

Rare earth chromites: a new family of multiferroics

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Heavy rare earth chromites of the formula LnCrO_3 with $\text{Ln} = \text{Ho, Er, Yb, Lu}$ and Y are shown to be multiferroic, exhibiting canted antiferromagnetism at low temperatures ($T_N = 113\text{--}140\text{ K}$) and a ferroelectric transition in the $472\text{--}516\text{ K}$ range.

Multifunctional materials, especially multiferroics, have attracted great attention recently because of their potential applications.¹ A few metal oxides are known to exhibit ferroelectricity at relatively high temperatures and a magnetic transition at lower temperatures, typical examples being BiFeO_3 ² and YMnO_3 ³ both of which are antiferromagnetic. Heavy rare earth manganites LnMnO_3 ($\text{Ln} = \text{Ho, Er}$ and Yb) also exhibit multiferroic properties.⁴ It is of great interest to discover materials which are simultaneously ferroelectric and ferromagnetic. BiMnO_3 is found to be ferroelectric (FE) below 450 K (T_E) and ferromagnetic (FM) below 105 K (T_C).⁵ BiCrO_3 is reported to exhibit a ferroelectric transition at 440 K and parasitic ferromagnetism below 114 K .⁶ $\text{Bi}_2\text{Mn}_{4/3}\text{Ni}_{2/3}\text{O}_6$ and $\text{Bi}_2\text{MnNiO}_6$ are found to show both ferroelectric and ferromagnetic properties.⁷ It has been shown recently that YCrO_3 is a canted antiferromagnet (CAF) below 140 K and undergoes a ferroelectric transition around 473 K .⁸ By analogy with the rare earth manganites,^{3,4} it appeared to us that the heavy rare-earth chromites (LnCrO_3 , $\text{Ln} = \text{Ho, Er, Yb}$ and Lu) may also show such multiferroic behavior. We have, therefore, investigated the properties of several rare-earth chromites to explore their possible multiferroic nature.

Several rare-earth chromites (LnCrO_3 , $\text{Ln} = \text{La, Nd, Ho, Er, Yb}$ and Lu) were prepared by solid state reactions and characterized by X-ray diffraction. They were all found to belong to the orthorhombic system ($Pbnm$) as reported in the literature. Although these chromites are formally considered to be antiferromagnetic, low-temperature magnetic measurements show them to be CAFMs just like YCrO_3 .⁹ In Fig. 1, we show typical magnetization data of LaCrO_3 and LuCrO_3 . They exhibit non-linear behavior of the magnetization with respect to the field below T_N as shown in the inset of Fig. 1b. Detailed magnetic measurements have shown the weak ferromagnetic moment of the Cr^{3+} spins to be due to Dzialoshinski–Moriya (D–M) interaction in the chromites. There is some evidence for temperature-independent constant-canting-angle coupling in LuCrO_3 . These chromites also show magnetic domain effects below T_N .

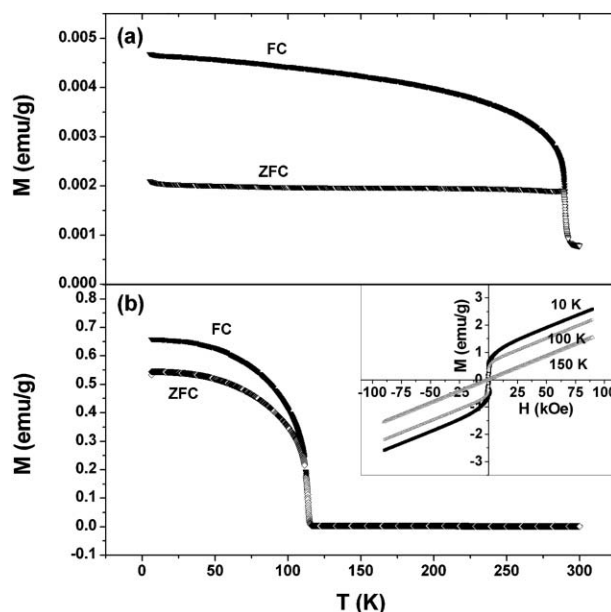


Fig. 1 Temperature variation of the magnetization of (a) LaCrO_3 and (b) LuCrO_3 under field-cooled and zero-field-cooled conditions ($H = 100\text{ Oe}$). The inset in (b) shows the field dependence of magnetization of LuCrO_3 .

