



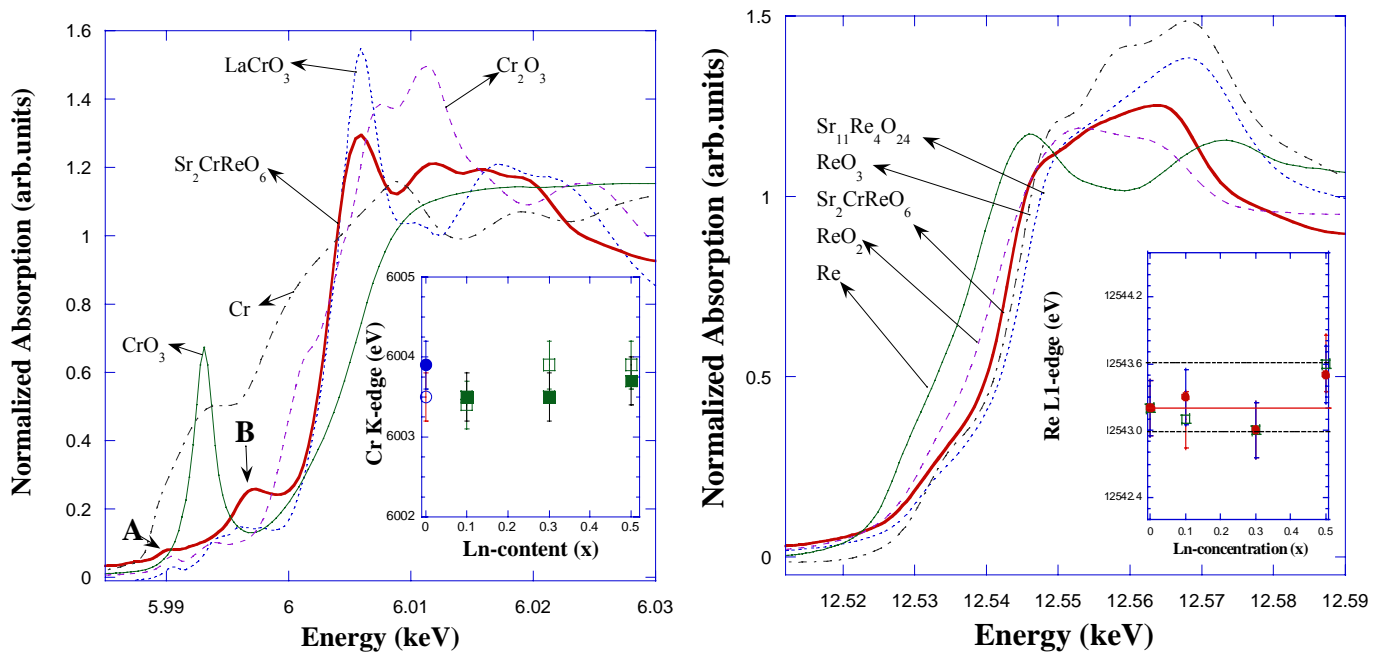
	<b>Experiment title:</b> XAS study on electron doped of Re-based double perovskites.	<b>Experiment number:</b> HS-3077
<b>Beamline:</b> BM29	<b>Date of experiment:</b> from: 15-JUNE-06 to: 18-JUNE-06	<b>Date of report:</b> 25-09-07
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### Report:

There is much interest in the study of ferromagnetic oxides with a Curie temperature ( $T_C$ ) well above room temperature and with a high spin polarization of the conduction electrons. There are several members belonging to the so-called double perovskites (DP) family, namely Re- and Mo-based compounds, exhibiting a half-metallic ground state and a high  $T_C$ . Among them,  $Sr_2CrReO_6$  has one of the highest  $T_C$  and a large conductivity. One successful route to further increase  $T_C$  in Mo-based DP was via electron doping, i.e. partial substitution of Sr with rare-earth (Ln) in order to fill the  $4d$   $t_{2g}$  minority spin band. In this work, we have studied the effects of the Sr replacement by different lanthanides in  $Sr_2CrReO_6$ . Our attempts at electron doping of  $Sr_2CrReO_6$  led to multiphasic systems. Single phases are only obtained with the stoichiometric formula  $Sr_{2-x}Ln_xCr_{1+x/2}Re_{1-x/2}O_6$ .

