ESRF	**Experiment title: Static phase diagram of tin above 1 Mbar**	**Experiment number**: HC-5077
Beamline: ID27	**Date of experiment**: from: 6/12/222 to: 9/12/2022	**Date of report**:
Shifts: 9	**Local contact(s)**: Mohamed Mezouar, Gaston Garbarino	*Received at ESRF:*

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Report:

-Objective & expected results-

We planned to use laser-heated diamond anvil cell to measure the phase diagram of tin in the 0.6-2 Mbar range, and especially the melting curve at high pressure. We had already a large set of data collected on synchrotron Soleil but very few on the melting curve because of the difficulty to keep molten in the laser hot spot. In the 1.6-Mbar range, we wanted to test the effect of temperature increase on the hcp phase which forms at 1.6 Mbar.

-Results and conclusions of the study-

Five laser-heated diamond anvils cells (LHDAC), shortly described in **Table 1**, have been bought to ESRF. Laser-heating of tin is a challenge due to its high reflectivity in the infrared range. Starting sample for large diamond culet size (Sn47 and Sn48) were thin foils ($e = 5\ \mu m$) of Tin, with a surface roughing to decrease reflectivity, and Tin and KI powder grains for small diamond culet size (Sn44 and Sn45) and run KI. We used KI as pressure transmitting medium (PTM) and as pressure gauge. This was one of the best PTM for laser-heating experiments on Tin (determined in a previous experiment), with a low thermal conductivity. We used the run KI to measure its EOS at 0- 20 GPa (KI loaded in He, with W as pressure gauge [1])

Experiments were carried out at the ID27 beamline, with an X-ray beam focused to a 0.8x0.8 µm FWHM spot on the sample with KB mirrors, and cleaned with a pinhole. On-line laser-heating system has been used for LHDAC. XRD data were collected using an EIGER detector with a sample to detector distance calibrated with a reference sample.

Run name	Diamond culet diameter (µm)	Sample	Pressure range (GPa)	Temperature (K)
Sn44	70	Sn in KI	125 -> 160	300->2000
Sn45	70	Sn in KI	100 -> 190	300->2000
Sn47	300	Sn in KI	20 -> 65	300 -> 3750
Sn48	200	Sn in KI	25 -> 70	300 -> 3500
KI	400	KI + W in He	0 -> 20	Room T

Table 1: Conditions of the 5 runs.

1. *Melting curve of Sn up to 70 GPa*

The two runs Sn47 and Sn48 were used to study the melting curve of tin between 20 to 70 GPa and the stability of the different crystaline phases. The liquid was identified on XRD patterns thanks to the fast and sensitive detector as presented in **Figure 1**. This allows the precise determination of melting curve of tin in this high pressure domain. We obtain a higher melting curve than the previous one reported in the litterature [2].

