



**Experiment title:** Synchrotron X-ray study of structure and cation distribution in  $RE_{1.2}Sr_{1.8}Mn_2O_7$ .

**Experiment number:**

CH195

**Beamline:**

BM16

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9

**Local contact(s):**

Andy Fitch

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### Names and affiliations of applicants (\*indicates experimentalists):

R.Seshadri\* and C Martin

Laboratoire CRISMAT, ISMRA

6 Boulevard Maréchal Juin

Caen 14050, France

seshadri@crismat.ismra.fr & martin@crismat.ismra.fr

### Report:

While the original proposal envisaged the collection of data on three different samples (RE = La, Pr, Nd) at (totally) four different wavelengths, the final strategy decided upon was to collect data on only one of the samples,  $La_{1.2}Sr_{1.8}Mn_2O_7$ , but at three wavelengths near the La K edge in the vicinity of  $\lambda = 0.3 \text{ \AA}$ , and one data set far from the edge ( $\lambda \sim 0.4 \text{ \AA}$ ). The near edge wavelengths were chosen by scanning the fluorescence yield from the sample as a function of the monochromator angle.

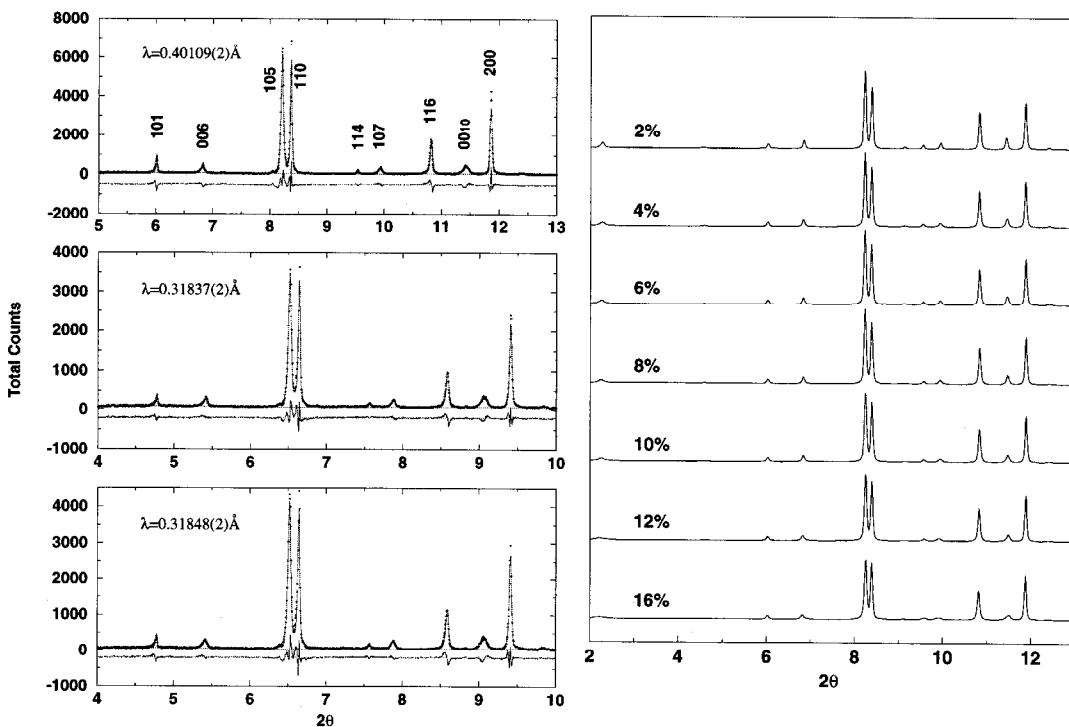
The idea of the experiment was to verify what had been proposed based on lab data, that the RE and Sr in the structure occupy two different sites, and while stoichiometry does not permit their ordering over these two sites, there can nevertheless be preferential distribution. This distribution affects the in-plane MnOMn bond angle and therefore is crucial to factors such as the in-plane d band stiffness. It would also affect Mn - Mn (double) exchange.

Data were collected at room temperature in the Debye-Scherrer geometry with the sample in a 0.3 mm glass capillary. The use of small wavelengths obviated the need for absorption corrections. The off-edge data were refined using the Rietveld program XRD (J.F.Berar, ESRF) and could be treated routinely except that the very high instrumental resolution showed up considerable 001 broadening. The near edge data were treated in two ways; the first, by refining  $f'$  and using tabulated  $f''$  values to account for the anomalous scattering. The second, and possibly more elegant scheme was to use a special feature of XRD that allows refinable parameters to be expanded as a linear polynomial in some dummy variable. This permitted the treating of the anomalous scattering as a perturbation on the normal.

The results were consistent with a slight excess of Sr in the 12 coordinate *A* perovskite site within the double perovskite unit of the structure. We have noted earlier (Seshadri et al. *J. Mater. Chem.* 6 (1996) 1585) that as the rare-earth becomes smaller, the propensity of the larger *Sr* to occupy the 12 coordinate site increases, driven by a tendency of the *MnO*<sub>2</sub> sheets to remain flat.

We have also exploited the very high resolution of the SXPD pattern to quantify the defect structure, which from microscopy we know to comprise extra perovskite slabs that result in faulting along along *C*: Using the computer program *DIFFAX* (M.M.J. Treacy, NEC Research, Princeton, NJ, USA) we have simulated the SXPD patterns for different percentages of the extra perovskite intergrowth, and arrive at the estimate, that approximately every ten or so unit cells along the *c* axis are interrupted by a stacking fault corresponding to the insertion of an (La,Sr)MnO<sub>3</sub> unit. In a highly lamellar material such as the present one, this is a negligible percentage of stacking faults, and the interpretation of properties is safely achieved within the hypothesis that the phase is pure.

The panel on the left shows typical SXPD data at different wavelengths along with the fitted Rietveld profiles. The panel on the right shows simulated (*DIFFAX*) patterns for different probabilities for the insertion of adventitious perovskite intergrowths.



A paper has resulted from this work:

R.Seshadri, M.Hervieu, C.Martin, A.Maignan, B.Domenges, B.Raveau and A.Fitch, A study of the layered magnetoresistive perovskite,  $La_{1.2}Sr_{1.8}Mn_2O_7$  by Synchrotron X-ray powder diffraction and high resolution electron microscopy.