Supporting Information

Experimental and theoretical studies on α-In_2Se_3 at high pressure

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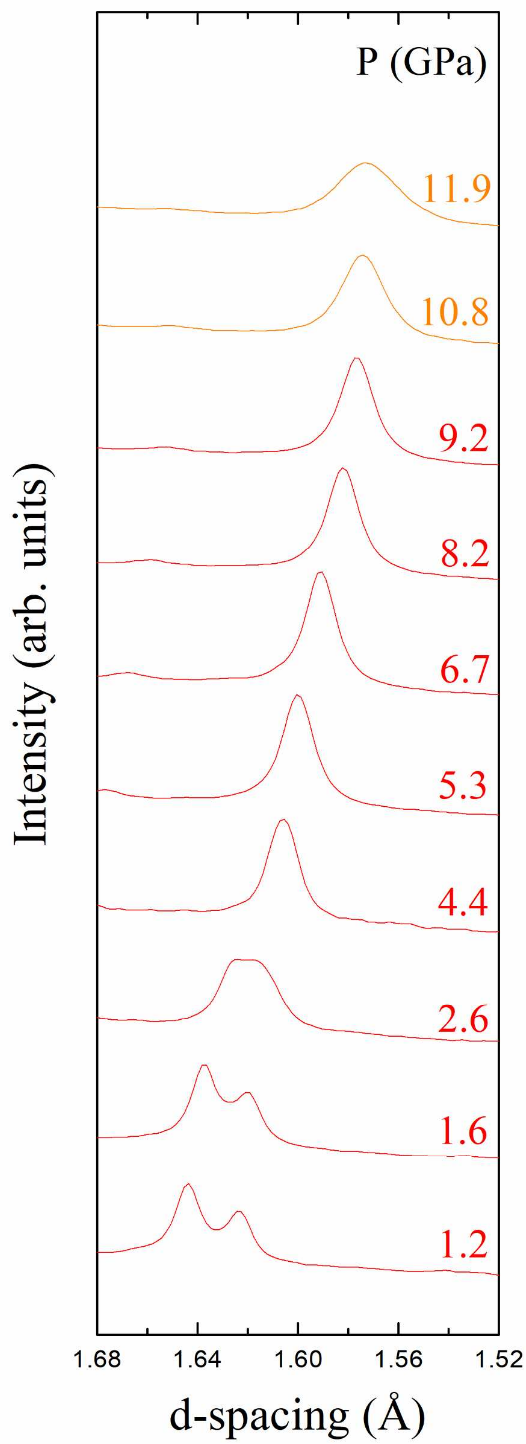

Figure S1. Selected x-ray powder diffraction patterns of β'- and β-In_2Se_3 under compression. Red and orange lines indicate the some reflections between 1.68 and 1.52 of the d-spacing of the β' and β phases, respectively.

