Electronic Supplementary Information

Pressure-driven structural and electronic transitions in quasimolecular layered compound of antimony triiodide

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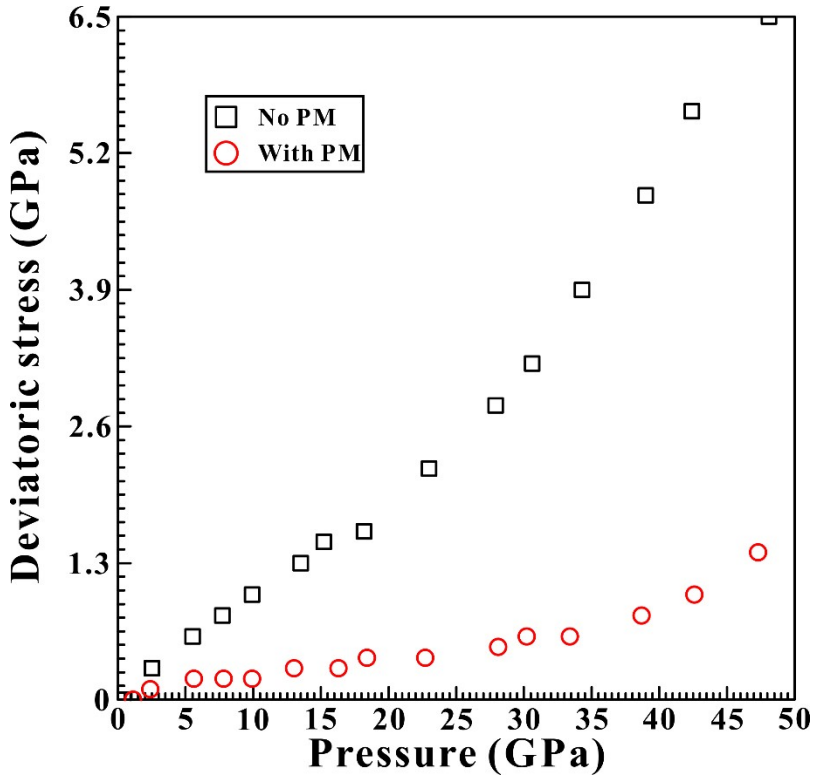

Fig. S1 The relationship between deviatoric stress and pressure under different hydrostatic environments. Herein, PM stands for pressure medium.

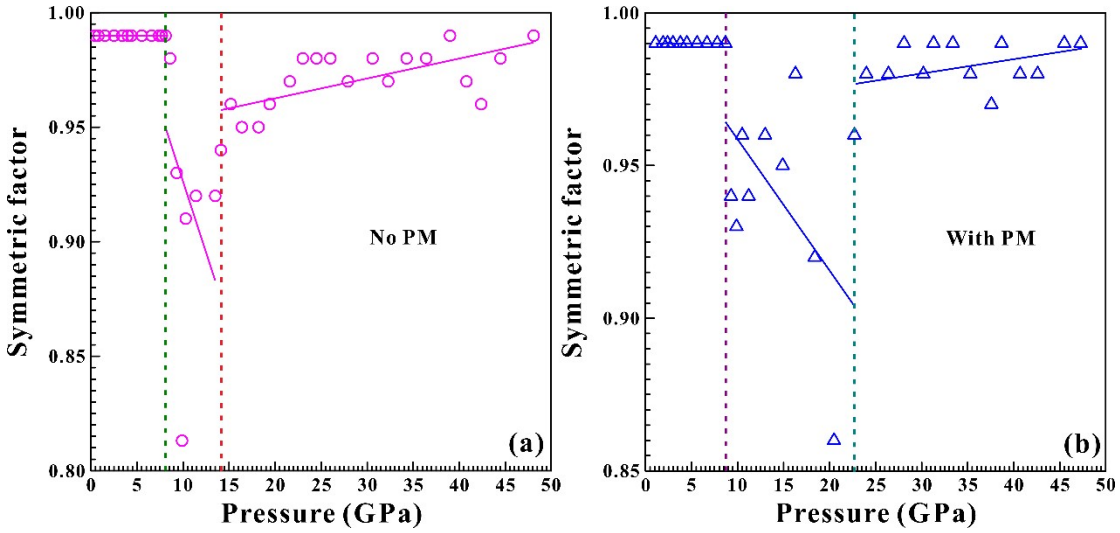

Fig. S2 The evolution of symmetric factor as a function of pressure for the characteristic Raman peak of ν_1 under (a) non-hydrostatic condition and (b) hydrostatic condition, respectively. In here, PM denotes pressure medium.