In order to determine the extent of doping, x-ray absorption spectroscopy has been used to independently determine the electronic structure and local geometry around both the Re and Cr atoms [1]. XANES and EXAFS spectra were recorded for  $Sr_{2-x}Nd_xCr_{1+x/2}Re_{1-x/2}O_6$  and  $Sr_{2-x}Sm_xCr_{1+x/2}Re_{1-x/2}O_6$  ( $x \leq 0.5$ ) series at Cr K and Re L edges at BM29 beam line. The measurements were carried out in transmission mode on powder samples at selected temperatures between 35 and 295 K. The beam was monochromatized by a fixed-exit Si(111) double crystal at both the Cr K- and the Re  $L_{1,2,3}$ -edges. Harmonic rejection better than  $10^{-5}$  was achieved by using a Si mirror coating of the double flat mirror installed after the monochromator. A Cr foil and a pellet of metallic Re were simultaneously measured for energy calibration at each respective absorption edge.

The chemical shift of the Cr K-edge revealed the presence of  $\text{Cr}^{3+}$  ions for all compounds, although changes with increasing the rare-earth content are visible at the pre-edge features (see Figure 1, left panel). These changes suggest a change in the Cr-O-Re covalency of the samples with increasing Ln-content. On the other hand, the edge position of the Re  $L_1$ -spectra agrees with the presence of  $\text{Re}^{5+}$  in the same compounds, as shown in Figure 1 (right panel). Accordingly, we have tested the relationship between the area of the Re  $L_{2,3}$  white lines and the unoccupied 5d electronic states. We have found a linear relationship at the  $L_2$ -edge whereas the  $L_3$ -edge seems to be less appropriate for this goal due to multiplet effects, as reported previously for 4d-systems. The inferred 5d occupation also agrees with the presence of  $\text{Re}^{5+}$  for all compounds in agreement with the Re  $L_1$ -edge results.



**Figure 1.** **Left panel:** Normalized Cr K-edge XANES spectra for metallic Cr (---),  $\text{Cr}_2\text{O}_3$  (----),  $\text{LaCrO}_3$  (.....),  $\text{Sr}_2\text{CrReO}_6$  (thick line) and  $\text{CrO}_3$  (thin line). A and B denote pre-edge features at the  $\text{Sr}_2\text{CrReO}_6$  spectrum. Inset: Edge position for  $\text{Sr}_{2-x}\text{Nd}_x\text{Cr}_{1+x/2}\text{Re}_{1-x/2}\text{O}_6$  (filled squares) and  $\text{Sr}_{2-x}\text{Sm}_x\text{Cr}_{1+x/2}\text{Re}_{1-x/2}\text{O}_6$  (open squares) at 295 K. The filled and open symbols for  $x=0$  correspond to the values at 35 and 295 K, respectively. **Right panel:** Normalized Re  $L_1$ -edge XANES spectra for selected samples. Inset: Re  $L_1$ -edge position for  $\text{Sr}_{2-x}\text{Nd}_x\text{Cr}_{1+x/2}\text{Re}_{1-x/2}\text{O}_6$  (circles) and  $\text{Sr}_{2-x}\text{Sm}_x\text{Cr}_{1+x/2}\text{Re}_{1-x/2}\text{O}_6$  (squares) series.

The EXAFS analysis gave Re-O and Cr-O bond-lengths, which do not vary with the doping ratio and concur with the expected values for  $\text{Re}^{5+}$  and  $\text{Cr}^{3+}$  oxides. Therefore, our spectroscopic study reveals the absence of change in the oxidation state of Cr and Re after the addition of Ln.