

# Neutron Scattering Investigation of Multiferroic $\text{Ce}_{1-x}\text{Eu}_x\text{CrO}_3$ Nanopowders

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Magnetic multiferroic materials with the coexistence of ferroelectric and ferromagnetic ordering have attracted increasing interest in recent years not only because of their potential for applications in multifunctional devices but also for the basic understanding of their fundamental properties. The perovskite rare-earth orthochromites with the general formula  $\text{RCrO}_3$  (where R is a rare-earth ion) are one such family of multiferroic materials with the great potential applications in optics and magnetism such as catalysts, electrolytes, fuel cells and refractory ceramics. These compounds with 4 formulas per unit cell are orthorhombically distorted from the ideal cubic structure at room temperature with space group of  $\text{Pbnm}$  [1-3].  $\text{RCrO}_3$  has two antiferromagnetic sublattices consisting of  $\text{Cr}^{3+}$  ( $3d^3$ ) and  $\text{R}^{3+}$  ( $4f^n$ ) moments. The ideal bond angle of Cr-O-Cr is  $180^\circ$  and their magnetic moments should be antiparallel, however, the mismatch of R-O and Cr-O bond lengths causes the crystal distortion and weak ferromagnetism. Most members of the  $\text{RCrO}_3$  family are canted antiferromagnetic and exhibit the magnetoelectric effect due to the Dzyaloshinskii-Moriya interaction [3, 4]. The relative size of the  $\text{R}^{3+}$  appears to have an important role in the magnitude of this tilting which in turn strongly affects on physical properties, including magnetization. Variations of rare earth ions also change the electronic configuration [4-6].

Recent studies [7] on pure nanocrystalline  $\text{CeCrO}_3$  has revealed that it exhibits multifunctionalities such as antiferromagnetism, relaxor-like dielectric behaviour and an optical band gap in the visible region. To understand how the ionic radius size and electronic configuration affect on the structural, magnetic and electrical properties of this  $\text{CeCrO}_3$  compound, we have undertaken a systematic study of this material by substituting the  $\text{Ce}^{3+}$  (with  $1.2 \text{ \AA}$  ionic radius size and  $4f^1$  electron configuration) with the  $\text{Eu}^{3+}$  (with  $0.94 \text{ \AA}$  ionic radius size and  $4f^6$  electron configuration). A new series of nano-sized powder  $\text{Ce}_{1-x}\text{Eu}_x\text{CrO}_3$  ( $x = 0.0$  to  $1.0$ ) with

orthorhombic structure were synthesized using a solution combustion method. All samples were sintered at  $950 \text{ }^\circ\text{C}$  for 12 h.

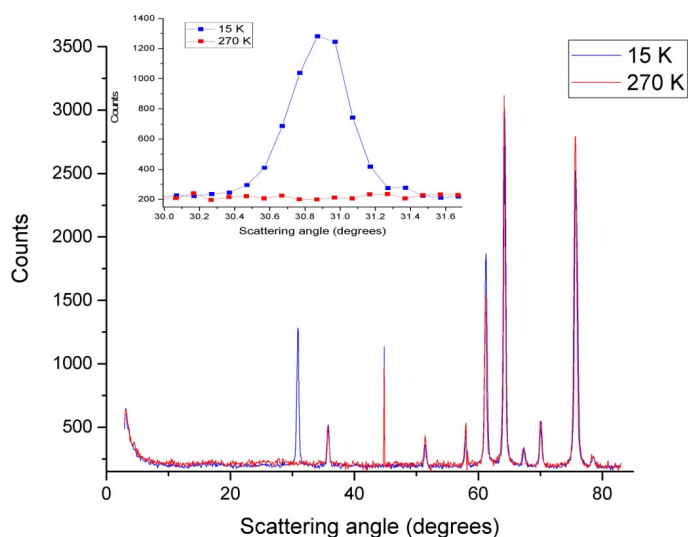
In order to determine the nuclear and magnetic structure and how they evolve with Eu-doping, we performed neutron powder diffraction measurements at C2 powder diffractometer on nanopowders  $\text{Ce}_{1-x}\text{Eu}_x\text{CrO}_3$  (with  $x = 0, 0.1, 0.5, 0.9$  and  $1$ ). The diffraction patterns were collected using  $2.37 \text{ \AA}$  and  $1.33 \text{ \AA}$  wavelengths. Since Eu has a large neutron absorption cross section, we used flat-plate geometry for mounting the sample in the beam [8]. With this geometry we took advantage of the large size of the beam and hence larger sample volume but with small thickness to minimize the neutron path length within the samples. In order to determine the Neel transition temperature, we collected the diffraction pattern as a function of temperature from room temperature down to  $3 \text{ K}$ .

The refinement of the diffraction pattern at room temperature indicated that for all doping levels the nuclear structure remained orthorhombic with no additional structural phase transitions down to  $3 \text{ K}$ . Furthermore, from the temperature dependence of the observed patterns, we determined that  $\text{Cr}^{3+}$  ions order below Neel temperature of  $T_N=260 \text{ K}$  in  $\text{CeCrO}_3$  (Fig. 1) while it decreases with Eu-doping ( $180 \text{ K}$  in  $\text{EuCrO}_3$ ). The refinement of the low-temperature neutron diffraction patterns reveals that ordering of the Cr ions leads to a G-type antiferromagnetic structure. In fact, the magnetic moments of  $\text{Cr}^{3+}$  are aligned along the b-axis in a G-type antiferromagnetic arrangement where a  $\text{Cr}^{3+}$  spin is aligned antiparallel to its six nearest neighbours. These results and the value of the ordered  $\text{Cr}^{3+}$  moment of  $2.42(\pm 0.01) \mu_B$  are in good agreement with previous results [7] on  $\text{CeCrO}_3$ . Similar analysis on  $\text{EuCrO}_3$  indicates that the  $\text{Cr}^{3+}$  magnetic moment is  $2.5(\pm 0.1) \mu_B$ . None of the diffraction patterns collected for different

doping levels revealed any additional peak at low temperatures down to  $T=3\text{K}$ . Thus, we couldn't detect the magnetic ordering of the rare-earth ions in these samples which is in disagreement with the previous literature on pure  $\text{CeCrO}_3$  where weak magnetic ordering for  $\text{Ce}^{3+}$  ions was reported [7].

