Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electroic Supporting Information
Pressure and thermal effects of topological electronic materials X_2Y_3 (X=As, Sb, Bi; Y=Se, Te) from first-principles

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Taking Bi_2Se_3 as an example, we compare the calculated c/a ratio with the experimental data [1], as shown in FIG. S8. According to the results, the electronic topological transition in Bi_2Se_3 leads to changes in compressibility rather than volume, with pronounced changes in the c/a ratio behavior at pressures below and above the 5 GPa (around 6 GPa in the experimental data [1]), suggesting the pressure induced electronic topological transition in Bi_2Se_3 near 5 GPa. Similar behavior has been observed in Bi_2Te_3 and Sb_2Te_3, and the electronic topological transition of Bi_2Te_3 is around 3.2 GPa [2, 3], that of Sb_2Te_3 is around 3.5 GPa [4].

References

[1] H. Cheng, J. Zhang, Y. Li, G. Li and X. Li, *J. Appl. Phys.*, 2017, **121**, 225902.

[2] A. Polian, M. Gauthier, S. M. Souza, D. M. Trichês, J. C. de Lima and T. A. Grandi, *Phys. Rev. B*, 2011, **83**, 113106.

[3] J. Zhang, S. Zhang, H. Weng, W. Zhang, L. Yang, Q. Liu, S. Feng, X. Wang, R. Yu, L. Cao *et al.*, *Proc. Natl. Acad. Sci*, 2011, **108**, 24–28.

[4] O. Gomis, R. Vilaplana, F. Manjón, P. Rodríguez-Hernández, E. Pérez-González, A. Muñoz, V. Kucek and C. Drasar, *Phys. Rev. B*, 2011, **84**, 174305.

[5] X. Chen, H. Zhou, A. Kiswandhi, I. Miotkowski, Y. Chen, P. Sharma, A. Lima Sharma, M. Hekmaty, D. Smirnov and Z. Jiang, *Appl. Phys. Lett.*, 2011, **99**, 261912.

