vibration related to A-site cation, *i.e.* A(x), A(z) out-of-plane and A(y) motion, respectively. B3g(1) mode has not been found in the high-temperature hydrothermal synthesized YbCrO3 and LuCrO3 samples49. Peaks of B1g(2), a mode of reverse motion for A-site and O1 in z-direction, shifts from 397.3 to 416.0 cm-1 for Er-to-Lu, which indicated that the increment of A-site cation mass improve the vibration frequency of Raman scattering. Other modes that pertinent to the synergetic motion of A-site and O1, *i.e.* Ag(4) and B2g(2), show similar increasing of vibration frequency with an exception of ErCrO3. Three modes that results from the motion of BO6 show clear A-site dependent vibration frequency evolutions, *i.e.* Ag(5), Ag(6) and B2g(3), that relates to BO6 out-of-phase x rotations, BO6 bendings and BO6 out-of-phase bendings, respectively. Ag(3) mode is activated by the synergetic effect of rotation along [010] and Jahn-Teller distortion, that results in BO6 in-phase y rotations, which shows mode inconsistency to the A-site rare-earth cations with unknown reasons. The O2 scissors-like motion (B3g(2)) and O2,O1 antistretching (B3g(3)) also show A-site dependent vibration frequency increasing with the exception of ErCrO3. Bands association of the 700 cm-1 have been assigned as to some kind of local structural imperfection or the presence of octahedral Cr4+ at the surface of the samples[[64]](#endnote-65).

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E:\WRITINGS\王珊文章\Hydrothermal YbCrO3 ErCrO3\Raman-yuanlong\TmCrO3-Raman.tif

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E:\WRITINGS\王珊文章\Hydrothermal YbCrO3 ErCrO3\Raman-yuanlong\LuCrO3-Raman.tif

Figure 5. Room temperature unpolarized Raman spectra of as-prepared micro-sized crystals of (a) ErCrO3, (b) TmCrO3, (c) YbCrO3 and (d) LuCrO3, respectively. Mode assignments have been marked based on references of 49. NA is designated for the Raman modes have not been assigned.

Factors of the distortion of CrO6 octahedral along [010] and [101] directions and A-site discrepancy from ideal perovskite positions could affect the peak intensity and position of Raman modes for different RECrO3 crystals (Figure 6). In comparison with the Raman peaks of the active modes of YbCrO3 and LuCrO3 in previous work, all peaks that related to the motion of BO6 bending shift to higher frequency, while the other peaks that mainly resulted from the motion of A-site keep a near scattering vibration frequency as that in previous work49. These results suggest a more intensive symmetry vibration originated from the bending of CrO6 octahedral units in our synthesized samples. For example, the Ag(5) mode represents the CrO6 octahedral rotation vibration along [101], that alternately rotates four equatorial oxygens (O2) clockwise and counterclockwise along this direction with oppositely vibration of O1 consecutively. This vibration mode is definitely affected by the distortion angle of CrO6 octahedral that determined by the size and atomic mass of A-site RE3+ cations. Positions for ErCrO3 and TmCrO3 Raman peaks show a linear relation along with that of YbCrO3 and LuCrO3 dependent on the CrO6 octahedral distorted angle along [101], especially for the modes that related to the CrO6 octahedral and RE-O bonds.

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Figure 6. Raman phonon wave numbers as a function of octahedral distorted angles for selected modes and the representation of Ag(5) mode that represented of CrO6 [101] rotation for the four heavy rare-earth chromites.

Optical UV-vis-NIR absorbance spectra of the samples were collected in the wavelength of 200-1200 nm (Figure 7). The peaks for electronic transition of Cr3+ in RECrO3 samples were seen at 452.5, 610.5, 691.0, 734.5 nm, which are originated from the 4A2g→4T1g, 4A2g→4T2g, 2A2g→2T1g and 2A2g→2E2g transitions[[65]](#endnote-66). These absorption bands show near peak positions that resulted from the internal energy level transitions of 3d electrons in the octahedral ligand-coordinated fields of the as-synthesized RECrO3 samples.

