ESRF	**Experiment title:** **Study of the high-pressure phase transitions of $BiCrO_3$ by single crystal and powder diffraction**	**Experiment number**: HC-1333
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Report:

1) Technical aspects

In accordance with the proposal, both single crystal and powder experiments were carried out. XRD was performed in diamond-anvil cells with helium as pressure-transmitting medium.

The powder experiment was carried out safely up to 70 GPa, and data were acquired in small pressure steps (0.5 to 1 GPa) upon compression and decompression without any technical problem. The quality of the powder pattern is very good, even at the highest pressures.

The single crystal experiment was carried out up to 59.1 GPa. The DAC chosen did not allow to go much further, and unfortunately, one of the diamonds broke at the beginning of the decreasing pressure run so that data could be collected upon increasing pressure only. The quality of the diffraction patterns is good, although the crystal is twinned. Besides, we have evidence that the domain structure (or in other words the domain volume ratio) changes during the experiment, which complicates the analysis further. Since this is very difficult to avoid twinning anyway, we carried out the experiment with this crystal in spite of this, instead of spending time to check other crystals that would likely have been equally twinned.

In addition, a diffraction pattern was collected on another DAC, which had been previously pressurized up to 62 GPa for the need of a high-pressure Raman experiment. Only one pressure point was made on this cell, as a complement to the main single crystal experiment.

2) Results obtained

We review below the objectives stated in the proposal and the corresponding results. Mind that analysis is just at its beginnings and that those preliminary results should be taken with great care.

1 - Confirmation and thorough characterization of the first phase transition C2/c→Pnma expected at 1-1.5 GPa but hardly documented in the literature.

→ We confirm this *C2/c→Pnma* transition, and we certainly have all the necessary data with good enough quality for a detailed characterisation. Notably, it is clear that the detailed structure of the *Pnma* phase, which is not reported in the literature, will be obtained from the powder patterns. Also, the comparison with the single crystal data will enable us to treat the issues of phase coexistence, volume jump, order of the transition, etc.

2 - Confirmation/or invalidation of the occurrence of a further transition to a polar phase at higher pressure.

→ We could have expected that $BiCrO_3$ might undergo under pressure the same transition *Pnma→Cm* seen in $BiMnO_3$. Even at this early stage of the analysis, we can already safely say that it is not the case in the pressure range investigated. The full significance of this difference between the two compounds still has to be worked out, with the help of theorists.

3 - Characterization of any other transition at HP, especially related to a possible insulator-to-metal transition.

→ Several points have to be mentioned here. An additional phase transition does seem to occur in the 60 GPa range, as seen in the powder diffraction patterns (and our complementary Raman study). We don't know yet what structure this is, but it does not seem to be associated to a IM transition. But in fact, the most striking feature of the pressure evolution is that the *Pnma* structure remains stable in a very large pressure range, even though the spontaneous strains change very rapidly and bring the crysta structure in a strain state that is not usually found in perovskites, because a phase transition happens before, as the relevant comparison with $LaCrO_3$ shows. It is unclear how the *Pnma* structure can accommodate such strains; this is the main puzzling result in this experiment.

3) Perspectives

Future detailed analysis includes:

- Rietveld refinements of the powder patterns. It is probable that at some pressure, Rietveld refinement won't be possible anymore because of peak broadening caused by intergrain stresses, but it should be nonetheless possible to follow the details of the structure (bond angles, bond lengths etc.) up to 40 GPa at least.
- Structural refinements of single crystal patterns. Although it could be in principle of better quality, the twinning of the crystals considerably complicates the full crystal refinements. It is yet unclear whether we can succeed in refining fully those patterns, especially in the 30 GPa range where the volume ratio of domain changes during the experiment. If it fails, a rougher analysis based on the intensities of superstructures peaks could be attempted.
- Strain analysis from the lattice parameters, and interpretation in the framework of Landau's formalism.

Publication is not yet in preparation, but given the quality of the data obtained, and according to past experience, it makes little doubt that these XRD results, together with our high-pressure Raman data, will be published in a decent journal.