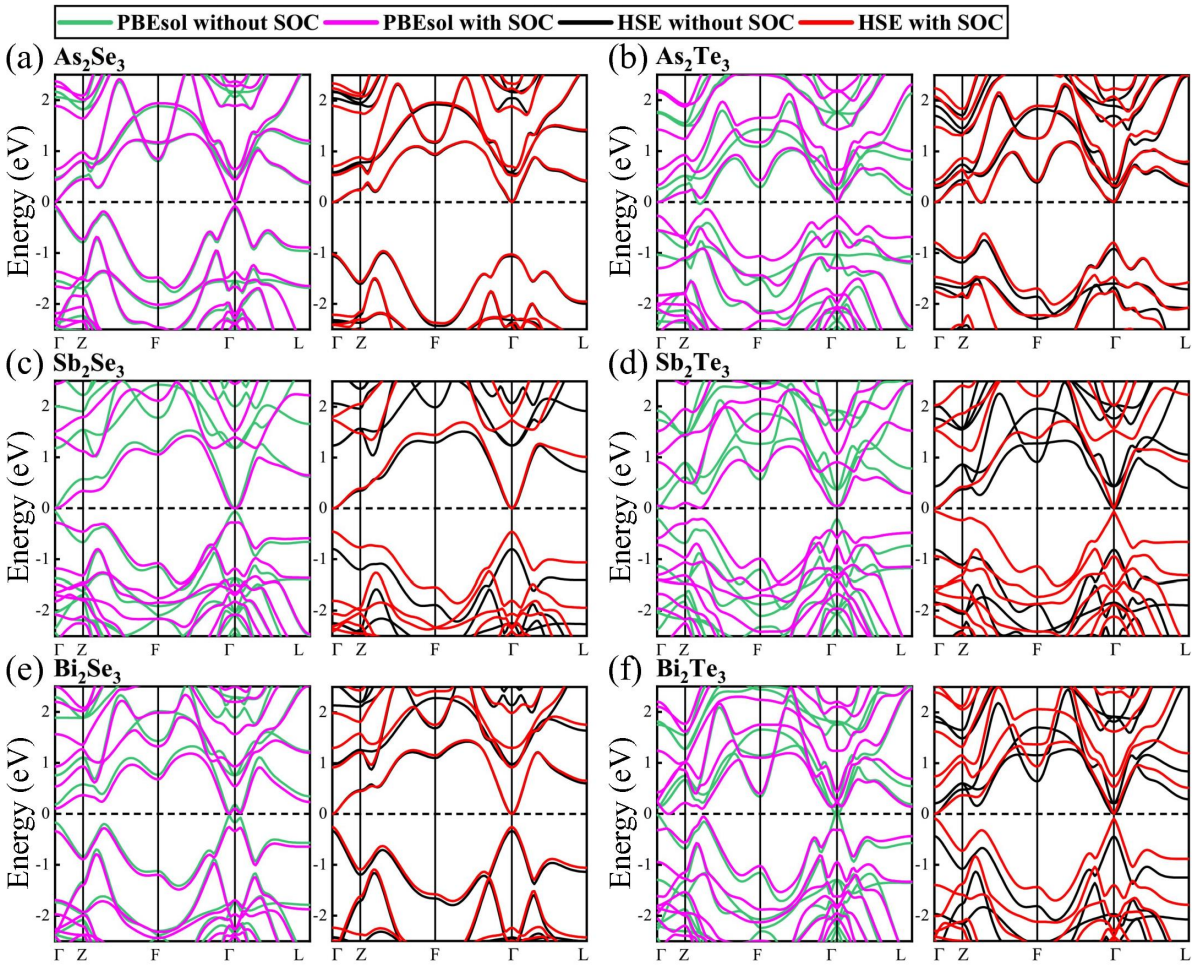

Figure S1: The calculated electronic band structure of X_2Y_3 (X=As, Sb, Bi; Y=Se, Te) using PBEsol and HSE06 methods, the Tkatchenko-Scheffler vdW is considered in all calculations.

Table S1: The calculated lattice parameter a (Å) and c (Å), c to a ratio, volume (Å^3), band gap (eV) of X_2Y_3 (X=As, Sb, Bi; Y=Se, Te) using different methods, in which, D and I represent the direct and indirect band gaps, respectively.

