



	Experiment title: Formability of Solid Solutions of Spinel type Ge_3N_4 and Sn_3N_4 at High Pressure and High Temperature	Experiment number: HC-3639
Beamline: ID06-LVP	Date of experiment: from: 08/03/2018 to: 12/02/2018	16/11/2018
Shifts: 12	Local contact(s): Dr. K. Spektor	<i>Received at ESRF:</i>
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Report:

Spinel type nitrides formed by the group 14 elements, namely Si_3N_4 , Ge_3N_4 and Sn_3N_4 , offer a new class of compounds with potentially useful mechanical and optoelectronic properties [1-6]. This project aims to investigate the formation and stability of a novel $(\text{Ge}_{1-x}\text{Sn}_x)_3\text{N}_4$ in the spinel structure (called γ -phase) at high pressures and high temperatures (HP-HT). In the first efforts, we studied the HP-HT behavior of γ - Sn_3N_4 and 1:1 mixture of γ - Sn_3N_4 and α & β - Ge_3N_4 (Sigma-Aldrich). The starting materials, spinel- Sn_3N_4 was synthesized [7] by ammonolysis of $\text{Sn}(\text{NMe}_2)_4$ complex at TU Darmstadt (Prof. Ralf Riedel group). At the ID06-LVP beamline, we performed following experiments.

	Starting material	Oil pressure (bar)	P (GPa)	T (°C)
Exp1	γ - Sn_3N_4	200	15.8	1480
Exp2	γ - Sn_3N_4	250	18.9	1800
Exp3	CrTe_3 (as additional sample)	100	10.5	230
Exp4	γ - Sn_3N_4 + α & β - Ge_3N_4 (1:1)	250	17.9	1630
Exp5	γ - Sn_3N_4	250	17.6	1500

During *in situ* investigations, Spinel type tin nitrides under above mentioned P-T conditions (Exp1,2 and 5) show a few new unknown reflections (Figure 1). Unfortunately, we were unable to refine the structure or identify the chemical composition. Recovered samples appear altered with a yellow (with reddish tinge), and results from the Exp4, 1:1 mixture of tin and germanium nitride experiment also appear inconclusive. When we tested these mixtures using the six ram large volume press (LVP) installed at DESY beamline P61.2, we obtained the mixture of γ - Ge_3N_4 and γ - Sn_3N_4 (Figure 2) without additional unknown reflections seen at ID06. Therefore, we were unable to reproduce our *in situ* experiment results and in both cases no solid solution could

be obtained. These outcomes can be attributed to mainly the following, a) reaction of sample with surrounding materials when no metal capsule is used (for X-ray transparency), b) starting materials contained considerable amount of oxygen (based on later analysis).

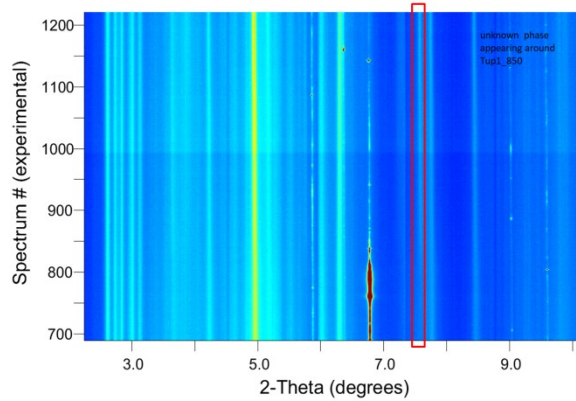


Figure 1. *In-situ* diffractograms of Tin nitride including reflections from sample environment (Exp5; 54 keV, 17.6 GPa and 500-1200 °C)

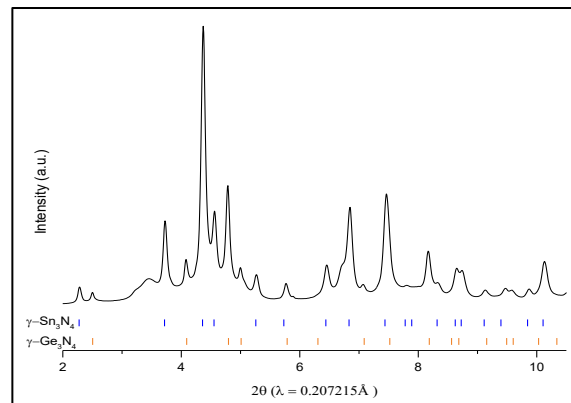


Figure 2. Ex-situ angle dispersive X-ray diffraction patterns of 1:1 mixture of Tin nitride and Germanium nitrides collected after 15-20 GPa and 800-1000 °C (acquired at DESY beamline P02.1, 60 keV)

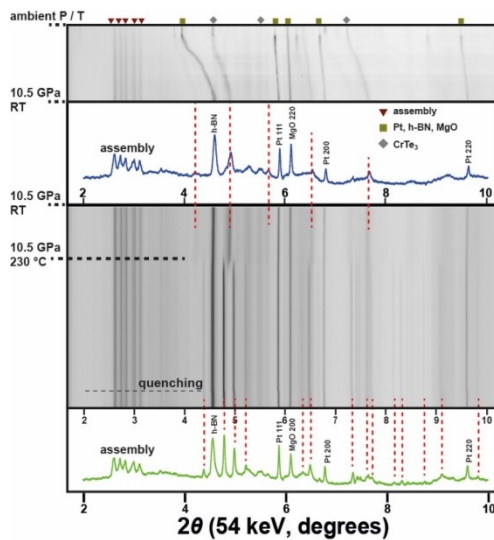


Figure 3 Combination of in situ diffractograms demonstrating the phase transformation from monoclinic CrTe_3 to an orthorhombic phase.

During beamtime, we carried out an experiment on one additional sample namely, chromium telluride CrTe_3 . Chromium tellurides reveal a large variety of structural, electrical and magnetic properties and became increasingly attraction since the discovery of ferromagnetism in CrTe [8]. Most chromium tellurides are metals and have a transition into the ferromagnetic state at higher temperatures [9]. High-pressure high-temperature (high-*PT*) *in situ* synchrotron X-ray diffraction experiments were performed to study the high-*PT* stability of the CrTe_3 compound at the ID06-LVP beamline at ESRF. High-*PT in situ* investigations reveal a temperature-induced phase transformation of CrTe_3 from the monoclinic to the orthorhombic crystal structure at pressure of 10.5 GPa and temperature of 230°C. The monoclinic structure remains stable during pressurization up to 10.5 GPa. The phase transformation can be clearly identified in the 2D diffraction patterns in

Figure 3. The monoclinic CrTe_3 reflection (023; 22-3) around 4.6° 2Θ diminish, while two new reflections occur at 4.5° and 4.8° 2Θ . This result is promising for further investigations.

References:

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