Supplementary Information

Compressive behavior and electronic properties of ammonia ice: a first-principles study

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Table S1. Lattice constant (a, b, c), bond lengths of covalent ($d_{N–H}$) and hydrogen ($d_{N–H…N}$) bonds and H–N–H angle (θ) in $P2_12_12_1$, $Pca2_1$, $P2_1/m$ and $Pnma$ phases under various pressures P (GPa). Q_N and BO respect the average Mulliken charge on nitrogen and bond order along N–H bonds, respectively.

Structure	P (GPa)	a (Å)	b (Å)	c (Å)	$d_{N–H}$ (Å)	$d_{N–H…N}$ (Å)	θ (°)	Q_N (e)	BO
$P2_12_12_1$	0	3.43	5.58	5.78	1.03	2.35	106.20	–1.10	0.70
	30	2.82	4.68	5.00	1.02	1.87	106.80	–0.96	0.80
	100	2.57	4.22	4.48	1.01	1.56	107.83	–0.86	0.88
$Pca2_1$	0	13.58	4.17	4.50	1.03	2.26	105.68	–1.11	0.68
	40	9.49	2.83	4.43	1.04	1.68	103.94	–0.90	0.79
	100	8.93	2.57	4.13	1.03	1.52	104.00	–0.84	0.84
$P2_1/m$	0	4.60	4.12	5.24	1.13	1.87	105.14	–1.00	0.51
	40	2.87	4.36	4.69	1.11	1.72	102.71	–0.89	0.71
	100	2.60	4.12	4.38	1.08	1.55	103.44	–0.83	0.79
$Pnma$	0	5.93	4.74	4.43	1.03	2.25	106.47	–1.12	0.69
	40	4.60	4.59	2.93	1.02	1.78	106.21	–0.94	0.81
	100	4.32	4.25	2.64	1.01	1.62	106.89	–0.86	0.85

Table S2. The Hirshfeld charge analysis of $P2_13$ phase of ammonia ice under 0, 5, 13, 100, and 500 GPa.

P (GPa)	atom	Q_N (*e*)
0	H	0.08
	N	–0.25
5	H	0.08
	N	–0.24
13	H	0.08
	N	–0.23
100	H	0.07
	N	–0.20
500	H	0.06
	N	–0.17

Table S3. The Hirshfeld charge analysis of *P*ma2 phase of ammonia ice under 0, 5, 15, 100, and 500 GPa.

P/GPa	group	atom	CT_1/e	CT_2/e
0	NH_4^+	H_1	0.11	0.18
		H_2	0.07	
		N_1	–0.18	
	NH_2^-	H_9	0.06	–0.18
		H_{10}	0.06	
		N_3	–0.30	
5	NH_4^+	H_1	0.11	0.18
		H_2	0.07	
		N_1	–0.18	
	NH_2^-	H_9	0.06	–0.18
		H_{10}	0.05	
		N_3	–0.30	
15	NH_4^+	H_1	0.10	0.19
		H_2	0.07	
		N_1	–0.15	
	NH_2^-	H_9	0.05	–0.20
		H_{10}	0.05	
		N_3	–0.30	
100	NH_4^+	H_1	0.07	0.12
		H_2	0.07	
		N_1	–0.16	
	NH_2^-	H_9	0.06	–0.11
		H_{10}	0.06	
		N_3	–0.23	
500	NH_4^+	H_1	0.06	0.05
		H_2	0.06	
		N_1	–0.19	
	NH_2^-	H_9	0.06	–0.06
		H_{10}	0.06	
		N_3	–0.18	

