High Pressure Research: An International Journal

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/ghpr20

Melting and homogeneity in germanium-silicon alloys and a modified micro-manufactured assembly for stable high pressure and temperature measurements†

G. Serghiou[a], N. Odling[b], R. Hunter[a], A. Abbie[a], B. Armstrong[a] & C. Lathe[c]

[a] School of Engineering, University of Edinburgh, Kings Buildings, Mayfield Road, Edinburgh EH9 3JL, UK

[b] The Grant Institute, School of Geosciences, University of Edinburgh, Kings Buildings, West Mains Road, Edinburgh EH9 3JW, UK

[c] Helmholtz Zentrum Potsdam, GeoForschungsZentrum GFZ, D-14473 Potsdam, Germany

Published online: 31 Jan 2014.

To cite this article: G. Serghiou, N. Odling, R. Hunter, A. Abbie, B. Armstrong & C. Lathe , High Pressure Research (2014): Melting and homogeneity in germanium-silicon alloys and a modified micro-manufactured assembly for stable high pressure and temperature measurements†, High Pressure Research: An International Journal, DOI: 10.1080/08957959.2013.856896

To link to this article: http://dx.doi.org/10.1080/08957959.2013.856896

High Pressure Research, 2014
http://dx.doi.org/10.1080/08957959.2013.856896

Taylor & Francis
Taylor & Francis Group

Melting and homogeneity in germanium–silicon alloys and a modified micro-manufactured assembly for stable high pressure and temperature measurements†

G. Serghiou[a]* N. Odling[b], R. Hunter[a], A. Abbie[a], B. Armstrong[a] and C. Lathe[c]

[a]*School of Engineering, University of Edinburgh, Kings Buildings, Mayfield Road, Edinburgh EH9 3JL, UK;* [b]*The Grant Institute, School of Geosciences, University of Edinburgh, Kings Buildings, West Mains Road, Edinburgh EH9 3JW, UK;* [c]*Helmholtz Zentrum Potsdam, GeoForschungsZentrum GFZ, D-14473 Potsdam, Germany*

(*Received 30 August 2013; final version received 10 October 2013*)

We present a modified assembly for high pressure and temperature measurements in a MAX80 press. The designs include a T-shaped power coupler with a ring-shaped insulator, a precision made, all-in-one single-piece crucible, with mirror-image located, flat-bottomed sample and pressure marker chambers, with press-fit lids and thermocouple insert in the middle of the crucible. These features facilitate assembly stability, reproducibility of *in situ* measurements, avoidance of chemical contamination, portability of assembly and ease of sectioning for further analysis. These attributes are important in evaluating phase relations at high pressure, especially where melting of the charge is investigated. While the cubic-diamond structured silicon–germanium system exhibits a complete solid solution, in practice, homogeneous solid solutions are not readily accessible because of the considerable difference in temperature between the liquidus and solidus and concomitant segregation coefficients. We use our designs, for *in situ* X-ray diffraction measurements and melting of germanium–silicon alloys at high pressure for both a germanium-rich and a silicon-rich starting composition.

Keywords: alloys; high pressure phase relations; melting; synthesis; manufacture; diffraction

1. Introduction

Cubic diamond GeSi alloys are important for a range micro, opto and thermoelectric applications.[1,2] In these applications, well-defined, controllable and generally homogeneous chemical distributions are essential. While the silicon-rich side of the phase diagram is more accessible, because the segregation coefficients are smaller than those for germanium-rich starting compositions, homogeneous reaction products are a challenge throughout.[3] Silicon and germanium are stable in the cubic diamond structure to about 10 GPa.[4] Within this pressure regime, their melting points decrease [5,6] as a function of pressure because the liquids are denser than the solids. Indeed by 8 GPa, their respective melting points are reduced by about 30% and concomitantly the absolute melting temperature disparity between the two elements is less by

*Corresponding author. Email: george.serghiou@ed.ac.uk,
†This paper was presented at the LIth European High Pressure Research Group (EHPRG 51) Meeting at London (UK), 1–6 September 2013.

