Microwave-Assisted Synthesis, Microstructure, and Physical Properties of Rare-Earth Chromites

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ABSTRACT: The full rare-earth (RE) chromites series (RE)CrO3 with an orthorhombic distorted (Pnma) perovskite structure and the isostructural compound YCrO3 can be synthesized through a simple microwave-assisted technique, yielding high-quality materials. Magnetization measurements evidence that the Néel temperature for antiferromagnetic Cr3+-Cr3+ ordering strongly depends on the RE3+ ionic radius (IOR), and a rich variety of different magnetic spin interactions exists. Dielectric spectroscopy on sintered pellets indicates electronic inhomogeneity in all samples as manifested by the presence of at least two dielectric relaxation processes associated with grain boundary and grain interior bulk contributions. X-ray diffraction, Raman spectroscopy, and temperature-dependent dielectric permittivity data do not indicate potential noncentrosymmetry in the crystal or concomitant ferroelectricity. Strong correlations between the magnetic and dielectric properties were not encountered, and microwave-synthesized (RE)CrO3 may not be classified as magnetolectric or multiferroic materials.

1. INTRODUCTION

Rare-earth (RE) orthochromites (RE)CrO3 with distorted perovskite structure are currently attracting research interest because of their potential application as multifunctional materials.1 Chromites in general are under intense investigation nowadays,7 where the particular interest in the RE species is debited to potential magnetoelectric coupling. Initial studies had claimed that certain rare-earth chromites belong to a new family of ferroelectric and antiferromagnetic multiferroics.3 Such claims are somewhat surprising though because (RE)CrO3 chromites adopt a centrosymmetric orthorhombic structure with space group Pnma (No. 62) (frequently given in its nonstandard setting Pmmn). Ferroelectricity in centrosymmetric space groups is unusual, and it was attempted recently4 to explain this by chromium off-centering with a local character and a small value of displacement, leading to weak polarization.

The magnetic properties of the (RE)CrO3 series contain a rich variety of different magnetic spin interactions, where three different types may occur: (1) Cr3+-Cr3+, (2) Cr3+-(RE)3+, and (3) RE3+-RE3+, with isotropic, symmetric, and anisotropic magnetic exchange interactions, respectively.6,² A weak ferrimagnetic moment in some of the species was claimed to arise from Dzialoshinski–Moriya (D–M) interactions between Cr3+ spins.⁶,⁹ The antiferromagnetic Néel temperature TN,Cr for Cr3+-Cr3+ ordering increases with the RE cationic radius,¹⁰ which is associated with diminishing lattice distortions and increasing Cr3+-O5–Cr3+ bond angles approaching the ideal 180°.¹¹

The charge-transport properties in (RE)CrO3 materials have been claimed to involve p-type semiconductivity with sensitivity toward humidity, methanol, ethanol, and several gases, which is useful for potential sensor applications.¹²,¹³ Furthermore, LaCrO3 and its doped variants are candidates for application as interconnect materials in solid oxide fuel cells¹⁴,¹⁵ and as catalysts for hydrocarbon oxidation.¹⁶

Usually, rare-earth chromites are synthesized by solid-state reactions where the process involves multiple heating (≥1200 °C) and regrinding steps to help overcome the solid-state diffusion barrier.¹⁷ Other more efficient synthetic methods reported in the literature include self-propagating high-temperature synthesis, metathesis of metal chlorides, decomposition of coprecipitated precursors, a citrate sol–gel route, and hydrothermal synthesis.¹⁸–²⁰ Here in this work we present an alternative route of microwave-assisted synthesis.

In fact, the use of microwaves for the synthesis of solid oxide materials dates back to the late 1980s,²¹ although it is only in
the past decade that this technique has been more widely employed, and plenty of functional materials have recently been synthesized by these means.\textsuperscript{22–25} The most commonly applied procedure involves mixing the precursors, pressing them into pellet form, and placing the pellets in a microwave oven in an adequate crucible (usually porcelain, alumina, or SiC). In certain cases of insufficient heating, an additional microwave absorber such as black carbon, graphite, or SiC can be intermixed with the precursor materials to improve coupling between microwaves and material for enhancing microwave energy absorption.\textsuperscript{26}