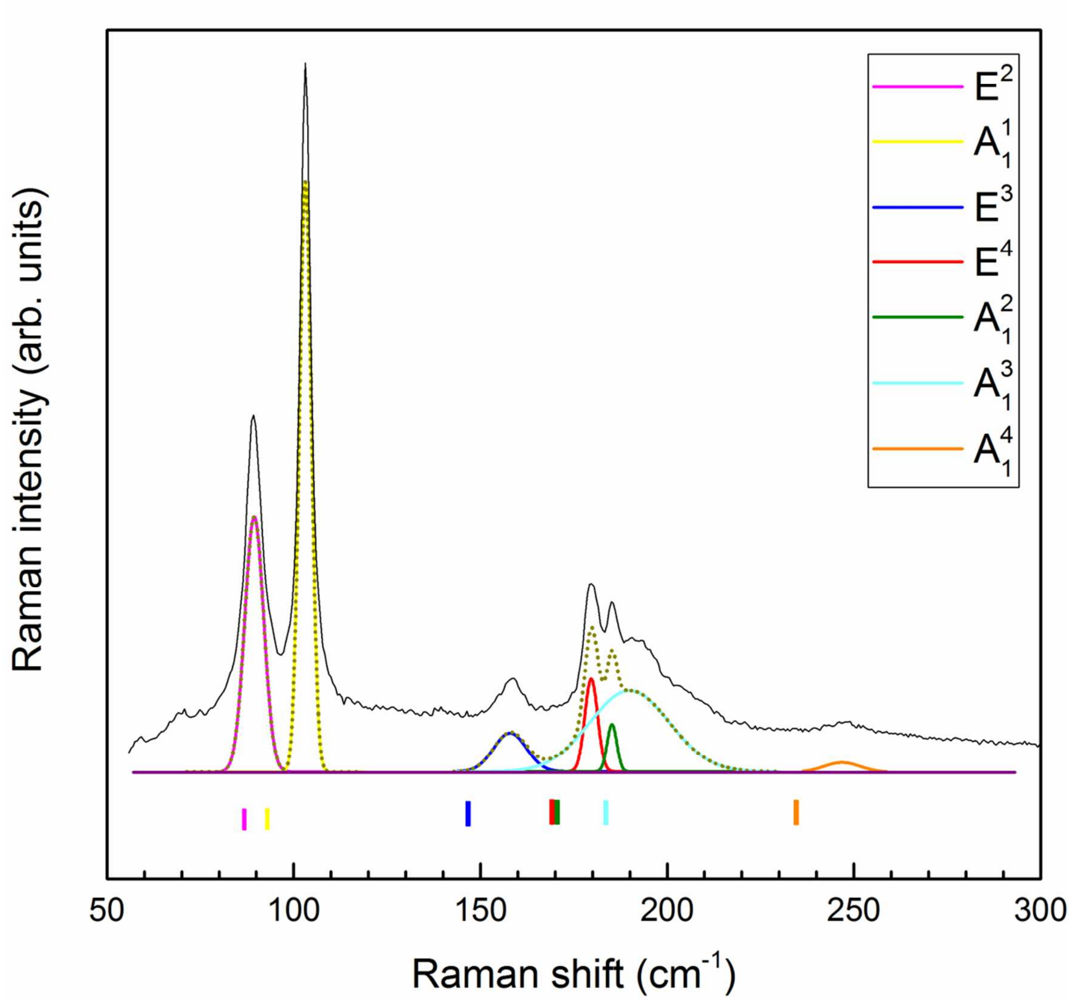

Figure S2. Raman spectrum of α-In_2Se_3 at room pressure. Bottom marks represent the theoretical frequencies at 0 GPa for identification of the Raman-active modes of the α phase. Due to its low frequency, E^1 mode has not been observed experimentally.

