Structural and vibrational study of Bi_2Se_3 under high pressure

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Supplementary materials

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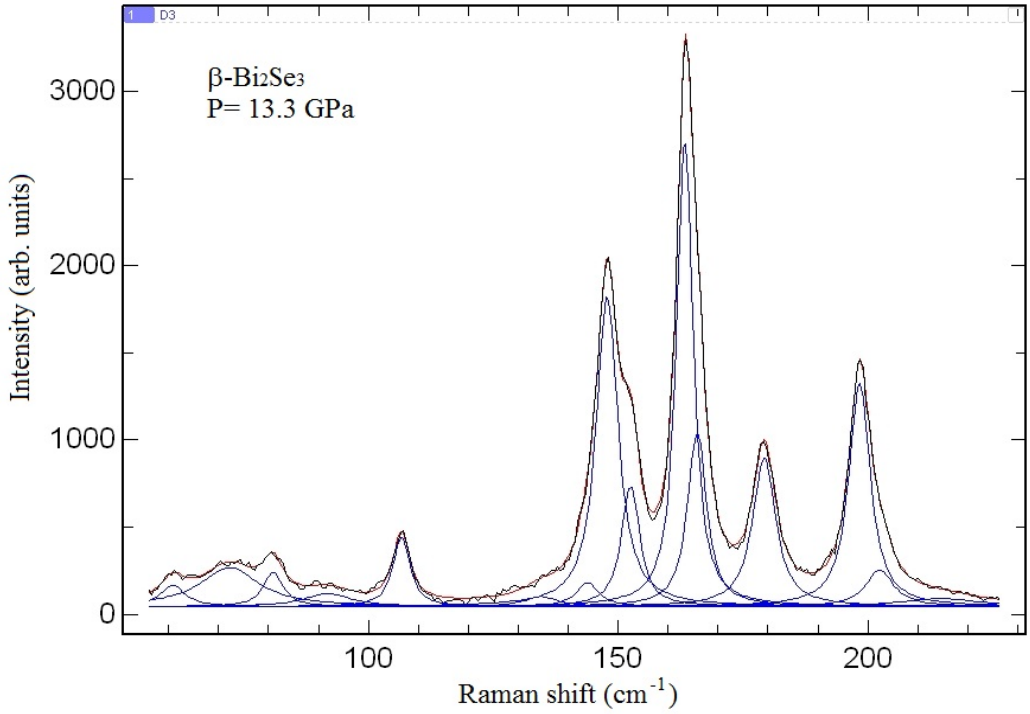
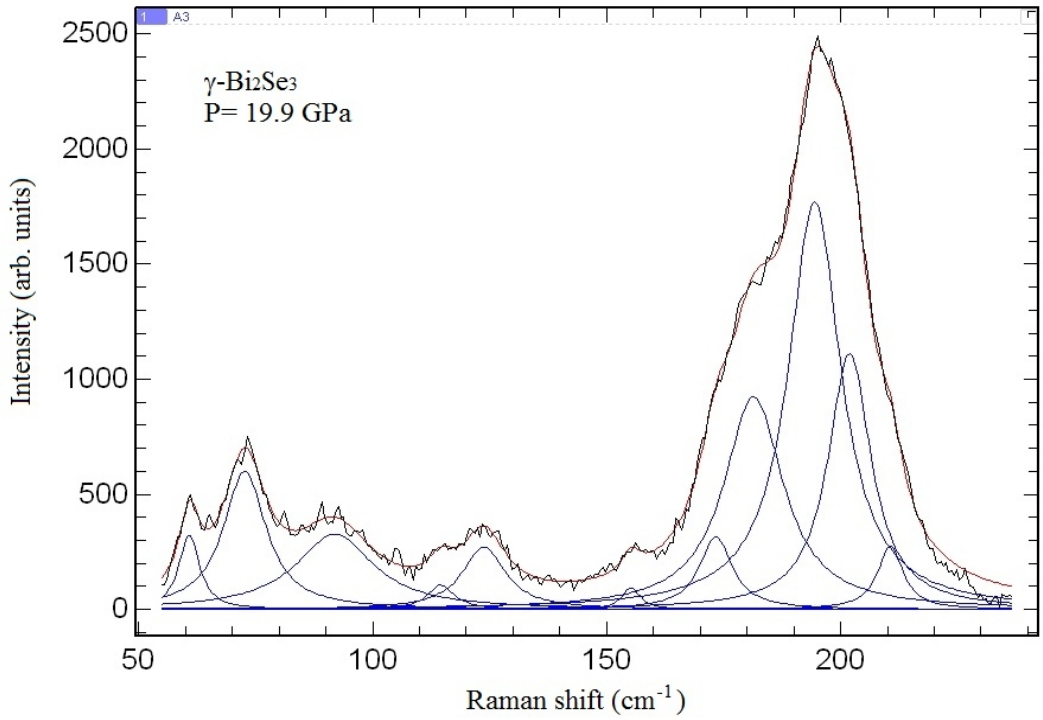
Supplementary Figure 1.