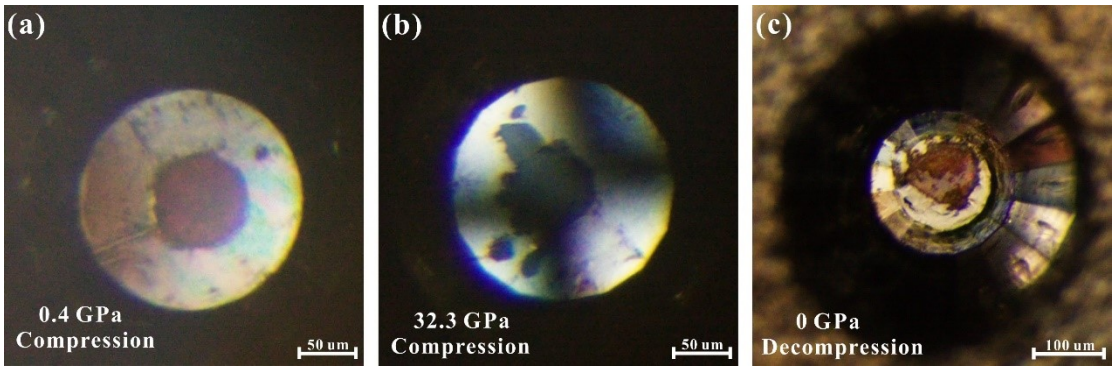

Fig. S3 Optical photographs of the sample chamber in a diamond anvil cell at (a) 0.4 GPa and (b) 32.3 GPa during compression, and as well as (c) 0 GPa after releasing to ambient pressure, respectively.

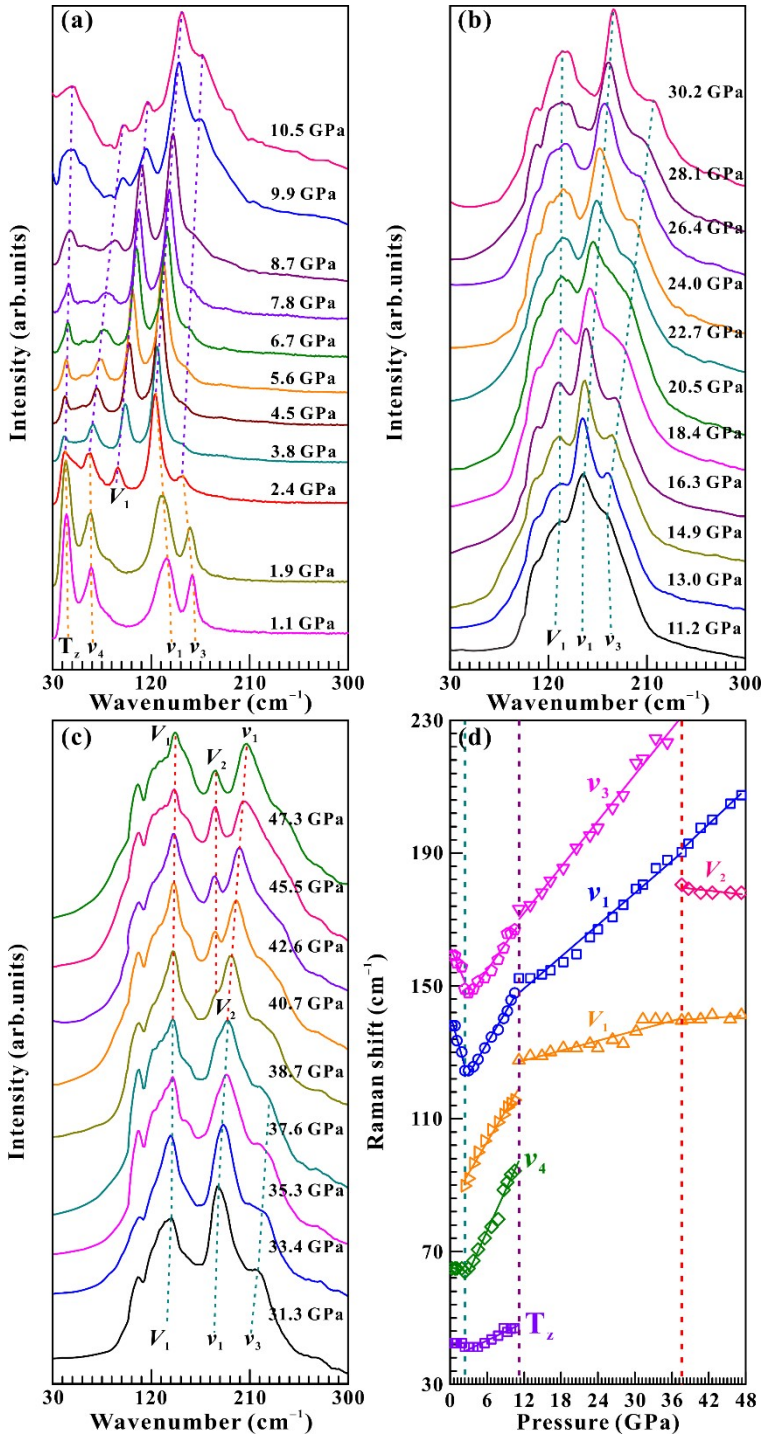

Fig. S4 High-pressure Raman spectroscopic results of SbI_3 under hydrostatic condition within the pressure range of (a) 1.1–10.5 GPa; (b) 11.2–30.2 GPa and (c) 31.3–47.3 GPa, respectively. (d) Correspondent evolution of Raman shift versus pressure during pressurization. Errors in both Raman shifts and pressures are within the size of the symbols.