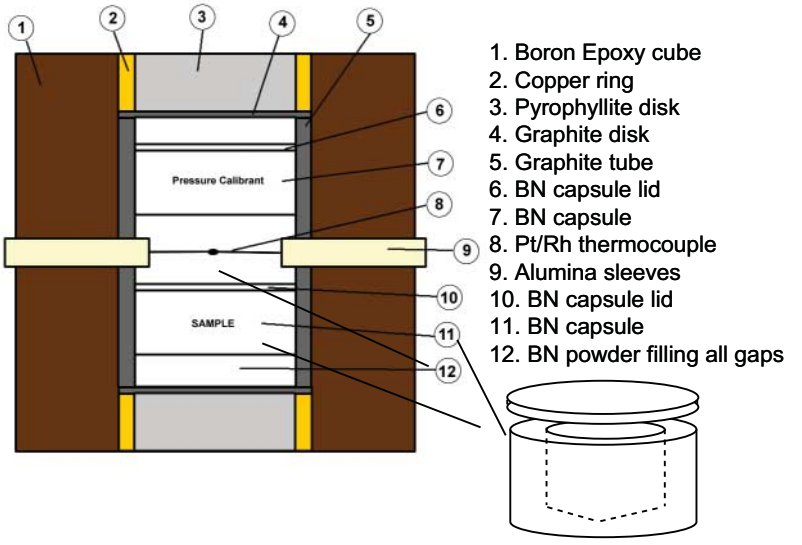

Figure 1. Original sample assembly utilised for high pressure and temperature measurements with the MAX80 press.

about 30%. In addition, with this melting point reduction, further ambient pressure attributes conducive to segregation, such as atomic mobility in the liquid state, can be decreased. The single stage MAX80 press is a relatively easy to operate, effective multi-anvil device in this pressure regime.[7] Also, advantageous are the low Z components of the sample assembly, typically, a graphite heater, a boron nitride (BN) crucible and boron epoxy cube, in which the crucible is contained, which result in *in situ* X-ray diffraction measurements which do not generally suffer from high background or dominant overlapping spurious diffraction patterns. However, particularly in experiments where higher temperatures and/or higher pressures are used, a standard configuration employed, suffered from frequent failures including inability to heat, and *blowouts*. This standard configuration we employed is shown in Figure 1. This configuration consists of the boron epoxy cube, insulating pyrophillite disks, a graphite tube and disks for resistive heating and contact with copper rings and a thermocouple for temperature measurement, NiCrSi for lower temperatures and Pt/Rh for higher temperatures and BN filler powder in various locations. The copper rings serve as power couplers for the current, which passes from the top anvil via the copper rings to the graphite heater and down to the lower anvil. We list principal weaknesses we sought to modify including the particular source of frequent blowouts. One weakness is the use of BN powder as packing filler between the upper and lower capsules and between the upper and lower graphite disks and corresponding capsules (Figure 1), because this results in considerable void space, component mobility and significant arbitrariness in assembly, from load to load. The use of capsule lids which simply sit on the top of the crucibles is also a weakness (Figure 1), because this arrangement may not seal the sample as securely as it could, an element which is particularly important during melting where material is more prone to escape the chamber. Furthermore, the loose lids do not allow for portability or ease of loading, since both capsules need to face upwards. Hence for the bottom crucible, one needs to drop reagent into a crucible which is already deeply entrenched at the bottom of the graphite tube and sitting unevenly on filler BN powder. Furthermore, the initial crucible manufacture with standard drills generates a conical base, meaning that during X-ray line scanning, the diffraction pattern profile and signal to noise ratio vary non-uniformly because the X-ray beam is traversing varying amounts of sample to BN crucible material (Figure 1). Finally, we established the source of the loss of contact and blowouts, by cross-sectional analysis to be, at least in part, due to a selective bevelling of the pyrophillite

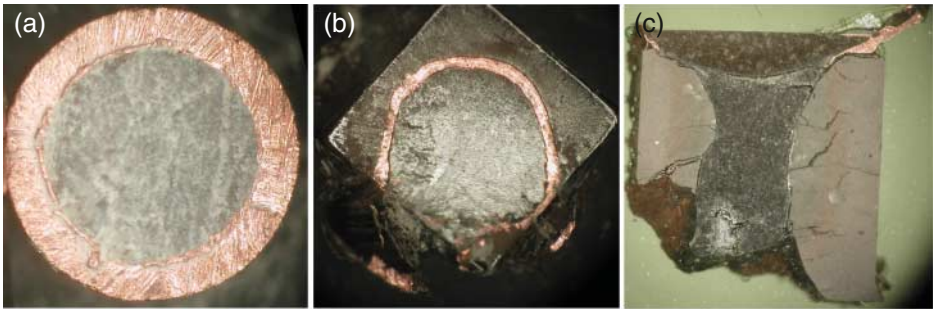

Figure 2. (a) A copper ring power coupler with thermally insulating pyrophillite at ambient pressure, (b) a drastically deformed and ruptured copper ring after release from high pressures and temperatures and (c) cross-sectional view of a recovered assemblage revealing the deformed copper ring and the bevelling of the pyrophillite, amongst others, contributing to loss of copper contact with the heater.

insulating disks which push weaker couplers (in this case copper rings) outwards, leading to loss of contact with the graphite heater and disruption of the boron epoxy cube (Figure 2).

