Pressure-induced phase transformation of In$_2$Se$_3$

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Indium selenide (In$_2$Se$_3$) is a III–VI semiconductor that exists in multiple crystalline phases, including the layered $\alpha$ and $\beta$ phases and the defect wurtzite $\gamma$ phase. Recently, In$_2$Se$_3$ has received attention as a phase-change material that could be used in phase-change random access memory (PRAM) applications. In$_2$Se$_3$ may be preferable over Ge$_2$Sb$_2$Te$_5$ as a potential PRAM material because of its high resistivity and the large difference in resistivity between the crystalline and amorphous phases. In addition, the crystalline-crystalline phase transitions of In$_2$Se$_3$ may allow for multi-level memory. The use of In$_2$Se$_3$ in a PRAM device requires the ability to precisely control the switching between phases. To accomplish this, it is important to understand the phase transformations of the material under various conditions of temperature and stress.

Known temperature-dependent phase transitions for bulk In$_2$Se$_3$ include the $\alpha \rightarrow \beta$ phase transition at 473 K and the $\beta \rightarrow \gamma$ phase transition at 793 K. While the temperature-induced phase transitions in In$_2$Se$_3$ have been well studied, the pressure dependence of these phase transitions has not been reported. In this paper, we report the results of x-ray diffraction experiments (XRD) performed on In$_2$Se$_3$ powder for pressures up to $\sim$10 GPa. Phase transitions observed in XRD were verified with Raman spectroscopy. In addition, we report the bulk modulus for the $\alpha$ and $\beta$ phases.

Samples of $\alpha$ phase In$_2$Se$_3$ powder (99.99%), purchased from Alfa Aesar, were loaded into a piston-cylinder diamond-anvil cell. A stainless steel gasket was pre-indented for the 600 $\mu$m or 1000 $\mu$m culet diamonds to a thickness of $\sim$50 $\mu$m. A 300 $\mu$m diameter hole was drilled in the center of the indentation and the sample was loaded into the hole along with a pressure transmitting medium of either 4:1 methanol-ethanol mixture or mineral oil. The 4:1 methanol-ethanol mixture is known to provide hydrostatic conditions up to 10 GPa. Mineral oil is hydrostatic up to 4 GPa, as determined by the width and splitting of the ruby lines. Ruby microspheres were inserted for in situ pressure measurements. The pressure was measured before and after each XRD spectrum by the R1 and R2 peak shifts using the Mao scale and the average used as the experimental pressure value with estimated precision of 0.1 GPa. The opening of the DAC limited the maximum 2-theta value to $15^\circ$–$20^\circ$.

XRD experiments were performed at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LLNL), beamline 12.2.2 (Ref. 11) and the Cornell High Energy Synchrotron Source (CHESS), Cornell University, beamline B2. Samples were loaded to a pressure of $\sim$0.2 GPa and spectra were taken for both compression and decompression. All experiments were done at ambient temperature. Spectra were collected at wavelengths between 0.4859 and 0.6199 $\AA$ by a high resolution MAR3450 plate detector. Diffraction images were integrated using the FIT2D program.

Volume and lattice parameters were obtained through Le Bail fitting using the GSAS program. A Raman study assigned the $\alpha$ phase to the rhombohedral $R3m$ space group (No. 160). However, our XRD spectra for the $\alpha$ phase are in agreement with those of Popović et al., who assigned peaks to the $R3m$ space group (No. 166). For consistency, we assigned the peaks of the $\alpha$ and $\beta$ phases to $R3m$. Since the Le Bail fitting only extracts the $a$ and $c$ parameters of the rhombohedral unit cell, and not the atomic positions, our results do not rule out $R3m$ for the $\alpha$ phase. Pressure-volume data were fit to the third-order Birch-Murnaghan equation of state (EOS)

$$P = \frac{3}{2} K_0 \left[ \frac{V_0}{V} \right] - \frac{3}{4} \left[ \frac{V_0}{V} \right]^2 \times \left[ 1 - \frac{3}{4} \left( K' - 4 \right) \left( \frac{V_0}{V} \right)^2 - 1 \right].$$

where $P$ is the pressure, $V_0$ is the lattice volume at ambient pressure, $K_0$ is the bulk modulus at ambient pressure, and $K'$ is the pressure derivative of bulk modulus at ambient pressure.

Figure 1 shows XRD spectra for In$_2$Se$_3$ at pressures of 0.4 GPa, 0.7 GPa, and 1.2 GPa. The intensity of the (104) peak decreased, while the intensity of the (105) peak increased, at 0.7 GPa. In addition, a discontinuous drop in both the $a$ and $c$ lattice parameters, obtained from the GSAS Le Bail fitting, was observed at 0.7 GPa. From the splitting

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of the (0 0 6) peak, in spectra that showed a mixture of the two phases, we find the c lattice parameter drops by ~2%. The change in intensities and the drop in lattice constants are consistent with the $\alpha \rightarrow \beta$ phase transition previously observed at elevated temperatures. The strong (1 0 5) peak persisted upon decompression down to ambient pressure and the lattice parameters at ambient pressure remained lower than the ambient $\alpha$ phase lattice parameters. These observations indicate the persistence of the $\beta$ phase upon decompression to ambient pressure.

