ESRF	**Experiment title:** In-situ X-ray diffraction study of the superconducting MgB_2 synthesis and its single crystal growth at high pressure and high temperature	**Experiment number**: HS-1889
Beamline: ID30	**Date of experiment**: from: 28/07/2003 to: 02/08/2003	**Date of report**: 14/09/2005
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Report:

Aims of the experiment and scientific background

Following the discovery of superconductivity in magnesium diboride in january 2001, the necessity of MgB_2 single crystals was crucial to determine precisely the physical parameters governing the its superconducting properties. At this time, two major groups were able to produce these single crystals with a significant size. The first one was the group of Prof. Karpinski based in Zürich, Switzerland. They directly grew their crystals under high pressure – high temperature (HP-HT) in a multi anvils press working in the binary Mg-B system, typically at 3 GPa and around 1700 °C. The second one was the group of Prof. Tajima who worked in the range 4-5 GPa and 1400-1700 °C in the pseudo ternary system Mg-B-N.
In the group of Prof. Flükiger in Geneva, Switzerland the HP-HT synthesis of MgB_2 was also studied in a cubic multi anvil press. To be able to grow MgB_2 single crystals by a reproducible method, we had to understand what are the relevant parameters which drive the crystal growth of MgB_2: i.e. chemical composition of the flux, temperature and pressure. The aim of the experiment HS1889 was to study precisely by in situ X-ray diffraction the MgB_2 formation and its single crystal growth under high pressure. In addition, the last experiment was dedicated to the in-situ XRD study of the HP-HT synthesis of a new silicon sp^3 superconductor, the Ba_8Si_{46} clathrate.

Experimental

The ESRF large volume high pressure cell (in Paris-Edinburgh press) was used to investigate the synthesis and the crystal growth of MgB_2 single crystals by in situ X-ray powder diffraction under extreme conditions of pressure and temperature. This method was already successfully used in the investigation of the HP-HT synthesis mechanism of the high-T_c superconducting mercury cuprates by XRD on the same ID 30 beamline from 1997 to 1999 (see previous experimental reports).
For the MgB_2 experiment, pellets in the Mg-B-N system were prepared, starting from powders of boron, magnesium and boron nitride, fitting the size of the BN crucibles, typically used in the Paris

Edinburgh press of the ID 30 beamline. In the binary system, a Mg:B = 1:1 stoechiometry was used to obtain a magnesium rich flux. In the pseudo ternary system a Mg:B:BN = 1:1:1 composition was prepared. Three different assemblages were tested: a Mg-B pellet directly introduced in its BN crucible surrounded by the carbon heater, a Mg-B pellet wrapped into a thin 25 µm Ta foil itself placed into the BN crucible and a Mg-B-BN pellet in its BN crucible. The role of the Ta foil was to protect the carbon furnace in case of too strong reaction between the B+Mg mixture and its BN crucible. And finally, two assemblages with MgB_2 (from Alfa Aesar) pellets were also prepared using the two kind of setups (with or without an isolating Ta foil). Six experiments were carried out for the study of MgB_2 at pressure around 3 - 4 GPa and temperature up to 1200 °C.

For the six Mg-B-BN experiments, the high quality diffraction images were recorded at 20 keV in 1-3 minutes, using an online image plate detector. In the case of the Ba_8Si_{46} clathrate, the energy was increased to 61.33 keV (Yb K-edge absorption, λ = 0.2122 Å) because of the stronger absorption of barium. Despite the absorption of the B-epoxy gasket and the environment of the sample (furnace, Ta/BN crucible) the high brilliance synchrotron X ray beam of ESRF allowed us to follow the MgB_2 and Ba_8Si_{46} formation.

Results

In all cases, an explosion happened at the end of each experiment (between 3 and 8 h of heating time). It is probably because at the high temperature reached at the end of each experiment (around 1200 °C), the high pressure assembly can not resist mechanically in such aggressive environment (Mg rich flux). For this reason it was not possible to explore the 1200-1700°C domain as expected in the proposal. Nevertheless, from the two experiments performed with MgB_2, it was possible to observe solid MgB_2 up to 1200°C at 3-3.5 GPa (figure 1), suggesting a higher melting point (as observed by Baranov. et al. in their in-situ synchrotron XRD study, Supercond. Sci. Technol. 16 (2003) 1147). Concerning the Mg-B experiments, no intermediate phase was observed in Ta/BN crucible. Only in the case of the Mg+B+BN mixture (without a protective Ta foil), intermediate(s) phase(s) were observed around 700-1000°C (see upper part of fig. 1).