Driven by these challenges associated with this initial standard configuration, we developed a robust and more generic assembly. We did this by changing the geometry of the assembly, as well as, selective materials employed in the micro-manufacturing of the assemblies. The experimental section describes the materials of construction we employed, and the processing tools used. The results and discussion section presents the new assembly geometry, discusses its merits and illustrates these merits with high pressure and temperature measurements in the solid and liquid states on both a germanium-rich and a silicon-rich starting composition mixture. Finally, we conclude by addressing further assembly configuration challenges and germanium–silicon alloy phase relation directions.

2. Experimental techniques

The boron epoxy cubes were made of 75% amorphous boron and 25% boron epoxy. The copper rings were replaced by molybdenum (Goodfellow 99.9% MO007904 rods, centreless ground). The BN was purchased from Kennametal Ltd (BN7000, diffusion bonded sawn bar 7 × 7 × 105 mm). The graphite is from Ceramisis Ltd (GP25 Graphite 5 mm dia × 300 mm long rod, average grain size 5 microns). The pyrophillite is from Ceramic substrates and components Ltd (Ceramit 10 rod 5 mm × 150 mm). The Pt/PtRh10% thermocouple wire is from Goodfellow (Pt wire 0.2 mm thick, 20 cm long 008-736-37; Pt/PtRh 0.2 mm thick, 20 cm long 544-592-43). The starting material reagents were Ge pieces (99.9999+% puratronic Alfa Aesar) and Si pieces (99.999% Alfa Aesar). MgO was purchased from Ozark Technical Ceramics Inc. (high purity rods). High purity BN is essential to avoid binder contamination. It is further easy to machine, relatively inert and a low Z material markedly minimising interference with diffraction measurements. Molybdenum is hard and has a high melting point, making it much more stable than copper, albeit with a lower thermal conductivity. The GP25 graphite is low porosity, machinable and low Z. The pyrophillite is semi-sintered to withstand deformation, yet not so hard that it is not machinable. The MgO rods are chosen, because they are inert, refractory and ideal for machining plug-shaped pressure markers. These are press-fit into the BN chambers hence further reducing porosity. Pt/PtRh10% is robust and the alumina sheaths vital for avoiding breakages. The components required for the microreactor assemblies were micro-manufactured at the University of Edinburgh utilising both manual fabrication (EMCO Unimat 3 Jeweller's lathe) (tolerance of about 10 microns) and computerised numerical control (CNC) fabrication (ProtoTRAK SLX CNC lathe) (tolerance

