ESRF	**Experiment title:** In-situ XRD study of the High Pressure - High Temperature synthesis of the multiferroic $BiCrO_3$ compound: HP-HT phase diagram, and single crystal growth	**Experiment number**: CH-2675
Beamline: ID27	**Date of experiment**: from: 06/03/2008 at 8:00 to: 11/03/2008 at 8:00	**Date of report**: 08/10/2009
Shifts: 15	**Local contact(s)**: M. Mezouar	*Received at ESRF:*

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Report:

Aims of the experiment

The in-situ synthesis of the distorted perovskite $BiXO_3$ (with X = Mn and Cr) under high pressure - high temperature (HP-HT) conditions was studied. The main interests of these experiments were firstly to collect accurate information on the HP-HT phase diagram of $BiXO_3$ (phase transitions, optimal synthesis conditions, melting point) and secondly, to get thermodynamic data needed to achieve the single crystal growth of these compounds using the flux method based on boric acid H_3BO_3.

The experiment was carried out on the ID27 beam line using a MAR CCD detector at a wavelength of 0.173Å, using the Paris-Edinburgh cell with standard tungsten carbide anvils and 7 mm boron-epoxy gaskets. The starting mixtures were put into gold or platinum capsules (1.4 mm diameter and 2.4 mm height) specially fabricated by us for the ESRF experiment. To provide suitable conditions for the x-ray diffraction (XRD) patterns acquisition on an image plate detector of potential fast phase transitions or reactions during the heat treatments at fixed pressure, we worked at moderate heating rates (around 10°C/min). In order to reduce the exposure time to typically 30seconds, the radial Soller slits were generally not used.

Results on the in-situ study of the HP-HT synthesis and phase diagram of $BiCrO_3$

The initial powder was a stoichiometric mixture of Bi_2O_3 and Cr_2O_3. The pressure and temperature, estimated from the XRD peaks of BN and Au using their equation of state, was first increased up to 2 GPa, then the temperature was ramped to about 1000°C.

A 2D and 3D-illustration of the in-situ synthesis of $BiCrO_3$ at 2 GPa are shown on figure 1a and 1b, respectively. After an amorphization under pressure of the initial Bi_2O_3 and Cr_2O_3 powders, followed by a progressive recrystallization during the heating, two abrupt transitions are observed around 550°C and 670°C. The first one corresponds to the formation of $BiCrO_3$, and the second one is identified as a structural transition of remaining Bi_2O_3, from a monoclinic to a cubic symmetry.

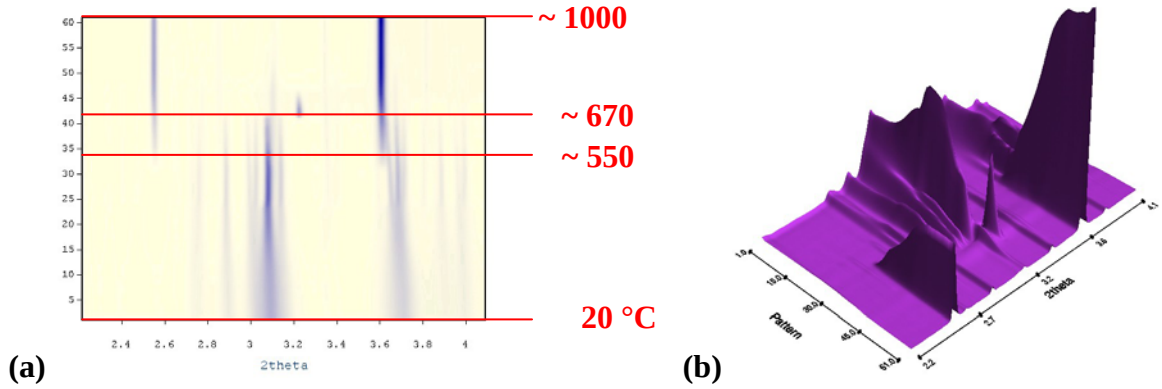


Figure 1 : In-situ synthesis of $BiCrO_3$ at 2 GPa : (a) 2D-illustration ; (b) 3D-illustration.

A similar experiment was carried out at 6 GPa. The data analysis is in progress.

Results on the in-situ study of the HP-HT synthesis and phase diagram of $BiMnO_3$

As for $BiCrO_3$, $BiMnO_3$ HP-HT synthesis was studied starting from a stoichiometric mixture of Bi_2O_3 + Mn_2O_3 at 4.5 GPa and 6 GPa. As shown on figure 2, after the broadening of the XRD peaks during the pressurization a first recrystallization of the initial reactants occurs, then at relatively low temperature an intermediate phase crystallized. The identification of this phase is underway. Then, at higher temperature the $BiMnO_3$ phase appears in its orhtorhombic form. When the heating is stopped at 4.5 GPa, $BiMnO_3$ undergoes a phase transition towards its monoclinic phase which is recovered after complete decompression. The 6 GPa experiment is not shown in this report.

