



	Experiment title: The role of Pb-environment on the structure and electric properties of ordered $\text{Pb}_2\text{Mn}(\text{W}_{1-x}\text{Re}_x)\text{O}_6$ perovskites studied by XAS	Experiment number: HS-3605
Beamline: BM25A	Date of experiment: from: 17/04/2009 to: 21/04/2009	Date of report: 01/03/2010
Shifts: 12	Local contact(s): Felix Jimenez-Villacorta	<i>Received at ESRF:</i>
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Report:

Pb-based double perovskites $\text{Pb}_2\text{BB}'\text{O}_6$ usually exhibit spontaneous electric polarization as a result of the lead $6s^2$ lone pair that strongly distorts the coordination. In Pb_2WMnO_6 , our previous XAS study pointed out a phase transition of the order-disorder type. Above 445 K, Pb_2WMnO_6 is cubic and paraelectric whereas it is orthorhombic and antiferroelectric below such temperature. Our results showed that the local structure around the Pb and W atoms remains distorted in both high and low temperature phases. Furthermore, in the $\text{Pb}_2\text{ReMnO}_6$ double perovskite which is monoclinic at room temperature (RT), nearly regular MnO_6 and ReO_6 octahedra and a more symmetric coordination polyhedron around Pb than in Pb_2WMnO_6 is expected [1]. Hence, a similar structural effect as the one observed by heating up in temperature above 445 K in Pb_2WMnO_6 is likely to occur when replacing W by Re. In this regard, the XAS experiment on the series $\text{Pb}_2(\text{W}_{1-x}\text{Re}_x)\text{MnO}_6$ ($x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1$) was proposed.

Recent x-ray diffraction results for the solid solution $\text{Pb}_2(\text{W}_{1-x}\text{Re}_x)\text{MnO}_6$ at RT confirm a structural phase transition at $x = 0.5$. Samples with low Re doping fraction ($x < 0.5$) are orthorhombic while high Re doping fraction ($x \geq 0.5$) samples show monoclinic structure.

EXAFS spectra for the entire series were collected at the BM25A beamline on powder samples at the Pb L_3 and Re L_3 edges in transmission mode at both RT and low temperature (~ 60 K). For both edges, the low temperature data are preferable due to the longer useful k range. The Fourier transform (FT) of the k -weighted EXAFS spectra has been calculated for the ranges $1.8 - 9.5 \text{ \AA}^{-1}$ at the Pb L_3 edge and $3.5 - 11.5 \text{ \AA}^{-1}$

at the Re L₃ edge using a sine window. Fig. 1 and fig. 2 show the modulus of the FT for the different samples at the Pb L₃ and Re L₃ edges respectively.

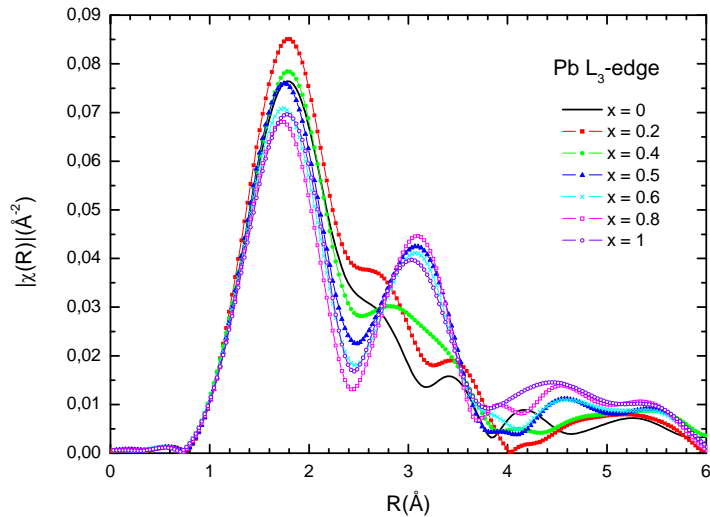


Figure 1. Modulus of the FT of the k-weighted EXAFS data at the Pb-L₃ edge at low temperature (60 K) for the samples $x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1$ (uncorrected for phase shift).

