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 using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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.

	Experiment title: Bi-K edge Anomalous Differential PDF study to unveil the short and medium range environment of Bi in multiferroic BixCo2-xMnO4 oxides	**Experiment number**: CH-4018
Beamline: ID22	**Date of experiment**: from: 02.07.2014 to: 04.07.2014	**Date of report**: 26.08.14
Shifts: 6	**Local contact(s)**: Christina Drathen	*Received at ESRF:*

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Report:

The Bi-doped cobalt, manganese oxide, $Bi_xCo_{1-x}MnO_4$, is a candidate multiferroic compound. Specifically, literature [1a] reported ferro-magnetism below $T_{FM}=180$ K and ferroelectric ordering up to $T_{FE}\sim400$ K, leading to magneto-electric behaviour. The authors suggested a diffusive phase transition below the electric behaviour anomaly [1b], but, to date, no structural characterization was known other than room-temperature XRPD as a function of doping.

XPRD patterns were collected on a BCMO sample (x=0.2, referred to as BCMO-2) and the undoped Co_2MnO_4 (CMO) in a temperature range from 100 to 450 K. Samples were scanned by $3°$ min^{-1} while heated at 1 K min^{-1}. During the same T ramp, additional "long" scans ran by $1°$ min^{-1} at fixed 100, 200, 350, and 450 K. A BCMO sample with x=0.1 composition (BCMO-1) underwent a "long" scan at 293 K. Wavelength used was $\lambda=0.2958$ Å in each case.

The reciprocal space analysis has been performed using the software GSAS **[2]** and its graphic interface EXPGUI **[3]**. The samples were single-phase spinels throughout the temperature range and for each composition but some trends are worth being remarked.

The curves in Figure 1 show the cubic cell parameter increasing for both CMO and BCMO-2, following a similar trend. For $100 < T < 200$ K, cell parameter slowly increases for both samples; a sharp cell expansion is found above 200 K, with a slower segment observed at ~340 K for BCMO-2 and a marginally slower rise just under 400 K for CMO. Such inflection points seemingly reflect the reported magnetic and electric anomalies referred to above, which were also paralleled by our ESR measurements. The values for the cell parameter from the scans at fixed T perfectly fit into the values from the ramp scans and are included in the figure below. Two isotropic thermal parameters were applied to the A and B cations in BCMO-2 and their evolution is shown in Figure 2. Both fixed-T measurements and heat ramp measurements show the atomic displacement at the tetrahedral site being more dependent on temperature than at the octahedral site. The more sloping *msd* at the tetrahedral site is confirmed by the ramp scans, though such data are obviously more affected by the uncertainty.
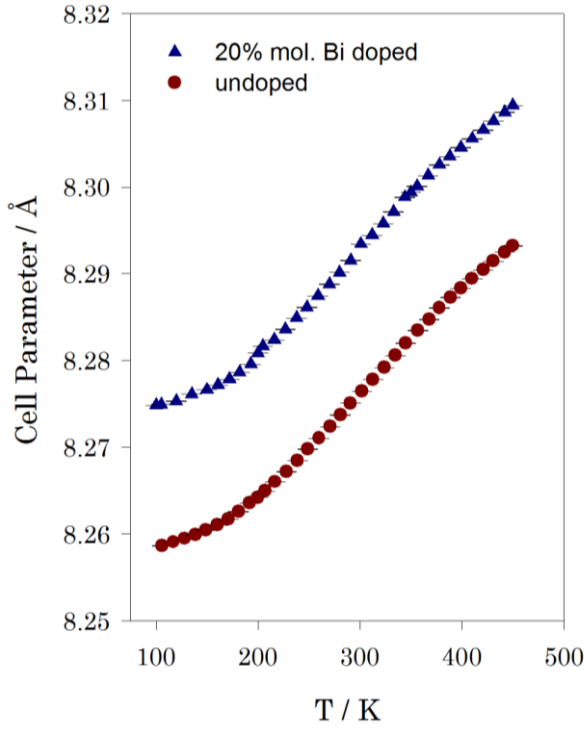
Figure 1: Temperature evolution of cell parameters for the doped (blue, triangles) and the undoped (red, circles) samples.
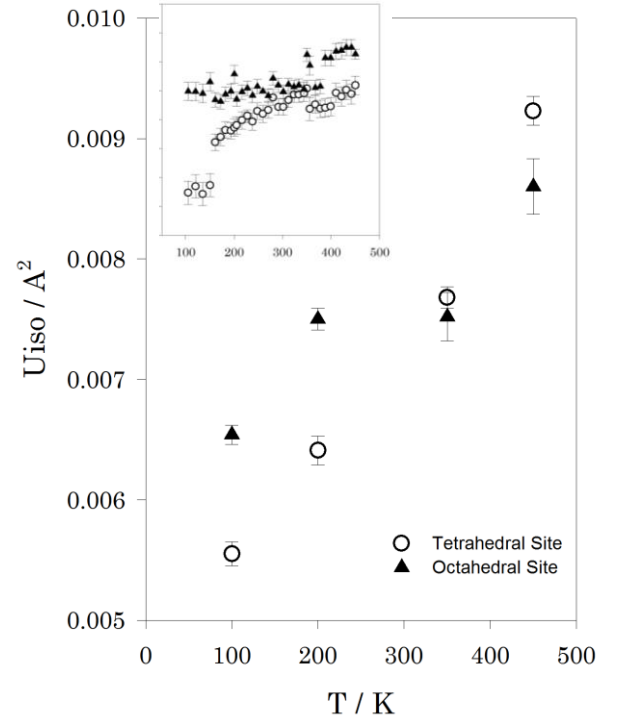