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Figure 7. Room temperature UV-Vis-NIR spectra of RECrO3 samples. Dotted lines are guided for eye to discriminate the four main bands that indicated energy level transitions of 3d electrons in CrO6 octahedral ligand-coordinated fields in the four RECrO3 samples.

Fourier-transform infrared (FT-IR) spectroscopy is also a sensitive technique to detect local structure evolution inside of solid materials, which characterises the vibrations of specific chemical bonds related to the characteristic active modes. FT-IR spectra of as-synthesized RECrO3 samples are shown in Figure 8. Transmission peak at c.a. 420-456 cm-1 is associated to the O-Cr-O deformation vibrational mode[[66]](#endnote-67). The peak shifts from 422.39 cm-1 to 435.89 cm-1 from ErCrO3 to LuCrO3, which indicates the higher energy needed to bend the bond-linkage of O-Cr-O for heavier A-site RECrO3 samples. This mode shift towards higher wavenumbers is related to the CrO6 octahedral distortion, which determines the deformation degree and absorption energy of O-Cr-O bonds. Similar structure evolution can also be found in the FT-IR spectra with the peaks around 493-515 cm-1, that could be assigned to RE-O stretching vibrations[[67]](#endnote-68). The displacement of this set of FT-IR peaks may be resulted from the increased relative atomic mass (Mr) from Er (Mr=167.260) to Lu (Mr=174.967). Transmission peaks at 586-590 cm-1 are referenced as stretching modes involving of the displacements of Cr and O[[68]](#endnote-69), which reflects the vibrational motion inside of CrO6 octahedral for each RECrO3 sample. Because of the same structure and near Cr-O bond length for the four samples, peaks of this mode show at nearly the same wavenumber in the FT-IR spectra.

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Figure 8. Room-temperature FT-IR spectra of as-synthesized RECrO3 crystals. Dotted lines are plotted for the guide of eye.

**Magnetic properties**. Magnetic properties of mild hydrothermally synthesized RECrO3 samples were measured using vibrating sample magnetometer (VSM) as shown in Figure 9. Temperature-dependent FC and ZFC magnetization curves of heavy rare-earth RECrO3 perovskites, recorded with an applied magnetic field of 100 Oe, show clear temperature affected magnetization evolution in the range of 2-300 K. Magnetization evolution for the four samples, either in FC or ZFC mode, show similar tendency with two transition points, i.e. antiferromagnetism to paramagnetism for Cr3+ sublattice at ~100 K and spin reorientation temperature at ~20 K. In all the four RECrO3 samples, the magnetic moments of Cr3+ ions antiferromagnetic arrangement occurs below TN with a typical G-type magnetic structure. At high temperatures, all of the as-synthesized RECrO3 samples show clear Curie-Weiss behavior, and the temperature-dependent inversed magnetization 1/M-T data is shown in the inset of Figure 9. Based on the Dzyaloshinsky-Moriya antisymmetric exchange mechanism, the magnetic moment of Cr3+ in RECrO3 is not totally antiparallel arranged to that of the nearest neighbor Cr3+, but is normally canted at a small angle dependent on the size of A-site cation40. Due to the distortion of CrO6 octahedral units and increased canting of Cr moments in small-sized RECrO3 perovskites, weak ferromagnetism shows below TN for these samples. This phenomenon is most clearly seen in the temperature-dependent magnetization curves for LaCrO3, YCrO3 and LuCrO3, because of the inexistence of magnetic moments carried on the rare-earth sites40. Temperature dependent magnetization curves of ErCrO3 show clear incretion when the temperature is lower than 100 K with slightly divergence of ZFC and FC curves (Figure 9 (a)). According to the derivative curve of FC (Figure S22(a)), the extreme point is 93 K, which indicates that magnetic moment of Cr for ErCrO3 changes from paramagnetism to antiferromagnetism at this transition point of TN. The magnetization is getting increased with cooling the sample till a maximum at 20 K and then decreased greatly below this temperature for both of FC and ZFC curves. This phenomenon is ascribed to spin reorientation (Morin transition) of Er3+ at A-site of ErCrO3[[69]](#endnote-70), which is resulted from the contribution of the magnetic moment of rare-earth cations, especially of Er3+ carried with an estimated effective magnetic moment of 9.59 μB. Generally, the magnetic ordering of Cr3+ in RECrO3 is typical Γ4(GxAyFz) for RE=La-Tb and Er below Néel temperature28. For the heavy rare-earth chromites, the basic magnetic order of Cr is Γ2(FxCyGz). ErCrO3 undergoes a second-order magnetic transition at 22 K changed from Γ4(GxAyFz) to Γ1(AxGyCz), while other heavy rare-earth RECrO3 keeps as Γ2(FxCyGz) magnetic ordering till to the Néel temperature[[70]](#endnote-71). However, Yin et.al. reveals two spin reorientation points in the single crystal of ErCrO3 obtained by high-temperature flux method14, which could also be observed in the field cooling magnetization curve at 6 K. This result should be ascribed to the antiferromagnetic arrangement of Er3+ spin ordering, which is reported to be ordered at about 4.3 K according to neutron diffraction[[71]](#endnote-72). The calculated Weiss constant for ErCrO3 is 213.18 K, which is 35 K for the samples obtained via high temperature solid state method[[72]](#endnote-73).