Materials	Methods	a (Å)	c (Å)	c/a	Volume (Å^3)	Band gap (eV)	
						w/o SOC	with SOC
As_2Se_3	LDA	3.743	26.738	7.143	324.435	0.021 (D)	0.043 (D)
	PBE	3.810	30.142	7.911	378.964	0.487 (I)	0.443 (I)
	PBE+vdW	3.811	28.277	7.420	355.681	0.351 (I)	0.304 (I)
	PBEsol	3.760	27.469	7.306	336.266	0.225 (D)	0.169 (D)
	PBEsol+vdW	3.746	27.111	7.238	329.433	0.136 (D)	0.075 (D)
	HSE06	3.779	29.634	7.841	366.573	1.144 (I)	1.096 (I)
	HSE06+vdW	3.771	28.160	7.468	346.783	0.996 (I)	0.949 (I)
As_2Te_3	LDA	4.027	28.250	7.015	396.760	0.160 (D)	0
	PBE	4.093	30.233	7.387	438.607	0.157 (D)	0
	PBE+vdW	4.111	28.690	6.979	419.873	0.189 (D)	0
	PBEsol	4.044	28.533	7.056	404.036	0.235 (D)	0
	PBEsol+vdW	4.028	28.345	7.037	398.251	0.367 (I)	0.138 (I)
	HSE06	4.083	30.107	7.375	434.567	0.841 (I)	0.667 (I)
	HSE06+vdW	4.107	28.948	7.049	422.837	0.735 (I)	0.590 (I)
Sb_2Se_3	LDA	3.994	27.611	6.913	381.482	0.039 (I)	0.265 (I)
	PBE	4.070	30.397	7.469	436.041	0.268 (D)	0.194 (D)
	PBE+vdW	4.079	28.378	6.957	408.864	0.045 (I)	0.180 (I)
	PBEsol	4.014	28.169	7.018	392.955	0.025 (I)	0.229 (I)
	PBEsol+vdW	3.999	27.915	6.981	386.568	0.050 (I)	0.258 (I)
	HSE06	4.035	29.808	7.387	420.376	0.654 (D)	0.580 (D)
	HSE06+vdW	4.038	28.548	7.069	403.157	0.335 (D)	0.257 (D)
Sb_2Te_3	LDA	4.251	29.498	6.939	461.594	0.039 (I)	0.047 (I)
	PBE	4.332	31.165	7.194	506.440	0.137 (D)	0.124 (I)
	PBE+vdW	4.329	29.935	6.914	485.897	0.045 (I)	0.095 (I)
	PBEsol	4.267	29.779	6.978	469.635	0.044 (I)	0.067 (I)
	PBEsol+vdW	4.248	29.666	6.984	463.534	0.049 (I)	0.055 (I)
	HSE06	4.289	31.535	7.352	502.376	0.662 (D)	0.334 (D)
	HSE06+vdW	4.295	30.491	7.099	487.133	0.439 (D)	0.088 (D)
Bi_2Se_3	LDA	4.105	27.956	6.810	407.971	0.023 (D)	0.328 (I)
	PBE	4.108	30.669	7.325	465.587	0.593 (D)	0.324 (D)
	PBE+vdW	4.193	28.662	6.835	436.438	0.199 (D)	0.121 (D)
	PBEsol	4.127	28.541	6.916	421.012	0.111 (D)	0.218 (D)
	PBEsol+vdW	4.112	28.306	6.884	414.484	0.069 (D)	0.277 (I)
	HSE06	4.158	29.878	7.186	447.295	1.105 (D)	0.804 (D)
	HSE06+vdW	4.164	28.580	6.864	429.111	0.769 (D)	0.432 (D)
Bi_2Te_3	LDA	4.354	29.928	6.873	491.390	0.154 (D)	0.176 (I)
	PBE	4.442	31.697	7.137	541.519	0.457 (D)	0.076 (I)
	PBE+vdW	4.428	30.474	6.882	517.438	0.267 (D)	0.161 (I)
	PBEol	4.374	30.241	6.914	500.964	0.210 (D)	0.203 (I)
	PBEsol+vdW	4.352	30.153	6.928	494.605	0.209 (D)	0.209 (I)
	HSE06	4.412	31.490	7.138	530.776	0.974 (D)	0.259 (D)
	HSE06+vdW	4.409	30.664	6.955	516.124	0.811 (D)	0.061 (D)