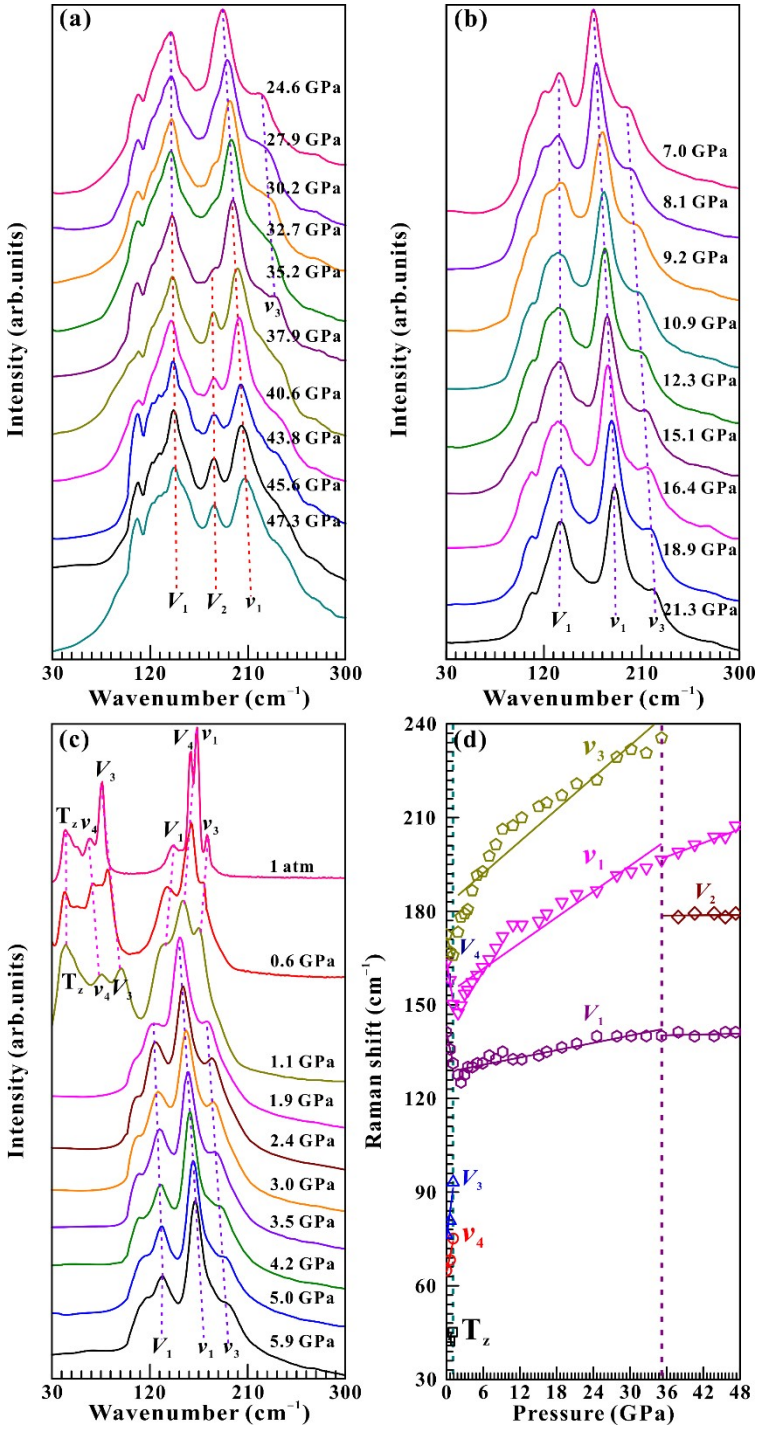

Fig. S5 High-pressure Raman spectra of SbI_3 under hydrostatic condition within the pressure range of (a) 47.3–24.6 GPa; (b) 21.3–7.0 GPa and (c) 5.9–0 GPa, respectively. (d) The relation between Raman shift and pressure at atmospheric temperature during decompression. Errors in both Raman shifts and pressures are within the size of the symbols.