Dielectric measurements show that the heavier rare-earth chromites (LnCrO_3 , $\text{Ln} = \text{Ho, Er, Yb}$ and Lu) undergo a transition in the temperature range $439\text{ K}\text{--}485\text{ K}$ (T_{max}) accompanied by a maximum in the dielectric constant. In Fig. 2, we show the temperature variation of the dielectric constant in the

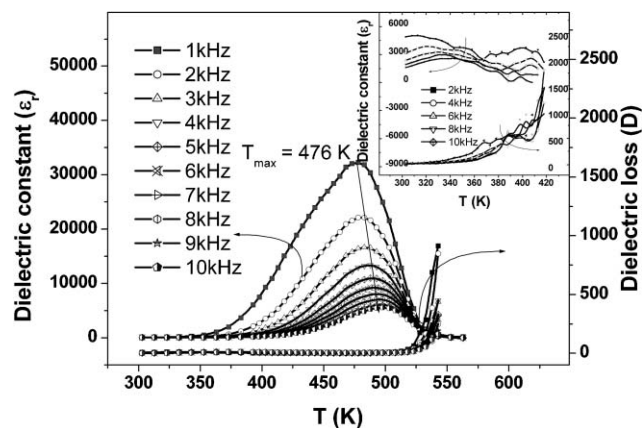


Fig. 2 Temperature variation of the dielectric constant, ϵ' , of LuCrO_3 at different frequencies. Inset shows the $\epsilon'\text{--}T$ curves for LaCrO_3 , at different frequencies.

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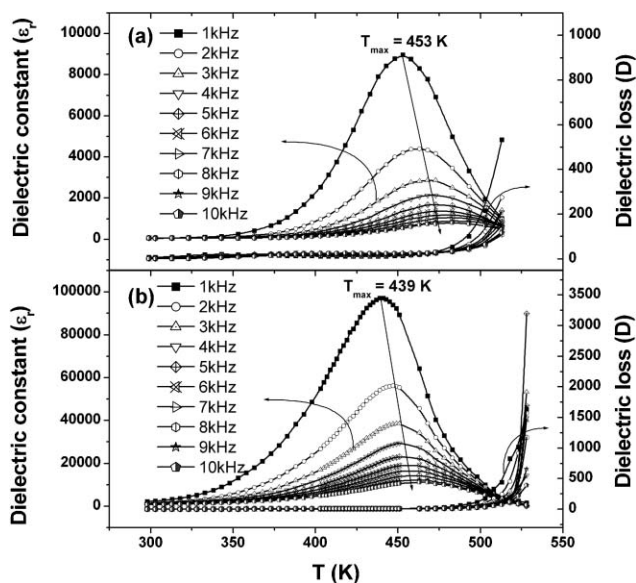


Fig. 3 Temperature variation of the dielectric constants of (a) ErCrO₃ and (b) YbCrO₃ at different frequencies.

case of LuCrO₃. We do not, however, find such a transition in the cases of LaCrO₃ or NdCrO₃ as exemplified for LaCrO₃ in the inset of Fig. 2. The temperature variation of the dielectric constant of YbCrO₃ and ErCrO₃ is similar to that of LuCrO₃ as can be seen from Fig. 3. We see from Fig. 2 and 3 that the T_{\max} is frequency dependent. In order to obtain the FE transition temperature, we employed a Curie–Weiss plot, wherein the reciprocal of dielectric constant in the high-temperature region ($T > T_{\max}$) was plotted against temperature.¹⁰ The Curie–Weiss plots yielded frequency-independent T_E values which are in the 472–516 K range for HoCrO₃, ErCrO₃, YbCrO₃ and LuCrO₃. The dielectric constants of the rare earth chromites show a large dispersion below T_E , but are frequency independent above T_E (see Fig. 2), behavior commonly observed in relaxor ferroelectrics.¹¹ It is noteworthy that the value of dielectric constant increases as the size of the rare-earth ion decreases. The maximum value of the low frequency dielectric constant is around 5000 in LaCrO₃ and 32000 in LuCrO₃. The polarization–electric field hysteresis loops of the heavier rare-earth chromites are similar to those of leaky dielectrics and are comparable to the hysteresis loop in YCrO₃.⁸ Like YCrO₃, the heavy rare earth chromites show low values of polarization and may, therefore, be considered to be weakly ferroelectric.

