Experimental report

09/04/2026

Proposal:	**5-24-761**	**Council:**	10/2024

Title: Study of the crystal and magnetic structures of La0.3Ca0.7Fe1-xCrxO3-¿ solid solution

Research area: Materials

This proposal is a new proposal

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Samples: La0.3Ca0.7Fe1-xCrxO3-¿, ¿x = 0.1

Instrument	Requested days	Allocated days	From	To
D2B	3	3	09/05/2025	12/05/2025

Abstract:

ABO3 oxides accommodate a variety of chemical compositions, crystallize with several structures in competition and develop diverse physical properties, being intensively studied in the search for new functional materials. Transition metal oxides with perovskite structure are of major interest, where A/B chemical substitution is a common strategy towards physical properties modification. Attainability of very rich phase diagrams are proven by, eg.La1-xCaxMnO3 system, with different electronic/magnetic properties, and charge ordering effects, that can be controlled via chemical composition. We propose the study of the La0.3Ca0.7Fe1-xCrxO3-¿ oxygen deficient perovskite solid solution for harnessing thermoelectric energy.
Preliminary NPD data on one sample showed two high temperature structural transitions at ~800 and 600K from Pnma to R3c. Bulk magnetic properties of our samples reveal magnetic anomalies at these T, also related with different thermoelectric behaviors. The compositional range covers an unusual n- to p-like behavior. A high resolution and thermodiffrantion study on D2B will provide insight on the phase diagram and further understanding on their physiscal properties.

Study of the crystal and magnetic structures of $La_{0.3}Ca_{0.7}Fe_{1-x}Cr_xO_{3-\delta}$ solid solution

ABO_3 oxides accommodate a wide variety of chemical compositions, crystallize with several structures in competition and develop diverse physical properties, being intensively studied in the search for new functional materials. Among them, transition metal oxides with perovskite structure are of major interest, where the chemical substitutions into the A/B sites is a common strategy towards physical properties modification. Well studied materials like the $La_{1-x}Ca_xMnO_3$ system demonstrate the attainability of very rich phase diagrams, with different electronic and magnetic properties, as well as charge ordering effects, that can be controlled via chemical composition.

In experiment 5-24-761 we performed a high temperature neutron diffraction study to explore the phase diagram of the related $La_{0.3}Ca_{0.7}Fe_{1-x}Cr_xO_{3-\delta}$ oxygen deficient solid solution with perovskite structure. While the x = 0.3 member is reported as a promising electrode for reversible SOFC,[1] this solid solution has been found of interest in the context of harnessing thermoelectric energy from waste heat.

We prepared the full $La_{0.3}Ca_{0.7}Fe_{1-x}Cr_xO_{3-\delta}$ solid solution with $\Delta x = 0.1$ using a combustion method. Samples were measured in pellet form using 12mm V containers at D2B with $\lambda = 1.594$ Å for high resolution. In total, 8 different samples were studied in this experiment throughout the solid solution at room and high temperatures. From the collected data, the structural phase diagram depicted in Fig.1 could be determined.[2] The compounds with $x < 0.5$ crystallise with a rhombohedral (*R3c*) perovskite structure and those with $x \geq 0.5$ with an orthorhombic (*Pnma*) perovskite structure at room temperature. High temperature phase transitions are observed to the rhombohedral polymorph for all studied samples, as previously reported for x = 0.3 sample. [3]

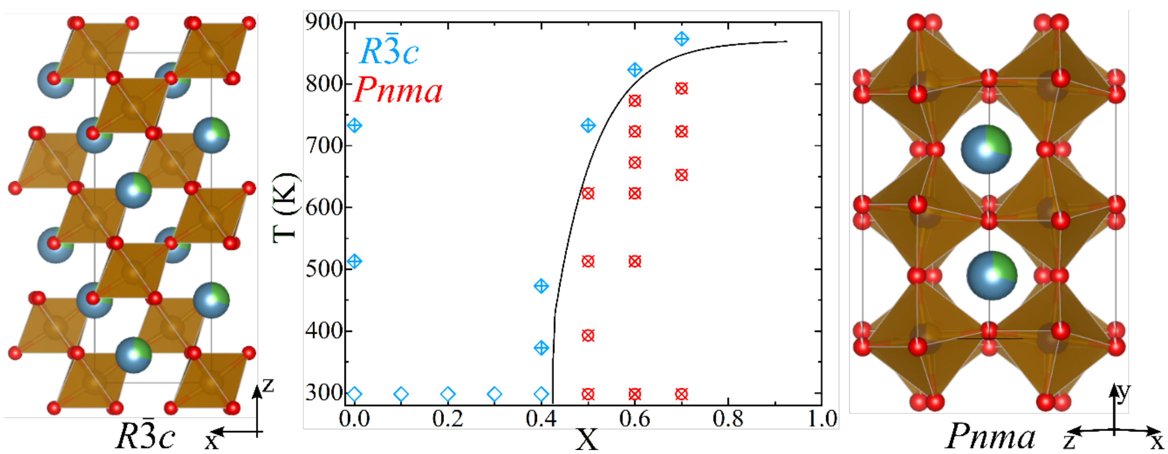

Figure 1. Phase diagram as a function of temperature and chromium content for $La_{0.3}Ca_{0.7}Fe_{1-x}Cr_xO_{3-\delta}$, from D2B data collected in experiment 5-24-761.

These results provided enough background for continuation experiments to i) complete the high temperature phase diagram (XtremeD, experiment CRG-3312), ii) explore the compositional phase boundary between both structures, performing a low temperature diffraction study in XtremeD for the compounds with x = 0.4 and 0.5 (EASY-1476), and iii) determine the magnetic structures at low temperature for the orthorhombic phases (CRG-3310).

References: [1] Molero-Sánchez, B. *et al. Int. J. Hydrogen Energy*, 40(4) (2015) 1902-1910. [2] Fernández-Gallego, L. *et al. Manuscript in preparation* (2026). [3] Sánchez-Ahijón, E., *et al. Journal of Solid State Chemistry,* 316 (2022) 123426.