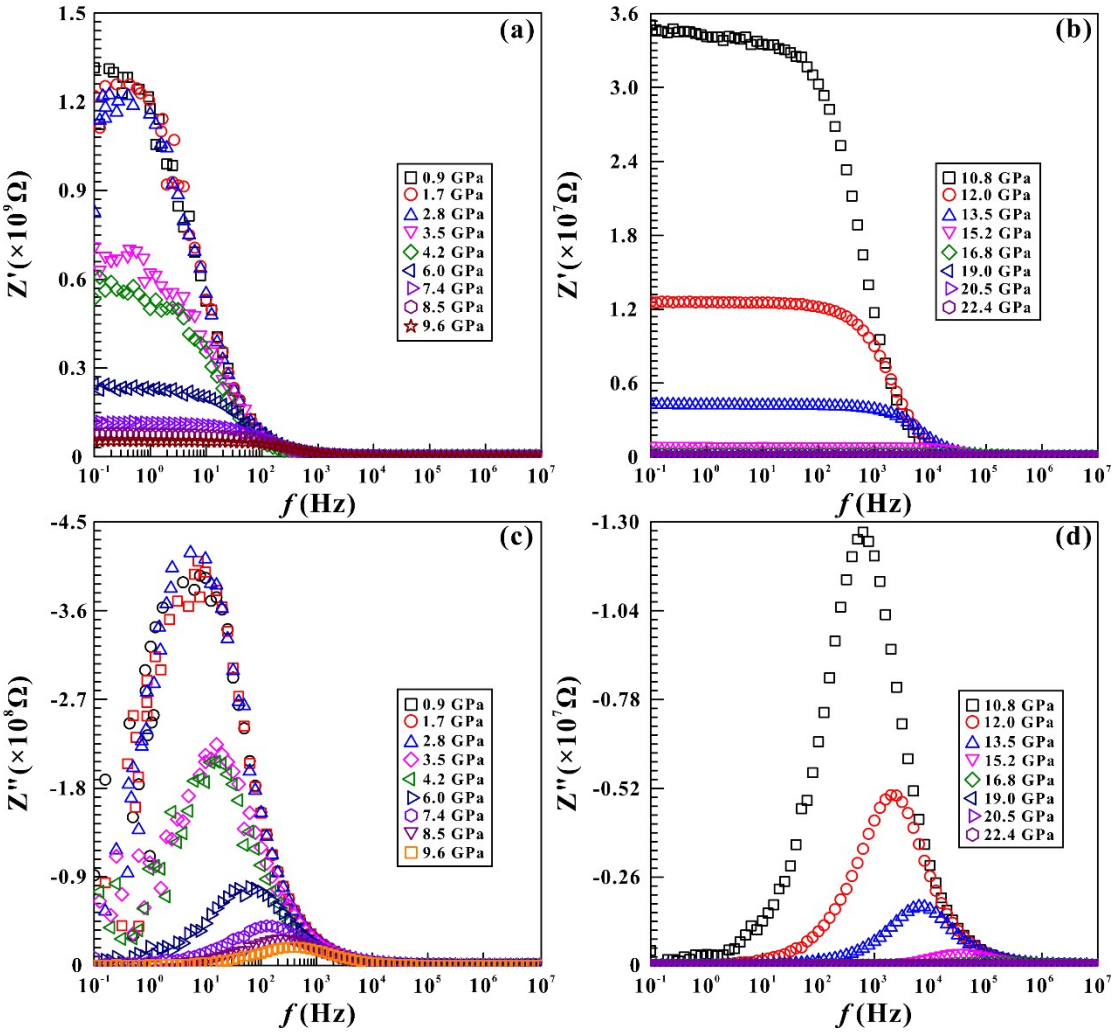

Fig. S6 The Bode diagrams of the complex impedance spectra for SbI_3 over the frequency range of 10^{-1}–10^7 Hz under the conditions of 0.9–22.4 GPa and atmospheric temperature. (a and b) The dependence of the real part of complex impedance (Z') on frequency (*f*). (c and d) The evolution of the imaginary part of complex impedance (Z'') on frequency (*f*).