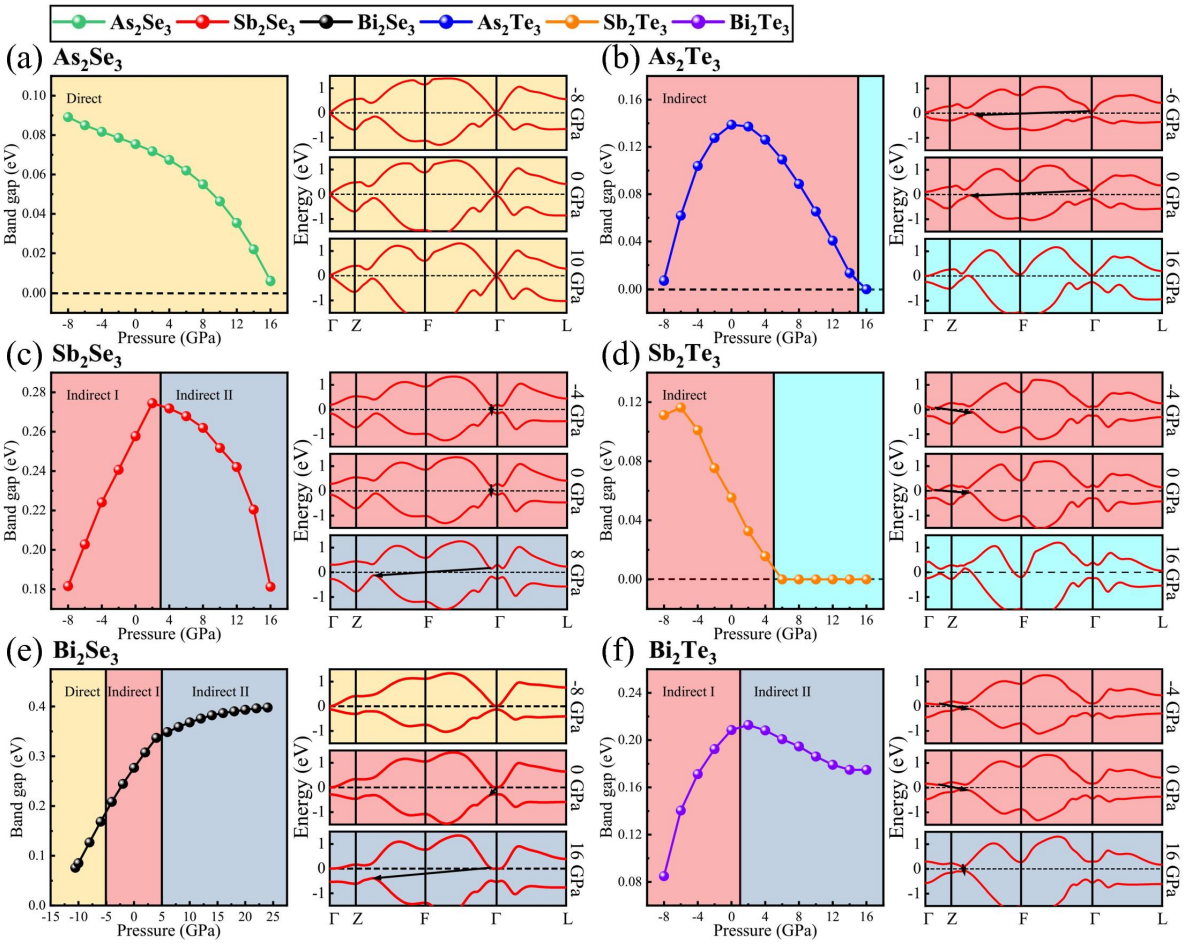

Figure S2: Band gaps *versus* external pressure of X_2Y_3 (X=As, Sb, Bi; Y=Se, Te) systems, and the electronic band structures of X_2Y_3 systems under different external pressure.

