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Supplementary Information for: Tunable band gap of layered semiconductor $Zn_3In_2S_6$ under pressure

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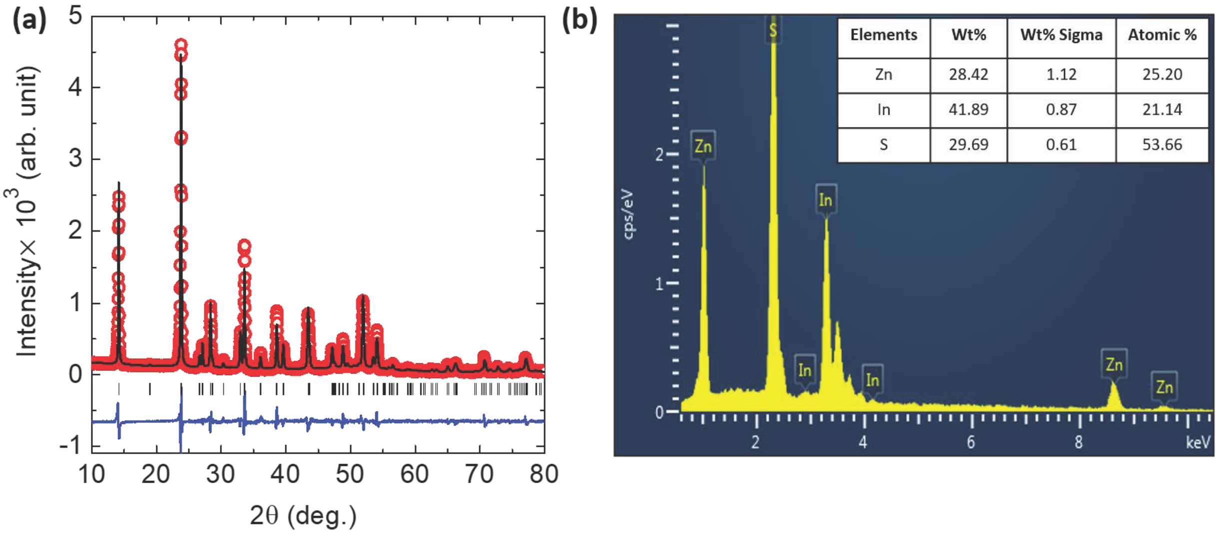

Elements	Wt%	Wt% Sigma	Atomic %
Zn	28.42	1.12	25.20
In	41.89	0.87	21.14
S	29.69	0.61	53.66

Figure S1. (a) Le Bail fitting to the X-ray diffraction pattern of pulverized $Zn_3In_2S_6$ at ambient condition. (b) Energy Dispersive X-Ray Spectroscopy (EDS) spectrum of the as-grown single crystal $Zn_3In_2S_6$. Chemical composition of the single crystal is found to be 2.7(1):2.3(1):6.