The aim of this work has been to carry out a systematic effort to synthesize the full (RE)CrO\textsubscript{3} series including the isostructural compound YCrO\textsubscript{3} using microwaves and to perform the structural and microstructural characterization and a detailed investigation of the magnetic and dielectric properties and their correlations with particular focus on possible magneto-electric or multiferroic behavior.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis. Appropriate amounts of precursor nitrates [98\% Cr(NO\textsubscript{3})\textsubscript{3}, 9H\textsubscript{2}O and 99.9\% (RE)(NO\textsubscript{3})\textsubscript{3}, Sigma-Aldrich] were weighed and mixed with 5\% by weight amorphous carbon acting as a microwave absorber, and the mixture was mechanically homogenized and compacted into pellets of 12 mm diameter.\textsuperscript{27} The pellets were placed in a porcelain crucible and irradiated in a domestic microwave oven for 10 min (2.45 GHz and 800 W). Afterwards, the pellets were crushed and the amorphous powder was heated in a conventional furnace in air at 500 °C for 2 h for crystallization to form the precursor (RE)CrO\textsubscript{3}. Such a precursor was then heated at 800 °C for 2 h to obtain (RE)CrO\textsubscript{3}. The resulting powders were compacted again into pellets in a 1 ton press for 5 min, and densification sintering was performed in air at 1300 °C for 15 h.

2.2. Structural and Microstructural Characterization. The phase composition and purity of all precursors and the final products were tested by powder X-ray diffraction (XRD) on a Bruker D8 high-resolution diffractometer using monochromatic Cu K\textalpha\textsubscript{1} radiation obtained from a germanium primary monochromator. X-rays were detected with a solid-state rapid LynxEye detector. Structural refinement of XRD patterns from (RE)CrO\textsubscript{3} powders were carried out using FullProf software.\textsuperscript{28}

Field-emission scanning electron microscopy (FE-SEM) of gold-coated powders was carried out using a JEOL 6335F microscope equipped with a detector for energy-dispersive analysis of X-rays (EDAX). Good homogeneity and the expected semiquantitative 1:1 cation compositions of RE/Cr for all powders were confirmed by EDAX. In each sample, analysis was performed on 10 microcrystallites (grains), where the cationic ratios on three different areas of each microcrystallite were measured and the overall average was calculated.

3. RESULTS AND DISCUSSION

3.1. Reaction Pathway. The reaction pathway for (RE)CrO\textsubscript{3} formation from nitrate precursors can be described by a three-step process, as indicated by the XRD pattern in Figure 1: (a) formation of an amorphous phase after 10 min of microwave irradiation; (b) formation of polycrystalline (RE)-

Figure 1. (a) Powder XRD pattern of the MW as-synthesized powders (amorphous), (b) XRD pattern of the 500 °C annealed powders showing monazite (LaCrO\textsubscript{3}), mixed monazite and zircon (PrCrO\textsubscript{3}), and a pure zircon (YCrO\textsubscript{3}) structure, and (c) XRD pattern of the 800 °C annealed powders all showing a pure perovskite phase.
CrO₄ at 500 °C (2 h); (c) formation of (RE)CrO₃ at 800 °C (2 h).

Notably, most of the intermediate (RE)CrO₄ phases show the zircon-type structure with tetragonal symmetry, space group I₄₁/amd (No. 141), except in the case of LaCrO₄ and PrCrO₄. For LaCrO₄, the monazite-type structure with monoclinic symmetry, space group P2₁/n (No. 14), is obtained because of the large La³⁺ cationic radius, whereas in PrCrO₄, zircon and monazite phases coexist. Another point of interest is the unusual 5+ oxidation state achieved for chromium in this intermediate phase. The (RE)CrO₃ final products adopt a distorted perovskite structure and orthorhombic symmetry, space group Pnma (No. 62), upon heating at 800 °C as expected.

3.2. Composition and Crystal Structure. All microwave-synthesized (RE)CrO₃ and YCrO₃ powders were single phase, as confirmed by XRD. Figure 2 shows examples of RE chromite XRD patterns and Rietveld refinement fits for RE = La, Nd, Tb, and Tm. The full set of XRD patterns and parameters obtained from the structural refinements are presented in the Supporting Information, Part I, including lattice parameters, atomic positions, bonding angles, and bonding distances.

The distorted perovskite structure with orthorhombic symmetry [space group Pnma (No. 62)] was confirmed in all RE chromites, in agreement with previous work. The unit cell vectors can be represented by \(\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p\), where \(a_p\) refers to the simple cubic perovskite cell. The perovskite tolerance factors for (RE)CrO₃ are \(t = 0.85-0.93\), which is within the reported limits of \(t = 0.8-1\) for perovskite structures of cubic (\(t = 1\)) or lower symmetry (\(t < 1\)). The cell parameters \(a\), \(b\), and \(c\) for the RE family are given in Figure 3 as a function of the RE ionic radius (IOR) and the perovskite tolerance factor for the (RE)CrO₃ series. An approximately linear increase of \(b\) and \(c\) with IOR implies an increasing unit cell size.

