Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** The rise of group IV systems: controlled melting, synthesis, and in-situ characterization of bulk and nanoalloys	**Experiment number**: CH4531
Beamline:	**Date of experiment**: from: 21/11/15 to: 23/11/15	**Date of report**: 09/02/16
Shifts:	**Local contact(s)**: Dr. Wilson Crichton	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The experiments involved developing and testing experimental assemblies to perform stable synthesis experiments in the GeSn system at pressures and temperatures up to 18 GPa and 1800 K with in-situ monitoring of compressional, reaction and structural evolution using X-ray diffraction up to melting at pressure, and crucially, upon decompression to ambient conditions, coupled with recovery of samples for further analysis using electron miscroscopy and diffraction. The overall objective is to correlate conditions of synthesis with formation, structural evolution and stability of bulk and nano Ge-Sn alloys in this system because of their importance towards overcoming limitations of silicon for efficient light emission applications [1-5].

Technical Developments

This being our first visit at ID06 for measurements under extreme conditions, meant that the designs evolved dynamically in response to the performance in each run. To this goal we exploited our beamtime to the fullest in exploring operational parameters for measurement. Indeed we managed to perform eight high pressure experiments in this time. There are several considerations in developing effective assemblies for measurement with merits whose relative benefits need to be evaluated by experiment. In conjunction with the assembly design and structural characteristics, the particulars of the phase relations of the samples under extreme conditions may also influence assembly stability [6]. The first trial employed a double chamber design using low Z h-BN and press-fit lids. One chamber contained the sample, ground 0.7:0.3 Ge:Sn mix and the other a 5:1 MgO:Pt mix for P-T measurement. A wrapped Re heater, a MgO sleeve and top and bottom h-BN plugs. A remarkable SiCBN X-ray cylindrical window was employed, which vitally remains amorphous even at high temperatures. Power coupling was via the folded Re heater. A beam diameter of order 0.5 x 1mm was employed. This run ended up in a blowout at ~3 GPa. The recovered charge exhibited hour-glassing. The overall view was that too much soft BN may have contributed to the instability, and potentially the window (hole) through the Re foil may have contributed to the instability as well. But to investigate whether this was indeed the case, this was reproduced, and indeed a second run had a similar fate, albeit at a pressure of ~8 GPa. In the third experiment, to investigate the effect of excess soft material and the effect of the Re foil with the drilled hole, we replaced the top and bottom spacers with unsintered MgO and the heater with a cylindrical low Z graphite heater, which hence required no potentially destabilizing hole.

This experiment was not destabilized until a somewhat higher pressure of ~10 GPa. To try to make a more dramatic change towards preventing structural destabilization, for the fourth run, we halved the length of the h-BN capsule and thinned the walls. This run was also destabilized at 7.6 GPa indicating that further significant assembly changes may be required. The results of this run were not conclusive because they were coupled with a potential feedback loop malfunction that may have led to premature decompression. Still, in the fifth run we embarked on the further signficant change with respect to the fourth one, of namely replacing MgO with harder ZrO_2 spacers to trigger a tigher coupling of oil pressure to assembly compression and likely a more stable structural assembly. This run met with significant success. We peformed a stable compressional run to ~13 GPa and were able to heat remarkably stably to ~1500 K the target temperature for this, where the sample was largely melted, followed by annealing for 1.5 hr at ~770 K and subsequent cooling to room temperature. In-situ diffraction measurements were performed throughout this process. Unfortunately vital decompressional measurements were not attained because of a further blowout proximally to the peak pressure. We were able however to recover the sample and collect numerous X-ray diffraction patterns at 1 atm as well as embed the recovered sample in epoxy resin, and arecurrently preparing this sample for field emission gun scanning electron microscopy and possibly transmission electron microscopy measurements [7]. We noted during run 5 that a significant oil 310 bar oil pressure was required to reach requisite, high enough pressures where the low pressure Sn and Ge phases had transformed completely to their high pressure modifications. We identified, that at least partly responsible for the high oil pressures required to attain these sample pressures, was the sluggish transition of c-Ge to β-Ge. During this transformation namely, the assembly pressure does not rise. To address this issue in the sixth run we increased the number of harder components, to try to make the oil pressure to assembly compression translate more efficient. While a reasonable pressure of 12 GPa was attained, a blowout was not avoided. Despite the blowout, we were able, as for run 5 to recover the sample and it is now also embedded in epoxy and is being prepared for electron microscopy analysis. This will serve as a control for samples recovered where heating was achieved (run5 above and run8, see below). Because run 6 did not improve on run 5, and to attempt to enhance the elastic response of run 5, potentially making gradual decompression possible, in contrast to run 5, we buffered the assembly employed in run 5 by cushioning the ZrO_2 spacers in run 5 with additional top and bottom MgO spacers. This however did not have the desired effect and the assembly destablized at 7.2 GPa. In run 8, we hence took a significant step back from run7 towards run5 by reverting to solely top and bottom ZrO2 spacers, but retaining a MgO sleeve which was not used in run 5. This led to a good run, improving somewhat on that of run5. In particular we reached 13 GPa and heated to our target temperature of 1500 K, largely melting the sample, followed by annealing at lower temperature for 20 minutes and a slightly better decompression to 11 GPa before blowout. Heating was again remarkably stable and in-situ X-ray diffraction patterns were collected throughout. Despite the blowout, as in run5 we were able, also here, to recover the sample and collect a pattern at ambient conditions, albeit not a very high quality one. This sample was also successfully embedded in epoxy and is being prepared for futher electron microscopy analysis.