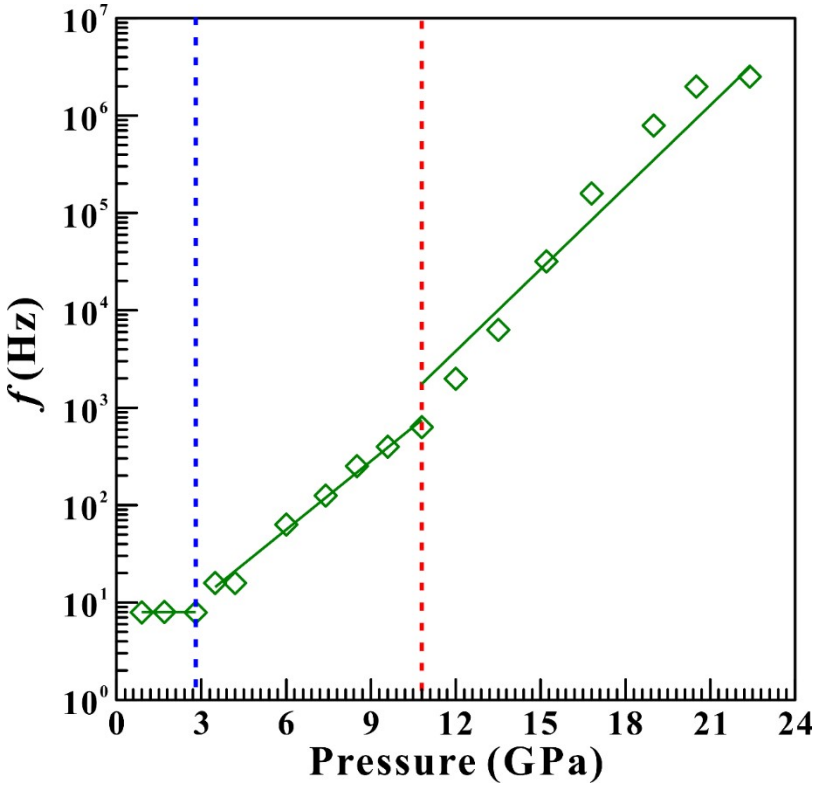

Fig. S7 The corresponding evolution of relaxation frequency (*f*) versus pressure for SbI_3 within the pressure range of 0.9–22.4 GPa. Therein, *f* stands for the relaxation frequency. Errors in both relaxation frequencies and pressures are within the size of the symbols.