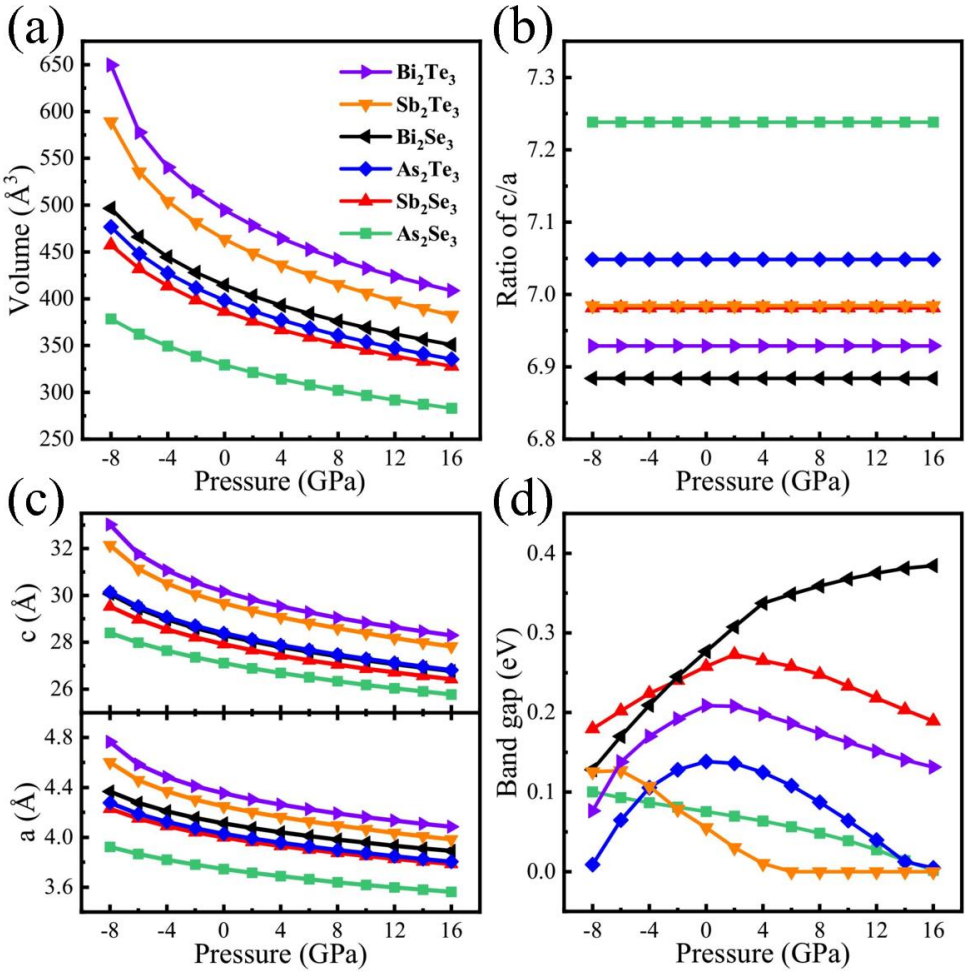

Figure S3: The pressure dependences of (a) volume, (b) fixed c to a ratio, (c) lattice parameters a and c, and (d) band gap of X_2Y_3 (X=As, Sb, Bi; Y=Se, Te) from -8 to 16 GPa. The green, red, black, blue, orange, and violet line plus symbol represent As_2Se_3, Sb_2Se_3, Bi_2Se_3, As_2Te_3, Sb_2Te_3, and Bi_2Te_3 systems, respectively.

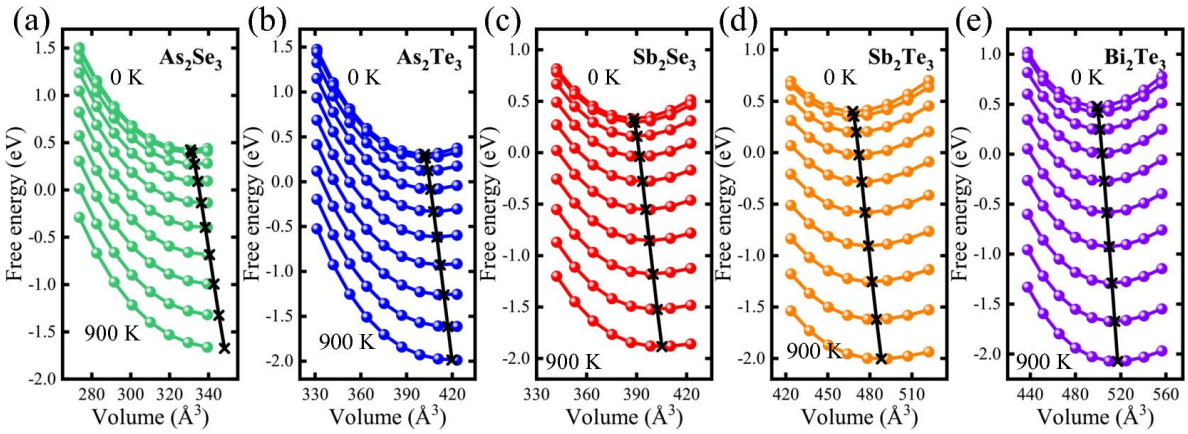

Figure S4: Free energy of X_2Y_3 (X=As, Sb, Bi; Y=Se, Te), except for Bi_2Se_3 in main text, with respect to volume at temperatures from 0 to 900 K in 100 K intevals are represented by colored solid circles, and the values are fitted by colored curves. The black cross symbols show the energy minima of the respective curves and the equilibrium volume.