![Figure 2. Rietveld refinement of XRD patterns: observed (red dotted lines), refined (black solid lines), and their difference (blue bottom line). Green vertical bars indicate the X-ray reflection positions.](image)

![Figure 3. Lattice parameters \(a\), \(b\), and \(c\) versus the RE IOR and the perovskite tolerance factor for the (RE)CrO₃ series. An approximately linear increase of \(b\) and \(c\) with IOR implies an increasing unit cell size.](image)
bonding distances can be determined with relatively low resolution only, but all of these distances appear to be similar (≈1.97 Å) and close to the expected value (1.9805 Å). The main effect of the RE size is observed in the octahedral tilting of the perovskite cell. θ, φ, and μ represent the tilting angles of the BO₆ octahedra along the three main directions of the ideal ABO₃ cubic perovskite structure, which implies that the larger these angles, the more distorted the structure. All angles decrease quite consistently away from the ideal 180° with decreasing IOR and increasing RE atomic number because the rigid CrO₆ octahedra accommodate A-site RE cations of decreasing size by decreasing the unit cell size and increasing the degree of octahedral tilting.

3.3. Microstructural Characterization. 3.3.1. FE-SEM. A full set of FE-SEM micrographs for (RE)CrO₃ powders is presented in the Supporting Information, Part II, where clear evidence for agglomeration of submicrometer particles is presented.

3.3.2. HRTEM. HRTEM images for (RE)CrO₃ (RE = La, Nd, Y, and Lu) are displayed in Figure 4. The experimental images taken along the [001] zone axis show excellent agreement with the simulated images depicted within the rectangles marked with (yellow) asterisks. In all images, the black dots are the projections of the atomic columns from the cationic RE and chromium sublattices, showing a well-ordered crystal without the formation of superstructures or defects such as dislocations and stacking faults. This is evidenced by a regular contrast across the HRTEM images and the absence of extra spots or streaking lines in the FFTs (Figure 4, insets). Enlargements of the HRTEM images with the projected model from each material set on top of the experimental image are displayed in Figure 5 showing good agreement. By careful analysis of the contrast of the images, it can be noticed that the darker dots (RE) and the less darker ones (chromium columns) are oriented in a zigzag fashion along the [010] direction with increasing amplitude in LaCrO₃ < NdCrO₃ < YCrO₃ < LuCrO₃. This feature is related to increasing octahedral tilting to accommodate RE cations of decreasing size in the octahedral framework.

3.4. Raman Spectroscopy. Figure 6 shows the Raman spectra of all chromite pellets. No secondary phases could be found on any of the samples, indicating a high degree of material homogeneity. Altogether 24 Raman modes are predicted by group theory for the orthorhombic and centrosymmetric Pnma structure with 4 formula units per unit cell. Only 9 of those Raman modes are easily observed in all of the samples (these modes are labeled in Figure 6) because of the measurement range used in this work. Additional symmetrically forbidden Raman modes characteristic of a potential (local) noncentrosymmetry were not encountered, and the observed spectra are in good agreement with a previous study and references therein.
The lower-energy modes (100−200 cm\(^{-1}\)) are quite stable across the full series, with the exception of YCrO\(_3\). Because these modes are mainly related to the vibrations of the A cations, they are independent of structural changes but highly sensitive to the mass of the cation. Most of the remaining Raman modes show a continuous tendency of decreasing mode position with increasing IOR (see also Supporting Information, Part III), which can be associated with an increase of the unit cell volume. Certain Raman modes display a higher dependence on IOR, for example, the mode \(A_1(5)\), which changes from 454 cm\(^{-1}\) in LuCrO\(_3\) to 278 cm\(^{-1}\) in LaCrO\(_3\). Furthermore, a mode crossing can be observed between \(A_1(5)\) and \(B_{1g}(2)\) for samples with IOR between 1.107 Å (Gd) and 1.12 Å (Eu), where both modes are almost indistinguishable. The \(A_1(5)\) mode has been previously associated with the [101] rotation of the CrO\(_6\) octahedra and is therefore strongly dependent on the different octahedral tilting angles. A plot of the \(A_1(5)\) mode position versus the octahedral tilting angle obtained from Rietveld refinement (\(\theta\) angle in Tables 2a and 2b of the Supporting Information, Part I) is shown in the Supporting Information, Part III, presenting a linear dependence for all samples (including YCrO\(_3\)) with a slope of \(\approx 21\) cm\(^{-1}/\)deg. This value is near to, but slightly smaller than, that previously reported.\(^{37}\) The \(A_1(3)\) Raman mode position also exhibits a linear tendency with the tilting angle with a slope of \(\approx 16\) cm\(^{-1}/\)deg.