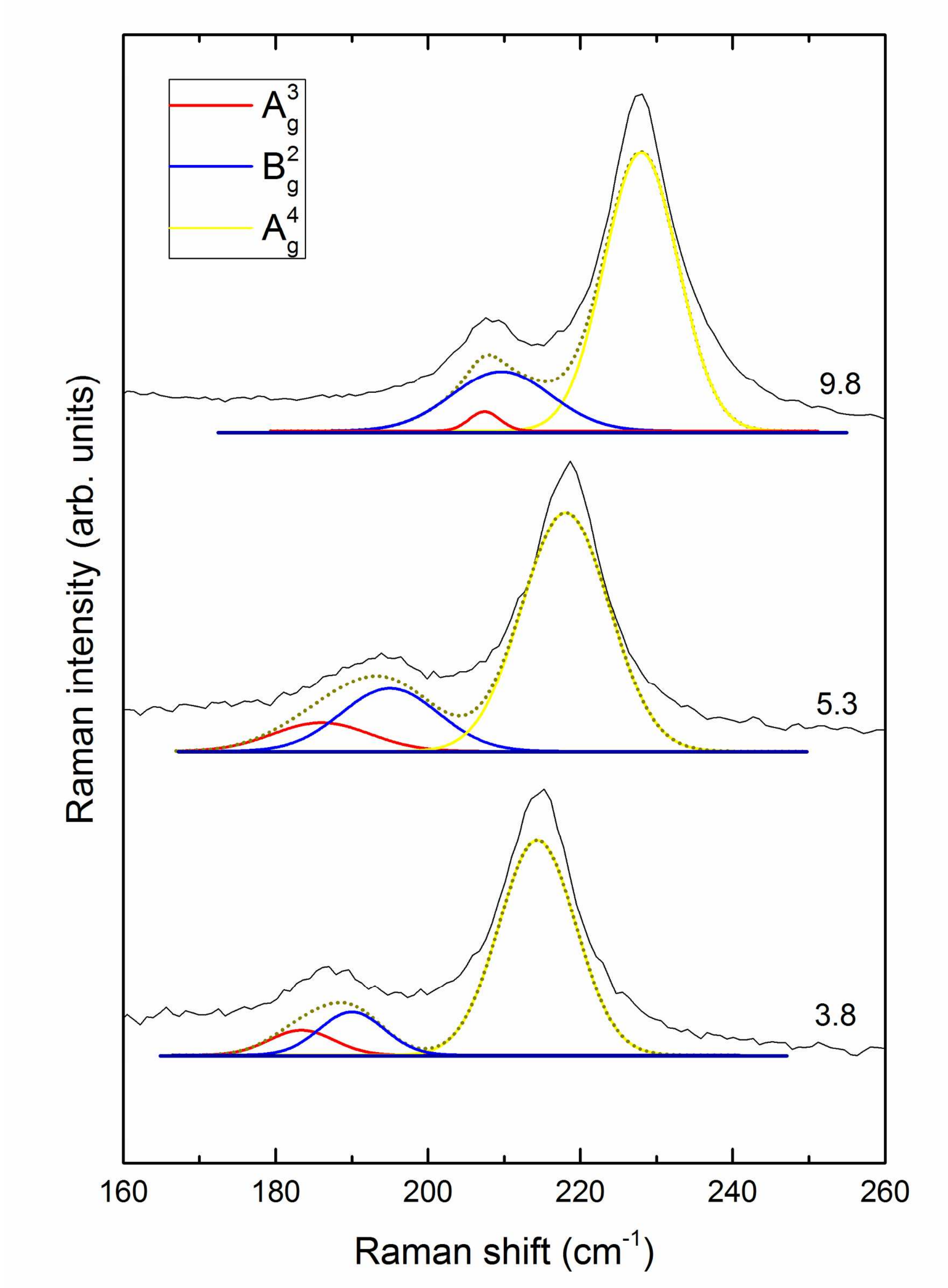

Figure S3. Detail of the RS spectra of the β´ phase at different pressures, where A_g^3 and B_g^2 modes are resolved, providing evidence of the stability of this phase up to 10 GPa. The A_g^4 mode is resolved for its proximity to the previous coupled modes as well.

