ESRF	**Experiment title:** **Melting Curve of GaN Determined by Energy-dispersive X-ray Absorption Spectroscopy**	**Experiment number**: HC-3479
Beamline: ID24	**Date of experiment**: from: 12.02.2018 to: 20.02.2018	**Date of report**: 28.02.2018
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Names and affiliations of applicants (* indicates experimentalists):

Izabella Grzegory	Institute of High Pressure Physics PAS, Warsaw, Poland
Bogdan Sadovyi	Institute of High Pressure Physics PAS, Warsaw, Poland
Svitlana Stelmach	Institute of High Pressure Physics PAS, Warsaw, Poland
Sylwester Porowski	Institute of High Pressure Physics PAS, Warsaw, Poland

Report:

1. The final goal of the proposal

The final goal of this proposal is determination of the **Melting Curve of GaN** to answer a fundamental question about melting temperature and its pressure dependence for this extremely important semiconductor. There are principal discrepancies in the reported data [1] on both the melting P-T conditions and the sign of dT/dP derivative. It is expected that melting of GaN can be reached at pressure exceeding 12 GPa since at low pressure a stoichiometric liquid of GaN cannot be reached due to thermal decomposition of GaN into Ga and N_2 or GaN prior to melting (<12GPa according to[1] or < 6 GPa according to [2]). The EXAFS (XANES) technique at HP-HT conditions seems to be ideal approach for evaluation of melting conditions of GaN because phase transition from tetrahedrally coordinated wurtzite crystal to both the stoichiometric liquid (melting) and N solution in liquid Ga (decomposition) can be clearly identified and distinguished.

2. Phase diagram of GaN BEFORE the HC-3479 session:

The melting curve of GaN derived from the experiments where high quality GaN bulk single crystals (10 mm in size) were studied in large volume pressure cells at pressure range of 6 – 10 GPa [1] was in principal disagreement (over 1000K at 10 GPa) with melting data obtained from XRD in multi-anvil cell [2] and simulation in [4] whereas in excellent agreement with predictions of Molecular Dynamics (MD) [5]. Results reported in [1, 2 and 3] are collected in the diagram shown in the HC3479 proposal and also at the end of Section 5. The MD simulations as well as our results [1] indicated that at low pressures, GaN should melt into a low density liquid of low coordination number (around 4). The extrapolation of these data by Drozd-Rzoska equation [6,7] based on Simon-Glatzel approach suggests a maximum of melting temperature at about 20 GPa and then its decrease down to the value corresponding to pressure of solid-solid phase transition of GaN from the low pressure wurtzite structure to the high pressure rock salt one. The pressure of this transition has been evaluated as 47-50 GPa at RT by Raman scattering and EXAFS studies in DAC [8].

3. Experimental

The experimental evaluation of the gallium nitride melting curve was planned for the pressure range 10 to 80 GPa, and temperature up to 4000 K. The samples were loaded in nanopolycrystalline diamond anvil cells in order to avoid Bragg peaks from the diamonds. Finely grained powders (compacted into 5 µm thick foils) obtained from the highest quality GaN single crystals grown in IHPP PAS laboratory were used. Both pure GaN and the one mixed with Pt to enhance the IR absorption in the sample, were studied. Two thin plates of KCl or MgO were used to thermally and chemically isolate the sample from the anvils and also as a pressure transmitting medium. Pressure was measured using the ruby method at ambient T. Two Nd:YAG lasers were used to heat the sample from both sides. The temperature from both sides was monitored by online spectro-radiometry, synchronized to both the laser heating and the x-ray acquisition.

4. **Beamline(s) and beam time used:**

The unique double sided laser heating system ID24 for XAS measurements in a laser heated diamond anvil cell was used during 18 shifts on beamline ID24: 3 shifts were used for setting up at the Ga energy, then Ga K-edge EXAFS on GaN was measured in different temperature runs up to 80GPa. 5 cells were prepared to perform different heating runs.