TmCrO3 shows a similar magnetization evolution behavior as a function of temperature for the FC and ZFC curves under 100 Oe direct current magnetic field as that of ErCrO3 (Figure 9 (b)). The two curves merged at 114 K for TmCrO3, i.e. with a same value of magnetization for FC and ZFC modes. According to the first-order derivative curve of FC to temperature (Figure S22(b)), the minimum value is 90.03 K, which indicates the TN value for hydrothermally synthesized TmCrO3. The literature value of TN for TmCrO3 synthesized via high-temperature method (1400 oC, 48 h, in air) is 125 K17,18. Although high-temperature method has been accepted as a general method to synthesize perovskite structure oxide powders with repeated grinding and re-calcination, oxygen-atoms would to be getting lost until the formation of a balanced oxygen defective concentration, which has now been generally adopted as a new technique for thermochemically splitting water and carbon dioxide molecules[[73]](#endnote-74),[[74]](#endnote-75). FC curve is getting increased with cooling temperature lowered than TN with a potential tendency of magnetization evolution similar as that of ErCrO3 in the range of the TSR to TN. Similar tendency also shows in their ZFC curves. However, it seems that TmCrO3 does not show its spin reorientation point with the temperature as low as 3 K. Negative magnetization could be observed in the literature below TN for TmCrO317,18, which keeps positive value for our sample. The magnetization obtained from ZFC curve, however, reduces below TN gradually, which imposes a negative field over the 4f electrons of Tm3+ in canted-antiferromagnetically ordered Cr3+-O-Cr3+ sublattice. This phenomenon has also been found in CeCrO3[[75]](#endnote-76) and perovskite structure manganites[[76]](#endnote-77).

YbCrO3 and LuCrO3 show a very near FC-ZFC temperature dependent magnetization evolution with near values of Néel temperature, compensation point, and negative magnetization of ZFC (Figure 9 (c and d)). FC and ZFC curves merge at 150 K for YbCrO3, while the minimum value of the first-order derivative curve of FC to temperature is located at 86.03 K (Figure S22(c)). The compensation point of YbCrO3 is 83.5 K. Antiferromagnetism to paramagnetism transition point for YbCrO3 is reported to be 115 K or 118 K for the samples synthesized with subcritical hydrothermal40 and solid state method[[77]](#endnote-78), respectively. This second-order phase transition point result is much lower than that of other method prepared YbCrO3 in literature19, which may be resulted from the local structural change and oxygen-rich surface structures for hydrothermally synthesized samples[[78]](#endnote-79). The most negative magnetization is -0.05811 emu/g at the point of 36.05 K. YbCrO3 seems to show a spin reorientation behavior at 19 K. However, unlike that of ErCrO3, spin reorientation of Yb3+ improved the magnetization of the samples, which may result from the parallel of the magnetic moments of Yb3+ to that of Cr3+ in hydrothermally synthesized YbCrO3 crystal lattice. Besides, the onset magnetization of YbCrO3 and LuCrO3 are much lower than that of ErCrO3 and TmCrO3, which is in consistency with the decrease of the increasing of the tilt angle of θ[101], that is further reduced in smaller ions at A-site, such as Sc3+ and In3+38,[[79]](#endnote-80). The Weiss constant is calculated as 170.86 K, slightly lower than the samples synthesized via solid state method77.