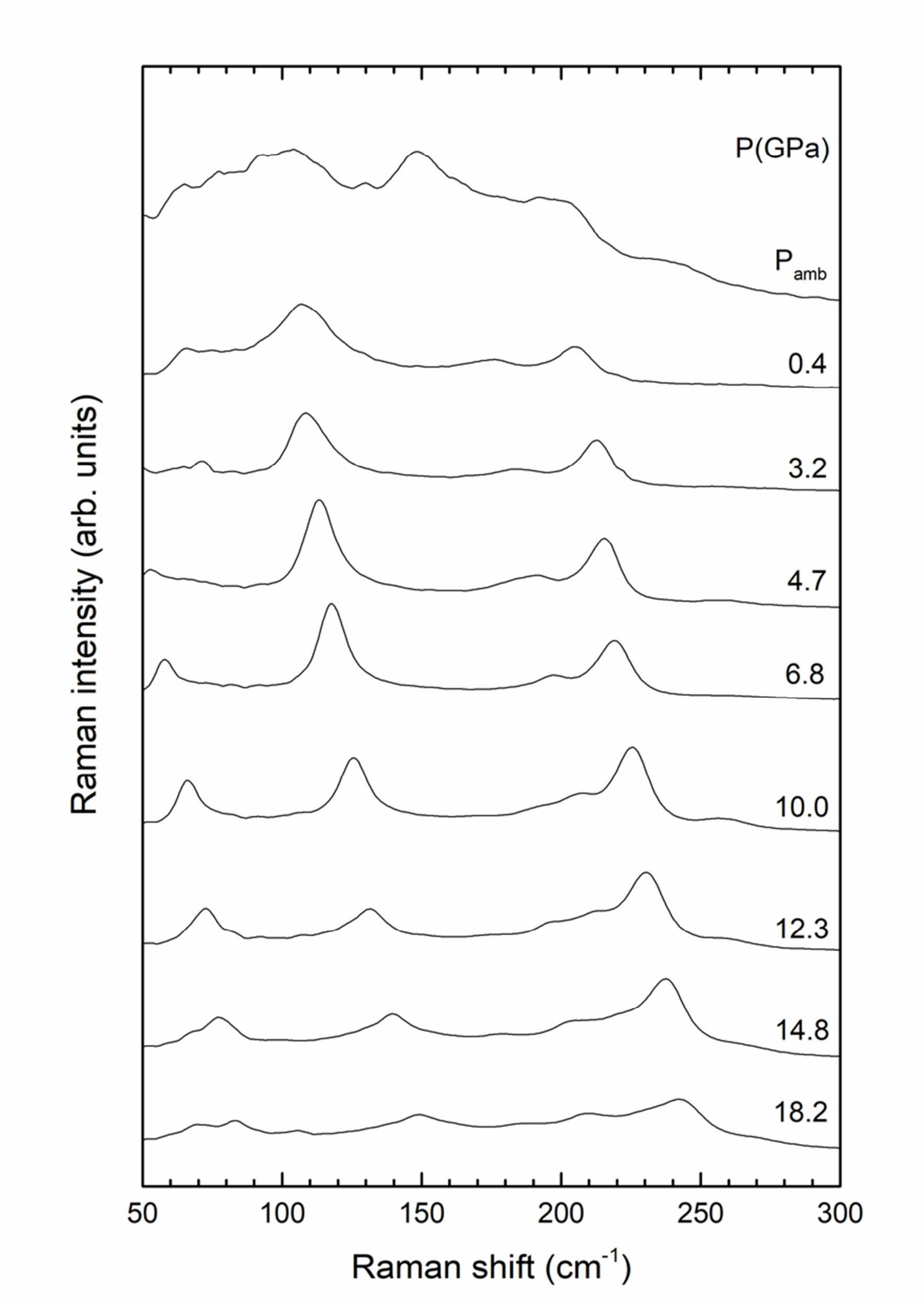

Figure S4. Raman spectra of In_2Se_3 at different pressures on downstroke from 20 GPa.