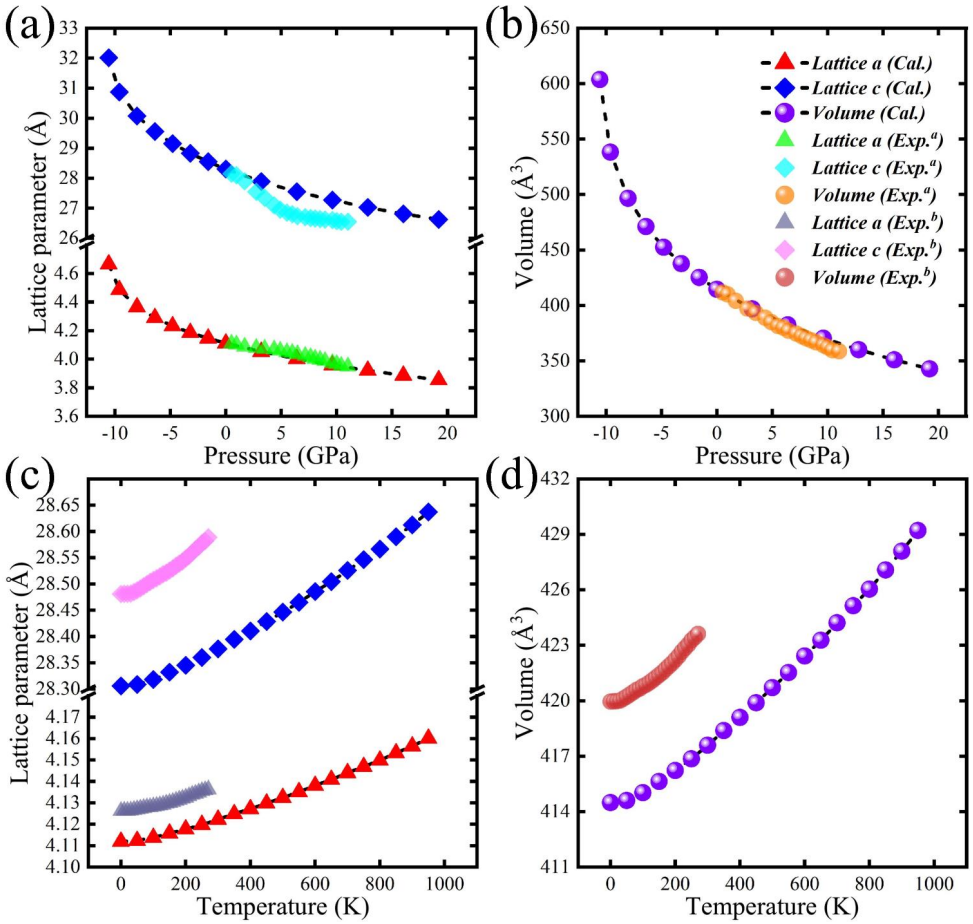

Figure S5: The relationships of (a) lattice parameter $versus$ pressure, (b) volume $versus$ pressure, (c) lattice parameter $versus$ temperature, and (d) volume $versus$ temperature for Bi_2Se_3. Note: Exp.^{a} and Exp.^{b} are from Reference [1] and Reference [5], respectively.

