ESRF	**Experiment title:** Structural characterization of phase transition in the $Pb_2Mn_{1-x}Co_xWO_6$ solid solution	**Experiment number**: **HC-1190**
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Report:

The experiments were carried out on five samples of the solid solution with x = 0, 0.25, 0.4 0.75, 1 and on an electric poled sample with composition Pb_2MnWO_6. The samples were closed in a fine capillary and the measurements were carried out in the temperature range 5-300 K with steps of 5 K. During the experiments we have found some issues with the cryostat set-up. In particular, the vibrations moved the sample during measurements in temperature making it necessary to centre the sample for each measurement. The procedure allows centring the sample in the direction perpendicular to the incident beam but unfortunately the direction parallel to the beam could not be calibrated in some cases, making the data in temperature unreliable.

The measurements performed on the Pb_2MnWO_6 (PMW) compounds confirm the non-centrosymmetric $Pmc2_1$ structure obtained from single crystal data[1]. On the contrary, the other compounds of the solid solution, containing both manganese and cobalt into the B site of the perovskite structure, present a centrosymmetric space group. In particular room temperature structure of the $Pb_2Mn_{0.6}Co_{0.4}WO_6$ compound was solved in the centrosymmetric *Pmcn* space group. The structural model is the classical orthorhombic double perovskite. This structure indicates an antiferroelectric nature of the system; furthermore from the analysis of the low temperature data, no phase transition with change of the system symmetry was detected down to 5 K. The same RT structure was found for the other two compounds of the solid solution and the structure is maintained down to the lowest temperature reachable by the instrumental set up. None of the solid solution compound presents new extra reflections down to 5 K. The analysis of the cell parameters versus temperature indicates some interesting features but since the experimental problems described above more physical characterizations are required to confirm or disprove the transitions, nevertheless any of the observed anomalies indicates a change of the system symmetry.

More interesting are the measurements conducted on the poled-PMW sample. This compound is a ferrielectric system characterized from the presence of two lead sublattices with different distortions[1]. In order to investigate the existence of a persisting effect of the application of a high electric field to the system, transmission diffraction experiments were performed on a thin sintered sample (t = 200 μm) metalized and

poled at 2 kV. The obtained diffraction pattern does not show significant changes of the reflection intensities with respect to the un-poled sample, instead some new weak reflections rise up by cooling below 230 K as shown in figure 1.

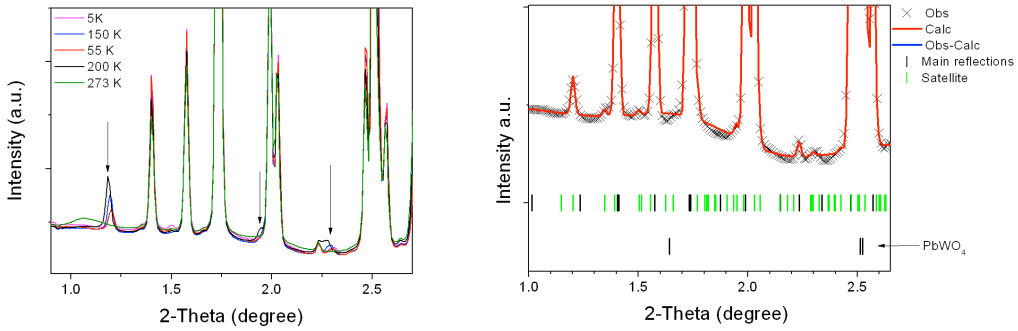

Figure 1 Left) Selected SPXRD patterns at low angle of the poled sample. Arrows indicate the satellite reflections arising below 230 K. Right) Le Bail fit of the 4 K data with the proposed modulation vector.

From the index with the k-search software and a Le-Bail fit of the 4 K data with the Jana2006 software, was obtained a modulation vector κ=(0.4388(2), 0.25, 0). By considering the modulation vector and the space group of the parent structure, the possible superspace group for the modulated structure is $P2_1(\alpha\beta 0)0$ (unique axis ***c***) corresponding to the V1 representation. Unfortunately owing to the small number and to the weakness of intensity of the observed reflections, it was not possible to obtain a plausible model for the incommensurate phase. In figure 2 are shown the integrated intensity as function of the temperature of selected reflections. The main reflections, attributable to the average nuclear structure, follow a classical behaviour increasing the intensity due to the reduction of the atoms ADP's. On the contrary the satellite reflections have a completely different behaviour. After the rise of the satellite peaks below 230 K the intensity decrease monotonically down to 80 K where start to rise again. The indication of extra reflections and the peculiar intensity evolution are indication of changes, with respect to the un-poled sample, of the crystal structure induced by the electric field. More physical characterizations are on going to better study the effect of the electric field on the crystal structure and on the system physical properties.

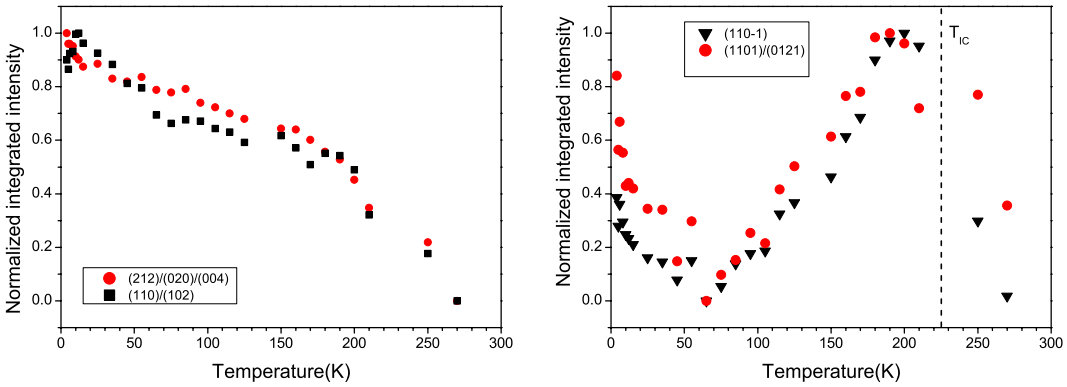

Figure 2 Integrated intensity of selected main reflections (left panel) and satellite (right panel) the index was conducted on the base of the 4 K modulation vector. The dot line indicates the appearing of the satellite reflection at 230 K.

Reference:

[1] Orlandi F.; Righi L.; Cabassi R.; Delmonte D.; Pernechele C.; Bolzoni F.; Mezzadri F.; Solzi M.; Merlini M. and Calestani G. Inorg. Chem. (2014) 53, 10283−10290