In order to determine the crystal field splitting level of  $\text{R}^{3+}$  ion, we also performed an inelastic neutron scattering experiment using N5 triple-axis spectrometer. These measurements on  $\text{CeCrO}_3$  sample (Fig. 2) revealed the splitting energy level of  $4.57 \pm 0.02 \text{ meV}$ , in good agreement with value obtained from Schottky heat capacity anomaly at low temperatures ( $4.41 \pm 0.03 \text{ meV}$ ),

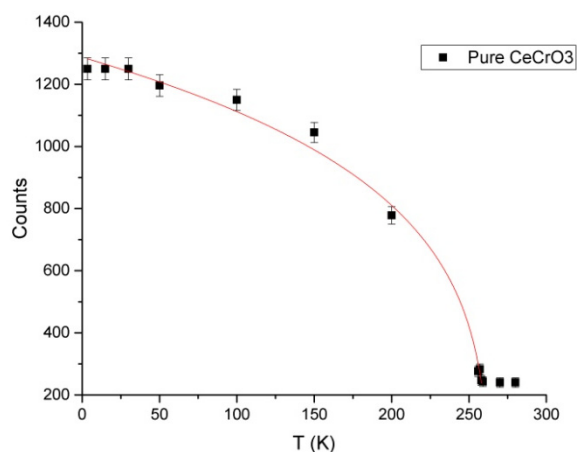
using an equation  $C_{Sch} = R \left(\frac{\Delta}{T}\right)^2 \frac{e^{\frac{\Delta}{T}}}{(1+e^{\frac{\Delta}{T}})^2}$ , where  $\Delta$  is the



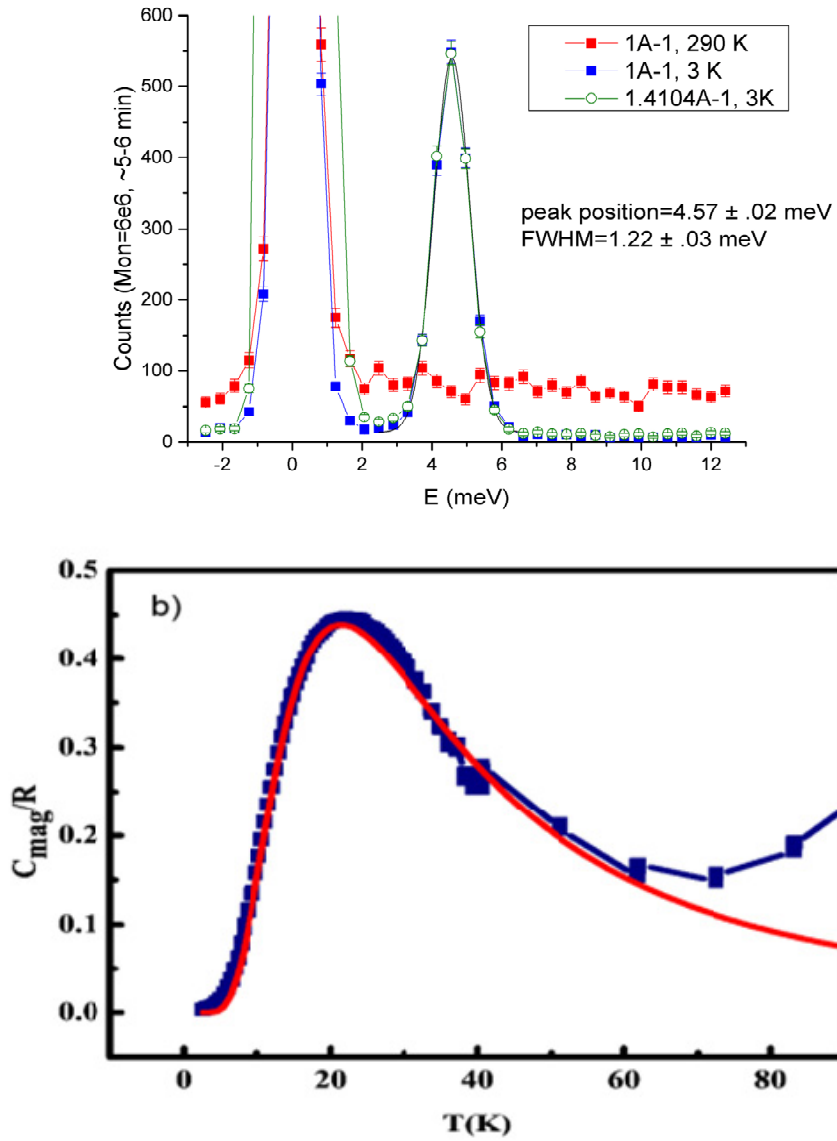
energy apart between the levels and  $R$  is the gas constant.

## References

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**Figure 1** Neutron powder diffraction of  $\text{CeCrO}_3$  at  $T=3\text{K}$  and  $T=280\text{K}$ , as well as its magnetic phase transition.



**Figure 2** Inelastic neutron scattering of CeCrO<sub>3</sub> at T=3K and T=290K, (b) Schottky heat capacity of CeCrO<sub>3</sub> at zero applied magnetic field.