ESRF	Experiment title: **Structural changes due to charge and orbital ordering in rare earth manganites and cobaltites: $R_{0.5}Ca_{0.5}MnO_3$ and $R_{0.5}Ba_{0.5}CoO_3$**	**Experiment number: CH-602**
Beamline: BM12	**Date of experiment:** from: **15/IV/99** to: **19/IV/99**	**Date of report:** **30/VII/99**
Shifts: 12	**Local contact(s):** **MASSON OLIVIER**	*Received at ESRF:*

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Report:

The main objective of this study was to characterise the structural changes and thermal behaviour of $Bi_{1-x}Ca_xMnO_3$ (x=2/3, 3/4, 0.85, 7/8), $Bi_{1-x}Sr_xMnO_3$ (x=1/2, 2/3) and $R_{0.5}Ba_{0.5}CoO_3$ (R=Pr, Gd) materials due to charge/orbital ordering at low temperature. To do that, many powder diffraction patterns at selected temperatures were collected with a short wavelength, 0.442377(2) Å, to minimise the absorption due to the heavy cations. The samples were loaded in borosilicate capillaries (ϕ =0.5 mm) and the standard cryostat was used to get the selected temperatures. The beam size was 7x0.8 mm. A second vertical re-alignment was necessary for each sample when temperatures were lower than 150 K. All other steps were programmed including the temperature control.

There were no problems with the beam, optic, diffractometer and cryostat (refilling) ! and many extremely good diffractograms. Patterns with range and statistic suitable for a full structural Rietveld refinement were collected averaging several recording cycles counting for ~180 min (overall) [2-40° (2Θ)]. Short patterns to determine the unit cell parameters and the microestructural and phase evolutions at the charge ordering temperatures (TCO) were collected in ~50 min [2-25° (2Θ)].

Some raw data have been fully analysed and others are currently under study. The series of highly doped manganites, $Bi_{1-x}Ca_xMnO_3$, has been studied and a selected part of the full Rietveld refinement plots is shown in Figure 1 above and below TCO. The RT structures are orthorhombic [$GdFeO_3$ type]. However, below TCO a monoclinic phase [previously unreported] appears for a given electron concentration (in the material). Because the high resolution of the synchrotron data, the phase ratios, unit cell parameters and in some cases the atomic positions could be refined for these strongly overlapped phases.

As an example, the orthorhombic peaks in the pattern for $Bi_{0.15}Ca_{0.85}MnO_3$ at 10 K were removed and the remaining peaks were autoindexed using TREOR90 in a monoclinic cell with M_{14}=76. The Rietveld refined unit cell parameters were [Pbnm, a=5.28375(6)Å, b=5.32027(7)Å, c=7.48290(8)Å, V=210.352(4)Å^3; $P2_1/m$, a=5.30881(4)Å, b=7.44383(5)Å, c=5.34186(4)Å, β=91.075(1)°, V=211.062(4)Å^3]. Full structural and microestructural data for this series will be soon reported elsewhere.

