

## Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:  
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

#### Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

### Deadlines for submitting a report supporting a new proposal

- 1<sup>st</sup> March Proposal Round - **5<sup>th</sup> March**
- 10<sup>th</sup> September Proposal Round - **13<sup>th</sup> September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

#### Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

#### Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Probing Charge and Orbital Ordering in the Solid Solution of the Multiferroic $\text{Ca}_{1-x}\text{Na}_x\text{Mn}_3\text{Mn}_4\text{O}_{12}$	<b>Experiment number:</b> HC2331
<b>Beamline:</b>	<b>Date of experiment:</b> from: 09/05/16 to: 13/05/16	<b>Date of report:</b>
<b>Shifts:</b>	<b>Local contact(s):</b> Andy Fitch	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists):  Mark Senn* Warwick University, UK Wei-tin Chen* National Taiwan University, Taiwan		

## Report:

### Proposal Summary:

Multiferroics – materials where an electric polarisation may be switch by the application of a magnetic field – will undoubtedly be the materials of choice for future generations of solid state storage devices, driving both capacity and data access speeds ever higher. To date,  $\text{CaMn}_7\text{O}_{12}$  is the multiferroic where this coupling between electric and magnetic polarisation is most pronounced. On the other hand, this coupling is absent in isostructural  $\text{NaMn}_7\text{O}_{12}$  due to the subtle change in average Mn valence state. We seek to learn more about the nature of this coupling mechanism by studying the solid solution  $\text{Ca}_{1-x}\text{Na}_x\text{Mn}_3\text{Mn}_4\text{O}_{12}$  by high resolution powder diffraction. Our results will allow us to ascertain the nature of any charge and orbital ordering which are intrinsically linked to the observed multiferroic phenomena and will point towards how new and improved materials can be designed.

### Results:

During our beamtime on high resolution powder diffractometer ID22 we measured a solid solution series  $\text{Ca}_{1-x}\text{Na}_x\text{Mn}_3\text{Mn}_4\text{O}_{12}$  and  $\text{La}_{1-x}\text{Ca}_x\text{Mn}_3\text{Mn}_4\text{O}_{12}$  at  $\Delta x = 0.1$  and  $0.2$  respectively as a function of temperature (from 700 K down to 10 K). The beamtime was highly successful with typical samples displaying peaks with FWHM of  $1/100^{\text{th}}$  degree at  $\sim 20$  degrees 2-theta with clearly resolvable diffraction peaks out to a d-spacing of  $0.45 \text{ \AA}$ . This has enabled us to map out the crystallographic phase transitions associated with the change of valence state on  $\text{Mn}^{\text{B}}$  implied by the doping (change in  $x$ ). Our work evidence four low temperature regmies that are coupled to the orbital ordering on the B site. At  $\text{Mn}^{3+}$  and  $\text{Mn}^{3.25+}$  our results are consistent with C-type orbital ordering in planes perpendicular to the [001] and [111] directions resepectivley. However at  $\text{Mn}^{3.5+}$  and  $\text{Mn}^{3.35+}$  two pseudo symmetric monoclinic phases are observed. Our Rietveld refinemetns suggest that these have distinct strucutre from each other. Single crystal experiemnts to ascertain more precisley the

microscopic nature of these orbital ordered phases will shed further detail on this. Work on analysing the data is ongoing and we anticipate it will lead to a journal article publication.

During our beam time we also measure analogous compound  $\text{HgMn}_7\text{O}_{12}$  at 10, 80, 300, 500 and 700K, demonstrating a sequence of novel charge transfer and charge and orbital ordering transitions (Fig 1) that drives and improper ferroelectric coupling (Fig 2). These results have now been published in PRB (Improper ferroelectric polarization in a perovskite driven by intersite charge transfer and ordering. W.-T. Chen, C.-W. Wang, H.-C. Wu, F.-C. Chou, H.-D. Yang, A. Simonov, and Mark S. Senn\*, Phys. Rev. B 97 (2018), 144102.)

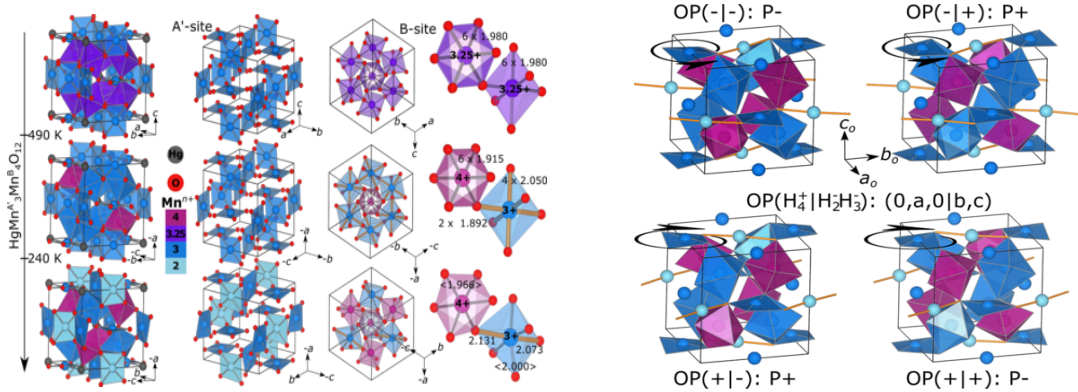


Fig1: The structure of the phases of  $\text{HgMn}_7\text{O}_{12}$ . Top panel, high-temperature cubic aristotype  $\text{Im}\bar{3}$ ; middle,  $\text{R}\bar{3}$  orbital disorder phase; bottom,  $\text{Pnn}2$ , double charge-ordered, polar phase. The color key indicates the formal valence states of Mn sites assigned based on analysis of the crystal structure. The orange bonds represent the Jahn-Teller long bonds ( $d_z$  orbital order) of the  $\text{Mn}^{3+}$ . The  $\text{R}\bar{3}$  phase has four apparent Jahn-Teller long bonds in the unit cell which are actually an average of two short and two long bonds, observed on account of the orbital disorder. There is a charge transfer of one electron per unit cell from B- to A'-site on going from  $\text{R}\bar{3}$  to  $\text{Pnn}2$ , which acts to remove the orbital disordered state and facilitates the double charge order on the A'- and B-site.

Fig2: The origin of the improper polarization in  $\text{HgMn}_7\text{O}_{12}$ . The reversal of one or the other of the two primary order parameters responsible for the double-charge ordering ( $\text{H}+4$  and  $\text{H}-2\text{H}-3$ ) on the A'- and B-sites is sufficient to reverse the direction of the polarization (P); reversal of both order parameters returns the polarization to its initial state. The short second-nearest-neighbor Mn-O distance ( $\sim 2.4\text{\AA}$ ) that is indicative of the  $\text{MnA}'^{2+}$  state is shown in yellow.

