High pressure γ-to-β phase transition in bulk and nanocrystalline In$_2$Se$_3$

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ABSTRACT
Pressure-dependent phase transitions of In$_2$Se$_3$ bulk powders and nanowire samples were studied at room temperature using synchrotron X-ray diffraction and a diamond anvil cell. γ-In$_2$Se$_3$, metastable under ambient conditions, transforms into the stable high pressure β phase between 2.8 and 3.2 GPa in bulk powder samples and at slightly higher pressures, between 3.2 and 3.7 GPa, in nanowire samples. While the γ phase bulk modulus is similar to that of the β phase, the decrease due to pressure in the unit cell parameter ratio, $c/a$, is less than half the decrease seen in the β phase. First-principles calculations show that γ-In$_2$Se$_3$ has a higher energy and unit-cell volume than β-In$_2$Se$_3$, consistent with the experimental observations.

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1. Introduction
Indium selenide (In$_2$Se$_3$) is a material that has a potential for use in phase-change memory applications.[1,2] Phase change memory relies on the ability to access metastable states with long lifetimes under ambient conditions. In addition to the ambient stable layered α phase, In$_2$Se$_3$ exists in two known metastable crystal structures at room temperature and ambient pressure: the layered β phase and the defect wurtzite γ phase.[3] To effectively control switching between metastable and stable states, the sensitivity of a metastable state to various pressure and temperature conditions must be understood.

Figure 1(a) and 1(b) illustrates the crystal structures for the β and γ phases, respectively.[4,5] Adopting the layered tetradymite crystal structure, space group $R\overline{3}m$, the β phase In$_2$Se$_3$ is isostructural with the ambient phases of the topological insulators Sb$_2$Te$_3$, Bi$_2$Te$_3$, and Bi$_2$Se$_3$.[6,7] Each layer of the β phase consists of five alternating sub-layers of selenium and indium atoms and interacts through van der Waals forces between neighboring layers. The γ phase is a defect wurtzite structure with vacancies ordered in a screw pattern on every third indium site.[5,8] It can crystallize in a number of related space groups, $P6_1$, $P6_5$, $P6_22$, or $P6_322$, corresponding to particular arrangements of the vacancy screws.[5,8,9]
Previously, we reported the discovery of the pressure-induced phase transformation from the $\alpha$ phase to the $\beta$ phase at 0.7 GPa. This critical pressure is an order of magnitude lower than phase-transition critical pressures typically observed in semiconductors. Ke et al. [4] found the $\alpha$ to $\beta$ phase transition to occur at a critical pressure of 0.8 GPa and determined the phase transition is due to a pressure-induced shear shift between neighboring layers. Zhao and Yang [6] report a transition from the $\alpha$ phase structure into an intermediate phase with a monoclinic structure around 0.8 GPa before transforming into the $\beta$ phase. In addition they found that In$_2$Se$_3$ begins to transform from the layered $\beta$ phase into a body center cubic structure at around 32 GPa and completes the phase transition around 50 GPa. In this paper we discuss the results of X-ray diffraction (XRD) experiments performed on In$_2$Se$_3$ bulk powder and nanowires initially in the metastable $\gamma$ phase.

2. Experimental methods

$\gamma$ phase In$_2$Se$_3$ bulk powder was obtained by annealing $\alpha$ phase In$_2$Se$_3$ powder (99.99%), purchased from Alfa Aesar, at 500°C for 24 or 48 h in a sealed ampoule filled with ~0.5 atm Ar gas. The nanowire samples were grown by a catalyzed vapor deposition method via vapor–liquid–solid growth using 100 nm gold colloids. As-grown nanowire samples are a mixture of the $\gamma$ and $\beta$ phases. Some of the nanowire samples were annealed for 24–48 h at ~500°C, transforming the $\beta$ phase components to the $\gamma$ phase.

Samples were loaded into a piston-cylinder diamond anvil cell (DAC) with 600 or 1000 $\mu$m culet diamonds. A stainless steel gasket was pre-Indented to ~50 $\mu$m thick and a 300 or 500 $\mu$m diameter hole was drilled for the 600 and 1000 $\mu$m culet sizes, respectively. The sample, a pressure-transmitting medium of 4:1 methanol–ethanol mixture or mineral oil, and ruby microspheres [12] for in situ pressure measurements were loaded
into the hole. The pressure was measured by the R1 and R2 peak shifts using the Mao scale [13] before and after each XRD spectrum, with the average used as the experimental pressure value. The maximum 2-theta value was limited to 20° by the opening of the DAC.