Based on the present findings, we can draw the phase diagram, shown in Fig. 4, to describe the multiferroic properties of the heavy rare-earth chromites. The phase diagram demarcates three distinct regions: CAFM FE, PM FE and PM PE where PM and PE stand for the paramagnetic and the paraelectric regimes respectively. The T_N decreases with the decrease in the radius of the rare-earth ion while the T_E increases slightly with decrease in size.

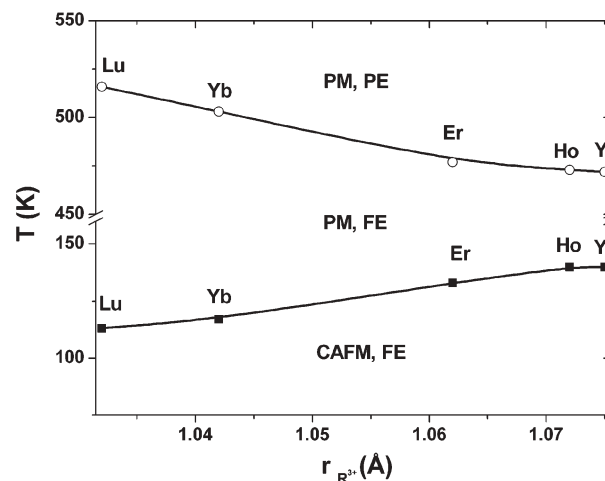


Fig. 4 Variation of the ferroelectric transition temperature T_E , and magnetic transition temperature, T_N , in the heavy rare-earth chromites.

Since the reported structures of the rare-earth chromites belong to the centrosymmetric orthorhombic system ($Pbmm$), it would be in order to comment on why ferroelectricity manifests itself. It has been pointed out recently that ferroelectric materials could be locally non-centrosymmetric although they are globally centrosymmetric, as exemplified by YCrO₃.⁸ A detailed study of the pair distribution functions¹² (PDF) of YCrO₃ based on neutron diffraction data indicates that in the short distance range (1–6 Å), the data give the best fit to a non-centrosymmetric $P2_1$ space group in the low-temperature FE phase. In the high-temperature PE phase, however, the PDF data conform to the centrosymmetric structure in the same distance range. The PDF data over the entire distance range of 1–22 Å can be fitted reasonably well with the centrosymmetric structure.

We have employed first-principles calculations to determine the effects of magnetic ordering and the size of the A-cation on the ferroelectricity of the chromites, through the cases of LuCrO₃ which exhibits ferroelectricity and of LaCrO₃ which is paraelectric at all temperatures. Our calculations are based on density functional theory within a gradient corrected (PW91) local spin density approximation (LSDA), as implemented in the PWSCF package¹³ with ultrasoft pseudopotentials¹⁴ and plane-wave basis with energy cut-offs of 25 Ry and 150 Ry in representing Kohn–Sham wave-functions and electron densities respectively. In all our calculations, we have used experimental lattice parameters of the crystal unit cell as ferroelectricity is known to be sensitive to unit cell volume.

We determined Λ point ($k = (000)$) phonons of LuCrO₃ and LaCrO₃ in the cubic perovskite structures (see Table 1) using the frozen phonon method. While LaCrO₃ has no Λ point instabilities in the PM form, it exhibits a weak ferroelectric instability upon ferromagnetic ordering. On the other hand, LuCrO₃ exhibits

Table 1 Calculated phonon frequencies at gamma point Λ (cm^{-1}) (i is imaginary)

	LaCrO ₃ (PM)	LaCrO ₃ (FM)	LuCrO ₃ (PM)	LuCrO ₃ (FM)
Λ_{15} (polar)	538.09	579.28	623.53	715.83
Λ_{15} (polar)	338.68	231.75	327.95	224.37
Λ_{25} (non-polar)	227.94	107.6	106.83	187.71 <i>i</i>
Λ_{15} (A off-center)	24.43	58.1 <i>i</i>	144.8 <i>i</i>	177.53 <i>i</i>