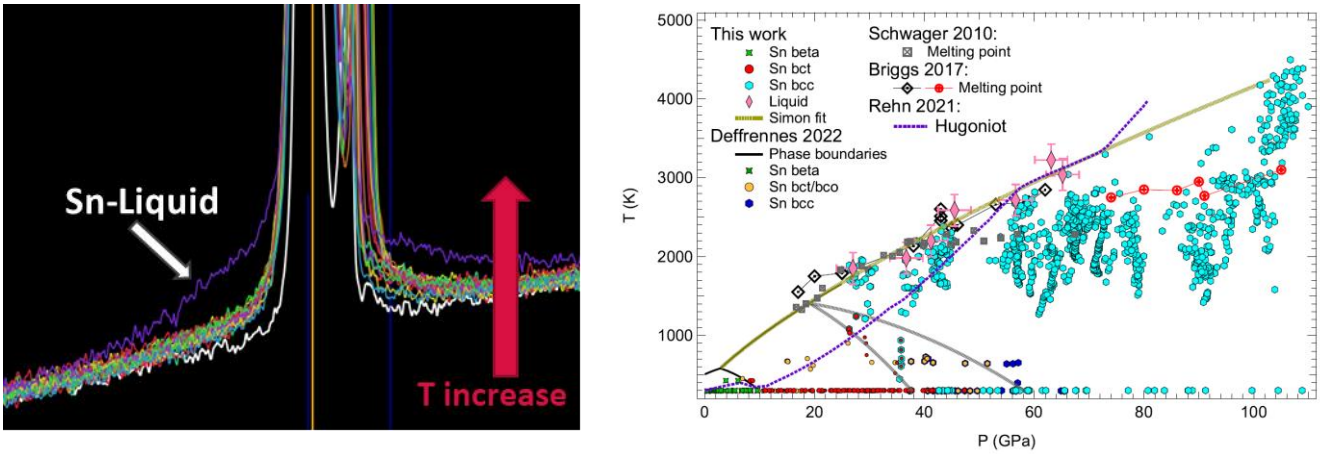

Figure 1: (left) XRD patterns at different temperature stack together. The diffuse signal of liquid is clearly identified. (right) Phase diagram of Tin up to 90 GPa including phase stability and melting curve analysed from data collected during our experiments as well as experiments carried out at synchrotron Soleil.

2. Stability of hcp phase

Around 160 GPa at room temperature, Sn-bcc undergoes a phase transition to an hexagonal structure Sn-hcp [3]. In a previous experiment, we detect the hcp phase under nonhydrostatic conditions at higher pressure. This high pressure phase was not detected under dynamic compression.

In runs Sn44 and Sn45, we used diamond with pits on the culet to increase the amount of KI and reach 160 to 200 GPa. Unfortunately, the pits reduced the maximum pressure reached (we could also measure large pressure gradients in the cell). We reached 190 GPa and 160 GPa at 300 K but the Sn-hcp phase was not observed. Sn44 and Sn45 Sn samples could be heated, which is a success, but even moderate heating resulted in a reaction between Sn sample and KI. It was clearly evidenced by XRD mapping of the sample after heating and the reaction product is likely SnI4. We plan to test one other thermal insulator, MgO, to repeat the experiments.

3. Equation of State of KI

The run KI was used to provide complementary data (between 0 and 20 GPa) to obtain the P-V relation for KI at room temperature. The collected data are consistent with the previous one collected at higher pressure. The obtained EOS is slightly different than the one proposed by Köhler [4] in 1997.

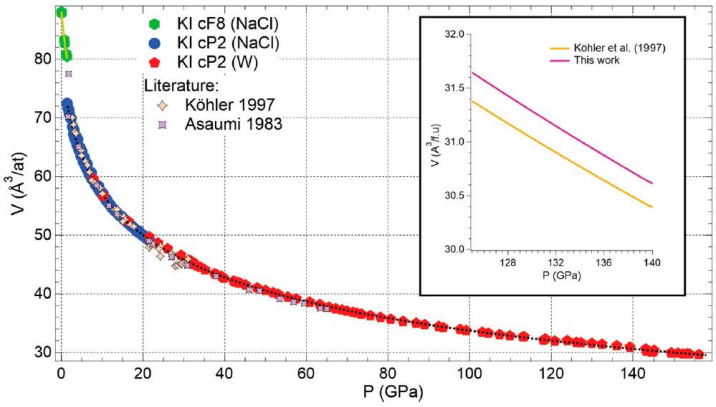

Figure 1: Equations of state for the two phases of KI up to 150 GPa.

-Justification and comments about the use of beam time-

After alignment of the beamline and calibration by the local contact on the first day, the beam time was used to align and collect date (XRD) for the five cells. The experiment went smoothly; we appreciated the very small spot size of the beamline and the fast and sensitive detector and the accurate sample holder motors.

The data collected have been published in Fréville et al., Equation of state of KI up to 150 GPa, High Press. Res. 43, 251, 2023 and another paper is in preparation (Fréville et al., High pressure-high temperature phase diagram of Sn).

-References-

[1] Akobuije et al., High-pressure equations of state of Al, Cu, Ta, and W, J. Appl. Phys. 98, 073526 (2005)

[2] Briggs et al., High-pressure melting behaviour of tin up to 105 GPa, Phys. Rev. B. 95, 054102 (2017)

[3] Salamat et al., Dense close-packed phase of tin above 157 GPa observed experimentally via angle-dispersive x-ray diffraction, Phys. Rev. B. 84, 140104 (2011)

[4] Köhler et al., Equation-of-state data for CsCl-type alkali halides, J. Phys.: Condens. Matter 9 (1997) 5581-5592.