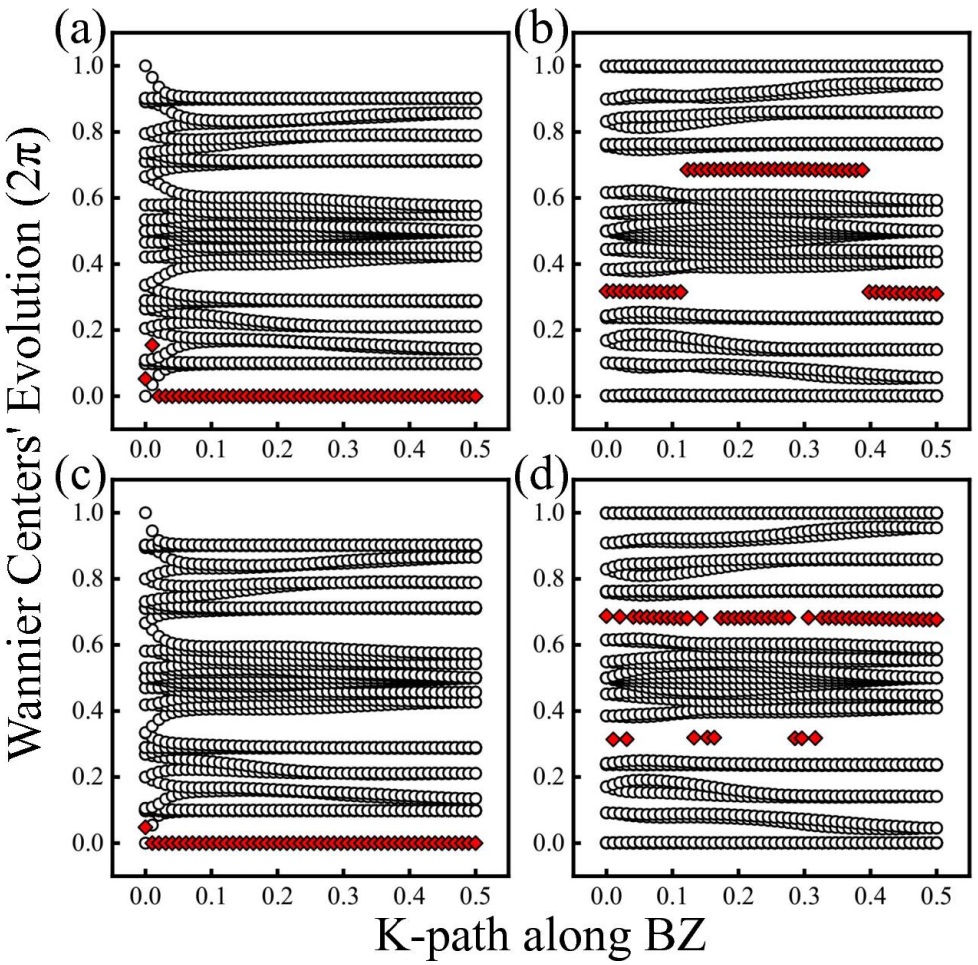

Figure S6: Wannier charge centers' evolution (black circles) $versus$ k_2 of Bi_2Se_3 at (a) k_1 = 0, (b) k_1 = 0.5, when the external pressure is 0 GPa, and (c) k_1 = 0, (d) k_1 = 0.5, when the external pressure is -8 GPa. The red diamond marks the midpoint of largest gap of Wannier charge centers' evolution, and k_2 is sampled in 50 equal increments from 0 to 0.5.

