

Tuning between Mixing and Reactivity in the Ge–Sn System Using Pressure and Temperature

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Group 14 (C–Si–Ge–Sn–Pb) systems are of primary importance.¹ C is the backbone of organic matter and of diamond. Si is a central component of computers. Si–Ge is principal in heterojunction bipolar devices. SiC is ideal for polishing and grinding applications. Pb–Sn is ubiquitous in materials textbooks. Ge and Sn, however, have virtually no mutual solubility at ambient pressure.² Recent work though, employing deuterated precursors, produced Ge–Sn thin films on Si substrates.^{3a} These and further studies³ underlining optoelectronic applications due to direct band gap formation and lattice matching with Si have sparked significant interest in preparing bulk Ge-rich, GeSn crystals. The challenge is to transform not only the structure, as in the graphite to diamond transition, but also the reactivity of Ge with Sn.

We identify a pressure region between 9 and 10 GPa where the two elements can adopt the same crystal structure (β -tin) (Figure 1a) and their atomic radii ratios are within 13% of each other (Figure 1b). The valency of diamond structured Ge and Sn is considered to be +4 and lowered to values between 2 and 0 in their metallic states, which β -tin already adopts at room conditions.⁸ Based on the Pauling scale, the electronegativities of diamond structured Ge and Sn are 2.01 and 1.96, respectively. The electronegativity of Sn (+2) is 1.8,¹ and that of Ge (+2) in the metallic state is arguably similar. Thus the two elements can be viewed as having similar valencies and electronegativities above \sim 9 GPa when they are both in the metallic state. Hence, high pressure could allow us to overcome the ambient pressure status quo by accessing conditions consistent with the Hume–Rothery rules for bulk Ge–Sn solid solution formation ((i) atomic radii difference <15%, (ii) similar electronegativities, (iii) same crystal structure, (iv) same valence).⁹ Indeed in work which may have a bearing on the Earth's core, the first rule has been exploited to dissolve up to 10 atom % Mg metal at 126 GPa in Fe metal.¹⁰ The region of most interest here upon compression seems to be between \sim 9 and 10 GPa where Ge becomes a metal like Sn, and the atomic size ratios could occur with a lower than 15% value. Several other issues should be noted with regards to the possible stability or metastability of novel bulk Ge–Sn alloys in a wider P – T range. First, Ge is metallic in the liquid state like Sn,¹¹ and its local structure becomes more β -Sn-like with increasing pressure.¹¹

Thus, fast melt-quenching even at ambient pressure should at least be considered in an attempt to recover a metastable Ge–Sn crystal.

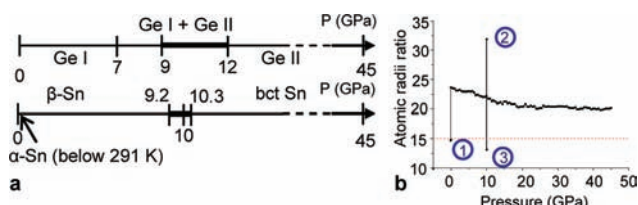


Figure 1. Ge and Sn crystal structure comparison upon room temperature compression. (a) Semiconducting GeI (diamond structure) transforms to metallic GeII (β -tin structure ($I4/amd$)) above \sim 9 GPa and coexists with GeII to 12 GPa.⁴ GeII can be retained to \sim 7 GPa upon decompression.⁴ The β -Sn-bct Sn ($I4/mmm$) transition occurs at 9.2–10.3 GPa.^{5,6} (b) Ge–Sn atomic radii ratio (%) pressure dependence.⁷ Points 1–3 show respectively the ratios, at 1 atm between α -Sn (below 291 K) and GeI; at 10 GPa between GeI and bct Sn ($I4/mmm$); and between Ge and Sn, both in the β -Sn structure.

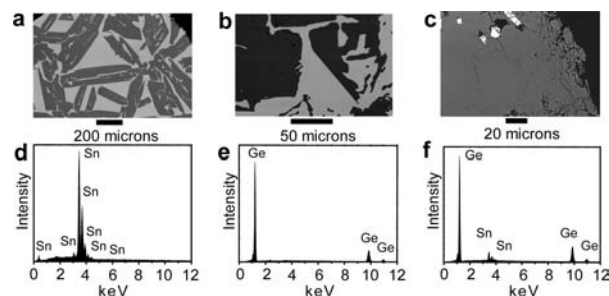


Figure 2. SEM images after heating a Ge/Sn mixture at (a) 1500 K at 1 atm for 10 min, (b) 1500 K at 8 GPa for 5 min followed by annealing at 8 GPa at 820 K for 1 h, and (c) 1500 K at 10 GPa followed by annealing at 770 K for 1 h, before temperature and then pressure quenching. (d,e) EDX analyses of the two regions of the samples recovered from 1 atm (shown) and 8 GPa reveal segregation of (d) Sn (light contrast regions) from (e) Ge (dark contrast regions). (f) EDX analyses from (c) reveal a uniform $Ge_{0.9}Sn_{0.1}$ composition.

