	Experiment title: **High-pressure and high-temperature investigation of nitrides of the IVA and IVB group elements**	**Experiment number**: HS-2845
Beamline: ID27	**Date of experiment**: from: 22-FEB-06 to: 28-FEB-06	**Date of report**: 28-FEB-07
Shifts: 15	**Local contact(s)**: Mohamed MEZOUAR	*Received at ESRF:*

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Report:

Compressibility and phase behaviour of a series of hard binary nitrides was investigated in a diamond anvil cell at high pressures up to 60 GPa. In particular, we performed experiments on cubic tin nitride having spinel structure, γ-Sn_3N_4 (*1*); β-phase of Si_3N_4 which transforms on compression at room temperature to the so-called δ-phase with a still unidentified structure (*2*) or, when heated, to a cubic phase with spinel structure, γ-Si_3N_4 (*3*); a mononitide of vanadium having the NaCl-type structure, δ-VN; and a boron subnitride $B_{13}N_2$ (*4*). In addition, at the maximal pressure tin nitride was heated to temperatures around 2000 K using the radiation of an infrared Nd:YAG-laser in order to explore a possibility of a post-spinel phase transition. In the present experiments we used the high-pressure equipment available at the hosting beam-line and from the sample environment support service of the ESRF. In most of the experiments we used argon or neon as pressure media which provide inert and quasi-hydrostatic load conditions.

Investigation of the compression behaviour of γ-Sn_3N_4 was performed for the following reasons. The bulk modulus, B_0, of γ-Sn_3N_4, discovered eight years ago, is still not determined experimentally. However, there are five different theoretical publications on B_0 of γ-Sn_3N_4 where the predicted values very between 186 and 218 GPa (*5-9*). The experimental value of B_0 of γ-Sn_3N_4 can be used to derive the shear modulus G_0 from the reduced modulus E_r measured in an earlier work using the nanoindentation technique (*9*). Thus, the G_0-value for a polycrystalline isotropic sample of γ-Sn_3N_4 can be determined using only experimental data without any unsupported assumptions. The obtained information on the bulk and shear moduli of γ-Sn_3N_4 can be compared with its hardness as well as with the elastic moduli and hardness of other two members of the spinel-nitrides family, γ-Ge_3N_4 and γ-Si_3N_4. From this comparison we can make a conclusion about dependence of elastic moduli and hardness on the size of the constituting cations.

X-ray powder diffraction patterns of γ-Sn_3N_4 were measured at room temperature to about 50 GPa. Neither new diffraction peaks nor sudden changes in the pressure dependences of the *d*-values were observed up to the maximal pressure. Accordingly, up to this pressure the spinel structure of Sn_3N_4 remains stable (or metastable) when compressed at room temperature. From the measured volume versus pressure dependence (Figure 1) we derived B_0 = 158(11) GPa and B_0' = 5.4(1.1) using the third order Birch-Murnaghan equation of state. The obtained B_0-value of γ-Sn_3N_4 is sufficiently lower then those predicted in the earlier theoretical publications. Thus, further improvements of the existing methods for calculation of elastic moduli are required.

At the maximal pressure, the sample of γ-Sn_3N_4 embedded in the argon pressure medium was heated with the radiation of a Nd:YAG laser to 2000-3000 K. The X-ray powder diffraction patterns collected after heating revealed appearance of new peaks. Currently we examine these XRD-patterns with respect to the question whether the new peaks are due to formation of a post-spinel phase or due to decomposition of γ-Sn_3N_4 to the constituent elements.

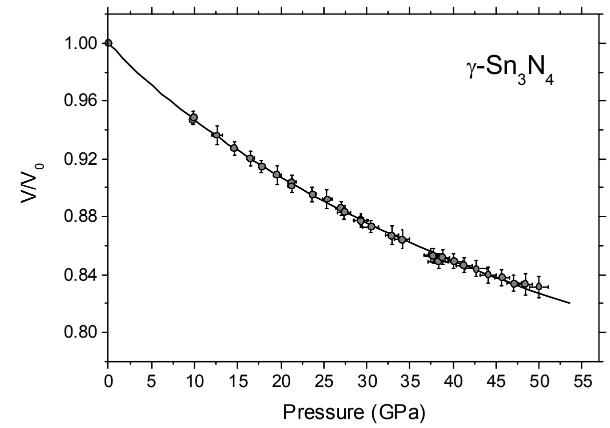

Figure 1 Pressure dependence of the relavive volume of γ-Sn_3N_4 measured to about 50 GPa.

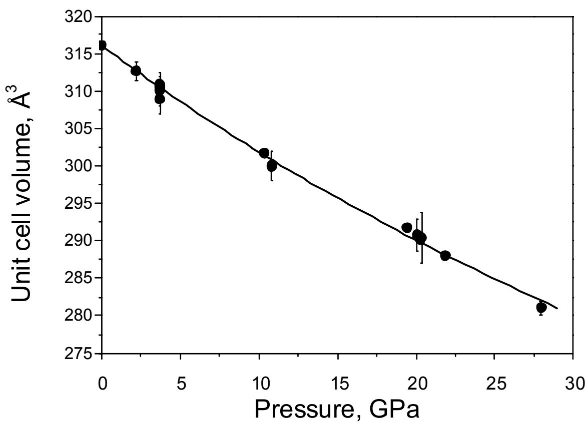

Figure 2 Equation of state of boron subnitride $B_{13}N_2$ measured to 30 GPa.

Determination of equations of state (EOS) of boron-rich compounds contributes to our understanding of their properties and bonding. Here, we performed an accurate measurement of the equation of state of boron subnitride, $B_{13}N_2$, up to 30 GPa. This compound has been recently synthesized from the B-BN melt at high pressures and temperatures (*4*). The sample, containing also some amounts of $B_{50}N_2$, hBN and β-rh boron, was compressed in a DAC in the neon pressure transmitting medium. Pressure was determined using both the hydrostatic ruby scale and the EOS of neon. The value of the bulk modulus, B_0 = 200(15) GPa, has been estimated using the Birch-Murnaghan equation with the first pressure derivative of bulk modulus, B_0', fixed to 4.

Proir to our work, elastic properties of δ-VN were investigated using different experimental techniques but its equation of state has never been measured. On the other hand, there are numerous theoretical calculations of bulk modulus of δ-VN (*10-16*). In this work we measured the pressure dependence of the specific volume of δ-VN at room temperature up to 29 GPa and derived, from the data, the bulk modulus B_0 = 288(12) GPa and its first pressure derivative B_0' = 4.3. The present value of the bulk modulus is at the bottom of the wide range of the theoretical values scattering between 282 GPa and 414 GPa (*10-16*) and similar to that derived from acoustic measurements, B_0 = 268 GPa (*17*).

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