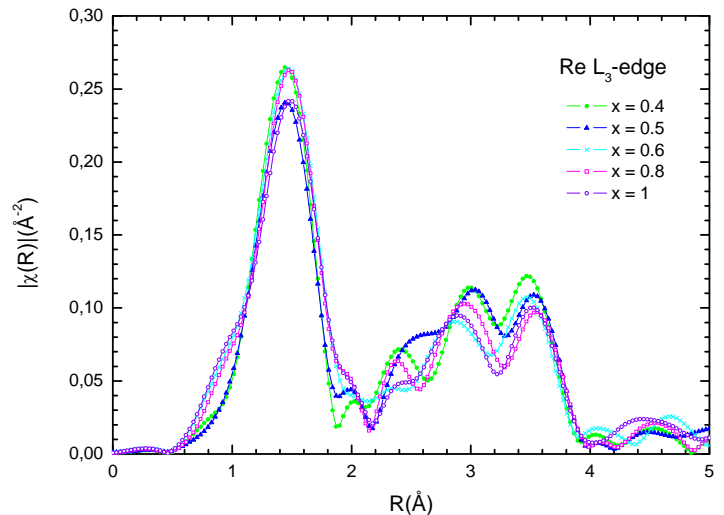


Figure 2. Modulus of the FT of the k-weighted EXAFS data at the Re-L₃ edge at low temperature (60 K) for the samples $x = 0.4, 0.5, 0.6, 0.8, 1$ (uncorrected for phase shift).

The Pb L₃-edge spectra display significant differences between samples with $x < 0.5$ and $x \geq 0.5$ mainly in the 2.4 – 4 Å region whereas the spectra at the Re L₃-edge roughly maintain the same profile for all the samples up to 5 Å within the experimental accuracy.

Due to the short k range and the considerable overlap beyond the first peak, only the first coordination shell has been fitted for both edges. The fit to the EXAFS spectra has been carried out by using the ARTEMIS programme [3]. We have fixed the overall amplitude reduction factor S_0^2 to 1 for the Pb L₃-edge and to 0.7 for the Re L₃-edge.

For the Pb L₃-edge, we have used the orthorhombic cell [2] as the structure model to fit all the spectra. The 12 O atoms in the first shell split into three sets of Pb-O bonds at average distances of 2.40 ± 0.03 Å ($x \times 4$), 2.86 ± 0.05 Å ($x \times 4$) and 3.05 ± 0.14 Å ($x \times 4$) that are nearly independent of the Re doping fraction (x). The same holds for the Pb-O average Debye-Waller factors σ^2 s.

The Re L₃-edge spectra first shell has been fitted by using the crystallographic distances of the monoclinic structure of Pb₂ReMnO₆ [1]. The distances to the 3 O pairs of the ReO₆ octahedron have been refined together resulting in an overall Re-O interatomic distance 1.885 ± 0.009 Å ($x \times 6$) that remains alike for all the samples. The Re-O σ^2 s do not vary notably either.

According to these results, the Re local structure agrees with a regular octahedron for $0.4 \leq x \leq 1$ as predicted. On the contrary, the PbO₁₂ polyhedron does not become more symmetric with the Re doping but keeps as distorted as in Pb₂WMnO₆. This indicates that the structural transition found at $x = 0.5$ for Pb₂(W_{1-x}Re_x)MnO₆ should be related to a Pb displacement in the cell, which would involve neighbouring atoms beyond the first coordination shell.

[1] K. Ramesha et al., Chem. Mater. **15**, 668 (2003)

[2] J. Blasco et al., J. Phys.: Condens. Matter **18**, 2261 (2006)

[3] B. Ravel and M. Newville, J. Synchrotron Radiat. **12**, 537 (2005)