ESRF	**Experiment title:** Phase transition of Pb_2MnWO_6 studied by means of XAS spectroscopy	**Experiment number**: HS-3205
Beamline: BM25A	**Date of experiment**: from: 15-Nov-06 to: 19-Nov-06	**Date of report**: 01-March-07
Shifts: 12	**Local contact(s)**: Germán Castro	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

J. Blasco, G. Subías*, J. García* and J. Herrero-Martín*.

Instituto de Ciencia de Materiales de Aragón, CSIC- Universidad de Zaragoza, Departamento de Física de la Materia Condensada, C/ Pedro Cerbuna 12, 50009 Zaragoza.

Report:

$Pb_2BB'O_6$ double perovskites are good candidates to show simultaneous electric and magnetic orderings, resulting in interesting technological applications. They usually exhibit distorted structures associated with the Pb^{2+} coordination, giving rise to spontaneous polarized states. Amongst them, Pb_2MnWO_6 undergoes an electrical transition coupled to a structural transition at ~445 K [1]. This compound is cubic paraelectric above 445 K and orthorhombic with antiferroelectric ordering below such temperature. An x-ray diffraction study of the cubic phase reveals the presence of regular MnO_6 and WO_6 octahedra together with a symmetric oxygen environment around the Pb atoms. However, a large value for the temperature factor for Pb atoms is noticeable. On the other hand, the orthorhombic phase shows distorted MnO_6 and WO_6 octahedra, coupled to displacements of the Pb atoms from the cubic special positions.

In order to investigate the influence of the order/disorder of Pb displacements (and associated distortions) on the local structural distortions around the Mn and W octahedral sites in Pb_2MnWO_6, we have measured XANES and EXAFS spectra at Pb L_3-edge and W L_3-edge at temperatures ranging from 300 K up to 500 K across the structural transition. We have also recorded XANES spectra of Pb and PbO as references for the Pb L_3-edge and W and WO3 as references for the W L_3-edge. Spectra were recorded at the BM25A beamline with a Si(111) double-crystal monochromator in transmission mode, using ionisation chambers as detectors. We have also tested to measure EXAFS spectra at the Mn K-edge in transmission mode but fluorescence detection using a 13 elements Canberra solid state detector is mandatory in this case due to the high photoabsorbing matrix. However, XANES spectra at the Mn K-edge of Pb_2MnWO_6 and Mn, MnO and Mn_2O_3 standards at room temperature were indeed recorded for checking the oxidation state of Mn atom.

XANES spectra were normalized to the high part of the spectrum (around 100 eV above the absorption edge) after a linear background subtraction. XANES spectra at temperatures above and below the transition confirm the expected oxidation states as Pb^{2+}, Mn^{2+} and W^{6+}.

EXAFS spectra ($\chi(k)$) were obtained by removing the smooth atomic absorption coefficient (μ_0) by means of a cubic spline fit. The Fourier Transform (FT) of the k-weighted EXAFS spectra was calculated between 2.0 and 10.0 $Å^{-1}$ for the Pb L_3-edge and between 2.3 and 11.3 $Å^{-1}$ for the W L_3-edge using a sine window. Figure 1 reports the modulus of the FT of Pb_2MnWO_6 for Pb L_3-edge (left) and W L_3-edge (right) as a function of temperature. The FT spectra at the Pb L_3-edge show two main peaks between 1 and 3 Å that correspond to the first coordination shell (Pb-O). The intensity of both peaks decreases as the temperature increases from 300 K up to 500 K. There is no discontinuity crossing the transition, indicating a similar local structure for the Pb^{2+} atoms above and below the transition. Thus, the Pb environment is already distorted in the high temperature cubic phase. We note that the intensity of these first oxygen shell peaks should increase if a symmetrical oxygen environment occurs in the cubic phase. An opposite trend in the temperature evolution of the FT spectra is observed at the W L_3-edge (Fig. 1, right), as the intensity of the peak between 1 and 2 Å (first coordination shell W-O) slightly increases with increasing the temperature contrary to the behaviour expected from thermal vibrations. This is an indication that the W local structure becomes more regular above 445 K.

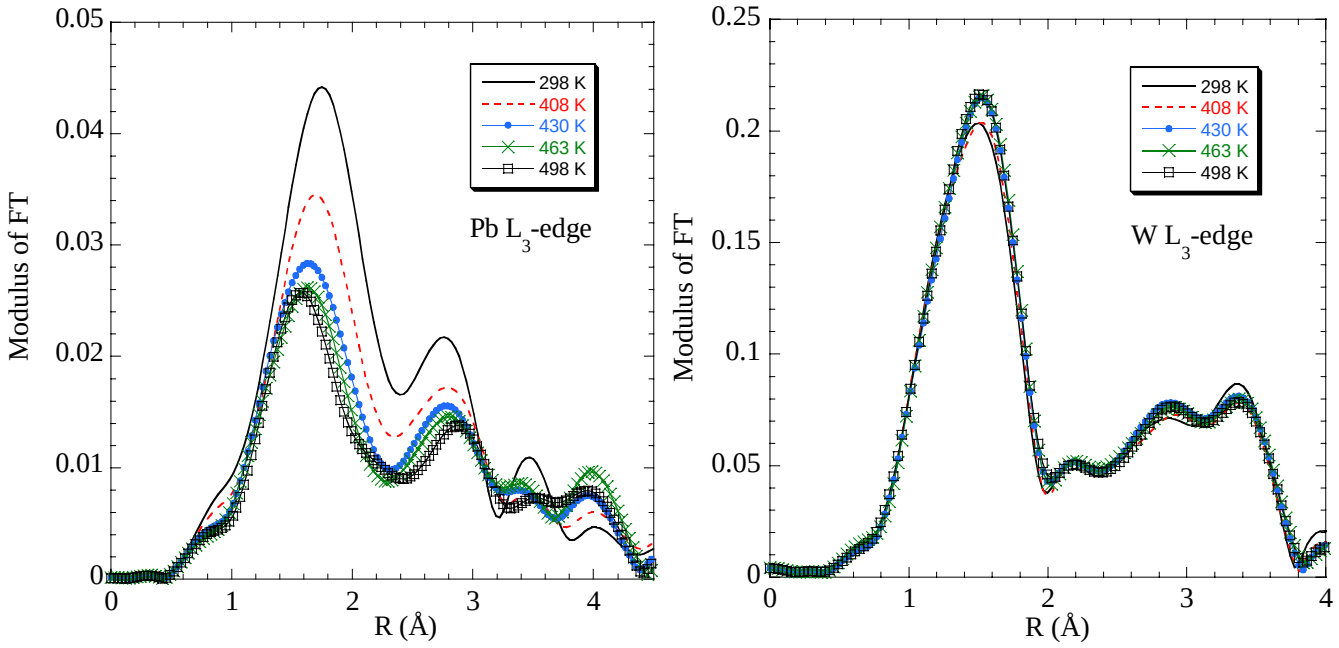

Figure 1. FT spectra (without phase shift correction) of Pb_2MnWO_6 at the Pb L_3-edge (left) and at the W L_3-edge (right) as a function of temperature across the structural transition at 445 K.

This preliminary analysis indicates that Pb-distortions, which are dynamically distributed in the cubic phase freezes at the transition, forcing W and Mn atoms to be distorted in the low temperature phase. This result will support an order-disorder structural type transition in Pb_2MnWO_6, though a quantitative analysis of the EXAFS data in order to confirm this point is still in progress.

[1] J. Blasco, R. I. Merino, J. García and M. C. Sánchez, J. Phys.:Condens. Matter 18, 2261 (2006).