Pressure-volume data for the $\alpha$ and $\beta$ phases are shown in Fig. 2 for both compression and decompression. It can be seen that, at ambient pressure, the $\beta$ phase is denser than the $\alpha$ phase. The $\alpha$ phase and $\beta$ phase data were fitted to the Birch-Murnaghan EOS and the bulk modulus for each phase was obtained. The ambient pressure derivative of the bulk modulus and the ambient lattice volume were held fixed at $K' = 4$ and $V_0 = 403.5 \text{ Å}^3$ for the $\alpha$ phase fitting. From this fit, the $\alpha$ phase has a zero pressure bulk modulus of $K_0 = 22 \pm 5 \text{ GPa}$. All parameters were allowed to vary for the $\beta$ phase fitting. The $\beta$ phase has an ambient pressure bulk modulus of $K_0 = 29 \pm 2 \text{ GPa}$, ambient pressure derivative of the bulk modulus of $K' = 6.5 \pm 0.7$, and ambient pressure volume of $V_0 = 389 \pm 1 \text{ Å}^3$.

Figure 3 shows the ratio $r = c/a$ as a function of pressure. The $\beta$ phase shows highly anisotropic compression at low pressures. The ratio has a nonlinear dependence on pressure

$$r = (6.68 \pm 0.03) + (0.38 \pm 0.02) \exp[-(0.23 \pm 0.04)P],$$

where $P$ is the pressure in GPa. In addition, we found the value for $r$ at ambient pressure for the $\beta$ phase is smaller than that for the $\alpha$ phase.

To complement the XRD experiments, we performed confocal Raman spectroscopy on our samples with the back-scattering geometry, using a 633 nm He-Ne laser and a Leica optical microscope which is coupled to a Renishaw InVia spectrometer. In order to avoid optical heating and phase transformation, we used the lowest possible optical excitation power of ~4 mW, which is higher than what was previously used for single-nanowire Raman. The reason we used more power is that the laser was applied to a relatively large amount of bulk powder instead of a single nanowire.

The In$_2$Se$_3$ powder was loaded and the pressures were measured in the same way as was done for the XRD experiments. The sample was loaded to a pressure of 0.5 GPa and a Raman spectrum was taken. (The higher background level in the high-pressure spectra is due to luminescence from the diamonds.) The sample was then compressed to 0.9 GPa. As shown in Fig. 4(a), there is a notable frequency shift ($\sim 3 \text{ cm}^{-1}$) of the main Raman peak from 0.5 GPa to 0.9 GPa, in addition to substantial broadening. We note that this frequency shift and peak broadening are larger than those between the Raman spectra at ambient pressure and 0.5 GPa. This suggests a phase transformation at a pressure between 0.5 and 0.9 GPa, consistent with the $\alpha \rightarrow \beta$ transformation at 0.7 GPa obtained from XRD.
To verify the Raman assignments, we annealed a sample of the α-In$_2$Se$_3$ powder from Alfa Aesar in argon at 948 K for 5 h, in a sealed silica ampoule. The sample was cooled by quenching the ampoule in room-temperature water. The annealing temperature is sufficient to transform the sample into β-In$_2$Se$_3$. As shown in Fig. 4(b), the Raman spectrum of the annealed β-phase powder is similar to that at 0.9 GPa. This confirms the presence of the β phase at 0.9 GPa.

In conclusion, using XRD, we discovered a pressure-induced phase transition in In$_2$Se$_3$, from the α to the β phase, at 0.7 GPa. Raman spectroscopy verified this result. The critical pressure is an order of magnitude lower than that for most materials. For example, InSe has a phase transition at 10 GPa, while GeSe has no phase transition up to 13 GPa. Bi$_2$Te$_3$ (Refs. 21 and 22) and Sb$_2$Te$_3$ (Refs. 23 and 24) undergo phase transitions at 10 and 8 GPa, respectively. Group IV, III–V, and II–VI semiconductors show phase transitions at 2 GPa or higher. We determined the EOS and c/a ratio for the β phase up to 11 GPa. The response to pressure was highly anisotropic with a nonlinear decrease of the c/a ratio. This anisotropy is related to the structure of the α and β phases In$_2$Se$_3$, in which α-plane layers interact via van der Waals interactions (Fig. 5). These relatively weak interactions result in a significant decrease in c/a as pressure is applied.

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FIG. 4. Raman spectra of In$_2$Se$_3$. (a) Ambient In$_2$Se$_3$ (α phase) and In$_2$Se$_3$ under pressure. The frequency shift and broadening is consistent with the α → β transformation at 0.7 GPa. (b) Comparison between β-In$_2$Se$_3$ (produced by annealing) and the 0.9 GPa spectrum. The similarity between the spectra confirms the presence of the β phase at 0.9 GPa.

FIG. 5. Ball-and-stick model for layered In$_2$Se$_3$, showing the rhombohedral R3m space group.
Trace amounts of reddish samples, attributed to the $\gamma$ phase, were found on the ampoule walls. The $\gamma$ phase has a much different Raman spectrum than the $\alpha$ and $\beta$ phases.