Raman spectrum of β-Bi_2Se_3 at 13.5 GPa and the corresponding fit of Voigt profiles corresponding to the Raman-active modes of the C2/m structure.



Supplementary Figure 2.

Raman spectrum of γ-Bi_2Se_3 at 19.9 GPa and the corresponding fit of Voigt profiles corresponding to the Raman-active modes of the C2/c structure.



Supplementary Table I. Theoretical (th.) *ab initio* IR-mode frequencies and pressure coefficients in α-Bi_2Se_3 (R-3m phase) at room temperature and P_0= 1 atm, as obtained from fits to the data using $\omega(P) = \omega(P_0) + a_1 \cdot (P - P_0)$. Experimental (exp.) and theoretical IR-mode frequencies at room pressure of other works are given for comparison.

Mode	ω_0(th.) (cm^{-1})	a_1(th.) (cm^{-1}/GPa)	ω_0 (th.) (cm^{-1})	ω_0 (th.) (cm^{-1})	ω_0 (exp.) (cm^{-1})	ω_0 (exp.) (cm^{-1})
E_u^1	80.3	3.29	64.69	85.1	65	61
E_u^2	129.9	1.44	126.8	133.0	129	133
A_{2u}^1	137.3	2.22	136.7	142.7		
A_{2u}^2	159.8	1.77	155.5	167.1		
Ref.	This work[a]	This work[a]	1[a]	1[b]	2	3

[a] GGA calculations including the spin-orbit coupling.
[b] GGA calculations without the spin-orbit coupling.

It can be observed that the room pressure frequencies of our calculations, which include the spin-orbit coupling using GGA-PBEsol for the exchange-correlation term, compare reasonably well with the experimental values already published and are intermediate between the theoretical results, obtained using GGA with and without spin-orbit coupling (see Ref. 1).

Supplementary Table II. Theoretical (th.) *ab initio* IR-mode frequencies and pressure coefficients observed in β-Bi_2Se_3 (C2/m phase) at room temperature at P_0= 9.8 GPa as obtained from fits using $\omega(P) = \omega(P_0) + a_1 \cdot (P-P_0)$. No spin-orbit coupling is included.

Mode	ω (P_0) (th.) (cm^{-1})	a_1 (th.) (cm^{-1}/GPa)
B_u^1	52.1	1.02
A_u^1	56.6	0.84
B_u^2	88.3	1.42
A_u^2	108.3	1.47
B_u^3	114.7	1.54
B_u^4	129.0	1.50
A_u^3	138.9	0.55
B_u^5	160.4	1.42
A_u^4	164.6	1.15
B_u^6	167.3	1.44
B_u^7	180.0	1.65
B_u^8	192.7	1.98

Supplementary Table III. Theoretical (th.) *ab initio* IR-mode frequencies and pressure coefficients observed in γ-Bi_2Se_3 (C2/c phase) at room temperature at P_0= 19.9 GPa as obtained from fits using $\omega(P) = \omega(P_0) + a_1 \cdot (P-P_0)$. No spin-orbit coupling is included.

Mode	$\omega(P_0)$ (th.) (cm^{-1})	a_1 (th.) (cm^{-1}/GPa)
A_u^1	57.0	0.51
B_u^1	66.5	0.15
A_u^2	83.4	0.68
A_u^3	121.6	0.11
B_u^2	127.8	-0.09
B_u^3	136.8	2.12
A_u^4	138.5	2.22
B_u^4	142.2	2.32
B_u^5	170.6	1.54
B_u^6	174.4	2.66
A_u^5	185.1	2.34
A_u^6	203.5	1.04

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