Despite the incremental improvements in our assemblies, there is still a further, possibly most significant observation, that despite the blowouts, the assemblies themselves were frequently recovered without substantial damage, whereas numerous anvils were lost, indicating that a significant source of the instability likely lies with the quality of the anvils. This is compounded by the sluggishness of the c-Ge to β-Ge transition. Hence next runs require a combination of higher quality anvils, likely examination of 7/3 assemblies for accessing higher pressures with greater ease. Also use the assembly of run8 as a reference to build some degree of elasticity to make the vitally important detailed decompressional behaviour of the synthetic products down to ambient pressure feasible. Coupled with this it is important to better optimize between signal to noise ratio, beam-size and sample chamber dimensions in order to measure with higher spatial resolution and likely minimize effects of temperature gradients on phase distribution during and after heating.

Scientific Advances

In two runs, as described in the technical section, we were able to continuously measure diffraction patterns in-situ to monitor the compressional behaviour of our Ge-Sn mix to 13 GPa in detail. In particular we documented the compression and sharp transition of β-Sn to its denser tetragonal modfication between 9.5 and 10 GPa over a small oil pressure range. In parallel we documented the compressional behaviour of c-Ge and its sluggish transition to its β-Sn modification at 10 GPa (Fig. 1a). The chamber pressure remained at 10

GPa until the transition was complete, and this required a significant change in the oil pressure. We accessed 13 GPa, and this pressure assignment varies somewhat depending on which system was used to calculate the pressure. MgO generally gave a higher pressure than using Sn for example. We state the more conservative value. Stable heating at pressure was achieved until the diffraction pattern of the sample had either dramatically weakened, or vanished, followed by annealing and then temperature quenching (Fig. 1b). The Sn or Sn rich parts of the pattern were retained to higher temperatures than β-Ge or β-Ge rich patterns. This is expected since the melting curves of Sn and Ge cross at about 8 GPa, making Sn the high melting component above this pressure. Upon temperature quenching the two principal Sn peaks of the tetragonal denser modification appear. Unfortunately a key target to monitor the evolutionof the diffraction pattern upon decompression was not achieved in this visit, because of blowouts in both run 5 and run 8 as the oil pressure is lowered, as discussed above. Plans on how to address this are also put forth above. Despite the structural collapse, we did manage to recover the samples and measure release diffraction patterns. These indeed, consistent with our ex-situ experiments [8], reveal sharp β-Sn diffraction patterns together with broad diffraction peaks from the Ge-rich cubic phase, supportive here too of recovery of nanocrystalline Ge-rich cubic diamond (Fig. 1c). While our complementary diamond cell high pressure and temperature experiments indicate a transition to nano-c-Ge rich diamond pahse from the β-tetragonal phase [9], the vital complementary decompresional behaviour from the multianvil experiments will require further measurement employing our suggestions discussed in the technical advance section above.

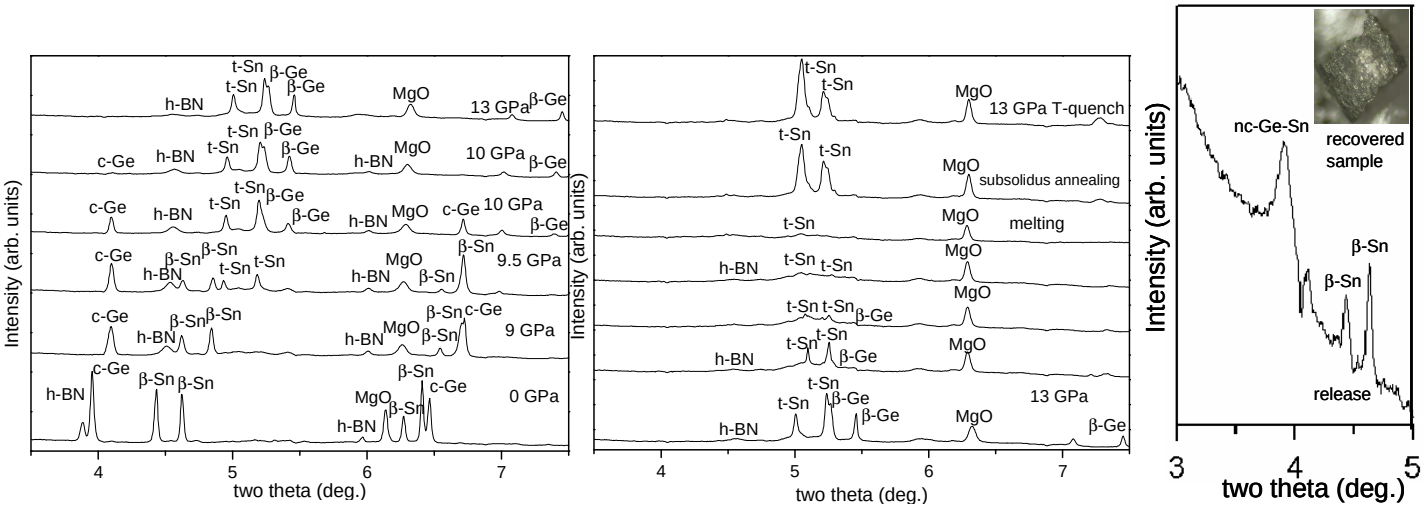

Figure 1. (a) High pressure x-ray diffraction patterns; (b) High pressure and temperature x-ray diffraction patterns; (c) recovered sample and x-ray diffraction pattern

References

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