Magnetic properties of LuCrO3 are similar as that of YbCrO3 with a smaller Néel transition point and more negative magnetization below TN (Figure 9 (d)). FC and ZFC curves merge at 90 K, with the first order derivative extreme value of 83 K (Figure S22(d)). The compensation point (magnetization become negative) of LuCrO3 is 78 K. The value of negative magnetization does not reach its extremity until the temperature lowered to 2 K, with a value of -0.33 emu/g. 1/M-T curve indicates a Curie-Weiss behavior for LuCrO3 with the temperature over 107 K. Néel temperature for LuCrO3 in the literature is in the range of 111-115 K40,[[80]](#endnote-81). TN of LuCrO3 is lower than that of the nanoparticles obtained from auto-ignition method,21 which should be resulted from the longer b-axis and more distorted CrO6 octahedral chains with smaller bond angle of Cr-O(1)-Cr for the mild hydrothermally synthesized samples. The Weiss constant is 612 K according to the linear fitting result of 1/M-T curve, which is higher than that of the samples obtained by auto-ignition high-temperature21 and solid-state methods[[81]](#endnote-82). Large Weiss constants have also been found in LaCrO3 and SmCrO3 in previous work40.

C:\Users\Yuan_Long\Desktop\FC-ZFC-ErCrO4.tif C:\Users\Yuan_Long\Desktop\FC-ZFC-TmCrO3.tif C:\Users\Yuan_Long\Desktop\FC-ZFC-YbCrO3.tif C:\Users\Yuan_Long\Desktop\FC-ZFC-LuCrO3.tif

Figure 9. Temperature dependent magnetization under the 100 Oe magnetic field or zero field cooling process of hydrothermally-synthesized crystals of (a) ErCrO3, (b) TmCrO3, (c) YbCrO3 and LuCrO3, respectively. Insets of (a)-(d) show the temperature-dependent inversed field cooling magnetization curves (blue open triangles) and the linearly fitted lines according to Curie-Weiss equation.

As discussed above, RECRO3 samples synthesized via mild hydrothermal method show much lower TN values of antiferromagnetism to paramagnetism transitions than the materials with same compositions that obtained via high temperature crystallization methods. Similar phenomena have also been found in perovskite structure rare-earth ferrites REFeO3[[82]](#endnote-83) and Fe-doped TbCrO3, ErCrO3 and YbCrO3 samples9. These results indicate that the Dzyaloshinsky-Moriya antisymmetric exchange interactions of the spins of neighbor corner-shared CrO6 octahedral units are getting reduced with increasing the distortion angle via the Cr3+-O-Cr3+ chain in mild hydrothermally synthesized perovskite structure heavy rare-earth orthochromites from ErCrO3 to LuCrO3. Figure 10 shows the TN evolution with the ionic radii of RE3+ in RECrO3 samples synthesized via mild hydrothermal conditions. Although the transition temperatures for the samples obtained with mild hydrothermal method are lower than the previous work, the TN value decreased almost linearly with the reduction of the radii of rare-earth cations, which is in consistency with that of the samples prepared via traditional hydrothermal method in the literature40 and other rare-earth-based perovskites, such as REMnO3[[83]](#endnote-84). The relationship of RE3+ radii dependent TN for RECrO3 could be divided in two parts, i.e. light and heavy rare-earth chromites as shown in the independent linear fitting lines with the transition compound of DyCrO3, which can be also confirmed from the samples obtained via other methods35,40.