XRD experiments were performed at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL), beamline 12.2.2 [14] and Cornell High Energy Synchrotron Source (CHESS), beamline B2. Spectra were collected by a MAR3450 plate detector at the wavelengths of 0.4959 Å at ALS and 0.4859 Å at CHESS. Starting at initial pressures of 0.4–2.1 GPa, spectra were taken for both compression and decompression at ambient temperature.

Diffraction images were integrated using the FIT2D program [15] and lattice parameters were obtained using the GSAS program through the Le Bail fitting method. [16] Le Bail refinement is a more limited refinement method than Rietveld refinement, as it only extracts the unit cell parameters and does not refine the atomic positions within the unit cell. Le Bail refinement provides a straightforward way to compare changes in the unit cell due to pressure or temperature changes even when the diffraction angle is limited and full Rietveld refinement would not be appropriate. We assigned the peaks of the γ phase to $P6_522$ and the β phase to $R\overline{3}m$. The lattice volume as a function of pressure was fit to the third-order Birch–Murnaghan equation of state (EOS)

$$P = \frac{3}{2} K_0 \left[ \left( \frac{V_0}{V} \right)^{\frac{7}{3}} - \left( \frac{V_0}{V} \right)^{\frac{5}{3}} \right] \times \left\{ 1 + \frac{3}{4} \left( K' - 4 \right) \left[ \left( \frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\},$$

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 the bulk modulus at ambient pressure.

3. Results and discussion

XRD spectra for an annealed In$_2$Se$_3$ bulk powder sample at pressures of 2.3, 2.8, and 3.1 GPa are shown in Figure 2. At 2.3 GPa, the sample is in the γ phase. When pressure is increased, (003), (006), and (105) peaks appear, indicating a transition into the β phase. From multiple samples, we determined that the β and γ phases coexist in a mixed phase state above 2.8 GPa and fully transitions to the β phase above 3.2 GPa (see supplementary data). The samples remained in the β phase upon decompression to ambient pressure. The Le Bail refinement results for the γ phase and the β phase are shown in Figure 3.

Figure 4 shows XRD spectra for an annealed nanowire sample at 3.1, 3.4 and 3.8 GPa. At 3.1 GPa, the XRD spectrum shows the nanowire sample is still in the γ phase. The 3.4 GPa spectrum shows the sample is in a mixed phase and at 3.8 GPa the sample is fully in the β phase. From multiple nanowire samples, the transition to the mixed phase state was determined to occur at 3.2 GPa and fully transitions into the β phase by 3.7 GPa. These values are 0.4 and 0.5 GPa higher than in the bulk, respectively. It is typical in semiconductors for nanocrystalline samples to exhibit transitions at higher pressures than in bulk samples. [17] In addition, we note that after transitioning to the β phase the peaks are quite broad in both the bulk and nano samples, suggesting a decrease in the average domain size.
Pressure–volume data for the $\gamma$ phase are shown in Figure 5 for the bulk powder samples. The data were fitted to the Birch–Murnaghan EOS and the bulk modulus was obtained. The ambient unit volume was held fixed at $V_0 = 853$ Å$^3$ and the ambient pressure derivative of the bulk modulus was set to $K' = 4$. The ambient pressure bulk modulus obtained by the EOS fitting for the $\gamma$ phase is $K_0 = 28.2 \pm 0.7$ GPa, similar to the $\beta$ phase bulk modulus of $29 \pm 2$ GPa. The $\gamma$ phase In$_2$Se$_3$ lattice parameters $c$ and $a$ are presented as a function of pressure in Figure 6. The slope of the $c/a$ ratio is $-0.029 \pm 0.005$ GPa$^{-1}$, determined by a linear least-squares fit, revealing that the compression of the $\gamma$ phase is anisotropic. The decrease in the $c/a$ ratio with pressure for the $\gamma$ phase is, however, less than half the decrease in the $c/a$ ratio for the $\beta$ phase over the same pressure range.\[10\] The unit cell parameters for the nanowire samples exhibited a similar dependence on pressure.

