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REGULAR ARTICLE

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

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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*

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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 throughout³. Silicon and Germanium are stable in the cubic diamond structure to about 10 GPa⁴. 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 thirty percent and concomitantly the absolute melting temperature disparity between the two elements is less by about thirty percent. 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 multianvil device in this pressure regime⁷. Also advantageous are the low Z components of the sample assembly, typically, a graphite heater, a boron nitride 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 pyrophyllite 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 boron nitride 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 boron nitride powder as packing filler between the upper and lower capsules and between 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. Further, 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. Further, 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 varies 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 pyrophyllite 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 state 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 boron nitride was purchased from Kennametal Ltd (BN7000, diffusion bonded sawn bar 7x7x105 mm). The graphite is from Ceramisis Ltd (GP25 Graphite 5 mm dia x 300 mm long rod, average grain size 5 microns). The pyrophyllite is from Ceramic substrates and components Ltd (Ceromit 10 Rod 5mm x 150mm). 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 boron nitride is essential to avoid binder contamination. It is further easy to machine,

relatively inert and a low Z material markedly minimizing 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 pyrophyllite 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, 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 of about 50 microns). A detailed schematic together with images of the components is shown in figure 3. Additional molybdenum rings were also tested. Further, 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 US and Japan⁸. The multiAnvil-type high pressure X-ray system, or MAX80, is a multi-anvil press consisting of a 2500N 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 assembly⁷. 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 analyzed using a liquid nitrogen cooled Ge-solid state detector. E_d was determined, using the MgO pressure marker. The pressure was evaluated using an equation of state of MgO⁹. 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 parameters¹⁰. 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 4a 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 4b conversely, of 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 coefficient¹¹ 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 5. Figure 4c of a 3:1 Ge:Si starting mix to 7.4 GPa, 2 GPa higher than our other Ge-rich experiment (Figure 4a), 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 regions¹², 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 pyrophyllite 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 pyrophyllite 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 pyrophyllite inside, to a T-bar with the pyrophyllite outside (Figure 3ab). 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 micro-manufacturing, include a single piece triple chamber BN assembly (for the sample, the MgO marker and the Pt/Rh) (Figure 3ac), 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 3abc). 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 suffices. This also allows more controlled comparisons between runs. More broadly the new assembly designs are transferable to other high pressure devices.

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.

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Figure Captions

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

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

Figure 3. (a) From left to right, (i) an image of the complete assembly inside the cube, (ii) a schematic of the assembly with a scale bar at the bottom, (b) from left to right, pyrophyllite ring press-fit on a molybdenum T-bar ((i) top view, (ii) same item side view, and (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.

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 GPa, and (c) a 3:1 Ge:Si atomic ratio starting mix to 7.4 GPa and 1290 K.

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 $\text{Ge}_{0.25}\text{Si}_{0.75}$ cubic diamond alloy.

Figure 6 (a) A molybdenum T-bar power coupler with thermally insulating pyrophyllite at ambient pressure, (b) a virtually undeformed molybdenum/pyrophyllite 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 analyzed in-situ at high pressures and temperatures with X-ray diffraction, followed by further electron microscopy analysis

