ESRF	**Experiment title: Structural and Microstructural study of intrinsically inhomogeneous manganites.**	**Experiment number**: HE1856
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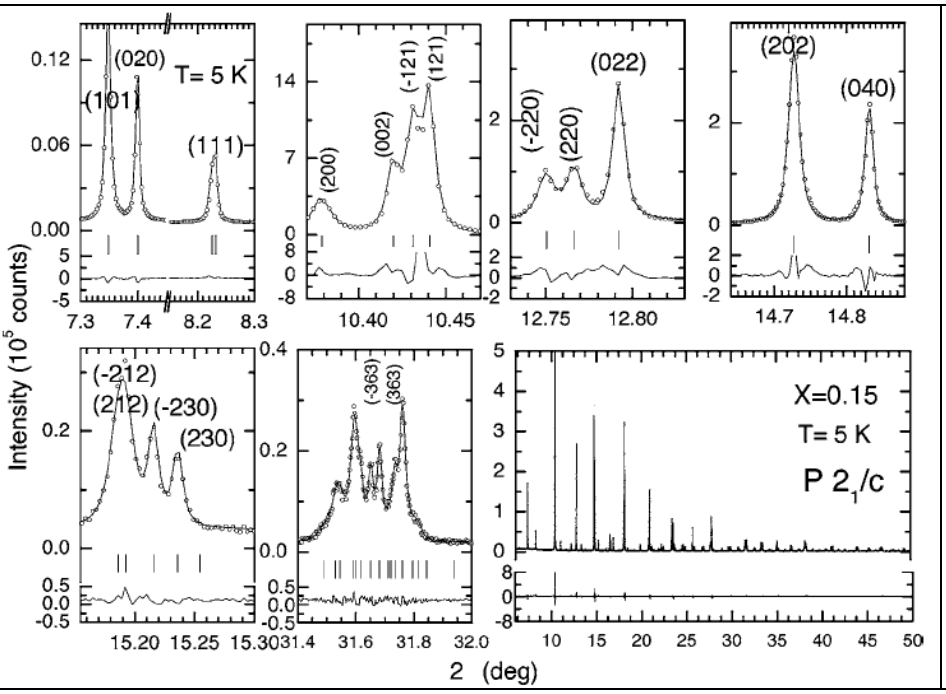
Report:

The very high resolution of ID31 beamline has allowed us to deeply investigate two families of compounds that are, at present, of high interest within the manganites family. With these studies, we have, once more, evidenced the deep relation between the electronic behaviour and the structural details of highly correlated oxides like manganites.

The first family studied corresponds to $La_{1-x}Ca_xMnO_3$ series in the region of low doping level. In contrast with the interest that the scientific community demonstrated on low Sr doped $La_{1-x}Sr_xMnO_3$ series, structural studies on Ca low doped compounds are scarce. One of the reasons responsible of this fact is that these compounds present quite easily non-stoichiometry (cationic vacancies). We have overcome this problem by annealing the samples under He atmosphere. This method allowed for the study of stoichiometric compounds and the precise determination of their structural properties at low temperatures. Therefore, we were able to visualize that the fact that when static Jahn Teller distortion appears, for the doping region $0.13 \leq x \leq 0.175$, the system undergoes an orthorhombic ($T > T_{JT}$) to monoclinic ($T < T_{JT}$) transition as evidenced by the splitting of (*hkl*) reflections with *h* and *k* different from 0 (see Fig. 1). Additionally, the space group below this transition is the $P\ 1\ 1\ 2_1/a$ (no. 14), presenting two different sites for Mn and two different sites for basal oxygen. This leads to the coexistence of two crystallographically different Mn ions in alternating planes along *b* axis ($b \sim 2a_p$). Based on the analysis of Mn-O bond distances obtained by NPD we propose that one site corresponds to Mn^{3+} ions and the other to a mixture of Mn^{3+} and Mn^{4+}.



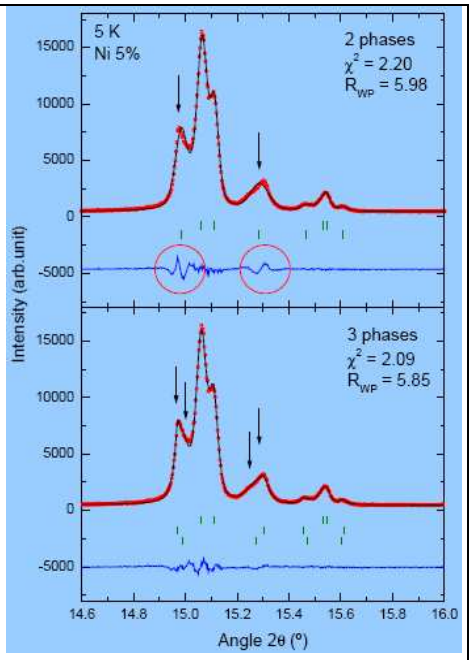


Fig 1 (left): Rietveld plot of $La_{0.85}Ca_{0.15}MnO_3$ at T=5K. The splitting of (*hkl*) peaks with *h*, *k* ≠ 0 are shown.

Fig 2 (right): Comparison of the pattern of $Pr_{0.50}Ca_{0.50}Mn_{0.95}Ni_{0.05}O_3$ compound refined using two and three phases.

On the other hand, we have measured four members of the family $Pr_{0.50}Ca_{0.50}Mn_{1-x}Ni_xO_3$ with x=0.005, 0.01, 0.03 and 0.05. We have found that, in contrast with previous works on different Mn substituted compounds like Cr, Ga, Co, etc, reporting the coexistence of two phases, that three phases are necessary to obtain a satisfactory fit of the collected data. In addition to an undistorted (and ferromagnetic according to NPD data) phase we have found two distorted phases. Their cell distortion is that of charge/orbital ordered half doped manganites. In addition, one of these two phases (the less distorted) is strongly strained and presents quite broad reflections. In addition, we did also measure $Pr_{0.50}Mn_{0.99}Ti_{0.01}O_3$ to compare with the case when the substituting ion has no *d*-electrons (as Ti^{4+}). For this compound we found two structural transitions on cooling. The first takes place at TCO and corresponds to the formation of two coexisting phases (no justification for a third phase was found), both present the typical distortion of CO half-doped manganites and anisotropic strain broadening, the more distorted being less strained than the less distorted. The second transition consists on a sudden change of the phase fractions that evolve towards the phase with strongest distortion. We have found that the superstructure peaks due to CO in the less distorted phase are very broad (more than expected from strain), signalling a short ranged charge ordering (~20 nm) in this phase.

References:

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