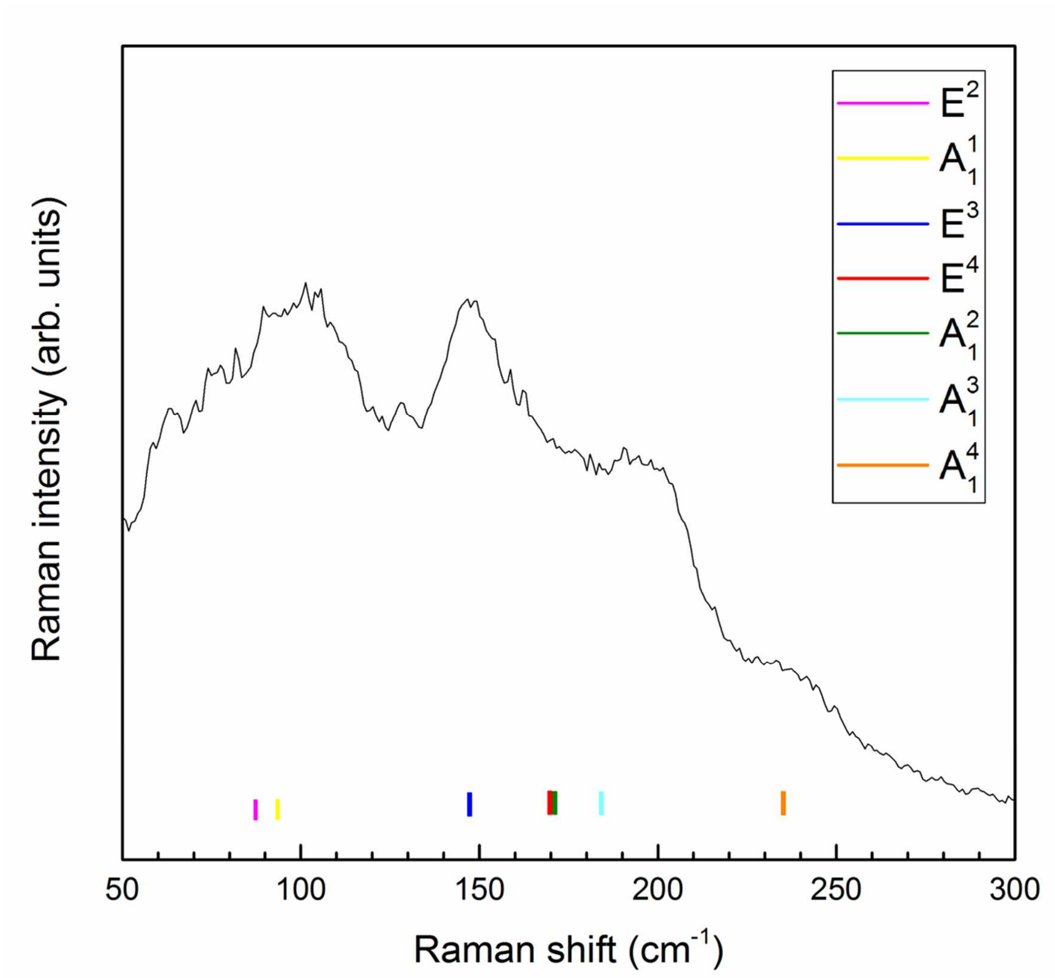

Figure S5. Detail of the Raman spectrum of In_2Se_3 at room pressure after decreasing pressure. Marks represent the theoretical frequencies of Raman-active modes of the α phase at 0 GPa.

