| ESRF | **Experiment title:** Development of a new HP-HT apparatus for X-ray studies | **Experiment number**: HS2532 |
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**Introduction**

All current applications of the PE press use an opposed anvils geometry. Experience shows that in such a geometry, the pressure and temperature range is limited to ~ 12 GPa and 2200 K, for various reasons. To overcome these limitations, we have designed a new device for *in situ* X-ray diffraction studies under HP-HT. The system consists of a 450-ton V7 Paris-Edinburgh press combined with a Stony Brook "T-cup" multianvil stage. The V7 has a capacity of 450 tons, i.e. almost twice as the standard presses, but still a weight of less than 90 kg. Here, we only present a yearly report since our last measurements within this LTP framework will occur in February and March 2008.

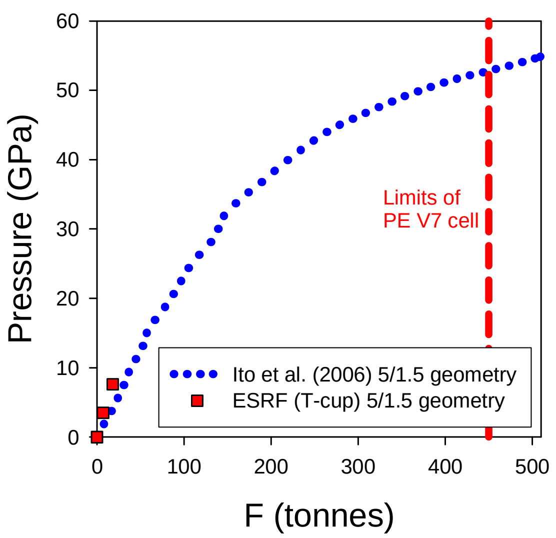
**2007 results**

***Technical part***

During this year (5 days of beamtime), we made several improvements of our PE/T-cup system :

1/ a new air-cooling system has been developped in order to protect the c-BN cubes during the heating at high pressure. This cooling system consists of a compressed air circulation inside a 4 thin grooves made in the first stage anvils. With this system, the occurrence of blowouts has been found to be reduced and in the meantime this modification did not lead to noticeable deteriorations of the (P,T) performance of our apparatus.

2/ In order to further improve the promptness of the installation, the efficiency and the speed of the first compression, the ease of the aligning, the reproducibility of the (P,T) performance of different set-ups, as well as lower the costs of the assemblies, severals improvements have been made amongst which was the development of a new anti-oscillating device for the first stage anvils, a less expensive octahedral pressure media fabrication by the technique of molding, the accurate laser cutting of rhenium furnaces which enhances the reproducibility from run to run, etc…



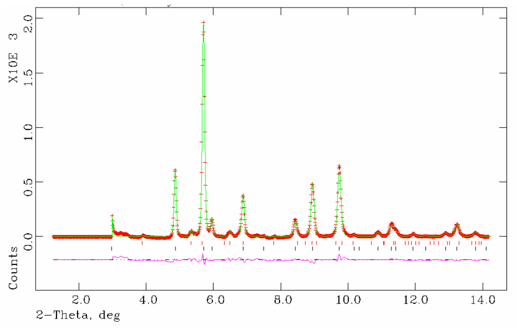

3/ We also tried a new geometry of the gasket assembly. Very recently, high pressure generation using an octahedral assembly with 5 mm edge length has been reported up to 69 GPa in a multianvil system with 1.5 mm corner truncation cubes (Ito *et al.*, IMA2006). By developing the same geometry, we demonstrated (Cf. figure) that we were able to reproduce the pressure efficiency given in the publication, at least at low pressure. For this experiment, the sample was simply a mixture of sodium chloride and magnesium oxide and the pressure efficiency was determined from the lattice constant of these compounds using their well-known equations of state (estimated error ~ 0.1 GPa). Unfortunately, in the course of this experiment, an oil leakage in the press prevented us from increasing further the oil primary pressure. New experiments are necessary to test this new geometry and (potentially) push back the pressure limit of our system.