Figure 2: Temperature evolution of the *msd* parameters for the A (tet) and B(oct) spinel sites in BCMO-2 long scans. Inset: parameters from the ramp scans.

As to the refinement strategy, better fits were obtained by accounting for some Bi^{3+} occupying the tetrahedral spinel site (about one-third of the total Bi^{3+}). This clashes with the commonly accepted octahedral occupation of Bi^{3+} and will be further clarified in the next leg of the experiment. Still, no clear indication can be drawn about site occupation from the reciprocal space analysis, especially for what concerns the Co and Mn ions.

Another noteworthy parameter is the atomic coordinate of the oxygen ion in the *32e* site of the spinel structure. Being the cobalt manganite spinel space group centro-symmetric, and in absence of sheer structural changes across the magnetic and electric transitions for such compounds, the evolution of $x=y=z(O)$ position could be a marker of a microscopic polarization, as reported for the $EuTiO_3$ system [4]. In fact, electric properties reported in [1] were attributed to a relaxor behavior of the CMO/BCMO system.

T-evolution of $x(O)$ for both BCMO-2 and CMO is shown in Figure 3. A slow contraction of the oxygen position is noticeable for CMO, with good agreement between the fixed-T scans and the heat-ramp ones.

Figure 2: Oxygen atom coordinate in BCMO-2 (blue) and CMO (red) as a function of T. Smaller symbols are used for the values from ramp scans.

In the doped compound, x(O) is virtually constant with temperature well within the uncertainties. Further analysis of the atomic positions was carried out in the other leg of the experiment, dealing with PDF analysis of the local structure.

As a further remark, the cell parameter, oxygen coordinate values were compared between the three Bi^{3+} concentrations (0, 0.1, 0.2). What is most evident is that the cell expansion is negligible between CMO and BCMO-1, while the oxygen coordinate is shifted for the BCMO-1 already.
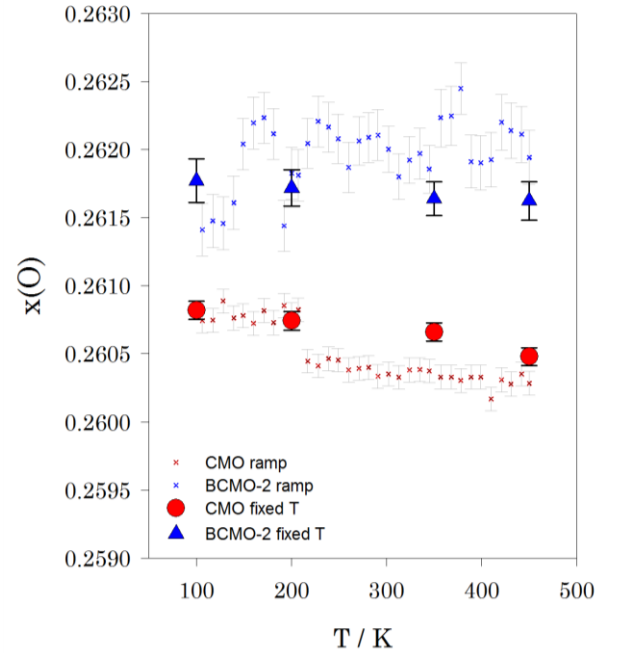
REFERENCES

[1] a) Rajeevan, N. E., Kumar, R., Shukla, D. K., Choudhary, R. J., Thakur, P., Singh, A. K., (2011) *Journal of Magnetism and Magnetic Materials*, *323*(13), 1760–1765; b) Rajeevan, N. E., Pradyumnan, P. P., Kumar, R., Shukla, D. K., Kumar, S., Singh, a. K., (2008). *Applied Physics Letters*, *92*(10), 102910.

[2] Larson, A. C.; Von Dreele, R. B. *General Structural Analysis System (GSAS)*; Los Alamos National Laboratory Report LAUR 86-748; Los Alamos National Laboratory, 2004.

[3] Toby, B. H. *J. Appl. Crystallogr.* **2001**, *34*, 210–214.

[4] Allieta, M., *et al*. (2012) *Physical Review B*, *85*(18), 184107.