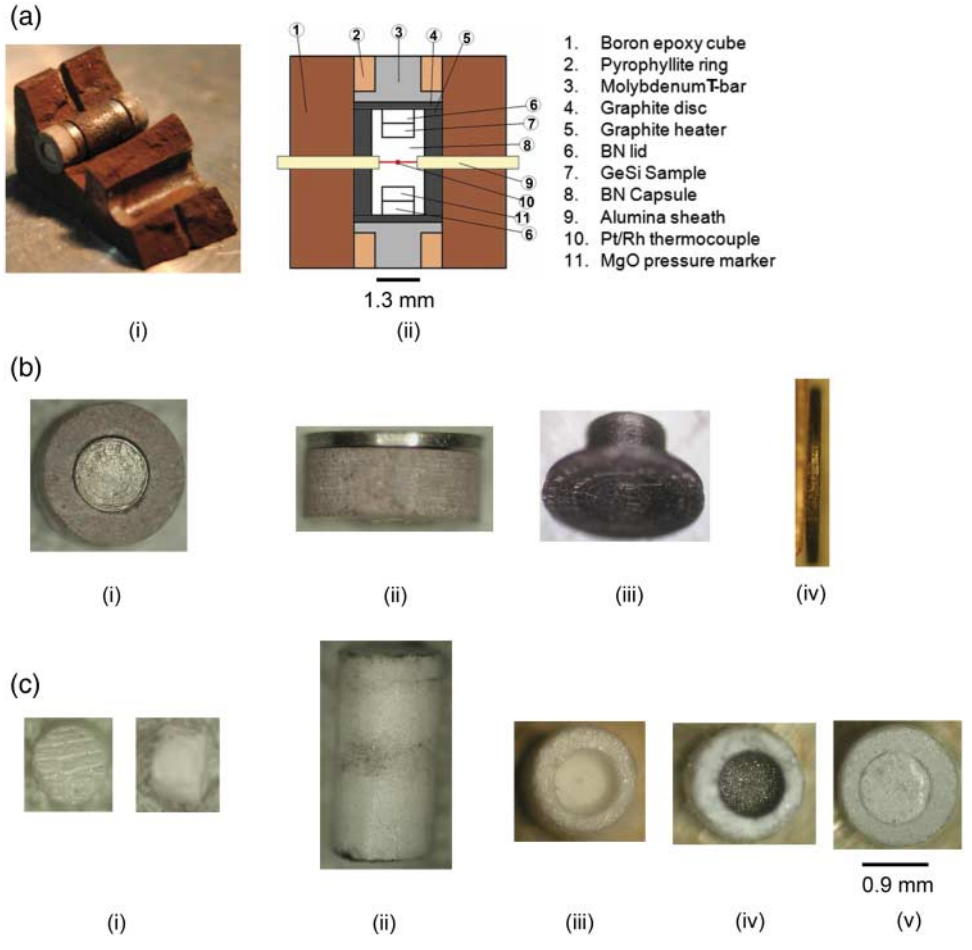

Figure 3. (a) From left to right, (i) an image of the complete assembly inside the cube and (ii) a schematic of the assembly with a scale bar at the bottom; (b) from left to right, pyrophillite ring press-fit on a molybdenum T-bar, (i) top view, (ii) same item side view, (iii) image of the T-bar in isolation and (iv) a side view of a graphite disk; (c) from left to right, (i) images of press-fitting MgO pressure marker and BN lid, (ii) fully packed all-in-one BN capsule, (iii) a top view of the capsule before sample loading showing the flat bottom, (iv) the capsule loaded half-way up with pressed powder and (v) with the press-fit lid flush across the top with another scale bar at the bottom.

of about 50 microns). A detailed schematic together with images of the components is shown in Figure 3. Additional molybdenum rings were also tested. Furthermore, carbide drills were employed for many of the micromachining processes.

The experiments were performed on F2.1 at DESY. Similar experiments for diffraction as well as deformation (D-DIA) are used in the USA and Japan.[8] The multiAnvil-type high pressure X-ray system, or MAX80, is a multi-anvil press consisting of a 2500 N hydraulic ram and two load frames. These drive four reaction bolsters for the lateral anvils which, together with top and bottom bolsters push six tungsten carbide anvils compressing the cube assembly.[7] In addition to this, the top and bottom anvils conduct a current through the cube, allowing for resistive heating to take place within the cube. The beam of collimated, white X-rays (energy dispersive mode) is guided through a gap in the tungsten carbide anvils and through the sample being investigated, where it is scattered at an angle of 2θ. The energy distribution of the scattered photons, and concomitant diffraction patterns were analysed using a liquid nitrogen cooled Ge solid-state detector. *Ed* was determined, using the MgO pressure marker. The pressure was evaluated using

an equation of state of MgO.[9] The temperature was measured using Pt/PtRh thermocouples. Diffraction line scanning was performed to evaluate the structure across the sample. Vanishing of peaks was employed to monitor melting. Ge fluorescence lines were used to ensure that the beam was hitting the sample. The sample composition was evaluated based on the position of the lattice parameters.[10] We refer to the schematic and images (Figure 3) of our modified design in the discussion below, and present three experiments here, one using a 1:3 Ge:Si starting atomic percent compositional mixture and two employing a 3:1 Ge:Si starting atomic percent compositional mixture.