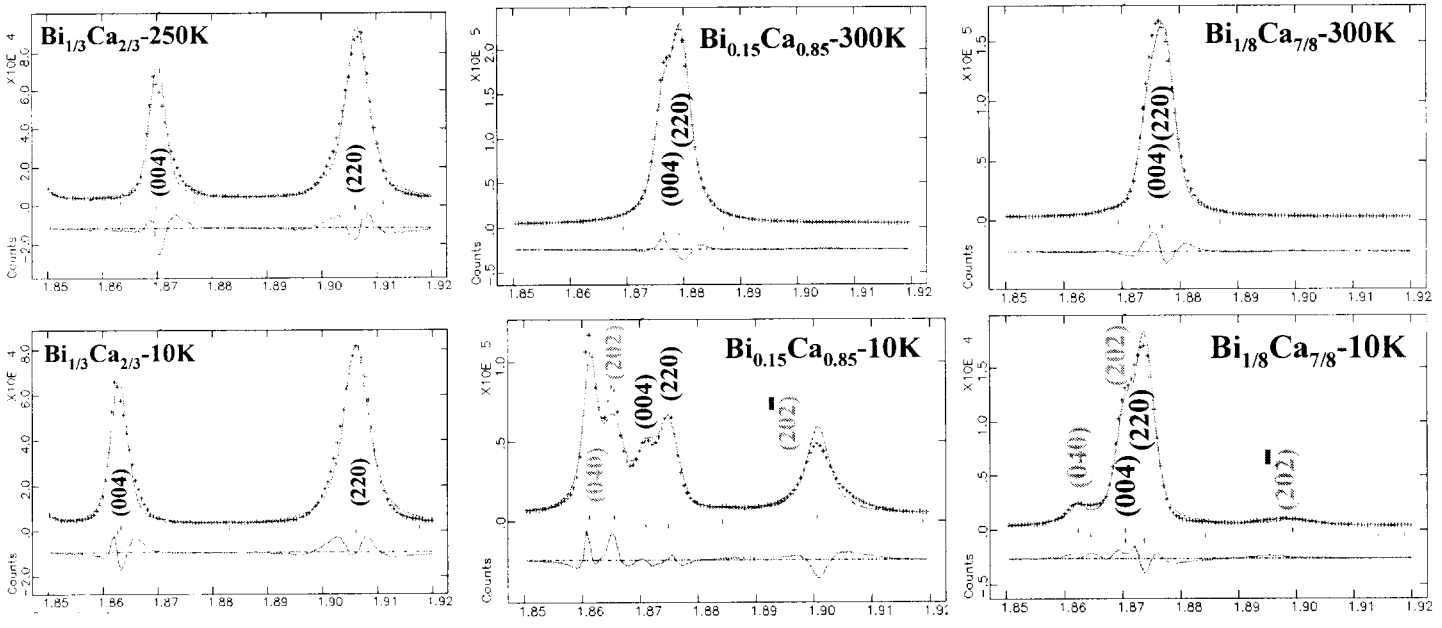

Figure 1. Enlarged view (in Å) for $Bi_{1-x}Ca_xMnO_3$ patterns showing "phase segregation" due to electron localisation at TCO, the new phase is monoclinic $P2_1/m$ (pale blue).

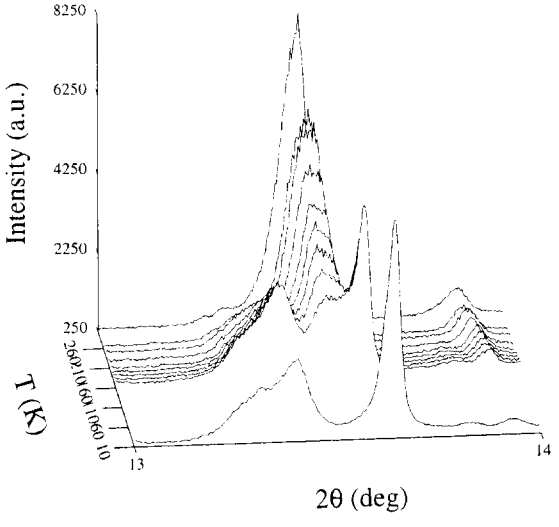

Figure 2. Patterns for $Bi_{1/4}Ca_{3/4}MnO_3$ showing the phase evolution at TCO

An astonishing example of phase evolution at TCO is shown for $Bi_{1/4}Ca_{3/4}MnO_3$ in Figure 2. The compound answers to the Mn^{3+}/Mn^{4+} ordering with very strong modification in the pattern.

On the other hand, and in spite of their similar compositions, the patterns for $\mathbf{R_{0.5}Ba_{0.5}CoO_3}$ (R=Gd, Pr) are quite different. The RT pattern for R=Gd has been indexed using TREOR in a simple orthorhombic cell [a=7.5364(6)Å, b=7.8273(7)Å, c=3.8786(6)Å, V=228.8Å^3] with M_{20}=139 and F_{20}=168 (0.005, 24). The pattern for R= Pr has also been indexed but in a much large (tetragonal) cell [a=7.8113(4)Å, c=15.2589(9)Å, V=931.1Å^3] with M_{20}=42 and F_{20}=47 (0.005, 87). The structural models and the temperature evolutions are being studied. Phase segregation is not observed in these compounds. The situation for R=Pr is much more complex than that for R=Gd. The superstructure peak which defines the large ordered cell strongly sharp with temperature indicating that the coherent diffraction domains growth when temperature is lowered. Further results will be reported elsewhere.