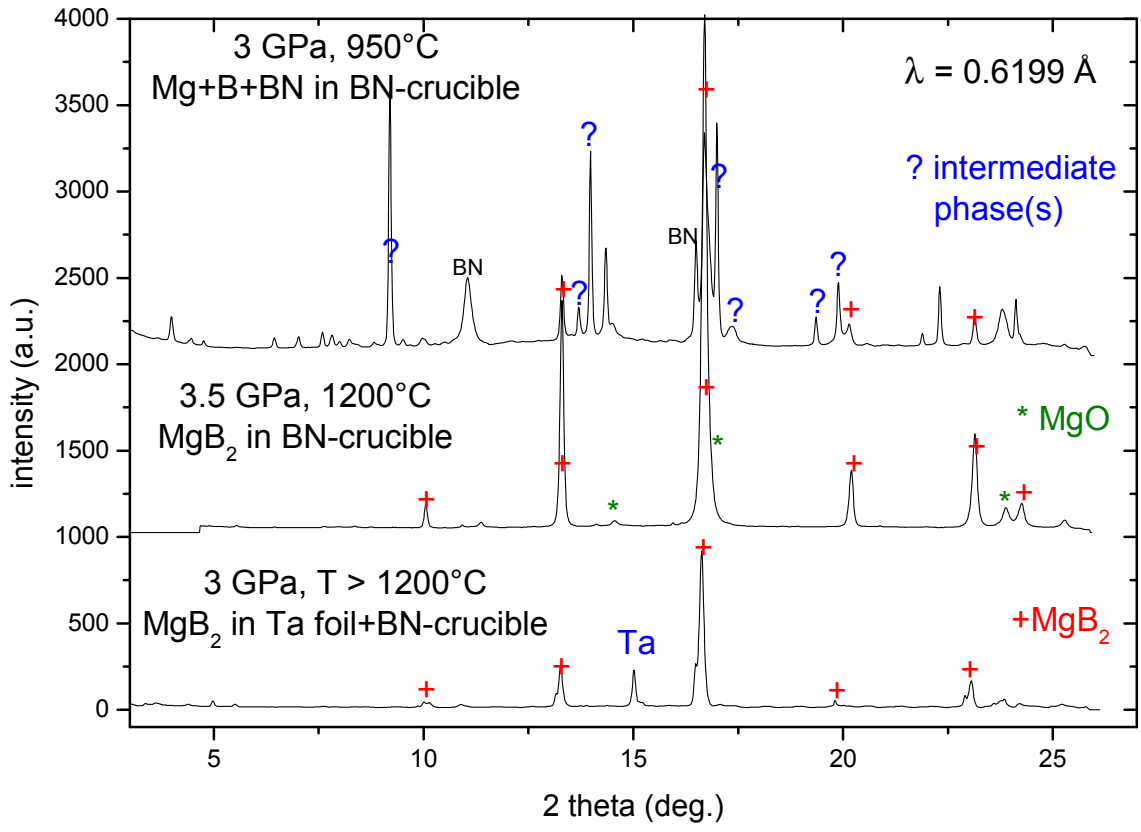

Figure 1. *Comparison of XRD patterns from the MgB2 and Mg+B+BN experiments at 3-3.5 GPa and temperature up to 1200 °C.*

In the last experiment, dedicated to the Ba_8Si_{46} clathrate, its formation at 3.5 GPa was observed in situ for the first time and an intermediate phase was clearly evidenced (figure 2). The reaction was not fully completed when, again, the B-epoxy cell exploded at high temperature. The causes of this explosion remain uncertain. Maybe the thickness of the BN crucible was too small to protect the furnace from contamination by the sample through reaction with the crucible.