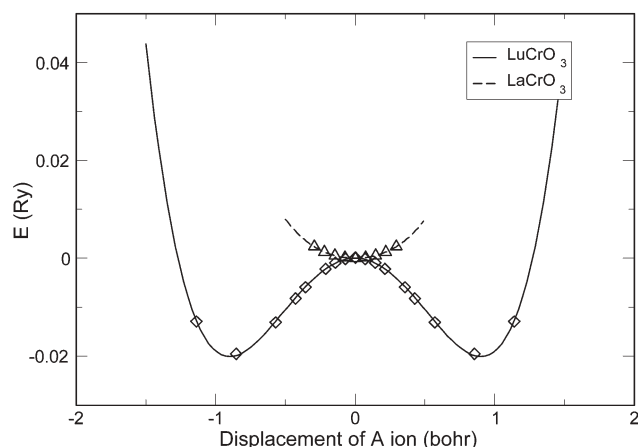


Fig. 5 Energy as a function of A-cation displacement along the (100) direction from their high symmetry site in the cubic structure with G-type AF ordering.

strong ferroelectric instabilities in both PM and FM orderings. We note that a change in magnetic ordering strongly affects the phonon frequencies, with a substantial softening upon FM ordering (relative to the PM phase) of the Λ_{25} mode which involves only the oxygen displacements. Since the modes of rotational instabilities belong to the subspace containing Λ_{25} , they are expected to behave similarly. Secondly, the softest polar (Λ_{15}) mode in both the chromites in the PM and FM phases involves A-cation off-centering, which softens upon FM ordering. In contrast, the hardest Λ_{15} mode is hardened further on FM ordering.

Since these chromites exhibit antiferromagnetism, we have determined the energetics of A-cation off-centering in the G-type antiferromagnetic ordering (involving two formula units per cell). As shown in Fig. 5, while the La displacement is stable at its high symmetry site, Lu exhibits a double energy well, with a tendency to be off-centered. It gains about 136 meV per formula unit due to off-centering by about 0.4 angstrom (comparable to the displacement of Pb in PbTiO_3). The frequency of the unstable Λ_{15} mode corresponding to Lu off-centering in the AFM ordered state is 64 cm^{-1} . The instabilities at the zone boundary are expected to compete with ferroelectric instabilities (we find more unstable modes, R_{25} (CrO_6 rotational mode) at $339i \text{ cm}^{-1}$ and R_{15} at $146i \text{ cm}^{-1}$ in AFM ordering) and the final ground state possibly involves a combination of these instabilities.

We have investigated the possibility of broken inversion symmetry in LuCrO_3 with respect to the theoretical structure optimized with the $Pbnm$ symmetry. The theoretical $Pbnm$ structure exhibits less distorted CrO_6 octahedra and more distorted LuO_8 polyhedra in comparison with the experimental structure. We then broke the inversion symmetry by off-centering Lu atoms along each Cartesian direction by 1% of the lattice constant and relaxing the structure with lower symmetry. This results in a small gain in energy (of about 1 meV per formula unit) and correspondingly small polarization (less than $0.35 \mu\text{C cm}^{-2}$, computed from the Berry phase formula¹⁵) upon breaking the

inversion symmetry along each of the three directions. These values are small and comparable to the magnitudes of computational errors. However, our results showing (a) the existence of a ferroelectric instability in the cubic structure, (b) its dependence on magnetic ordering, and (c) the small but non-zero values of polarization support the occurrence of ferroelectricity in LuCrO_3 . It would appear that local magnetic ordering can induce local non-centrosymmetry and weak ferroelectric polarization in these materials.

In conclusion, heavy rare-earth chromites HoCrO_3 , ErCrO_3 , YbCrO_3 , LuCrO_3 and YCrO_3 belong to a new family of multiferroics exhibiting canted antiferromagnetism at low temperatures. Further studies are necessary to fully understand the multiferroic properties of these chromites.

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