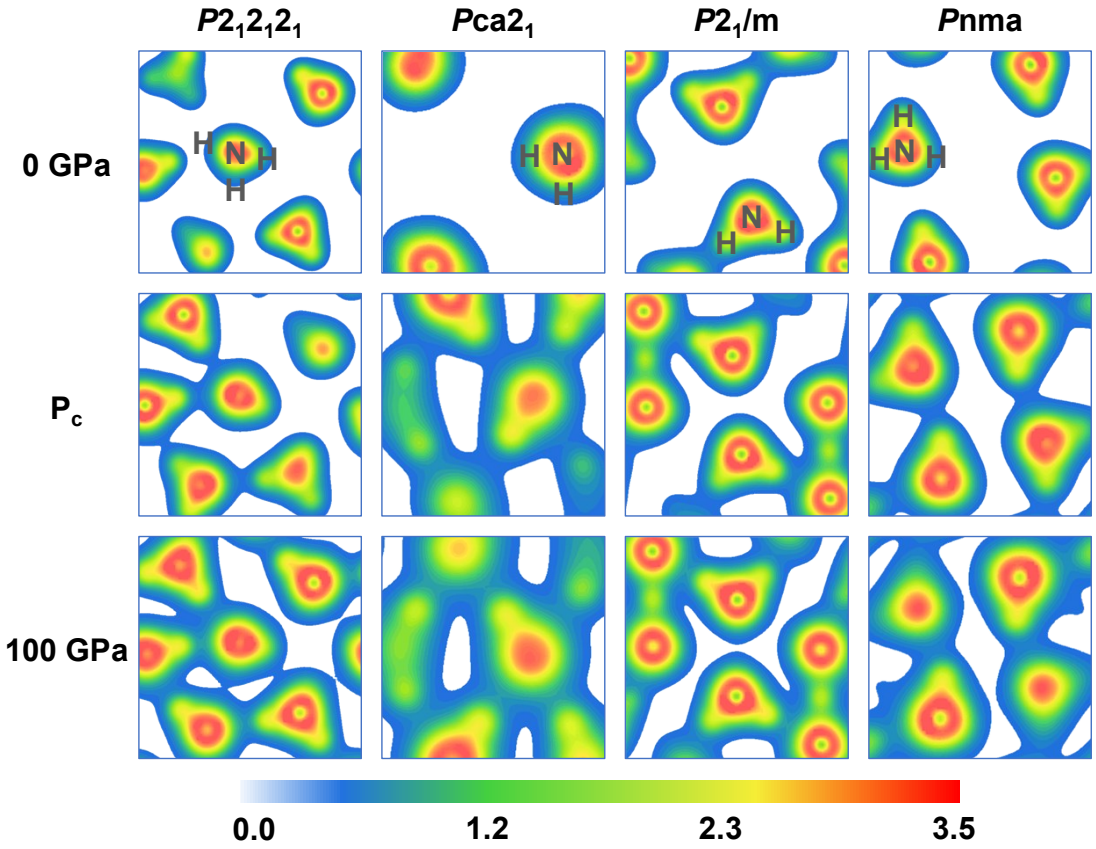

Fig. S1. The charge density distribution in (111) plane of $P2_12_12_1$, $Pca2_1$, $P2_1/m$ and *P*nma phases under 0, P_c, 100 GPa. (P_c: the critical pressure of the maximum band gap values)

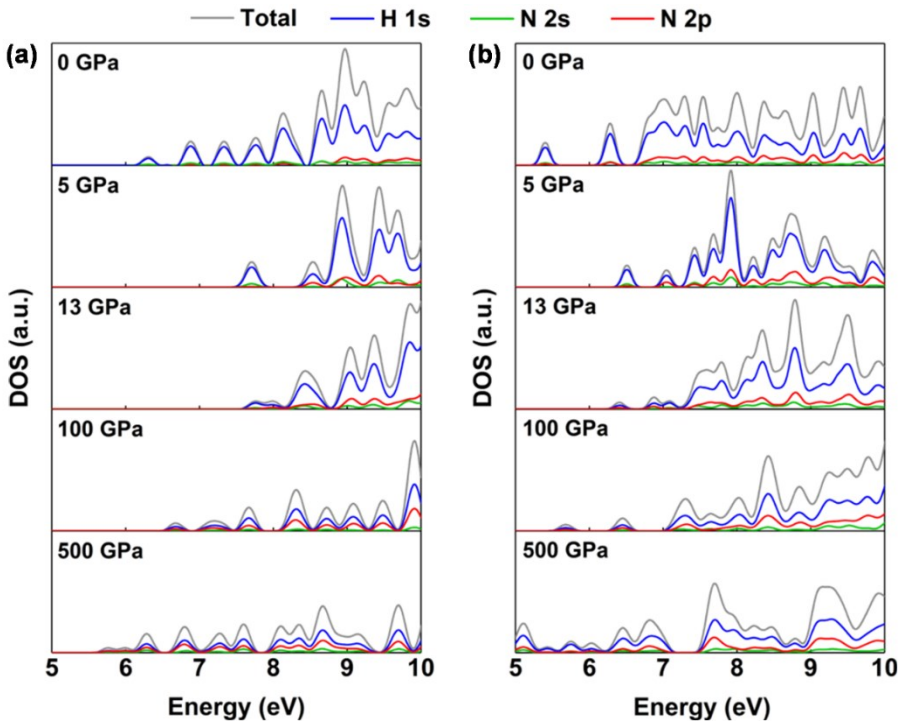

Fig. S2. The density of states (DOS) of (a) $P2_13$ phase and (b) *P*ma2 phase in the range of 5 – 10 eV under various pressures (0, 5, P_c, 100 and 500 GPa).