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Figure 10. Antiferromagnetic Néel temperature (TN) as a function of ionic radii of RE3+ (nine-coordination) in the mild hydrothermally synthesized perovskite structure RECrO3 samples. The TN values of La-, Pr-, Nd-, Sm-, Dy- and HoCrO3 are taken from reference 44, 45 and 52, respectively.

The magnetic properties of RECrO3 are mainly determined by the structure of corner-shared CrO6 octahedral subunit with bridge-ligand oxygen atoms. The 3d orbitals of Cr3+ split into two sets according to the crystal field theory with 2 high energy levels of eg and three low energy levels of t2g. Cr3+ is not a Jahn-Teller ion, with 3 valence electrons of the same spin orientation occupied the t2g orbitals that hybrids with O2p orbital. The spin orientation of Cr3+ in neighboring corner-shared CrO6 octahedral is antiparallel arrangement that leading to antiferromagnetic behavior through superexchange interactions. However, RECrO3 usually show remnant magnetization due to the strong canted tendency of CrO6 octahedral along <101> direction, that endows the materials net magnetic moments and ferromagnetic performance known as canted-antiferromagnetism. The magnetization of RECrO3 is dependent on the bond angle of Cr-O-Cr that affects the superexchange of neighbor t2g electrons through Dzyaloshinskii-Moriya (D-M) interactions. Magnetic field dependent magnetization hysteresis curves of as-synthesized RECrO3 materials are shown in Figure 11. ErCrO3 shows a remnant magnetization of 12.2 emu/g and coercive field strength of 2000 Oe at 4 K (Figure 11 (a)), which could be ascribed to the canted-antiferromagnetism induced net moment of distorted CrO6 octahedral units in perovskite lattice. No saturated magnetization could be obtained due to the slight non-compensated paramagnetic contribution up to 60 kOe[[84]](#endnote-85). This structural tendency keeps in dominating the magnetic hysteresis behavior in 50 K and becomes paramagnetism when the temperature is over 100 K to room temperature. The remnant magnetization of TmCrO3 is 2.57 emu/g at 4 K and the coercive field reduced to 1200 Oe (Figure 11 (b)), which increased to 2500 Oe at 50 K with the reduction of remnant magnetization to 1.31 emu/g. Paramagnetic behavior also found in the 100 K and 300 K hysteresis curves. A weak exchange-bias phenomenon was found in the hysteresis curve of YbCrO3 samples with the positive remnant magnetization of 0.37 emu/g and negative coercive field of 600 Oe at 4 K (Figure 11 (c)), which is improved to 0.61 emu/g and 3000 Oe respectively at 50 K, in agreement with the nanoparticle shape of YbCrO3 samples synthesized via sol-gel method19. LuCrO3 shows a remnant magnetization of 0.49 emu/g and coercive field of 1800 Oe at 4 K, both values reduced at 50 K (Figure 11 (d)). These results are much larger than that of La-, Nd-, Sm- and DyCrO3 and smaller than Pr- and HoCrO3 in our previous work44,45. The remnant magnetization and coercive field of RECrO3 are mainly determined by the ferromagnetic performance resulted from canted-antiferromagnetic of corner-oxygen-shared CrO6 octahedral that dependent on the size of A-site RE3+ cations and sample preparation methods. Besides, the coercive fields could be affected by the grain size[[85]](#endnote-86) and shape[[86]](#endnote-87) of samples for perovskite structure rare-earth transition metal oxides, which may be resulted from the preferential orientation in the magnetic fields during measurement.

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Figure 11. Magnetic field dependent magnetization hysteresis curves of hydrothermally-synthesized crystals of (a) ErCrO3, (b) TmCrO3, (c) YbCrO3 and (d) LuCrO3, respectively.

