ESRF	Experiment title: **Charge /orbital ordering and phase segregation in Bi-based manganese perovskites**	**Experiment number**: **CH-847**
Beamline: **BM16**	**Date of experiment**: from: **7/IV/00** to: **11/IV/00**	**Date of report**: **30/IX/00**
Shifts: **12**	**Local contact(s)**: **E.Dooryee**	*Received at ESRF:*

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Phase segregation tendencies seems to occur and have been theoretically predicted in several zones of the manganites phase diagram. The main objective of this study was to characterise the structural changes and to explore phase segregation in Bi based manganese perovskites. Although the size of Bi^{3+} ion (1.24 Å) is very similar to La^{3+} (1.22Å), the magnetotransport properties of La and Bi based manganites present deep differences probably due to the $6s^2$ lone pair of Bi^{3+} ion. Despite $La_{1-x}Sr_xMnO_3$ samples are metallic for x>0.15, $Bi_{1-x}Sr_xMnO_3$ are insulating at any doping. Data were collected on $Bi_{1-x}Sr_xMnO_3$ samples with x=1/3, 1/2, 2/3, $Bi_{1-x}(Ca_{2/3}Sr_{1/3})_xMnO_3$ and $Bi_{1-x}(Ca_{1/3}Sr_{2/3})_xMnO_3$ with x=1/3, 1/2 . A minor part of the beam time was used to collect data on $RBaCo_2O_{5+\delta}$ (R=Pr, Nd) samples prepared in both air and Ar atmospheres. Several patterns were obtained between 300 and 400 K, across the metal-insulator transition temperature at ~370 K.

A short wavelength, 0.450294(2) Å, was used to minimise the absorption due to the heavy cations. Capillar diameters ranging from ϕ =0.3 to 0.5 mm were used depending on the sample. The beam size on sample was 7x0.8 mm for measurements taken at room temperature, and 6x0.8 mm for high temperature measurements. For the latter, the working temperature was set using the hot air stream. Each SXRD run took about 3 hours to have good statistics over the angular range 6 to 43º (2Θ). Two kind of patterns were collected: (1) Patterns with range and statistic suitable for a full structural Rietveld refinement were collected averaging several recording cycles, tipically counting for ~150-180 min (overall) [2-40º (2Θ)]. (2) Shorter SXRD patterns (collected in ~20-30 min [4-25º (2Θ)] were also taken in order to determine the evolution of the unit cell parameters and phase segregation across the orbital ordering transition temperatures. Patterns were collected over the temperature range 295-650 K.

A two phase coexistence had been previously detected at RT from previous D2B and BM16 data on $Bi_{0.5}Sr_{0.5}MnO_3$. One of the phases presents CE type magnetic structure ,

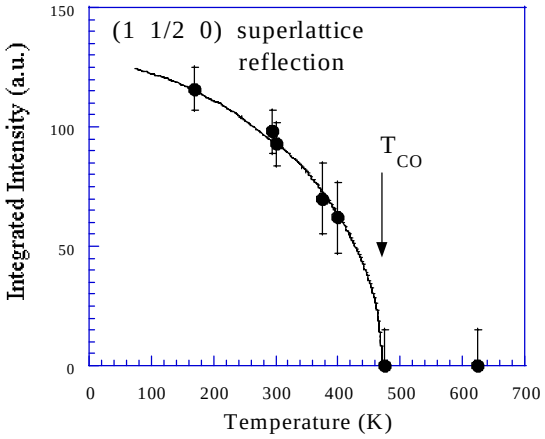

Fig. 1. Integrated intensity of the (1 1/2 0) superlattice peak as a function of temperature for $Bi_{0.5}Sr_{0.5}MnO_3$

while the second phase presents A-type magnetic structure. The charge-ordered phase of the former and the orbital-ordered phase of second are extremely stable when heating the sample (T_{OO}≈490 K, anomalously high). On cooling the samples below the transition, the SXRPD patterns show the presence of superlattice reflections which can be indexed by doubling the cell along *b*. As an example, the integrated intensity of the (1 1/2 0) superlattice peak is shown as a function of temperature in Fig. 1. As illustrated in Fig. 2, these samples splits into two macroscopic phases with different lattice parameters at T_{OO}. About this temperature the high resolution BM16 patterns are well described with a single Pbnm phase with microstrain. Further analysis will be reported elsewhere.(A manuscript has been submitted for publication in Phys. Rev. Letters).

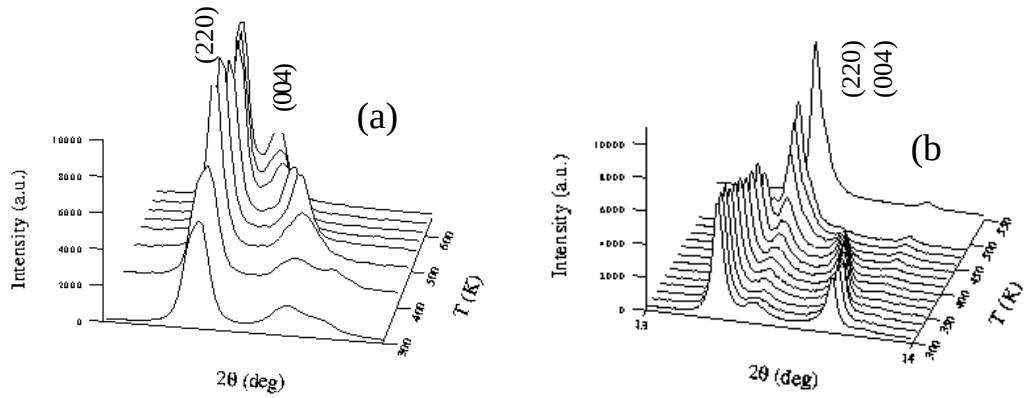

Fig. 2. Patterns for (a) $Bi_{1/2}Sr_{1/2}MnO_3$ and(b) $Bi_{1/2}(Sr_{2/3}Ca_{1/3})_{1/2}MnO_3$.

Below the metal-insulator transition the structure of $GdBaCo_2O_{5.5}$ (has been successfully refined (R_B=4.5% at 300 K) using the Pmm2 orthorhombic s.g. At 300 K the cell parameters are *a*=7.82653(4) Å, *b*=3.87627(2) Å and *c*=7.53574(3) Å, corresponding to a~c~2a_p and b~a_p (a_p is the unit cell of the primitive perovskite). The same s.g. successfully reproduces the diffraction patterns at 400 K above T_{MI}. We have found a disposition in (001) layers of the Gd and Ba ions and a concentration of the oxygen vacancies in the Gd planes. The evolution of the cell parameters is shown in Fig. 3. At T_{MI} an anisotropic change of the cell parameters and a sudden decrease of the unite cell volume can be clearly appreciated. Interestingly, the unite cell volume in the insulating phase is smaller than in the metallic phase. Further details about the structural and possible spin state changes at T_{MI}, oxygen vacancies ordering etc will be reported elsewhere.

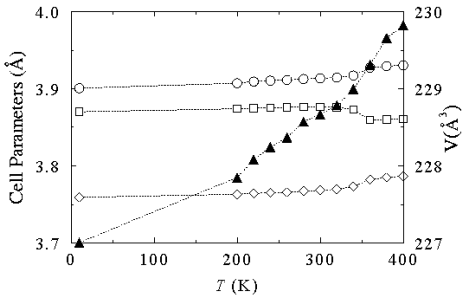

Fig. 3. Thermal evolution of the lattice parameters and unit cell volume for $GdBaCo_2O_{5.5}$