3. Results and discussion

Figure 4(a) is of a 3:1 Ge:Si starting mix to 5.4 GPa including patterns in the melt and upon recovery. The presence of two significantly different compositions demonstrates segregation ease at the pressures of this experiment for the Ge-rich sample. Figure 4(b) conversely, of a 1:3 Ge:Si starting mix including a pattern in the melt and upon recovery indicates only marginal segregation, indicating that pressure may assist in homogeneous alloy formation, supported also by the lower segregation coefficient [11] associated with the Si-rich section of the phase diagram, as noted in the introduction. A very detailed, evolution of the development of this Si-rich alloy from the component elements at high temperature, at pressure, all the way through melting is shown in

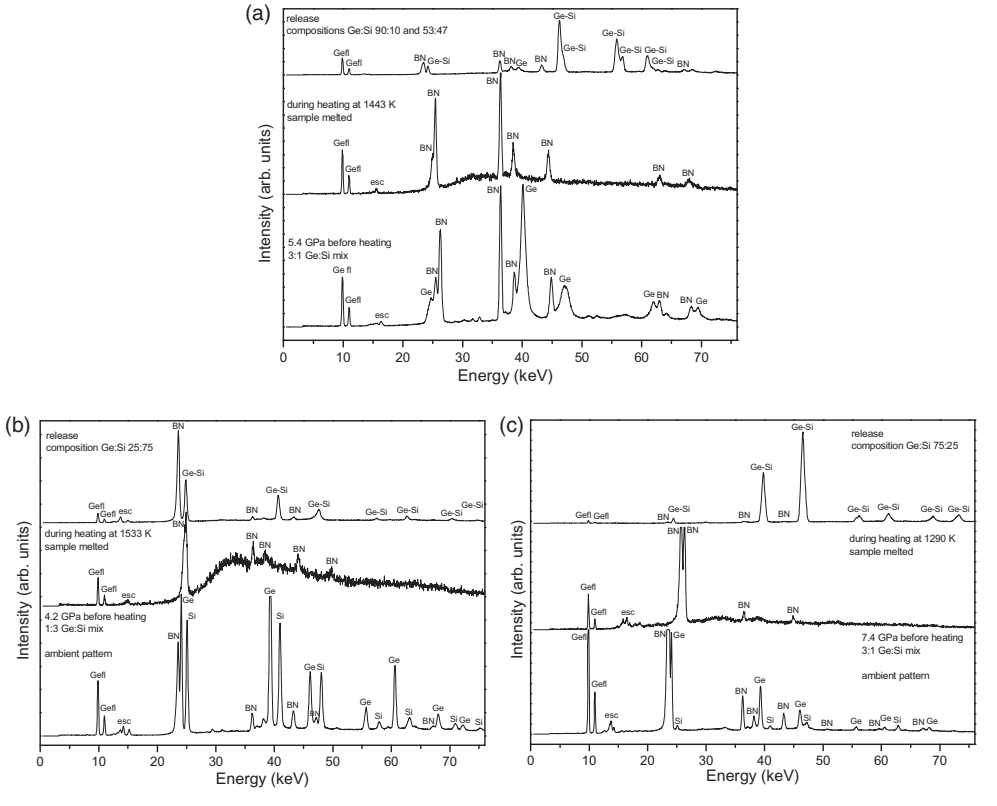

Figure 4. High pressure and temperature energy dispersive X-ray diffraction measurements through the solid–liquid transition of (a) a 3:1 Ge:Si atomic ratio starting mix to 5.4 GPa and 1443 K, (b) a 1:3 Ge:Si atomic ratio starting mix to 4.2 GPa and 1533 K and (c) a 3:1 Ge:Si atomic ratio starting mix to 7.4 GPa and 1290 K GPa.