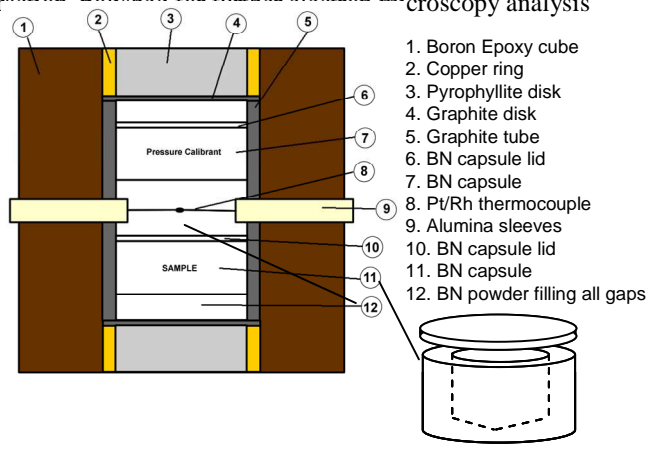


Figure 1

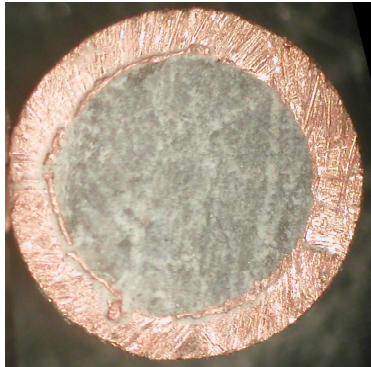


Figure 2a

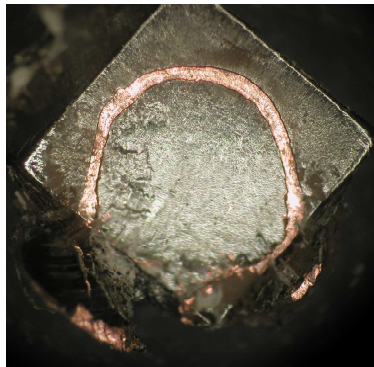


Figure 2b

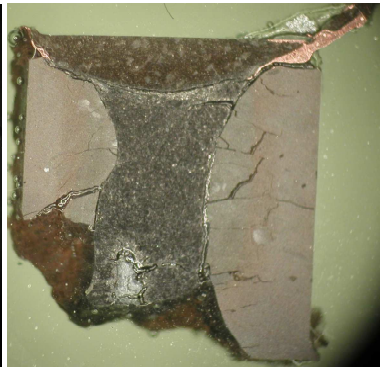


Figure 2c

Figure 3a

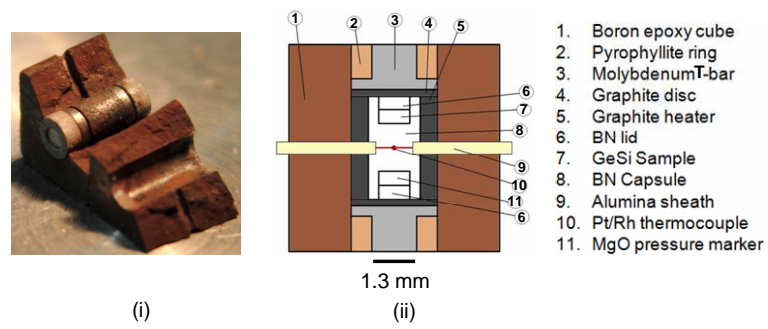


Figure 3b

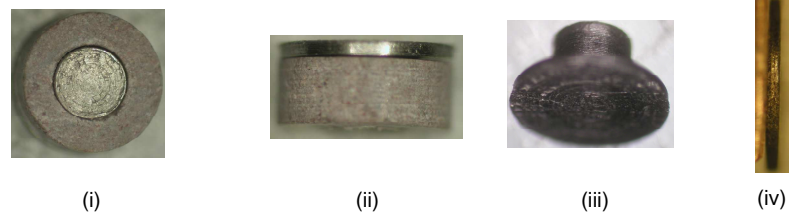
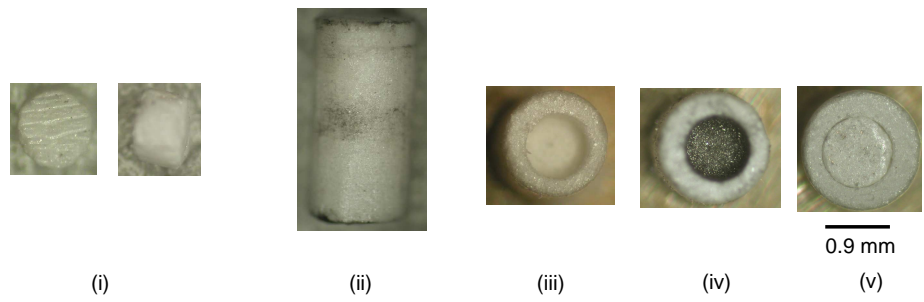