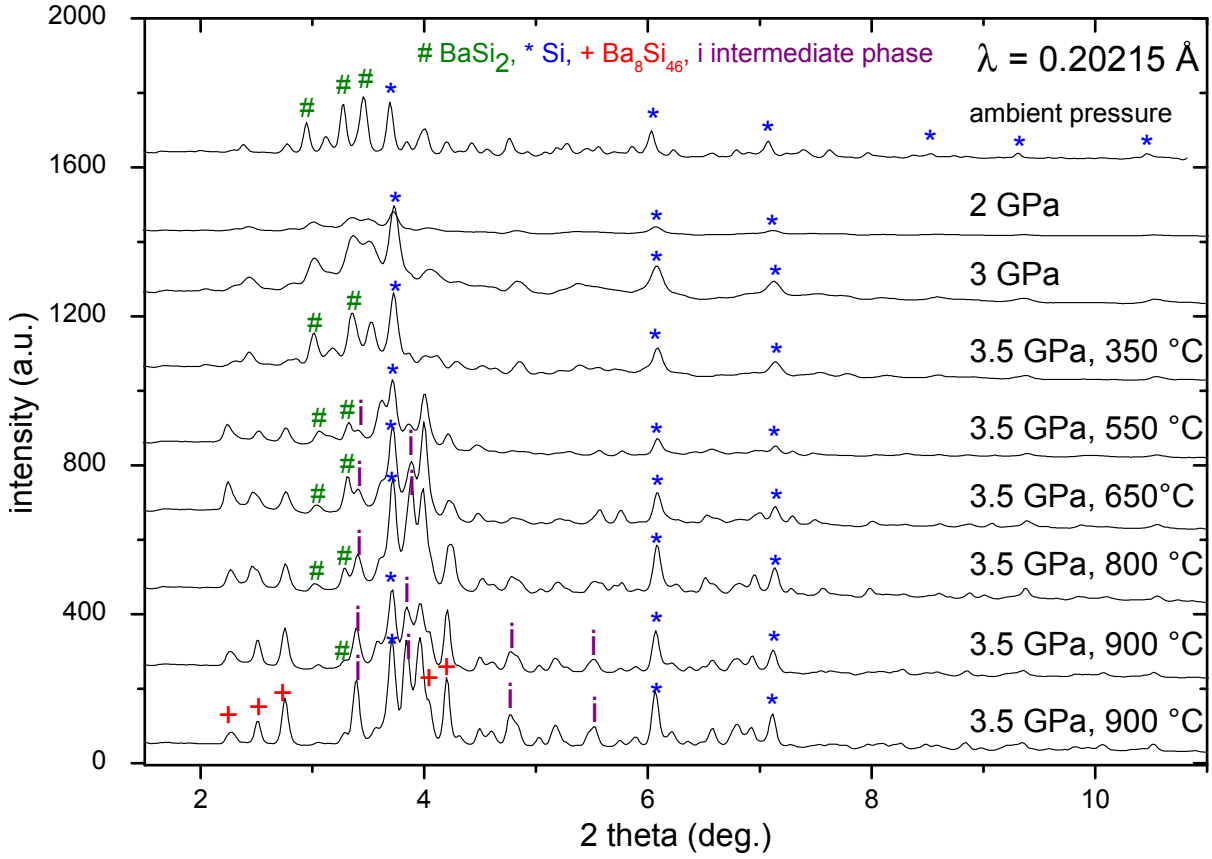

Figure 2. *XRD patterns of the Ba8Si46 experiment at 3.5 GPa, up to 900°C showing the intermediate phase..*

Despite preliminary heating tests off line in the PE press of ID30 with the same kind of sample before the HS1889 experiment (where no explosion was observed), we did not avoid this problem at each end of HP-HT exploration. As partially evoked above, due to the undesirable explosions but also due to technical problems (z-translation motor broken during the run), this HS1889 experiment was only a semi-success. It gives some indications in the Mg-B-BN ternary diagram to explain the crystal growth of MgB_2 and preliminary results on the Ba_8Si_{46} HP-HT synthesis. To fully understand the high pressure transformations involved in both systems, more experiments are needed.