Electronic Supplementary Information (ESI)

Theoretical predictions for low-temperature phases, softening of phonons and elastic stiffnesses, and electronic properties of sodium peroxide under high pressure

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Table S1. Structural data of Na_2O_2 for the *Amm2*, the *P*-62*m*, the $P2_1/c$, the *Pbam*, the *Pbam*‡, the *C*2/*m*, the *Pmmm*, the *Immm*, and the *I*4/*mmm* structures at different pressures.

Pressure (GPa)	Structure/ Space group	Lattice parameter				Atom	Site	Atomic coordinates (fractional)		
		a (Å)	b (Å)	c (Å)	β (degree)			x	y	z
0	*Amm2*	4.5103	10.8856	6.2819	90.000	O1	4c	-0.32927	0.00000	0.00000
						O2	8f	-0.17247	-0.16666	-0.50001
						Na1	4e	-0.50000	0.31748	-0.31745
						Na3	2b	-0.50000	0.00000	-0.36509
						Na2	4d	0.00000	0.15033	-0.15030
						Na4	2a	0.00000	0.00000	-0.69939
0	*P*-62*m*	6.2821	6.2821	4.5114	90.000	O1	2e	0.00000	0.00000	-0.17069
						O2	4h	0.33333	0.66667	0.32758
						Na1	3f	0.36521	0.00000	0.00000
						Na2	3g	0.69951	0.00000	0.50000
0 (RT)	*P*-62*m*†	6.22	6.22	4.47	90.000	O1	2e	0.00000	0.00000	0.16700
						O2	4h	0.33333	0.66667	0.33300
						Na1	3f	0.36600	0.00000	0.00000
						Na2	3g	0.72400	0.00000	0.50000
0 (RT)	*P*-62*m*⁋	6.208	6.208	4.469	90.000	O1	2e	0.00000	0.00000	0.33200
						O2	4h	0.33333	0.66667	0.16800
						Na1	3f	0.29500	0.00000	0.00000
						Na2	3g	0.63200	0.00000	0.50000
22	*Amm2*	4.1525	10.0080	5.7770	90.000	O1	4c	-0.32112	0.00000	-0.00004
						O2	8f	-0.18321	-0.16664	-0.50003
						Na1	4e	-0.50000	0.31479	-0.31479
						Na3	2b	-0.50000	0.00000	-0.37038
						Na2	4d	0.00000	0.14821	-0.14814
						Na4	2a	0.00000	0.00000	-0.70358
22	$P2_1/c$	4.6421	6.8657	3.6366	141.5836	O	4e	-0.49999	0.09003	-0.37268
						Na	4e	-0.00005	0.14092	0.66039
28	$P2_1/c$	4.5710	6.7955	3.5762	141.4831	O	4e	-0.49999	0.09082	-0.37198
						Na	4e	-0.00003	0.14129	0.65621
28	*Pbam*	3.5758	6.7976	2.8461	90.000	O	4g	0.12768	0.09089	0.00000
						Na	4h	0.15598	0.35872	0.50000
28	*Pbam*‡	3.5743	6.8001	2.8459	90.000	O	4h	-0.37247	0.40908	-0.50000
						Na	4g	-0.84429	0.35871	0.00000
100	*Pbam*	3.2502	6.2622	2.6121	90.000	O	4g	0.13333	0.09480	0.00000
						Na	4h	0.14474	0.35744	0.50000
200	*Pbam*	3.0575	5.9049	2.4648	90.000	O	4g	0.13688	0.09644	0.00000
						Na	4h	0.14323	0.35714	0.50000
300	*Pbam*	2.9413	5.6869	2.3741	90.000	O	4g	0.13887	0.09716	0.00000
						Na	4h	0.14311	0.35701	0.50000
0	*C*2/*m*	7.8720	3.6262	6.1470	141.4238	O	4i	0.84296	-0.00000	1.34321
						Na	4i	0.49998	-0.00000	0.72763
0	*Pmmm*	6.1415	3.6241	4.9218	90.000	O1	2s	0.50000	0.00000	0.15645
						O2	2r	0.00000	0.50000	0.65645
						Na1	2j	0.22799	0.00000	0.50000
						Na2	2k	0.72796	0.50000	0.00000
0	*Immm*	6.1414	3.6242	4.9213	90.000	O	4j	0.50000	0.00000	-0.84353
						Na	4f	0.22797	0.00000	-0.50000
0	*I*4/*mmm*	4.4082	4.4082	5.3359	90.000	O	4e	-0.50000	-0.50000	0.35278
						Na	4c	0.00000	0.50000	1.00000

† The *P*-62*m* structure of Na_2O_2 at ambient conditions proposed by Tallman *et al.*[2]

⁋ The *P*-62*m* structure of Na_2O_2 at ambient conditions proposed by Föppl.[3]

‡ The relaxed *Pbam* structure of Na_2O_2 predicted by Deng *et al.*[1]

RT: Room temperature

Table S2. Calculated bulk and shear moduli of the *Amm*2 and the *P*-62*m* structures at ambient pressure.