### 3.5. Magnetic Properties.

(RE)CrO\(_3\) orthochromites are paramagnetic at room temperature and undergo several magnetic transitions upon cooling. The chromium Cr\(^{3+}\)−Cr\(^{3+}\) sublattice is first to order at the Néel temperature \(T_{N1}\), which increases monotonically with IOR from 109 K in LuCrO\(_3\) to 288 K in LaCrO\(_3\), as demonstrated in Figure 7. Upon further cooling, RE\(^{3+}\)−Cr\(^{3+}\) interactions appear for certain RE cations, which leads to unusual ZFC–FC magnetic susceptibility (\(\chi\)) versus temperature (\(T\)) characteristics below \(T_{N1}\) in the range of \(\approx 50–100\) K, as demonstrated in Figure 8. The RE\(^{3+}\)−RE\(^{3+}\) sublattice orders last at very low temperature (\(T_{N2}\)) in the range of \(\approx 2–15\) K for certain species, where the variation of \(T_{N2}\) does not appear to be correlated with IOR. The \(\chi\) versus \(T\) curves recorded at 1 kOe fall into two different classes according to the magnitude of the magnetic susceptibility \(\chi\) below \(T_{N1}\). The samples with relatively low \(\chi\) include RE = Y, La, Nd, Sm, Eu, Tb, Dy, Ho, and Er. Figure 8 shows the temperature dependence of \(\chi\) for three representative powders each from the low-\(\chi\) (Figure 8a) and high-\(\chi\) (Figure 8b) species.
even dropped significantly below zero. Such a negative susceptibility was also encountered in the high-$\chi$ species HoCrO$_3$, as discussed below, in that case for the ZFC curve.

3.5.2. *Species with High Magnetic Susceptibility $\chi$.* The main panel of Figure 8b shows the magnetic properties of GdCrO$_3$, ErCrO$_3$, and PrCrO$_3$ as representative members of the high-$\chi$ species. GdCrO$_3$ and ErCrO$_3$ show no significant differences between the ZFC and FC susceptibility curves, and Cr$^{3+}$ ferrimagnetic ordering is not indicated. Contrarily, the PrCrO$_3$ sample does show differences between the ZFC and FC curves appearing below $T_{N1} = 239$ K, and Cr$^{3+}$ ferrimagnetism is indicated. The RE ordering temperature $T_{N2}$ can be identified by a peaklike structure in the $\chi$ versus $T$ curves at $T_{N2} \approx 2$ K.$^{41}$ $T_{N2}$ can be identified more clearly in the ErCrO$_3$ sample ($T_{N2} \approx 14$ K), as is the case in TbCrO$_3$ and DyCrO$_3$ (data not shown), whereas the GdCrO$_3$ sample does not reach the $T_{N2}$ peak at low $T$.

The upper inset in Figure 8b shows the $\chi$ versus $T$ curve for HoCrO$_3$, where an unusual negative $\chi$ value (diamagnetic-like) is observed at low $T$ in the ZFC curve. Because the negative magnetic susceptibility is unusually high for diamagnetism and seems unphysical, an experimental artifact may seem plausible at first sight. However, this phenomenon can only be observed in the HoCrO$_3$ sample and equivalent reports in the literature have shown precisely the same effect in HoCrO$_3$ only.$^{32,42}$ In ref 42, this extraordinary behavior was interpreted as an interaction between paramagnetic RE$^{3+}$ and canted Cr$^{3+}$ moments, but this argument may be open to debate and, certainly, further work is necessary to clarify this issue, not only in this case but also for the exotic magnetic susceptibility found in TmCrO$_3$ and YbCrO$_3$.

3.5.3. *Curie–Weiss Behavior.* The lower insets in Figure 8a,b show the temperature dependence of the reciprocal magnetic susceptibility $1/\chi$ for the respective samples. Above $T_{N1}$, the paramagnetic state follows the Curie–Weiss law: $\chi = C/(T - \Theta)$, where $C$ is the Curie constant related to the effective magnetic moment $\mu_{\text{eff}}$ and $\Theta$ is the Weiss constant. The Curie–Weiss fits are indicated by the solid lines. In the Supporting Information, Part IV, all fitted parameters are summarized and compared to the theoretical values for $\mu_{\text{eff}}$ from Landolt–Börnstein tables.$^{43}$ and generally good agreement is encountered. The $\Theta$ values obtained from the fits are all negative, which indicates predominantly antiferromagnetic exchange interactions.