Figure 2. Typical integrated XRD spectra for bulk powder In$_2$Se$_3$ initially in the $\gamma$ phase at 2.3 GPa, in a mixed $\gamma$–$\beta$ phase at 2.8 GPa, and in the $\beta$ phase at 3.1 GPa. The appearance of the (003), (006), and (105) peaks as the pressure increases indicates the transition into the $\beta$ phase.

Figure 3. Le Bail refinements for the $\gamma$ phase ($P6_522$ space group) at 2.3 GPa and the $\beta$ phase ($R\bar{3}m$ space group) at 3.1 GPa. The open circles and solid lines are the experimental and fitted data, respectively. The lower lines represent the residual intensities.
To elucidate the experimentally observed pressure-induced phase transformation of In$_2$Se$_3$, we performed first-principles calculations using the Vienna ab initio simulation package (VASP) [18] based on density functional theory with projector-augmented wave (PAW) pseudo-potentials [19,20] and the generalized gradient approximation in the parametrization of Perdew, Burke and Enzerhof [21] for the exchange-correlation functional. The plane wave expansions were determined by the default energy cutoffs given by the VASP PAW potentials. Van der Waals interactions were included using the semiempirical DFT-D3 method [22] with Becke–Johnson damping [23]. All atoms fully relaxed during structural relaxation until the force on each atom was smaller than 0.01 eV/Å.

Figure 4. Typical integrated XRD spectra for In$_2$Se$_3$ nanowires. The 3.1 GPa spectrum shows the nanowire sample is in the $\gamma$ phase. The 3.4 GPa spectrum shows the sample in a $\gamma$–$\beta$ mixed phase. At 3.8 GPa the sample is in the $\beta$ phase.

Figure 5. P-V data for $\gamma$ phase In$_2$Se$_3$ bulk powder. The solid line is the fit to the Birch–Murnaghan EOS (Equation (1)), $K_0 = 28.2 \pm 0.7$ GPa.

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The optimized bulk structure of the $\gamma$-phase In$_2$Se$_3$ has a volume of 143 Å$^3$ per In$_2$Se$_3$ unit, while the $\beta$-phase In$_2$Se$_3$ has a smaller volume of 128 Å$^3$ per In$_2$Se$_3$ unit. The detailed optimized lattice parameters are given in Table 1. Figure 7 shows the calculated total energy versus volume for the $\beta$ and $\gamma$ phases. The dashed tangent line connecting to the two energy-volume curves corresponds to a negative pressure, indicating that the $\gamma$-phase is a metastable state and a small perturbation may induce a spontaneous phase transformation to the $\beta$ phase that is not reversible. The results of these calculations are consistent with the experimental observation.

In conclusion, we discovered a pressure-induced phase transition in bulk powder In$_2$Se$_3$ from the metastable $\gamma$ phase to the high pressure stable $\beta$ phase between 2.8 and 3.2 GPa. While not a phase transition in the strictest thermodynamic sense, the

**Table 1.** Calculated lattice parameters of optimized $\beta$ and $\gamma$ phase In$_2$Se$_3$ at zero pressure. For comparison, experimental values (at 478 K for $\beta$ and 803 K for $\gamma$) are listed.[3]

|        | Calculated | Experimental |
|--------|------------|--------------|
|        | a (Å)  | c (Å)  | Volume (Å$^3$) | a (Å)  | c (Å)  | Volume (Å$^3$) |
| $\beta$ phase | 3.999 | 27.738 | 384.1 | 4.00 | 28.33 | 392.6 |
| $\gamma$ phase | 7.169 | 19.294 | 858.7 | 7.13 | 19.58 | 861.2 |

Figure 6. Plot of the $a$ and $c$ lattice parameters for $\gamma$ phase In$_2$Se$_3$ bulk powder as a function of pressure. Inset: Pressure dependence of the ratio $c/a$. The solid line is a linear least-squares fit (slope: $-0.029 \pm 0.005$ GPa$^{-1}$, intercept: $2.73 \pm 0.01$).
energy barrier between a metastable and stable state decreases at critical pressures and temperatures, enabling the transition into the thermodynamically stable state to occur over an experimentally observable time scale.[24] In nanowire samples, the phase transition occurs at a higher pressure, between 3.2 and 3.7 GPa. This higher phase transition critical pressure in the nanowires is consistent with prior observations in other nanocrystal semiconductors [25,26] and can be attributed to the large surface-to-volume ratio in nanocrystals.[27] The EOS was determined for the γ phase up to 3 GPa in bulk samples.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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