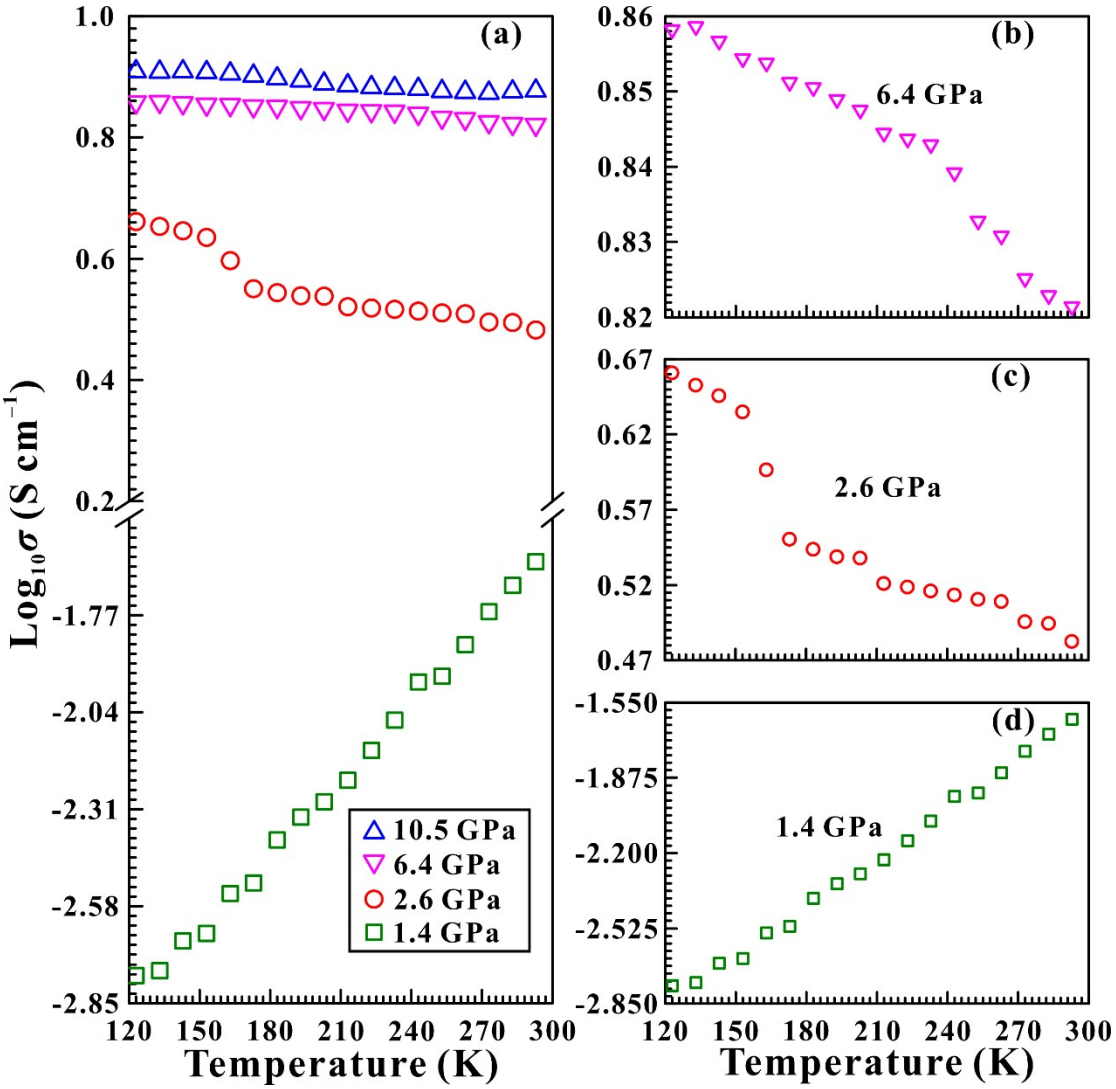

Fig. S8 A series of temperature dependence of electrical conductivity measurements for SbI_3 at some selected pressures of (a) 10.5, 6.4, 2.6 and 1.4 GPa during depressurization. (b and c) The metallic nature of sample at 6.4 GPa and 2.6 GPa. (d) The semiconducting characteristic of SbI_3 at 1.4 GPa, respectively.

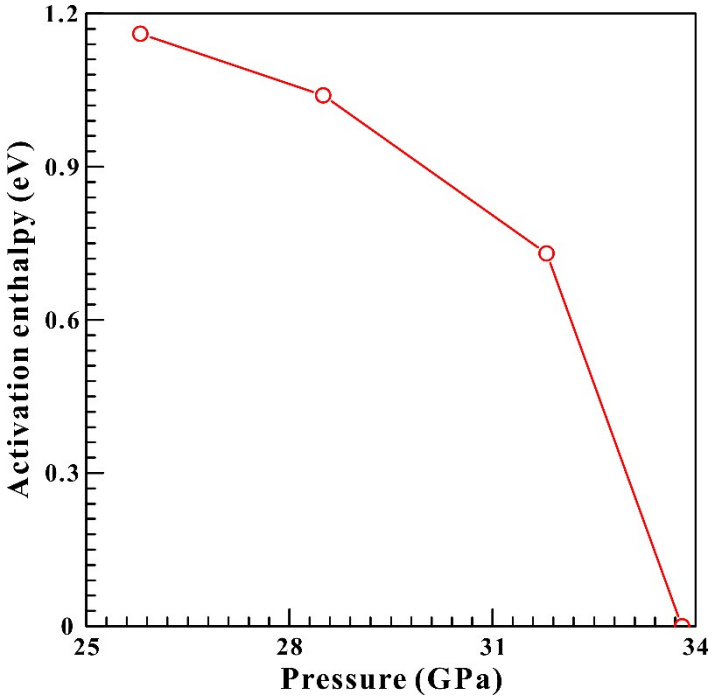

Fig. S9 The evolution of activation enthalpy as a function of pressure for SbI_3.

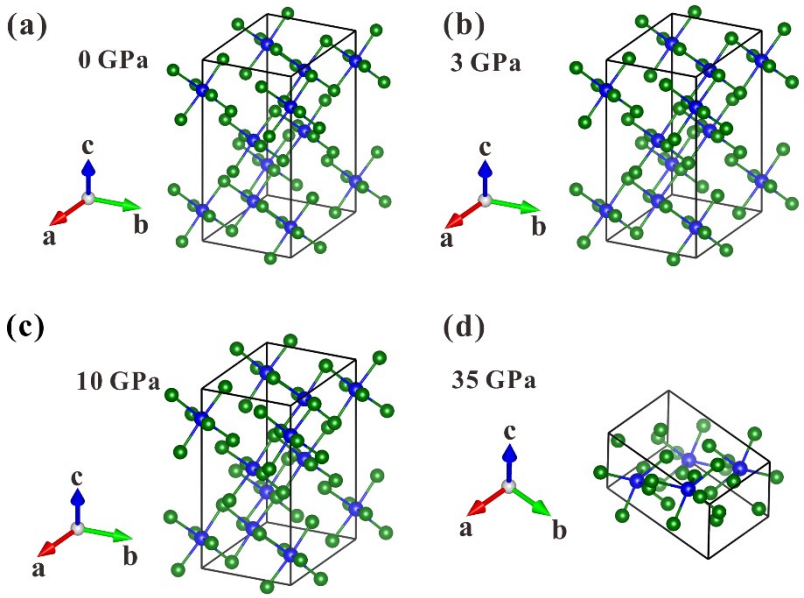

Fig. S10 Schematic representation on the crystalline structures of SbI_3 under high pressure. The rhombohedral $R\bar{3}$ structural phase at (a) 0 GPa, (b) 3.0 GPa and (c) 10.0 GPa, respectively. (d) The monoclinic $C2/m$ structural phase at 35.0 GPa. Herein, the blue and green spheres stand for antimony and iodine atoms, respectively. Black lines represent unit cells.

