Exploring Formation of a Novel Ge-Sn Phase at High Pressure-Temperature Conditions

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Intragroup alloys and compounds formed between the group-IV elements have varied technological applications in view of their excellent mechanical and optical properties [1]. For instance, SiC is used for polishing and grinding applications and SiGe is used in hetero junction bipolar devices. GeSn is another group IV-IV system which is predicted to be a direct band gap semiconductor with tunable band gap. Thin films of Ge\textsubscript{1-x}Sn\textsubscript{x} alloys with cubic diamond structure have been formed by non-equilibrium techniques such as chemical vapor deposition (CVD) and pulsed laser ablation [2]. Bulk synthesis of the Ge-Sn system has however been difficult due to the large atomic radii difference, different crystal structures and different electro negativities in their elemental states at ambient P and T conditions. The difference between the atomic radii can be minimized by subjecting Ge and Sn to ~ 9 GPa, when their crystal structures become same (beta-Sn) following the structural transition in Ge [3]. Subsequent application of high temperatures can lead to formation of Ge-Sn bonds.

Recently, we have adopted this methodology to explore formation of a Ge-Sn phases at high P-T conditions using a laser heated diamond anvil cell facility (LHDAC) developed at our laboratory [4]. In situ micro-Raman spectroscopy done on several regions of samples laser heated at P ~9 GPa revealed appearance of two new modes which we could ascribe to Ge-Sn bond formation [5]. Pressure variation of the frequencies of the new modes suggests that the Gruneisen parameter of the Ge-Sn phase and its pressure variation is intermediate between that of bulk Ge and beta-Sn. It can therefore be expected that high pressure XRD experiments on laser heated Ge+Sn mixtures will possibly confirm formation of a new Ge-Sn phase. XRD experiments at high pressure and high temperatures using laser heated diamond anvil cell technique was carried out at the Extreme Conditions Beamline P02.2 with an aim to obtain well resolved HPXRD patterns with good signal to noise ratio essential to clearly discern the features associated with the new phase formed, if any, under high P-T conditions from the parent phases.

Studies exploring formation of a novel Ge-Sn Phase at high P-T conditions were done during the nine shifts allotted. An intimate mixture of elemental germanium (Ge) and tin (Sn) was ground to fine powder in a glove box and loaded in a symmetric diamond anvil cell belonging to PETRA-III. A halide salt was coated on both anvils for thermal insulation for the simultaneous laser heating and HPXRD experiments. Pressure was raised slowly to ~ 9 GPa, just up to the threshold of a structural transition in Ge. While attempting to heat with the high power IR laser, it was seen that the coupling was not efficient. Further the HPXRD patterns revealed that the Ge was highly oriented as compared to Sn. A second attempt was made by increasing the thermal insulation layer thickness and loading another batch of Ge+Sn. This time the laser heating at ~ 9 GPa was efficient and estimated temperature was ~ 2000 K. After coinciding the laser focal spot and the x-ray spot on the sample, simultaneous heating and XRD runs were made by rocking the sample by ± 6° for several minutes and several cycles. This was found useful for eliminating secondary diffraction rings from the diamonds. Preliminary analysis based on comparing the HPXRD patterns before and after heating showed some drastic changes indicating formation of a Ge-Sn phase (Fig.1). The T-quenched sample was slowly de-pressurised and HPXRD patterns recorded at a few pressure steps.
to find the evolution of the new peaks. Detailed analysis is presently underway to eliminate possibilities of reaction products other than between Ge and Sn and identify unambiguously the newly formed phases.

Figure 1: Representative HPXRD patterns of Ge-Sn system before (black) and after laser heating (red) to ~2000 K at ~9 GPa. A pattern after pressure release to ~0.5 GPa (blue) is also shown and compared with the PC-PDF stick patterns of the starting elemental Ge (wine red) and Sn (greenish-yellow), as also the CaF₂ thermal insulator layer (violet). The photograph on the top right is a view through the anvils of the Ge-Sn reaction taking place at ~9 GPa and ~2000 K.

References