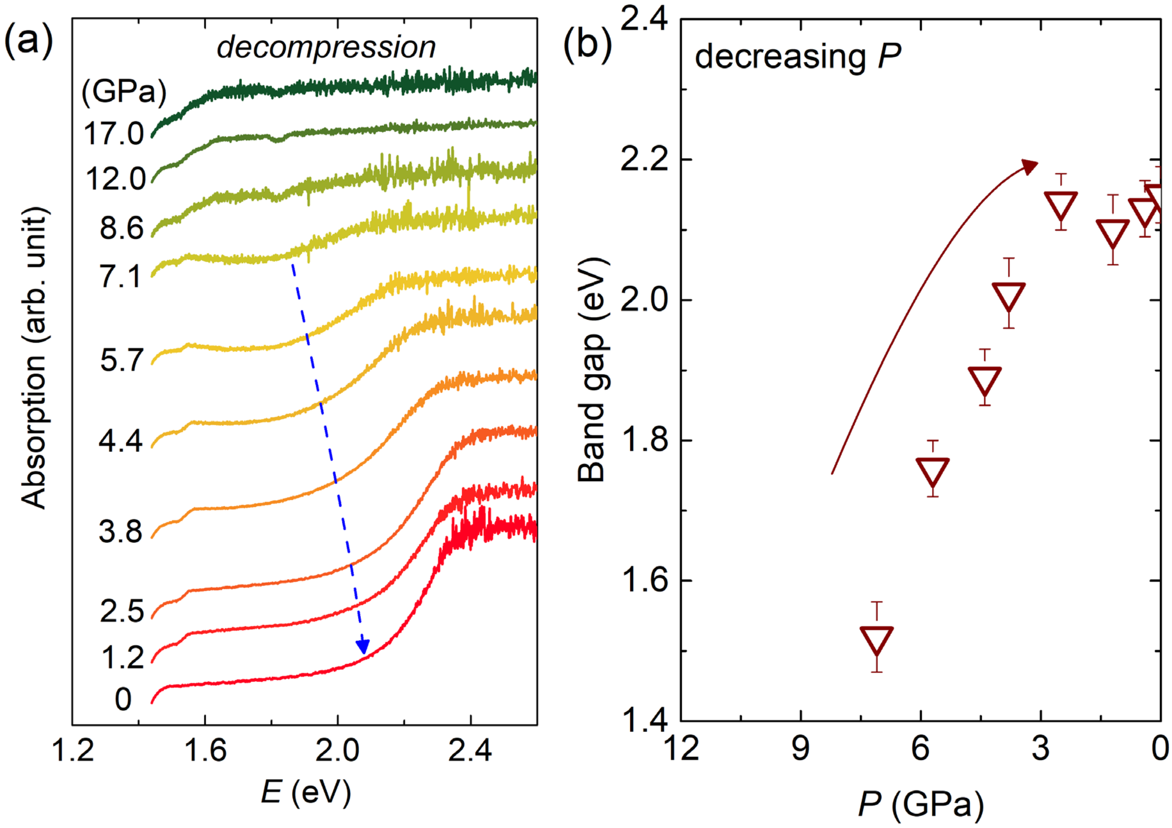

Figure S2. (a) Absorption spectra of $Zn_3In_2S_6$ at various pressures taken during releasing pressure (decompression). (b) The derived optical band gap as a function of pressure. Absorption edge starts to re-appear when the pressure is released below 8 GPa. The band gap increases on decreasing pressure reaching the value of 2.2 eV at ambient pressure as indicated by arrow in (a). The gap opening below 8 GPa, which is far below the gap closure at 20 GPa observed on increasing pressure, indicates the sluggish amorphous-amorphous (AM2-metallic to AM1-semiconducting phase) transition during decompression.

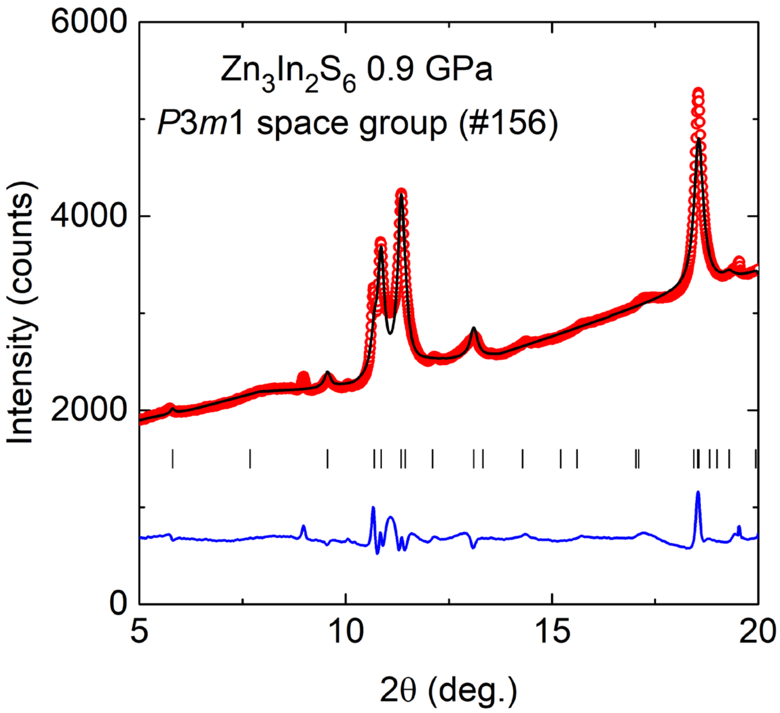

Figure S3. Le Bail fitting to the XRD pattern of $Zn_3In_2S_6$ at 0.9 GPa.

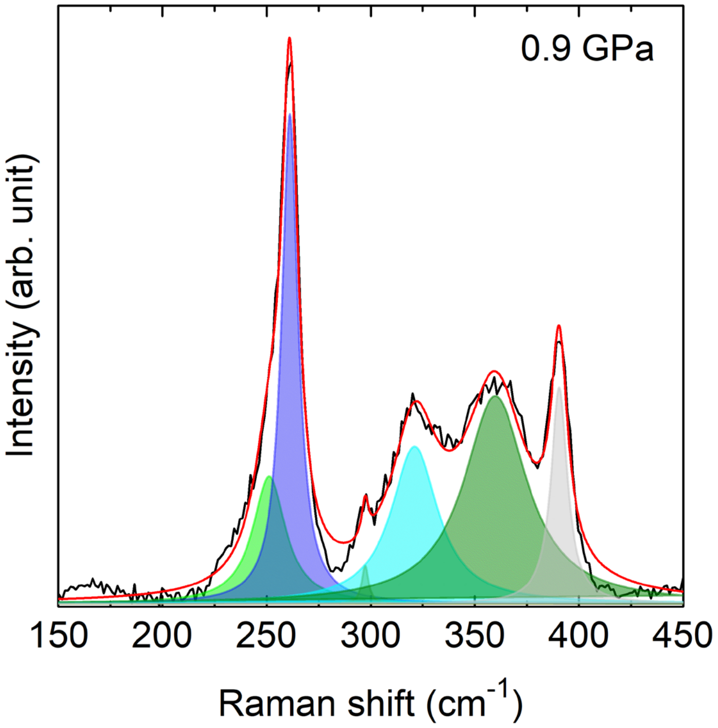

Figure S4. The deconvoluted Raman spectrum of $Zn_3In_2S_6$ at 0.9 GPa. The spectrum consists of six Lorentzian peaks as discussed in the main text.