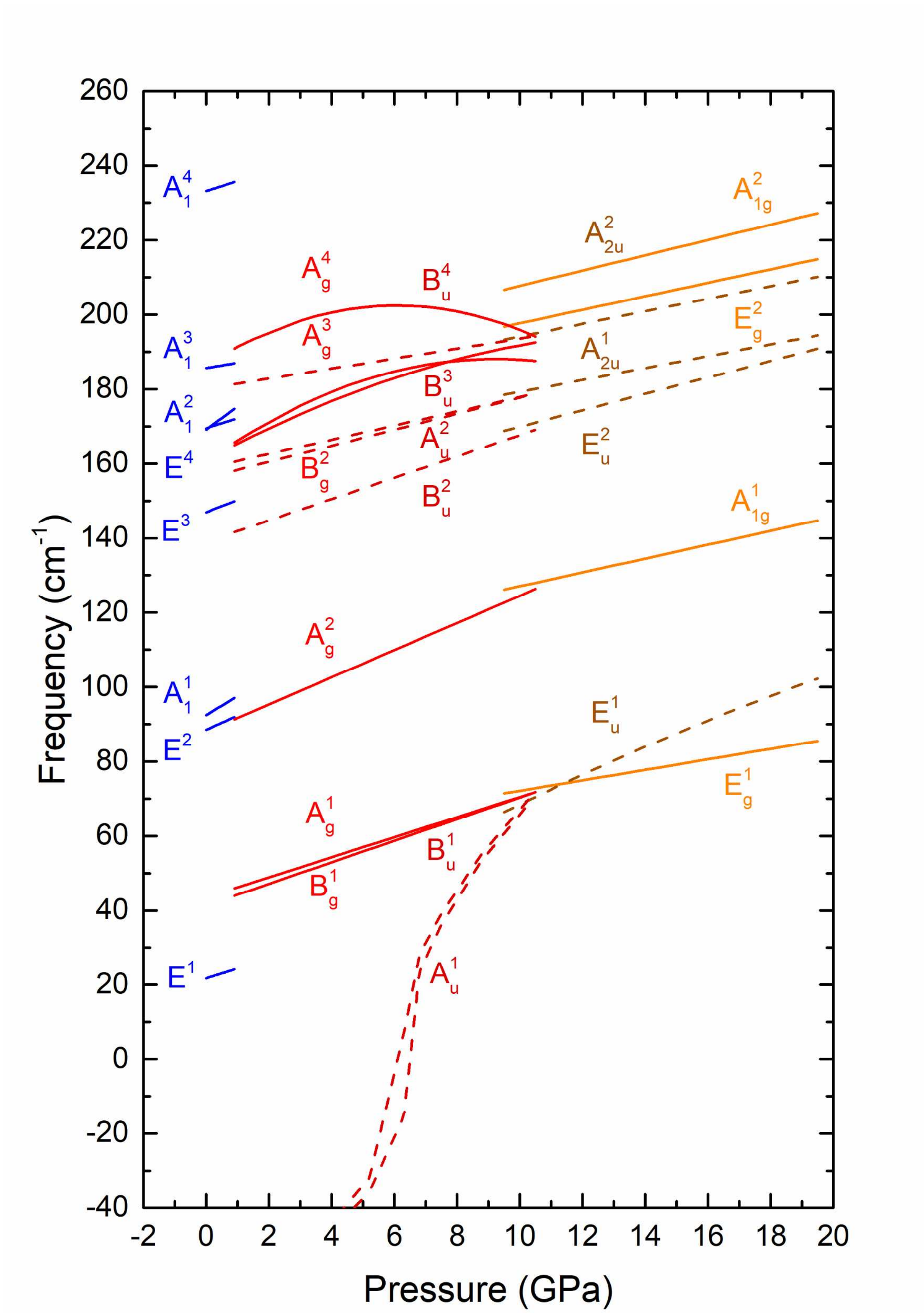

Figure S6. Pressure dependence of the theoretical frequencies of Raman-active (continuous lines) and IR-active (dash lines) modes of the α, β' and β phases in blue, red and orange, respectively. Modes of α phase are both Raman and IR.

Table S1: Experimental lattice parameters and unit cell volumes at different pressure up to 20.2 GPa of In_2Se_3.

Phase I	**R3m (Z=3)**				
P (GPa)	**a_I(Å)**		**c_I(Å)**		**V_I(Å^3)**
0.001	4.028(1)		28.731(6)		403.8(2)
0.3(1)	4.018(1)		28.666(6)		400.8(2)
0.5(1)	4.012(1)		28.622(6)		399.0(2)
Phase II	**C2/m (Z =2)**				
	a_{II}(Å)	**b_{II}(Å)**	**c_{II}(Å)**	**β**	**V_{II}(Å^3)**
1.2(1)	6.828(2)	3.973(1)	9.419(3)	103.25(3)	248.7(2)
1.6(1)	6.819(2)	3.967(1)	9.395(3)	103.25(3)	247.4(2)
4.4(1)	6.763(2)	3.928(1)	9.231(3)	103.30(3)	238.6(2)
5.3(1)	6.745(2)	3.916(1)	9.178(3)	103.32(3)	235.9(2)
6.7(1)	6.717(2)	3.896(1)	9.096(3)	103.34(3)	231.6(2)
8.2(1)	6.687(2)	3.876(1)	9.008(3)	103.37(3)	227.1(2)
9.2(1)	6.667(2)	3.862(1)	8.950(3)	103.39(3)	224.2(2)
10.8(1)	6.635(2)	3.840(1)	8.856(3)	103.42(3)	219.5(2)
11.9(1)	6.613(2)	3.825(1)	8.792(3)	103.44(3)	216.3(2)
Phase III	**R-3m (Z=3)**				
	a_{III}(Å)		**c_{III}(Å)**		**V_{III}(Å^3)**
12.7(1)	3.832(2)		25.16(1)		319.9(5)
14.2(1)	3.823(2)		24.88(1)		314.9(5)
15.1(1)	3.819(2)		24.72(1)		312.2(5)
16.6(1)	3.810(2)		24.44(1)		307.3(5)
18.2(1)	3.802(2)		24.14(1)		302.3(5)
19.2(1)	3.796(2)		23.96(1)		299.1(5)
20.2(1)	3.791(2)		23.78(1)		295.9(5)

Effective coordination number (ECoN)

The mean or ´effective´ coordination number (ECoN) is defined as

$$ECoN = \sum_i w_i \text{ where } w_i = exp\left[1-\left(\frac{l_i}{l_{av}}\right)^6\right] \text{ and } l_{av} = \frac{\sum_i l_i exp\left[1-\left(\frac{l_i}{l_{min}}\right)^6\right]}{\sum_i exp\left[1-\left(\frac{l_i}{l_{min}}\right)^6\right]}$$

being the l_{min} the smallest bond length in the coordination polyhedron