***Scientific part***

We carried out a number of experiments in 2007 which demonstrated the potential of our device.

*a/ Oxides under extreme conditions*

Various oxides were studied with our system in order to determine their high (P,T) behaviour, including magnetite $Fe_3O_4$, $CuGaO_2$ (which belongs to the delafossite conducting oxides family with potential optoelectronic applications) and finally $BaWO_4$ (another oxide of the scheelite family, used as scintillating detectors). As an illustrative example, the figure presents a Rietveld refinement of magnetite at 16.2 GPa and 580 K. All reflections are from the sample and there is no contaminant signal from the sample environment. Initial refinements were carried out using only the spinel structure but the small reflections at 5.3 and 6.5 Å indicate a minor amount of hematite $Fe_2O_3$ which was already present at ambient conditions. Including this phase in the refinements and varying the lattice parameters, the internal oxygen coordination z(O) of $Fe_3O_4$, two thermal and three profile coefficients for magnetite gives a = 8.19390(3) Å and z(O) = 0.25849. Upon increasing the temperature to 600 K at constant load the sample most likely spontaneously transformed into a multiphase compound (data are currently being analyzed). In a second study, high-quality spectra have been obtained for the $CuGaO_2$ sample. As occurred for magnetite, upon increasing the temperature to 600 K at 16 GPa, the sample spontaneously decomposed, and $CuGaO_2$ and $Ga_2O_3$ peaks have been identified; other phases are present and data are currently being analyzed. The full results will be presented in the final LTP report. Data for $BaWO_4$ are currently being analyzed, although there are some obvious initial qualitative results. The sample was pressurized at room temperature up to 6 GPa, and remained in the scheelite tetragonal phase, just below the transition to the intermediate fergusonite monoclinic phase (which takes place around 7 GPa). At this point the sample was annealed to reduce the non-hydrostatic stress. A further increase of pressure (at room temperature) induced a phase transition around 8.5 GPa; we increased temperature up to 300°C. Interestingly, the new phase obtained seems to be the high-pressure-high temperature BaWO4-II phase, and no evidence of the intermediate fergusonite phase was observed. On the other hand, after quenching to ambient conditions, the transition is completely reversible, and the recovered sample is the starting scheelite structure.




*b/ HP-HT synthesis of new advanced materials*

Phase stability of boron phosphide BP has been studied over a wide range of pressure and temperature. In particular, the melting curve of BP has been studied for the first time.

-The possibility of HP-HT solid-state synthesis of boron subnitride, $B_6N$, by chemical interaction between boron and boron nitride has been comprehensively studied. The results of our *in situ* studies has allowed us to conclude that the evidence for formation of boron subnitride $B_6N$ with $B_6O$-like structure by solid-state reaction reported by H. Hubert *et al.* [*J. Solid State Chem*. **133** (1997) 356.] is inconclusive.. At the same time, HP-HT treatment has resulted in strong and unpredictable preferred orientation of boron crystallites. This leads to the rise of some weak boron reflections that might be erroneously attributed to the appearance of a new phase.

The results of numerous *in situ* studies of HP-HT synthesis of new superhard phases in the B-C-N system will be mentioned in the final LTP report because at the moment they are the subject of European patent application.

***Publications arising from these measurements***


- Y. Le Godec, G. Hamel, D. Martinez-Garcia, T. Hammouda, V.L. Solozhenko et S. Klotz, *High Pressure Research* **25**, 243 (2005).
- V.L. Solozhenko, Y. Le Godec and O.O. Kurakevych, *Comptes Rendus Chimie* **9**, No. 11-12, pp. 1472-1475 (2006).
- Y. Le Godec, G. Hamel *et al.*, submitted to *Journal of synchrotron radiation*.