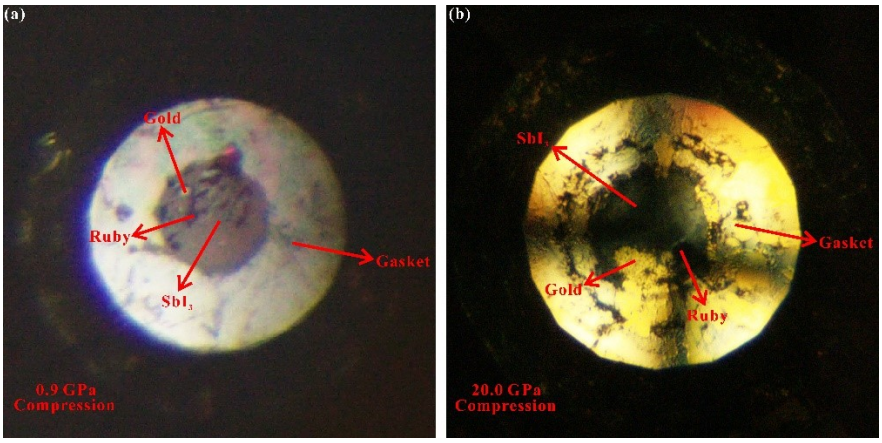

Fig. S11 Optical photographs of the sample chamber in a diamond anvil cell at (a) 0.9 GPa and (b) 20.0 GPa upon compression during the process of synchrotron X-ray diffraction experiments.

Table S1. Pressure-dependent Raman shift ($d\omega/dP$, cm^{-1} GPa^{-1}) for SbI_3 during compression and decompression under non-hydrostatic and hydrostatic environments. Herein, ω (cm^{-1}) and P (GPa) represent the Raman wavenumber and pressure, respectively.

Pressure condition		Pressure (GPa)	ω (cm^{-1})	$d\omega/dP$ (cm^{-1} GPa^{-1})	ω (cm^{-1})	$d\omega/dP$ (cm^{-1} GPa^{-1})
Non-hydrostatic	Compression	0.4–3.4	41.2 (T_Z)	–0.30	62.7 (v_4)	–0.33
			134.6 (v_1)	–3.45	156.9 (v_3)	–2.54
		3.4–10.3	40.1 (T_Z)	1.25	61.5 (v_4)	4.88
			123.4 (v_1)	3.71	147.9 (v_3)	3.24
			87.5 (V_1)	4.26	–	
		10.3–32.3	–		–	
			146.9 (v_1)	2.18	165.8 (v_3)	2.89
			114.5 (V_1)	0.63	–	
		32.3–48.1	–		–	
			192.8 (v_1)	1.46	–	
			139.9 (V_1)	0.35	180.5 (V_2)	–0.05
	Decompression	48.1–32.6	–		–	
			214.8 (v_1)	1.36	–	
			146.1 (V_1)	0.44	178.1 (V_2)	0.17
		32.6–1.2	–		–	
			195.2 (v_1)	1.66	235.5 (v_3)	2.21
			139.9 (V_1)	0.60	–	
Hydrostatic	Compression	1.1–2.4	42.4 (T_Z)	–0.84	64.9 (v_4)	–0.77
			133.5 (v_1)	–6.67	156.9 (v_3)	–5.58
		2.4–11.2	41.2 (T_Z)	0.83	63.8 (v_4)	3.97
			124.5 (v_1)	2.95	149.1 (v_3)	2.47
			89.9 (V_1)	3.13	–	
		11.2–37.6	–		–	
			152.3 (v_1)	1.61	173.1 (v_3)	2.31
			127.6 (V_1)	0.50	–	
		37.6–47.3	–		–	
			190.3 (v_1)	1.74	–	
			139.6 (V_1)	0.12	180.5 (V_2)	–0.20
	Decompression	47.3–35.2	–		–	

		207.4 (v_1)	0.81	–	
		141.2 (V_1)	0.04	179.3 (V_2)	0.05
		–		–	
	35.2–1.1	196.4 (v_1)	1.37	235.5 (v_3)	1.71
		140.0 (V_1)	0.39	–	

Table S2. The pressure dependence of activation energy (*dH*/*dP*, meV/GPa) for SbI_3 within three distinct pressure ranges of 0.9–2.8 GPa, 3.5–10.8 GPa and 12.0–22.4 GPa, respectively. Wherein, *H* (meV) and *P* (GPa) represent the activation energy and pressure, respectively.

Pressure range (GPa)	*dH*/*dP* (meV/GPa)	Error (%)
0.9–2.8	–0.01	0.43
3.5–10.8	–13.9	2.69
12.0–22.4	–19.0	5.97

Table S3. The detailed atomic positions of SbI_3 at the representative pressures of 0, 3.0, 10.0 and 35.0 GPa.