5. **RESULTS**

The results and conclusions are of preliminary character until the detailed data processing is terminated.
In the process of establishing the behaviour of GaN samples and their Ga K-edge EXAFS spectra in LH-DAC environment with the Nd-YAG laser heating, the following results have been obtained:

a. **Wurtzite – rocksalt solid-solid transition at RT**: starting from pure n-type GaN sample in the wurtzite phase and with KCl medium, at increasing pressure:
Upstream: wz-rs transition start at 46 GPa completed at 52 GPa
Downstream: rs-wz transition start at 22 GPa, completed at 16 GPa
The results were in agreement with the ones of [8].

b. **Wurtzite-rocksalt transition induced by heating:** pure GaN samples with KCl medium were heated at pressures where the wurtzite phase was stable at RT, going upstream:
37 GPa: at 1600 K, a thermal flash was observed. After quenching the pure NaCl phase has been identified.
43 GPa: at 1600 K, the wz-rocksalt transition started, completed at 1800K, further heated until 2200K where a thermal flash was observed.
45 GPa: at 1300K, the wz-rs phase transition started.
Preliminary interpretation
The results suggest that the borderline between the low pressure wz and the high pressure rs phases is inclined negatively towards low temperatures on P-T diagram. The thermal flashes at certain high T points may indicate abrupt changes in IR absorption at corresponding phase transitions: **wz to rs** – wide band gap semiconductor to narrower band gap semiconductor (37 and 45 GPa), **rs to liquid** – semiconductor to metallic liquid (43 GPa).

c. **Heating wurtzite GaN at 33 GPa**: **GaN mixed with Pt sample** with KCl medium was heated in its wurtzite phase.
At about **2200 K** a thermal flash was observed. After quenching a hole in the sample corresponding to the laser spot was found.
The proposed **preliminary interpretation** is that the melting of GaN from its wide band gap semiconductor phase to a metallic liquid occurred and due to abrupt change of the absorption coefficient a thermal flash happened.

d. **Heating wurtzite GaN at 20 GPa: GaN + Pt,** KCl medium, heating at 2 sample positions.
For both sample positions thermal flashes at 2000K and 2200K were observed. No sample was found for both cases (holes).
The proposed **preliminary interpretation** is that since **there is no nitrogen** in the pressure medium to assure stability of wurtzite GaN at high temperature, the crystals decompose into N_2 gas and liquid Ga. The liquid Ga abruptly enhances the IR absorption of the sample resulting in the observed thermal flash.

e. **Heating wurtzite GaN at 19 GPa: GaN + Pt, MgO medium**
At heating, the EXAFS spectrum of GaN transformed into the EXAFS spectrum of Gallium Oxide at about 1900 K (full conversion). A distinct change of the EXAFS spectrum was observed during further heating, at 2700 K. After quenching, the EXAFS spectrum of the oxide was recovered.
The proposed **preliminary interpretation** is that the MgO reacts with GaN at high temperature leading to formation of the gallium oxide which melts of at about 2700 K.

f. Heating rocksalt GaN at 55 GPa: pure GaN sample, KCl medium

After converting the initial GaN sample in its wz phase into the rs phase (result a), the pressure was raised further to 55 GPa, and the sample heated up to high T. **At 2650-2700K a distinct drop in intensities of 3 EXAFS peaks was observed.** A **preliminary interpretation** is that it is melting of GaN in its rocksalt phase at 55 GPa.

At further increase of the laser power, the temperature was increasing until 3800 K where the increase stopped, most probably due **to melting of KCl medium**.

6. CONLUSIONS

1. The EXAFS spectra of GaN have been successfully measured at pressures up to 70 GPa and temperatures approaching 4000K
2. The solid solid phase transition of GaN from wurtzite to rocksalt phase has been observed at both room temperature and high temperature conditions. Melting of the rocksalt phase at 55GPa has been probably, detected.
3. Due to the use of Nd-YAG laser (1064 nm) a direct heating of GaN being wide band gap semiconductor was difficult and required additional absorbing species (metal powders) for stable and efficient heat delivery to the crystal.
4. The heating of GaN with the Nd-YAG laser often resulted in thermal flashes at high temperatures due to abrupt changes in IR absorption at GaN melting and/or decomposition. In both processes a metallic liquid should appear.
5. To avoid GaN decomposition at high temperatures, the DAC should be loaded with nitrogen to assure a necessary chemical potential of N_2 around hot GaN.
6. It is proposed to continue the EXAFS experiment (YAG laser heating) at ID24 with DAC loaded with nitrogen and with GaN mixed with both Pt or Au powders. For low pressure range (10-30 GPa) and temperatures exceeding 2000K, an additional optimization of thermal insulators is necessary. KCl is not optimum choice due to its low melting temperature whereas the MgO leads to oxidation of GaN at high temperatures.
7. It is also proposed to perform a series of XRD experiments at ID27 where the CO_2 laser can be used for heating of GaN. This laser (9.4-10.6 μm) is more suitable for heating of semiconductors.

References

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