



	Experiment title: Structural investigation of the pressure induced insulator-to-metal transition in NaMn ₇ O ₁₂	Experiment number: HS-4594
Beamline: ID09	Date of experiment: from: 14/06/12 to: 17/06/12	Date of report: 07/01/13
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Report:

NaMn₇O₁₂ belongs to the class of the so called “Quadruple-perovskite” manganites, having general formula AA₃B₄O₁₂. By the structural point of view these materials can be considered highly distorted perovskites characterized by A site cation ordering, where ¾ of the original perovskite A sites are occupied by Mn³⁺ ions in square planar coordination, a condition that requires the application of high pressure during the synthesis process [1]. The valence of the A ion tunes the Mn³⁺/Mn⁴⁺ ratio on the octahedrally coordinated B site, determining the crystal symmetry based on the specific charge and orbital ordering. In the case of NaMn₇O₁₂, the presence of Na⁺ on the A site induces a 1:1 ratio of Mn³⁺ and Mn⁴⁺ on the B site, producing below 175K a charge and orbital ordering scheme which is described by the *I2/m* monoclinic symmetry [2]. Above 175 K the symmetry is cubic (*Im-3*) as a consequence of the melting of charge and orbital ordering, induced by the delocalisation of the Mn³⁺ e_g electrons on the B site. In these conditions all the B sites become symmetry equivalent.

Conductivity measurements were performed on NaMn₇O₁₂ as a function of pressure in a DAC cell, indicating a reversible semiconductor-to-metal transition above 18 GPa (see figure 1, left panel). The nature of the transition is unknown, as a consequence single crystal XRD experiments were carried out in the 0.3-40 GPa range at the ESRF ID09 beamline, allowing

the refinement of the crystal structure with good accuracy. A DAC cell was loaded with helium, a $\text{NaMn}_7\text{O}_{12}$ single crystal of approximate dimensions $10 \times 10 \times 10 \mu\text{m}$ and a ruby crystal, used as internal pressure calibrant. The wavelength of the incident beam was set at 0.4146 \AA , and data were collected in the whole reachable portion of the reciprocal space. The diffracted intensities were integrated by using the CrysAlis software and the refined data indicate a smooth variation of the compressibility coefficient at the electrical transition (fig. 1, centre), without the evidence of a change of the $Im\bar{3}$ symmetry.

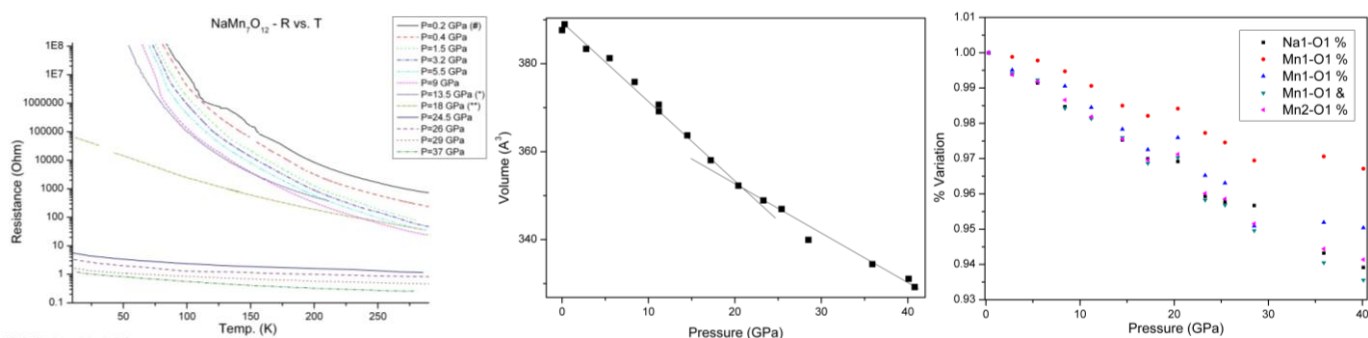


Fig. 1. Left: $\rho(T)$ curves collected at different values of applied pressure. Centre: cell volume as a function of pressure. Right: Selected bond length variations plotted as a function of pressure.

The process involves in particular the short Mn-O bond of the square planar coordinated site (Mn1 in fig. 1), showing a lower compressibility with respect to all the other cation-anion bonds, decreasing in the 0.3-25 GPa pressure range, then reaching an almost constant value (fig. 1, right panel). For what concerns the electrical properties of the system, a role could be played by the Mn-O-Mn angle, showing an anomaly in the pressure range where the electrical transition is observed. Ab-initio calculations taking as a starting point the structural data collected at ESRF are currently in progress, with the aim of understanding the nature of the metal-semiconductor transition allowing to relate the observed structural and electric properties.

References:

- [1] Marezio, M.; Dernier, P.D.; Chenavas, J.; Joubert, J.C., *J. Solid State Chem.* **1973**, *6*, 16.
- [2] Prodi, A.; Gilioli, E.; Gauzzi, A.; Licci, F.; Marezio, M.; Bolzoni, F.; Huang, Q.; Santoro, A.; Lynn, J.W., *Nat. Mater.* **2004**, *3*, 48.