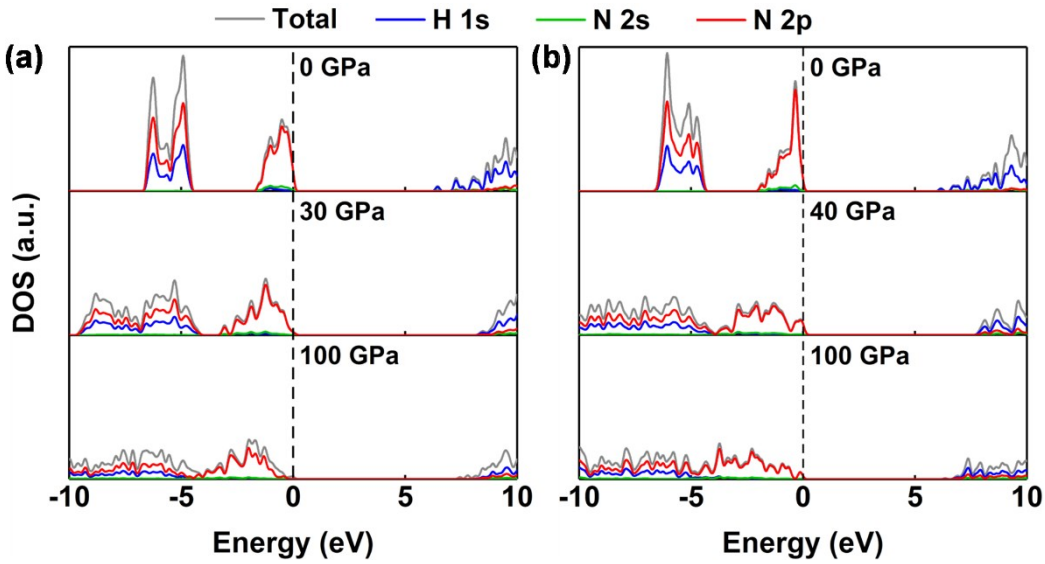

Fig. S3. The density of states (DOS) of (a) $P2_12_12_1$ and (b) *P*nma molecular phases under the various pressure.

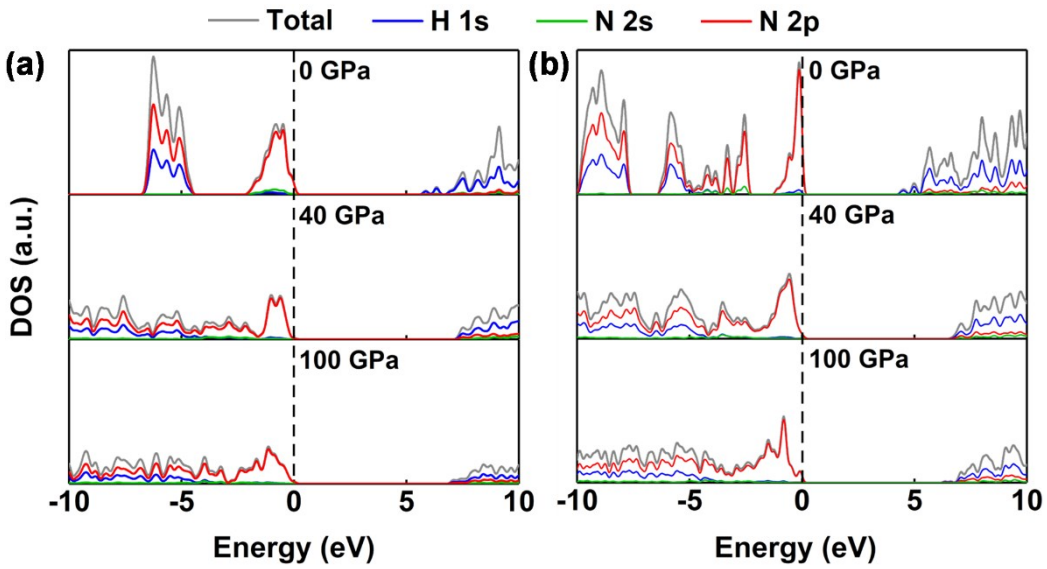

Fig. S4. The DOS of (a) *P*ca2$_1$ and (b) *P*2$_1$/m ionic phases under the various pressure.

