	Experiment title: EXAFS and XANES study of Re-based double perovskites.	**Experiment number:** HS-2458
Beamline: BM29	**Date of experiment**: from: 20-JUL-04 to: 24-JUL-04	**Date of report**: 22-JUL-05
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Report:

A renewed interest has been focused in the last years on the $A_2BB'O_6$ (A being alkaline-earth and B/B' being transition metal) compounds with perovskite structure. The reason is the outstanding magnetic and electronic properties they exhibit as a consequence of the strong interplay between structure, charge and spin ordering.

The electronic and geometrical local structure of Re-based double perovskites, A_2FeReO_6 (A=Ba, Sr, Ca), have been probed by using x-ray absorption spectroscopy at the Fe K- and Re $L_{1,2,3}$-edges [1]. X-ray absorption spectra were recorded at the BM29 beamline. The measurements were performed in transmission mode on powder samples. The incident and transmitted beams were detected by means of ionization chambers. The beam was monochromatized by a fixed-exit Si(311) double-crystal at both, the Fe K- and the Re L_i-edges. Harmonic rejection was achieved by 50% detuning of the monochromator from the parallel alignment. The energy resolution δE/E was estimated to be about 4×10^{-5} and 1×10^{-4} at the Fe K- and Re L_i-edges, respectively. XANES spectra were taken for the Fe K- and Re $L_{1,2,3}$-edges while EXAFS spectra were measured at the Fe K- and Re L_3-edges. Both kinds of spectra were collected at 40 K and at room temperature (~295 K). A Fe foil and a pellet of metallic Re were simultaneously measured for energy calibration. The XANES spectra were normalised to the high energy part of the spectrum (~100 eV beyond the edge) after background subtraction. The EXAFS structural analysis was mainly restricted to the first coordination shell by means of the FEFF 8.10 code and FEFFfit package.

Figure 1(a) shows the Fe K-edge XANES spectra of A_2FeReO_6 samples. The main traits of these spectra are a strong resonance at the threshold (W), some pre-peak structures at ~15 eV below W (P) and shoulders at intermediate energies (S). The main difference among the samples concerns to the edge position. The calculated edge values are 7125.0, 7125.7 and 7126.0 eV for Ba_2, BaSr and the rest of A_2FeReO_6 samples, respectively. Therefore, the edge position for the latter samples is consistent with the presence of trivalent Fe whereas a mixed valent Fe (~ +2.75) can be deduced for Ba_2.
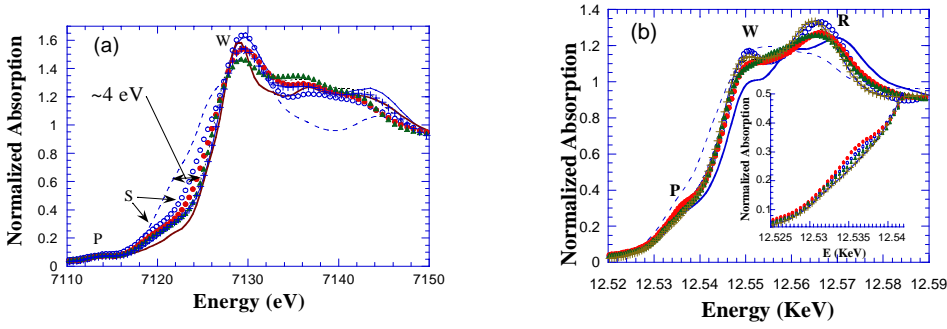
Figure 1. XANES spectra of the A_2FeReO_6 and reference samples at the (a) Fe K edge at 40 K and (b) at the Re L_1 edge at room temperature. A_2 being Ba_2 (open circles), BaSr (filled circles), Sr_2 (triangles), CaSr (dotted line), $Ca_{3/2}Sr_{1/2}$ (+), Ca_2 (solid line). The references $LaFeO_3$ or ReO_3 (chain curve) and FeO or ReO_2 (dashed line) are also included.

The XANES spectra at the Re L_1-edge for these samples are shown in Fig. 1b. The A_2FeReO_6 spectra are composed by a strong resonance (R) above the white line (W_L) and a pre-edge (P_L). The inset of Fig. 1b shows in detail the P_L and insulator samples (Ca_2 and $Ca_{3/2}Sr_{1/2}$) have the weakest P_L supporting a close relationship between *p-d* mixing and metallic behaviour. Comparison between references and A_2FeReO_6 compounds in Fig. 2b reveals an intermediate valence close to 5+ for the Re.

SAMPLE	Fe K-edge			Re L$_3$-edge		
	R_{Fe-O} (Å)	σ^2 (Å^2)	R	R_{Re-O} (Å)	σ^2 (Å^2)	R
Ba_2FeReO_6	2.063(6)	0.003(1)	0.037	1.949(4)	0.003(1)	0.025
$BaSrFeReO_6$	2.026(5)	0.003(1)	0.018	1.943(6)	0.004(1)	0.054
Sr_2FeReO_6	1.993(4)	0.003(1)	0.018	1.942(4)	0.002(1)	0.022
$CaSrFeReO_6$	2.003(5)	0.002(1)	0.017	1.949(4)	0.002(1)	0.018
$Ca_{3/2}Sr_{1/2}FeReO_6$	2.007(5)	0.003(1)	0.018	1.950(4)	0.001(1)	0.018
Ca_2FeReO_6	2.010(5)	0.002(1)	0.031	1.951(3)	0.001(1)	0.017

Table 1. Average interatomic distances R[Fe(Re)-O], Debye-Waller factors (σ^2) and reliability factors (R) for the A_2FeReO_6 samples at 40 K. Details of the fits can be found in ref. 1.

The EXAFS spectra were measured at 40 K and at room temperature. Table 1 compares the best fit results for both edges. The analysis was restricted to the 1st coordination shell in both cases. The EXAFS results are consistent with the presence of nominal Re^{5+} for all samples and Fe^{3+} for most of the samples. The exceptions would be Ba_2 and BaSr samples. According to Fe-O distances, the formal valence for Ba_2 sample would be +2.7 that nicely agree with XANES spectroscopy. Therefore, Ba strongly affects the charge distribution on the Fe-O-Re sublattice leading to mixed valence $Fe^{3-\delta}$ ions. We have explained our results in the frame of recent band models [1].

[1] J. Herrero-Martín, G. Subías, J. Blasco, J. García and M. C. Sánchez J. Phys.:Condens. Matter, in press.