3.5.4. *Ferrimagnetic Hysteresis.* Figure 9 presents the magnetization versus applied field plots at 10 K for DyCrO$_3$, HoCrO$_3$, and TbCrO$_3$, which all show weak ferrimagnetic hysteresis as a result of Cr$^{3+}$ spin canting. In previous studies, such a weak ferrimagnetic moment of the Cr$^{3+}$ spins has been explained with D–M interactions.$^{32,39}$

3.6. *Dielectric Properties.* Impedance spectroscopy data for the (RE)CrO$_3$ series were collected from sintered pellets. Selected impedance spectra are shown in Figure 10 in terms of the complex impedance plane plot of $-Z''$ versus $Z'$. The spectra for the Ho-, Gd-, Pr-, and Y-containing samples are normalized and shifted up the $Z''$ $y$ axes by increasing amounts for demonstration purposes. For the different compositions, two or three semicircles are displayed in $-Z''$ versus $Z'$, which is consistent with two or three conventional dielectric relaxation processes in series.$^{32,44}$ Not all semicircles are fully developed, and considerable overlap occurs, which is highlighted in the spectrum for TbCrO$_3$ by the dotted semicircles. All semicircles in Figure 10 are slightly suppressed in a way such that the
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Supporting Information, Part V). From the slopes of such graphs, the B and GB activation energies $E_A$ can be determined and are plotted versus IOR in Figure 11 (upper curves).

Although the absolute $\rho_1$ and $\rho_2$ values at 200 K and other example temperatures do not show any clear trends with IOR (see the Supporting Information, Part V), the $E_A$ values are quite consistent. Especially, the intrinsic bulk $E_A$ trend seems to show a slight decrease with increasing IOR above the Gd sample, whereas for lower IOR, the bulk $E_A$ trend appears approximately constant. A similar trend is observed in the intrinsic permittivity $\varepsilon_1$ versus IOR (lower curve in Figure 11), where again the trend seems to change near the Gd sample. The YCrO$_3$ sample, on the other hand, falls out of all of the trends in the $\varepsilon_1$ vs IOR (lower curve in Figure 11), which is consistent with the trends in the effective magnetization $\mu_{\text{eff}}$. Equivalent to the argument mentioned above, the RE electron configuration seems to play a major role here in determining the electronic charge-transfer rate (resistivity) and the electron cloud polarizability (permittivity) in (RE)CrO$_3$ chromites.

Most importantly, the permittivity $\varepsilon_1$ values are all relatively low and the electron cloud polarizability may well be the only contribution to the overall measurable polarizability in the (RE)CrO$_3$ series. Furthermore, the $\varepsilon_1$ values determined did not show any clear temperature dependence (see the Supporting Information, Part V). Therefore, a contribution from an ionic displacement to the overall polarizability, typical for ferroelectricity, is unlikely, and previous reports on ferroelectricity in these materials cannot be confirmed. The absence of ferroelectricity may be consistent though with the centrosymmetric space group used for Rietveld refinements of XRD patterns and the Raman spectra presented here. None of the trends of the magnetic parameters ($T_{\text{Nd}}, T_{\text{Nd}},$ and $\mu_{\text{eff}}$) versus IOR are correlated with any of the trends of the dielectric parameters $E_A$ and $\varepsilon_1$, and obvious magnetoelastic coupling effects are not indicated.

4. CONCLUSIONS

The perovskite (RE)CrO$_3$ series was synthesized by micro-wave-assisted methods. A comprehensive characterization in terms of the structural and physical properties was performed. The $b$ and $c$ unit cell parameters showed a consistent increase.
with increasing IOR of the RE cation. The concomitant increase in the octahedral tilting angle approaching 180° resulted in a consistent increase of the Cr\(^{3+}\)–Cr\(^{3+}\) antiferromagnetic ordering temperature \(T_N\). The magnetic susceptibility \(\chi\) versus temperature characteristics revealed a rich variety of different spin interactions. The intrinsic bulk charge-transport activation energy and bulk dielectric permittivity in sintered ceramics showed a change in the trend with IOR near transport activation energy and bulk dielectric permittivity in different spin interactions. The intrinsic bulk charge-transport activation energy and bulk dielectric permittivity in sintered ceramics showed a change in the trend with IOR near transport activation energy and bulk dielectric permittivity in different spin interactions.

**REFERENCES**