Figure 3c



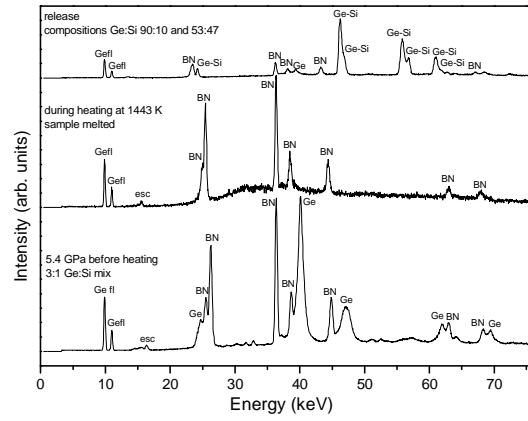


Figure 4a

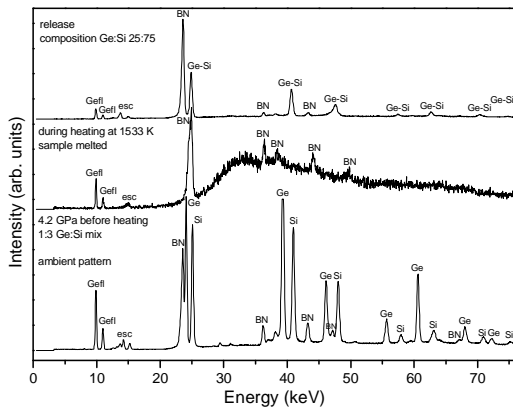


Figure 4b

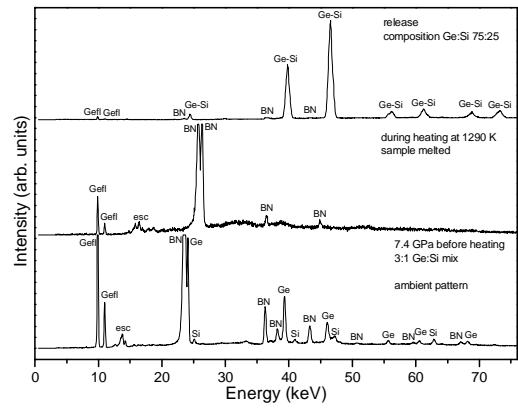


Figure 4c

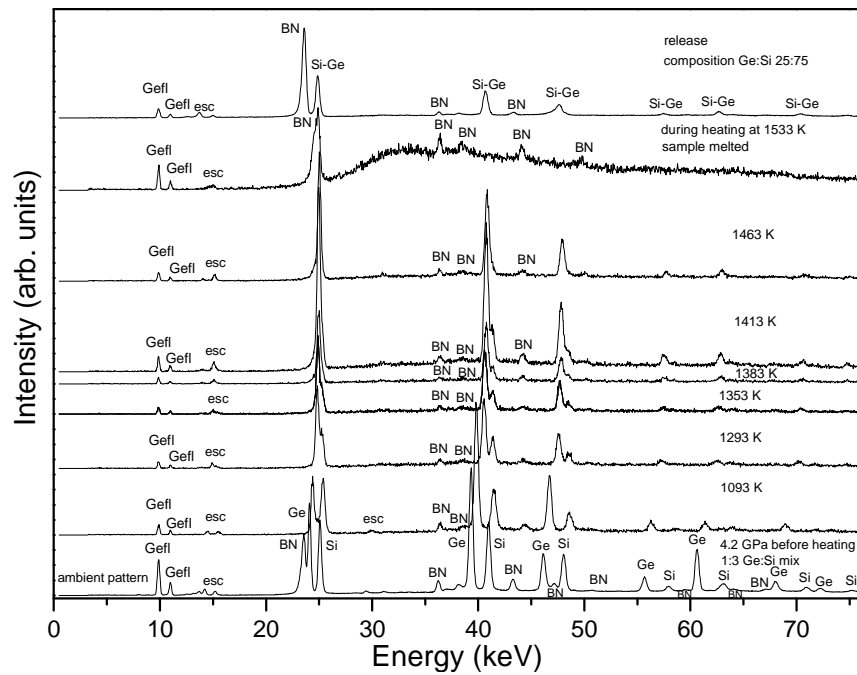


Figure 5



Figure 6a



Figure 6b

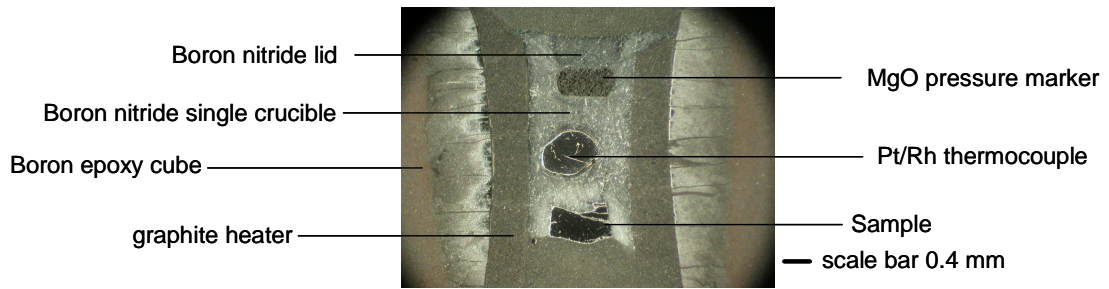


Figure 7