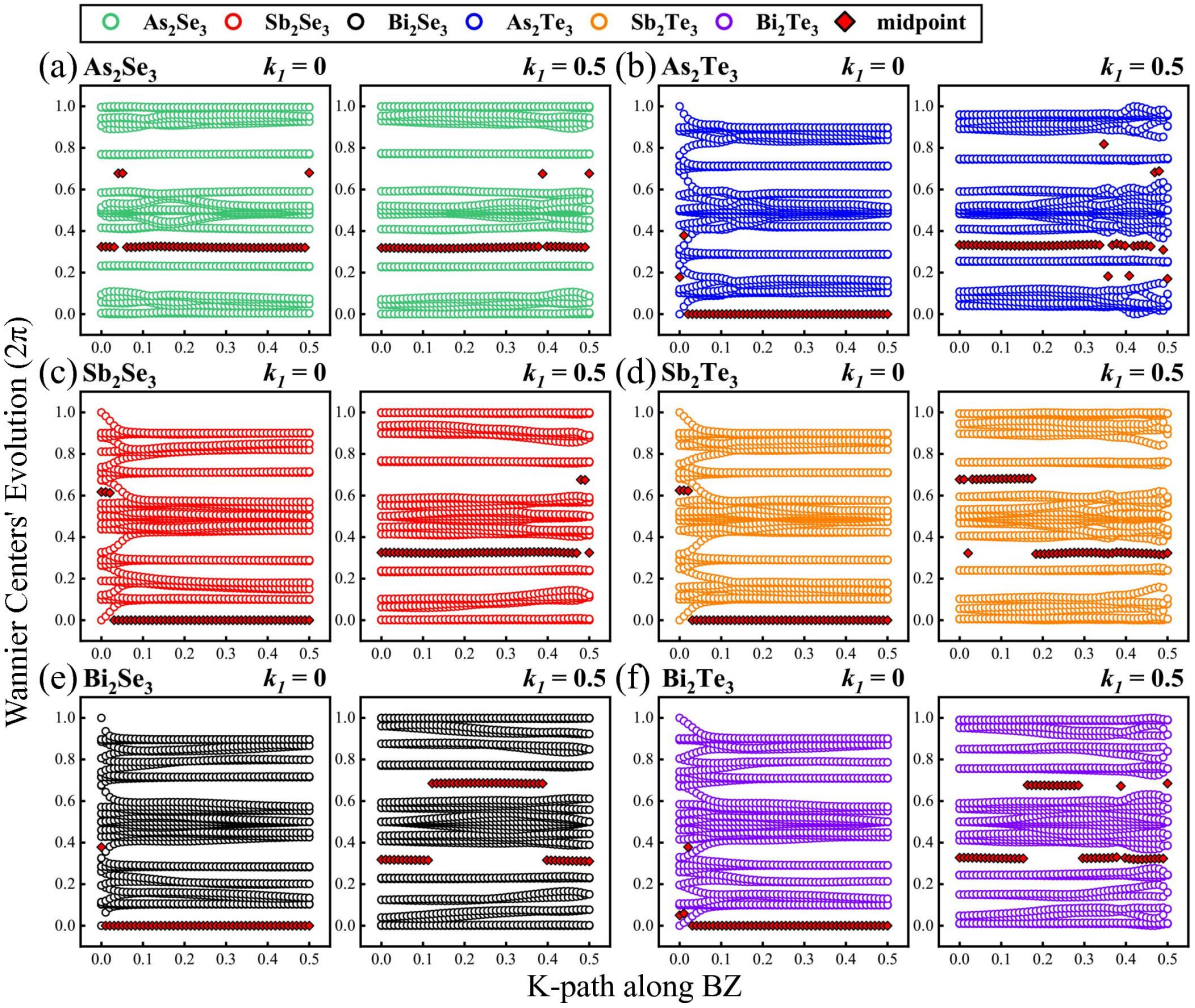

Figure S7: Wannier charge centers' evolution $versus$ k_2 of X_2Y_3 (X=As, Sb, Bi; Y=Se, Te) at (a) $k_1 = 0$, (b) $k_1 = 0.5$ when the temperature is 300 K. The green, red, black, blue, orange, and violet circle represent As_2Se_3, Sb_2Se_3, Bi_2Se_3, As_2Te_3, Sb_2Te_3, and Bi_2Te_3 systems, respectively, and the red diamond marks the midpoint of largest gap of Wannier charge centers' evolution.

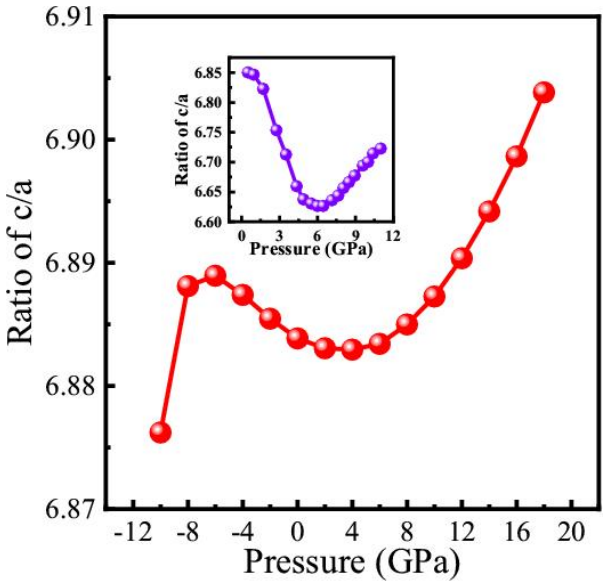

Figure S8: The calculated c/a ratio of Bi_2Se_3 system using PBEsol plue Tkatchenko-Scheffler vdW methods, the inset shows previous experimental data [1].