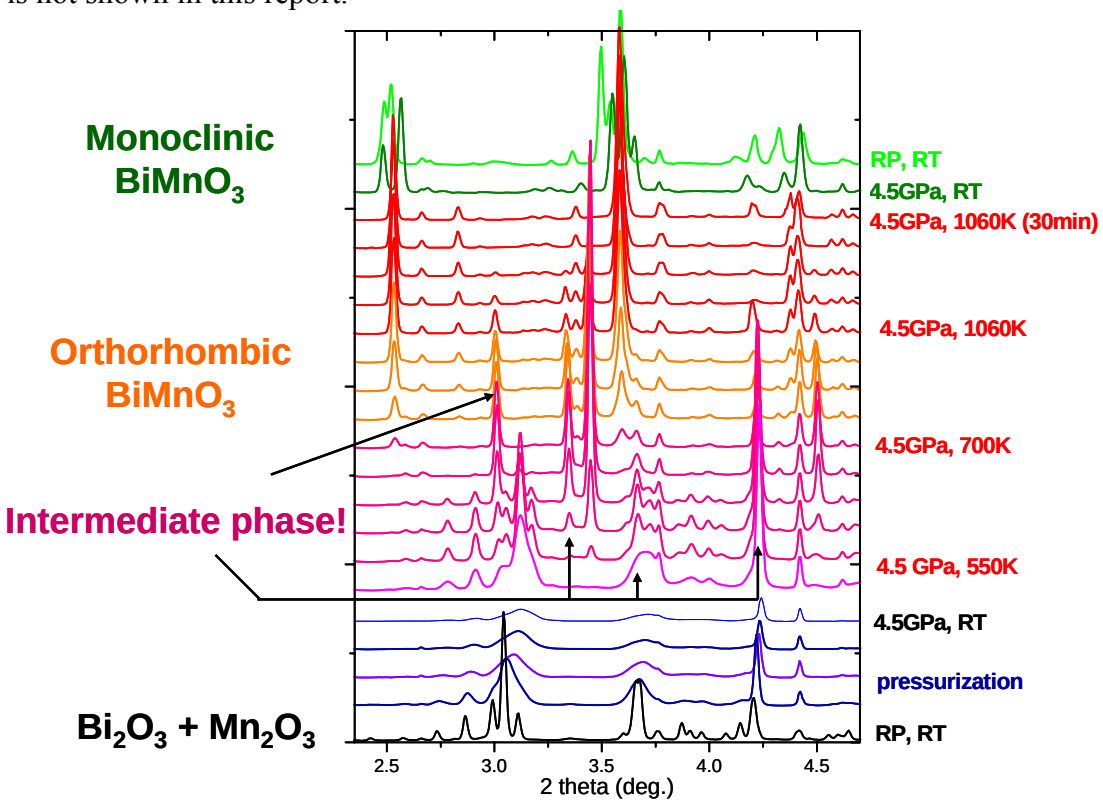


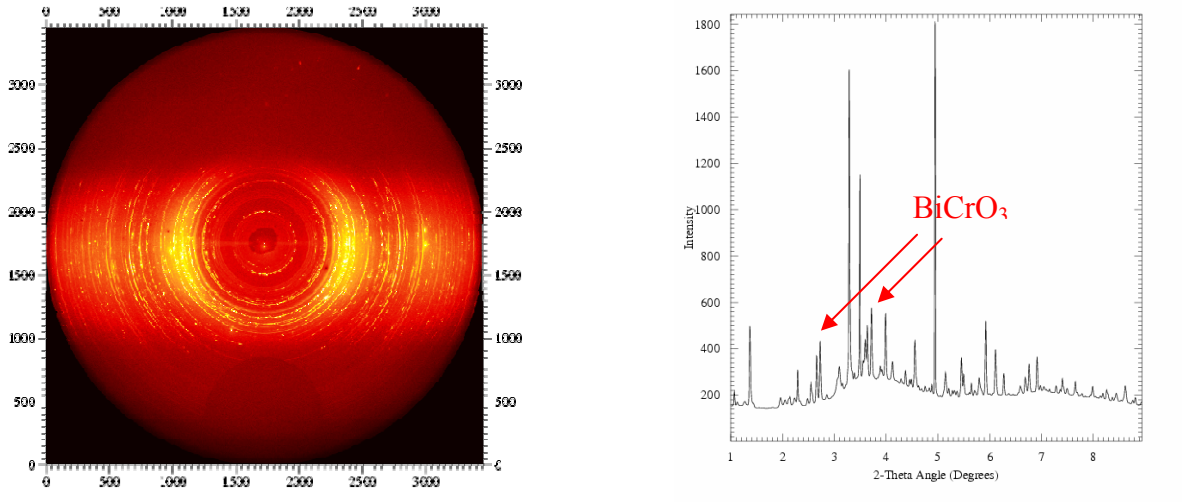
Figure 2 : In-situ XRD patterns acquired during the HP-HT synthesis of $BiMnO_3$ at 4.5 GPa.

Results on the study of HP-HT conditions for single crystal growth of $BiCrO_3$ and $BiMnO_3$

The initial mixture was Bi_2O_3 + Cr_2O_3 (or Mn_2O_3) + 5wt% of H_3BO_3. The pressure and thermal cycles were programmed as previously, except that after a dwell time at high temperature a very slow cooling rate was used to create adapted conditions for the growth of single crystals in the liquid.

At 2.5 GPa, the first peaks of $BiCrO_3$ are observed around 670°C which is little higher than the temperature observed during the « simple » synthesis, without boric acid, suggesting that a slightly different reaction mechanism occurs in presence of H_3BO_3. During cooling, diffraction spots are clearly identified on the

diffraction rings of $BiCrO_3$ (see figure 3a and 3b), showing that some single crystals were growing. In similar experiments at higher pressure, single crystals $BiMnO_3$ diffraction spots were also identified. A detailed analysis of these $BiXO_3/H_3BO_3$ data is still underway, to study precisely the reaction mechanisms and characterize the growth conditions.



(a) **(b)**

Figure 3 : In-situ XRD image (a) and corresponding integrated pattern (b) acquired during the crystal growth of $BiCrO_3$ in H_3BO_3 based flux at 2.5 GPa.