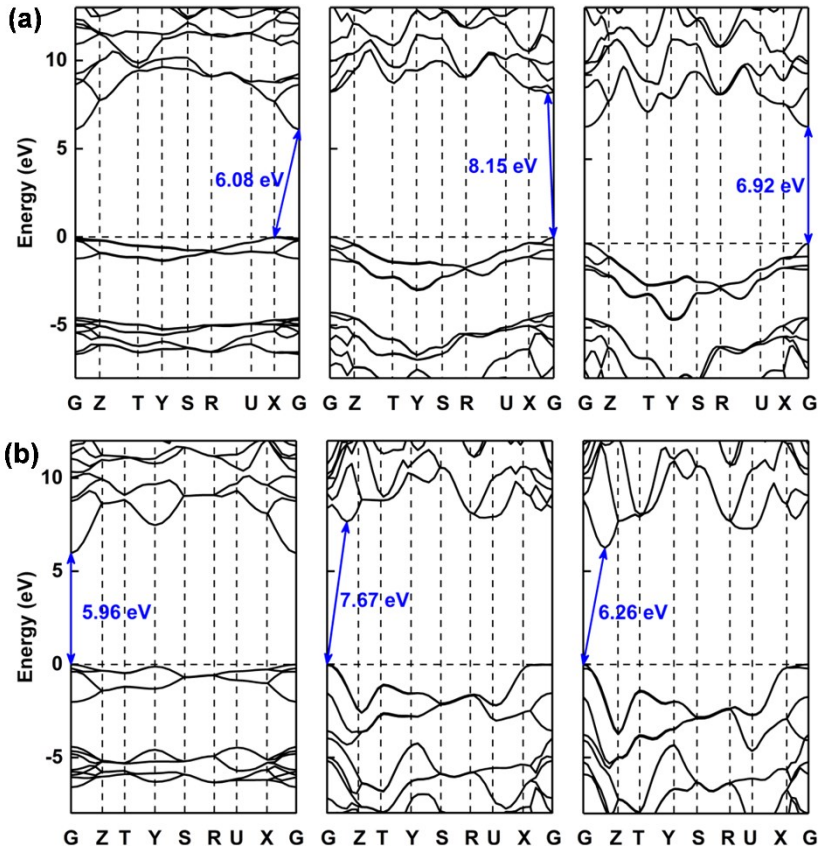

Fig. S5. The band structures of (a) $P2_12_12_1$ and (b) *P*nma molecular phases under 0 GPa, critical pressure (P_c: 30, 20 and 40 GPa) and 100 GPa.

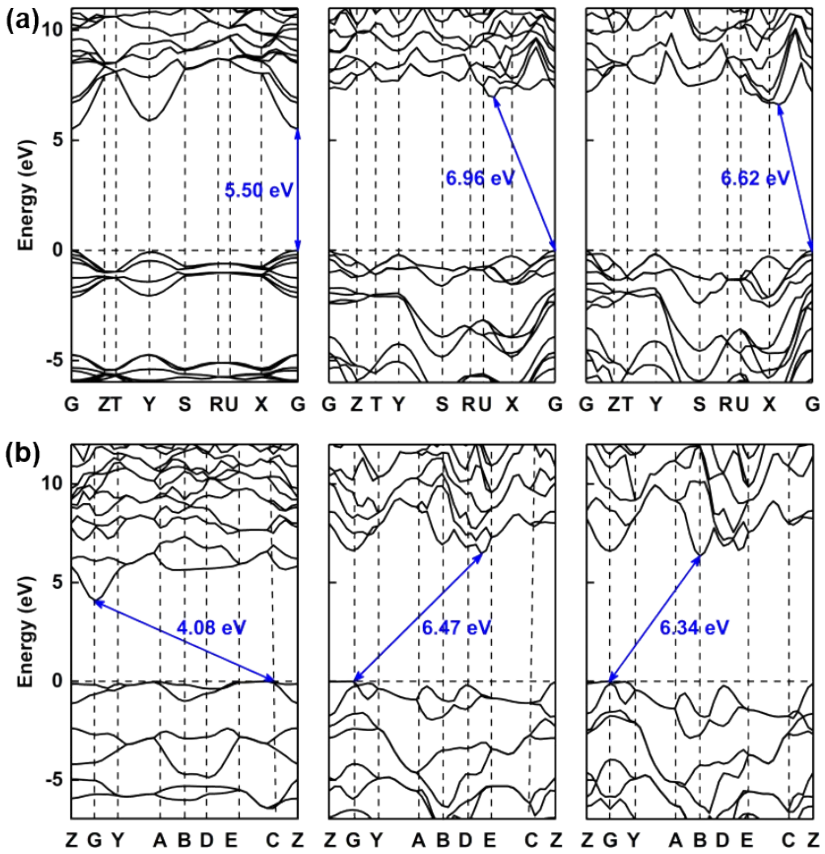

Fig. S6. The band structure of (a) *P*ca2$_1$ and (b) *P*2$_1$/m ionic phases under 0 GPa, critical pressure (P$_c$: 40 and 40 GPa) and 100 GPa.