Second, calculations suggested a Sn uptake in Ge of 20 atom % at 5 GPa and 1000 K and 50 atom % up to 9 GPa at 0 K.¹²

The samples recovered from experiments up to 9 GPa all show separation of Sn from Ge, either directly upon melt-quenching or after annealing (Figure 2a,b,d,e).¹³ The situation is drastically changed at 10 GPa where Ge and Sn react and a uniform single phase morphology is obtained after annealing (Figure 2c,f). In 14 multianvil experiments above 10 GPa regardless of heat treatment protocol or pressure, no such homogeneous region was observed, even though segregation into pure Ge and pure Sn was not attained (Figure 3a,b). At 10 GPa extensive chemical analysis throughout the sample revealed a uniform $Ge_{0.9}Sn_{0.1}$ composition (Figure 2f). No elemental Ge or Sn was detected anywhere. Zone-axis diffraction patterns from numerous crystals

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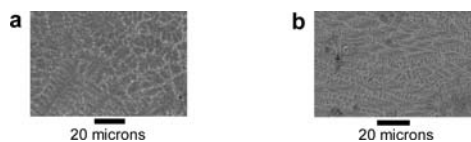


Figure 3. SEM images after heating (a) a Ge/Sn mixture at 1500 K at 14 GPa for 5 min followed by annealing at 770 K for 1 h and (b) a Ge/Sn mixture at 1500 K at 24 GPa for 5 min, followed by temperature and pressure quenching. In (a) and (b) the boundaries between the dark (Ge-rich) and light (Sn-rich) contrast agglomerates are diffuse and analysis is very challenging due to the small agglomerate sizes and the intimate mixture of the small crystallites within them.

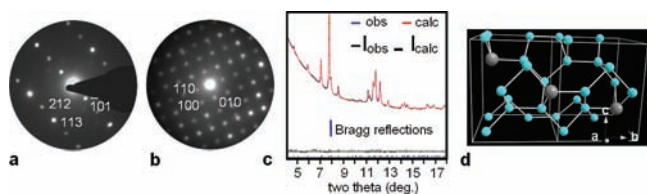


Figure 4. (a) [001], (b) [1-41] electron microdiffraction zone-axis and powder (c) X-ray diffraction patterns of the tetragonal (S.G. $P4_32_12$) $\text{Ge}_{0.9}\text{Sn}_{0.1}$ structure. (d) Schematic representation of the structure which consists of 4-fold coordinated Ge (turquoise) and Sn (gray) atoms.

throughout the homogeneous chemically analyzed region (Figure 4a,b) and a supporting angle dispersive X-ray powder diffraction pattern were collected (Figure 4c) and showed excellent fits to the $P4_32_12$ tetragonal structure ($a = 6.014$ (1) Å, $c = 7.057$ (1) Å, $Z = 12$) (Figure 4d). Our measurements thus show that a bulk crystalline $\text{Ge}_{0.9}\text{Sn}_{0.1}$ solid solution, unformable at ambient pressure, can be recovered from 10 GPa after melting and annealing. The a,c lattice parameters due to the solid solution of 10 atom % of the larger Sn atom in the structure are greater by 1.4% and 1.1%, respectively, than those of endmember Ge $P4_32_12$ which can also be recovered from high pressure.¹⁴ These results are consistent with our analysis that pressure promotes Ge–Sn reactivity and particularly favors alloy formation between 9 and 10 GPa (Figure 1). A caveat is that the temperature regime between 9 and 10 GPa at which this compatibility occurs is from ambient temperature to ~ 320 K⁷, which is below the temperature of synthesis. This region is nevertheless traversed upon cooling to room temperature. At lower pressures the incompatibilities are pronounced. The atomic size ratios are above 20%, Ge is a semiconductor, and the crystal structures are different at all temperatures from ambient upward. Above 10 GPa the size ratios plateau at $\sim 20\%$ (Figure 1). Further, while the electronegativities and valencies arguably become even more similar as pressure is increased, since the degree of metallicity increases¹¹ in Ge, the Ge and Sn crystal structures do not overlap again.¹⁵ These considerations also clarify the more detailed nature of the recovered products over the entire P – T range presented here (Figures 2,3). Thus to ~ 3 GPa the combination of still somewhat dissimilar liquid states both structurally and electronically¹¹ and distinctly dissimilar structurally and electronically solid states means that segregation into pure Ge and Sn will easily take place even directly after melt-quenching, whereas between ~ 3 and 9 GPa the liquid state likely becomes increasingly more homogeneous,¹¹ while the Ge and Sn solid states are still very different, necessitating annealing for segregation of Sn from Ge. In a window around 10 GPa, both the structural and electronic properties in the solid state satisfy the conditions for solid solution giving rise to a completely homogeneous recovered GeSn product. Above 10 GPa mixtures of Ge- and Sn-rich agglomerates of varying extent were always recovered, regardless of annealing time, likely because of the combination of an increasingly homogeneous liquid phase, followed by a metallic solid state. The atomic radii and crystal

structure incompatibility however make formation of a Ge–Sn solid solution problematic.

This is unlike the generally observed enhancement of emergent properties on further compression. Added factors that may promote Sn uptake by Ge near 10 GPa are that they undergo crystal and electronic transitions there⁶ and Ge is near a low-lying triple point,⁴ making this reconstruction region more conducive to reaction and bulk homogeneous solid solution formation. Notably this region also figures prominently in bulk homogeneous Ge-metallic glass formation¹⁶ by exploiting the low liquid diffusivity near the triple point, coupled there, with rapid quenching.

Tetragonal Ge is calculated to have a direct band gap.¹⁷ Hence, our novel tetragonal Ge-rich solid solution is of optoelectronic interest because, unlike the other ambient pressure prepared group IV elements and binaries, it most likely exhibits a tunable with Sn-content direct band gap. Further, that elusive $P4_32_12$ Si could upon doping have a higher superconducting temperature than those of other Si modifications¹⁸ can be pursued with the methods here. Si does not form the tetragonal phase, but a targeted solution with Ge which does should allow us to recover a bulk Si-based tetragonal phase. Several further elements undergo electronic and crystal transitions and exhibit low-lying triple points, selective groupings of which can also be targeted for new material designs.

Acknowledgment. High-pressure experiments were performed at the Bayerisches Geoinstitut under EU Contract No. 505320 (RITA) and were partially supported by the UK EPSRC.

Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA902466W