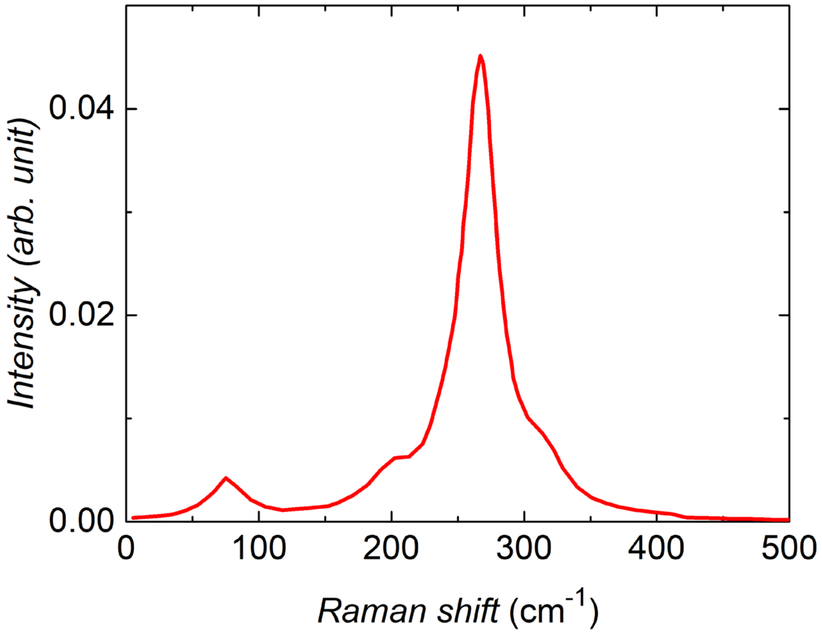

Figure S5. The calculated Raman spectrum of $Zn_3In_2S_6$ at 0 GPa based on the crystal structure shown in Figure 1. The calculated spectrum is consistent with the experimental data, in particular the strong Raman peak at ~260 cm^{-1} is fully captured by the calculation.

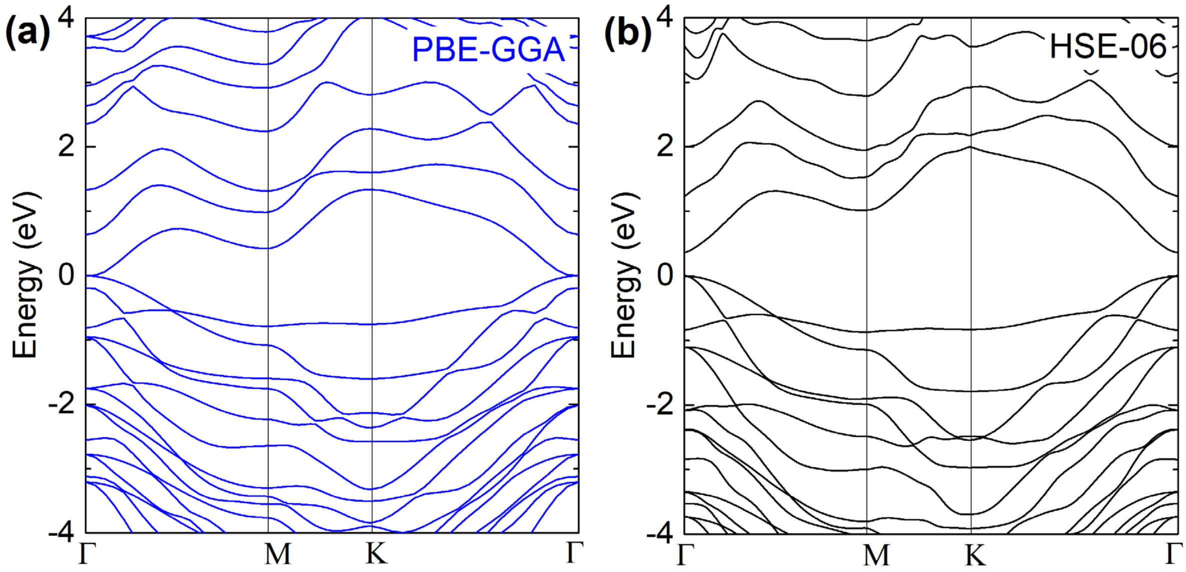

Figure S6. Band structures of $Zn_3In_2S_6$ at 0 GPa calculated with (a) PBE-GGA and (b) HSE-06 functionals. The PBE-GGA functional lead to the gapless electronic state which is inconsistent with the experimental results, whereas the HSE-06 functional opens a gap between the valence band maximum and conduction band minimum at the Γ point.