Pressure	Atom	Atomic position
0 GPa	Sb	(1.00000, 1.00000, 0.16806)
		(0.00001, 0.00001, 0.83195)
		(0.66666, 0.33332, 0.50131)
		(0.66666, 0.33333, 0.16537)
		(0.33334, 0.66667, 0.83463)
		(0.33333, 0.66666, 0.49869)
	I	(0.00329, 0.34758, 0.41630)
		(0.99671, 0.65243, 0.58370)
		(0.65243, 0.65571, 0.41630)
		(0.34757, 0.34429, 0.58370)
		(0.34429, 0.99672, 0.41630)
		(0.65571, 0.00329, 0.58370)
		(0.66987, 0.68067, 0.74961)
		(0.66364, 0.98590, 0.91702)
		(0.31933, 0.98920, 0.74961)
		(0.01410, 0.67774, 0.91702)
		(0.01080, 0.33013, 0.74961)
		(0.32226, 0.33636, 0.91702)
		(0.33636, 0.01410, 0.08298)
		(0.33013, 0.31933, 0.25039)
		(0.98590, 0.32227, 0.08298)
		(0.68067, 0.01080, 0.25039)
		(0.67773, 0.66364, 0.08298)
		(0.98920, 0.66987, 0.25039)
3.0 GPa	Sb	(1.00000, 1.00000, 0.16761)
		(0.00000, 0.00000, 0.83239)
		(0.66667, 0.33333, 0.50065)
		(0.66666, 0.33332, 0.16602)
		(0.33334, 0.66667, 0.83398)
		(0.33334, 0.66667, 0.49936)
	I	(0.00206, 0.32644, 0.41050)
		(0.99794, 0.67355, 0.58950)
		(0.67356, 0.67561, 0.41050)
		(0.32645, 0.32439, 0.58950)
		(0.32439, 0.99795, 0.41050)
		(0.67560, 0.00205, 0.58950)
		(0.66870, 0.65980, 0.74383)
		(0.66463, 0.00692, 0.92283)
		(0.34021, 0.00890, 0.74383)
		(0.99308, 0.65772, 0.92283)
		(0.99111, 0.33131, 0.74383)
		(0.34228, 0.33536, 0.92283)
		(0.33537, 0.99308, 0.07717)
		(0.33130, 0.34020, 0.25617)

		(0.00692, 0.34228, 0.07717) (0.65980, 0.99110, 0.25617) (0.65772, 0.66464, 0.07717) (0.00889, 0.66869, 0.25617)
10.0 GPa	Sb	(1.00000, 1.00000, 0.16761) (1.00000, 1.00000, 0.83239) (0.66667, 0.33334, 0.50094) (0.66667, 0.33334, 0.16573) (0.33333, 0.66666, 0.83427) (0.33333, 0.66667, 0.49906)
	I	(0.99819, 0.31097, 0.40701) (0.00181, 0.68903, 0.59299) (0.68903, 0.68722, 0.40701) (0.31097, 0.31278, 0.59299) (0.31278, 0.00181, 0.40701) (0.68722, 0.99819, 0.59299) (0.66486, 0.64430, 0.74034) (0.66848, 0.02237, 0.92631) (0.35570, 0.02055, 0.74034) (0.97762, 0.64611, 0.92631) (0.97945, 0.33515, 0.74034) (0.35389, 0.33151, 0.92631) (0.33152, 0.97763, 0.07369) (0.33514, 0.35570, 0.25966) (0.02238, 0.35389, 0.07369) (0.64430, 0.97945, 0.25966) (0.64611, 0.66849, 0.07369) (0.02055, 0.66485, 0.25966)
35.0 GPa	Sb	(0.00003, 0.71167, 0.50003) (0.99997, 0.78833, 0.99997) (0.00003, 0.21167, 0.00004) (0.99997, 0.28833, 0.49997)
	I	(0.83551, 0.50003, 0.23210) (0.63936, 0.63913, 0.75845) (0.63946, 0.86088, 0.25853) (0.36063, 0.86087, 0.74155) (0.63937, 0.13914, 0.25845) (0.36054, 0.63912, 0.24147) (0.16449, 0.49996, 0.76790) (0.83551, 0.00003, 0.73210) (0.16449, 0.99997, 0.26790) (0.63945, 0.36088, 0.75853) (0.36055, 0.13912, 0.74147) (0.36063, 0.36087, 0.24155)

Table S4. The refined lattice parameters of SbI_3 obtained from the synchrotron X-ray diffraction results at four characteristic pressures of 1.5, 8.0, 20.0 and 40.0 GPa, respectively.

Pressure (GPa)	*a* (Å)	*b* (Å)	*c* (Å)	*α* (º)	*β* (º)	*γ* (º)	*V* (Å^3)
1.5	7.113±0.002	7.113±0.002	19.293±0.009	90	90	120	845.35±0.55
8.0	6.819±0.004	6.819±0.004	18.973±0.007	90	90	120	764.03±0.48
20.0	6.696±0.003	6.696±0.003	18.295±0.002	90	90	120	710.39±0.65
40.0	6.187±0.004	10.440±0.005	5.850±0.001	90	98	90	374.19±0.43