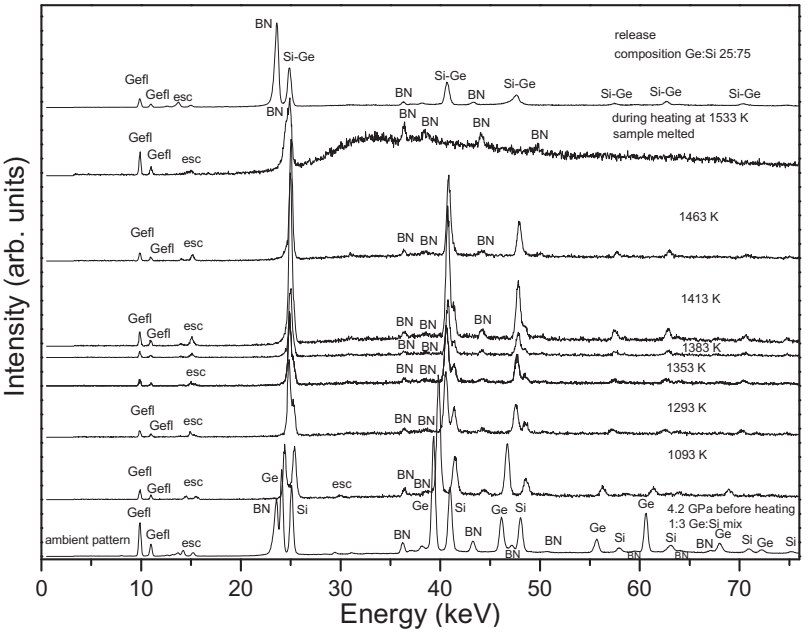

Figure 5. Detailed step-by-step evolution of the alloying transformation 1:3 Ge:Si starting mix as function of temperature at pressure through the melt transition and recovery of a $Ge_{0.25}Si_{0.75}$ cubic diamond alloy.

Figure 5. Figure 4(c) of a 3:1 Ge:Si starting mix to 7.4 GPa, 2 GPa higher than our other Ge-rich experiment (Figure 4(a)), indicates a much diminished segregation of a Ge-rich sample which may be consistent with decreased atomic mobility in the melt in targeted higher pressure regions,[12] but compositional variation and further experiments need to be considered for this.

From our investigations, we highlight here important sources of instability in our prior assemblies. Copper rings were used as the power coupler between the anvils and graphite heater with pyrophillite thermal insulation placed in the middle. The combination however of low strength, low melting point copper and its exposure to high pressures and temperatures as well as pronounced bevelling of the pyrophillite contributed to ruptures, flow, shorts, loss of contact with the heater and very frequently blowouts (Figure 2). One significant improvement was introduction of higher strength, higher melting molybdenum as the power coupler, concomitant with a re-design of the coupler from a ring with the pyrophillite inside, to a T-bar with the pyrophillite outside (Figure 3(a) and 3(b)). This combination contributed to an assembly, with significantly improved mechanical integrity and power coupling contact at high pressure and temperature conditions (Figures 6). Several further improvements through our materials selection and precision micromanufacturing, include a single-piece triple chamber BN assembly (for the sample, the MgO marker and the Pt/Ph) (Figure 3(a) and 3(c)), flat, rather than conical sample and marker bases, press-fit solid BN lids and MgO pressure markers, a denser small grain size, precision graphite heater and lid assemblies (Figure 3(a)–(c)). The additional improvements permit easy containment and sample measurement in its liquid state as well, reduce porosity, improve reproducibility of measurement during X-ray scanning, prevent contamination, and allow better structural and pressure-temperature profiling and facilitate portability and recovery for further complementary ongoing processing and analyses (Figure 7). Furthermore, prior procedure to revert to larger size boron epoxy cubes for higher temperature measurements at lower pressures, is not necessary. One-size cube and one set of crucible assemblies suffice. This also allows more controlled comparisons between runs. More broadly the new assembly designs are transferable to other high pressure devices.

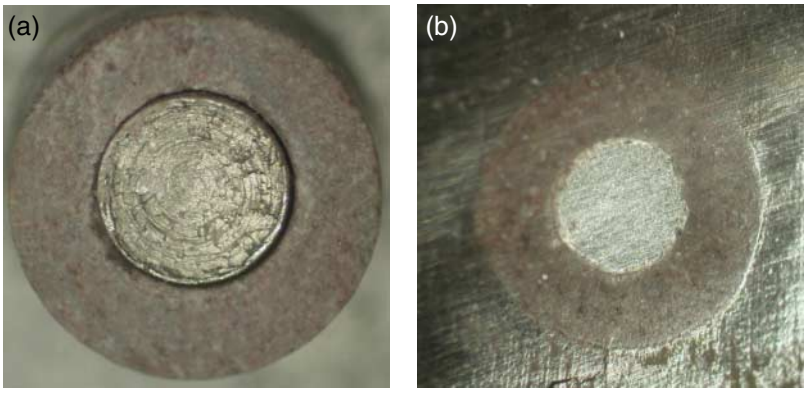

Figure 6. (a) A molybdenum T-bar power coupler with thermally insulating pyrophillite at ambient pressure and (b) a virtually undeformed molybdenum/pyrophillite assemblage after release from 8.52 GPa (before heating) and 1273 K.