**CONCLUSION**

In consideration of the amphoteric characteristics of Cr3+ that is sensitive to the aqueous solutions, it is challenging to synthesize RECrO3 in mild hydrothermal condition than that of REFeO3 and REMnO3. To explore the synthetic limitations of RECrO3, we compared reaction conditions and reactant addition routes and obtained a progressive dehydration method to synthesize the most “difficult” four heavy rare-earth chromites (*i.e.* ErCrO3, TmCrO3, YbCrO3 and LuCrO3) in a mild way. The as-synthesized samples show high crystallinity with a uniform particle size and rounded rectangular plate morphology. All of the samples crystalize into *Pbnm(62)* space group, with slightly longer unit cell parameters for a and c axis. Distortion angle of CrO6 octahedral in RECrO3 show a near value along φ[010] direction, while an increased distortion along θ[101] direction. Binding energy of Cr3+ in RECrO3 is in agreement with the chemical environment according to BVS calculation.

For the syntheses of rare-earth chromites in mild hydrothermal conditions, progressive dehydration is an essential route to crystalize the perovskite phase, via the following sequence: (i) formation of chromium hydroxide, (ii) formation of rare-earth and chromium hydroxides mixtures, (iii) interaction with adequate amounts of KOH mineralizer, (iv) hydrothermal crystallization at around 260 oC. No perovskite phase could be obtained below 240 oC during the hydrothermal process. Pure phase RECrO3 samples could be synthesized with well-controlled mineralizer concentrations in each step and a crystallization temperature at 260 oC. RE(OH)3 was the main impurity for reactions at insufficient temperature, while REO(OH) became the main impurity by overdosing the mineralizer. To our best knowledge, the synthetic method illustrated here demonstrated the lowest reaction temperature for the preparation of this family of materials.

The four as-synthesized RECrO3 (RE=Er, Tm, Yb, Lu) samples show higher distorted angle of the CrO6 octahedral units in comparison with the samples obtained via other methods. The corresponding Raman and FT-IR modes show a linear shift to high frequency wavenumbers from Er to Lu in RECrO3, which are also stronger than that of the samples synthesized via other methods in the literatures.

Temperature-dependent magnetization results of the RECrO3 samples show canted-antiferromagnetism properties with lower TN. The reduction of the antiferromagnetism to paramagnetism transition points are resulted from the larger distortion angle of CrO6 octahedral in mild hydrothermally crystalized samples. Hysteresis of field-dependent magnetization measurement indicates that the weak ferromagnetism was resulted according to asymmetric superexchange interactions of neighbor Cr-O-Cr bonds from corner-oxygen-shared CrO6 octahedral units.

In summary, ten RECrO3 (RE= La, Pr, Nd, Sm, Dy, Ho, Er, Tm, Yb, Lu) samples have been synthesized in mild hydrothermal conditions with controllable dehydration processes. The TN values are much lower than that of the RECrO3 synthesized via other methods. The low transition points may be resulted from the largely distorted CrO6 octahedral due to the special crystallization mechanism. Therefore, this paper illustrated a comprehensive synthetic technique to programmable dehydration for crystallization of binary metal oxides from amphoteric metal cations in mild hydrothermal conditions. It is important for the design and the syntheses of new functional oxides from amphoteric precursors, such as Al-, Sn-based multinary metal oxide materials.

ASSOCIATED CONTENT

**Supporting Information**. Supporting information file includes crystallographic data, E-pH diagrams, SEM, EDS, PXRD, TEM, SAED and the determination of Néel temperature results. This material is available free of charge via the Internet at http://pubs.acs.org.

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All authors have given approval to the final version of the manuscript.

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Synopsis

Four RECrO3 (RE= Er, Tm, Yb, Lu) samples with the smallest rare-earth cations at A-site were synthesized in mild hydrothermal condition for the first time. They show higher distorted angle of CrO6 octahedral units that results in the lower magnetization transition temperature and stronger magnetization reversal and exchange bias effect.

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