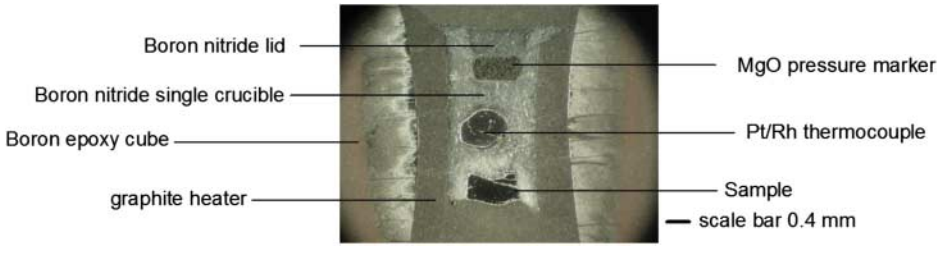

Figure 7. Section of a precision manufactured single-piece all-in-one reaction assembly analysed *in situ* at high pressures and temperatures with X-ray diffraction, polished for further electron microscopy analysis.

4. Conclusions

One significant area that still requires improvement is in preventing pressure relaxation after heating. This is interrogated through improvement of the boron epoxy composite and size scaling of the microreactor assembly. Augmentation of energy dispersive X-ray diffraction with angle dispersive X-ray diffraction, is important, for further correlation of the GeSi alloy phase relations and transport properties as a function of pressure and temperature, as well as *ex situ* electron microscopy analysis. Detailed higher pressure studies beyond the cubic diamond stability field are being prepared for publication as well.

Acknowledgements

We thank the workshops in Engineering and Geoscience at the University of Edinburgh, as well as the workshop at the Deutsches Elektronen-Synchrotron (DESY) in Hamburg for generous support

References

[1] Schilz J, Romanenko VN. Bulk growth of silicon–germanium solid solutions – review. J Mater Sci Mater Electron. 1995;6:265–279.
[2] Moontragon P, Ikonic Z, Harrison P. Band structure calculations of Si–Ge–Sn alloys: achieving direct band gap materials. Semicond Sci Technol. 2007;22:742–748.
[3] Dario A,. Sicim AO, Balicki E. A new approach for dopant distribution and morphological stability in crystals grown by the axial heat processing (AHP) technique. J Cryst Growth 2011;337:65–71.
[4] Young DA. *Phase diagram of the elements*. Berkeley: University of California Press; 1991.

[5] Kubo A, Wang YB, Runge CE, Uchida T, Kiefer B, Nishiyama N, Duffy TS. Melting curve of silicon to 15 GPa determined by two-dimensional angle-dispersive diffraction using a Kawai-type apparatus with X-ray transparent sintered diamond anvils. J Phys Chem Solids. 2008;69:2255–2260.
[6] Voronin GA, Pantea C, Zerda TW, Zhang J, Wang L, Zhao Y. In-situ X-ray diffraction study of germanium at pressures up to 11 GPa and temperatures up to 950 K. J. Phys Chem Solids. 2003;64:2113–2119.
[7] Mueller HJ, Schilling FR, Lathe C. Multianvil techniques in conjunction with synchotron radiation at Deutsches ElektronenSYnchotron (DESY) – HAmburger SYnchotron LABor (HASYLAB). Geol Soc Am. 2007;421:207–225.
[8] Wang YB, Rivers M, Sutton S, Nishiyama N, Uchida T, Sanehira T. The large volume high-pressure facility at GSECARS: a "Swiss-army-knife" approach to synchrotron-based experimental studies. Phys Earth Planet In. 2009;174:270–281.
[9] Jamieson JC, Fritz JN, Manghnani MH. Pressure measurement at high temperature in X-ray diffraction studies: gold as a primary standard. In: Akimoto S, Manghnani MH, editor. High Pressure Research in Geophysics., Tokyo: Cent. for Acad. Publ.; 1982. p. 27–48.
[10] Dimsukes JP, Paff RJ, Ekstrom L. Lattice parameter and density in germanium silicon alloys. J Phys Chem. 1964;68:3021–3027.
[11] Matsumura R, Tojo Y, Kurosawa M, Sadoh T, Mizushima I, Miyao M. Growth-rate-dependent laterally graded SiGe profiles on insulator by cooling-rate controlled rapid-melting-growth. Appl Phys Lett. 2012;101:241904-1–241904-5.
[12] Belashchenko DK. Modeling of liquid silicon at pressures up to 23 GPa from diffraction data. Inorg Mater. 2003;39:459–463.