Structure/Space group	Condition	Bulk modulus (GPa)		Shear modulus (GPa)	
		GGA-PBE	LDA	GGA-PBE	LDA
*Amm*2	0 GPa, 0 K	49.16	64.53	31.33	38.98
P-62*m*		48.95	64.72	29.88	37.59
P-62*m* [4]		56.40	-	-	-
P-62*m* [5]		49	-	29	-
P-62*m* †	ambient	55.82	40.19	31.14	27.92
P-62*m* §		57.16	41.37	32.11	29.08

†using the structural data proposed by Tallman *et al.*[2]
§using the structural data proposed by Föppl *et al.*[3]

Table S3. Vibrational modes, activity in the IR and Raman spectra for the *P*-62m structure at 0 GPa, the *Amm*2 structure at 0 GPa, the $P2_1/c$ structure at 22 GPa, and the *Pbam* structure at 30 GPa.

Structure/ Space group	Vibrational mode	Frequency (cm^{-1})	Activity	Structure/ Space group	Vibrational mode	Frequency (cm^{-1})	Activity
P-62*m* at 0 GPa	A''_2	129.3, 195.0, 292.3	IR	*Amm*2 at 0 GPa	B_1	223.4, 232.7, 260.4, 263.6, 271.8, 305.1, 314.5, 340.8, 779.1	IR / Raman
	E'	169.6, 203.4, 224.9, 286.4, 316.3, 338.0	IR / Raman				
	A''_1	125.5	-				
	A'_1	169.6, 278.8, 780.8, 821.0	Raman		B_2	124.4, 183.2, 216.3, 219.7, 283.8, 294.0, 331.3, 337.2	IR / Raman
	A'_2	180.8, 275.5, 773.5	-		A_1	225.0, 227.9, 254.8, 261.4, 295.3, 310.9, 317.7, 331.4, 784.9, 821.5	IR / Raman
	E"	221.8, 226.5, 242.5, 293.2, 318.4	Raman		A_2	108.2, 196.7, 210.9, 262.2, 307.5, 358.0	Raman
$P2_1/c$ at 22 GPa	A_u	194.9, 237.2, 295.1, 341.9, 418.5	IR	*Pbam* at 30 GPa	B_{1u}	405.9	IR
					B_{2u}	262.5, 318.7, 449.9	IR
					B_{3u}	305.9, 332.1, 432.6	IR
					A_u	199.3, 359.7	-
	B_u	262.3, 305.3, 380.5, 415.3	IR		B_{2g}	236.2, 361.1	Raman
					B_{3g}	255.8, 336.8	Raman
	A_g	237.2, 268.2, 345.8, 372.8, 433.3, 780.8	Raman		A_g	274.1, 378.0, 461.3, 815.3	Raman
	B_g	244.4, 337.4, 348.7, 412.6, 440.0, 766.6	Raman		B_{1g}	357.6, 431.6, 461.9, 797.2	Raman

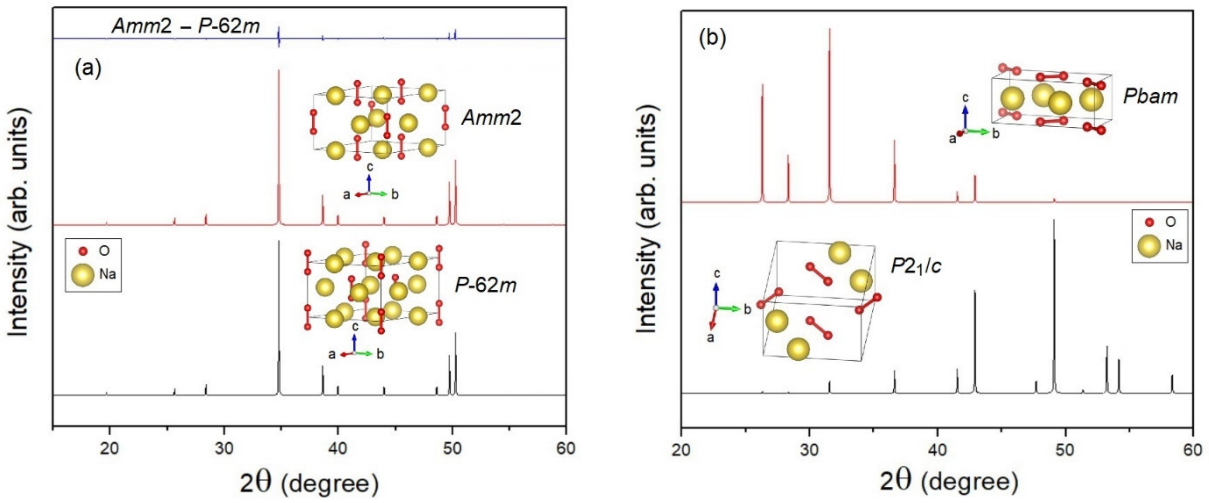

Figure S1. Simulated XRD pattern of various structures: (a) the *Amm*2 and *P*-62*m* structures at ambient pressure and the intensity difference between both structures, (b) the $P2_1/c$ and *Pbam* structures at 22 GPa.

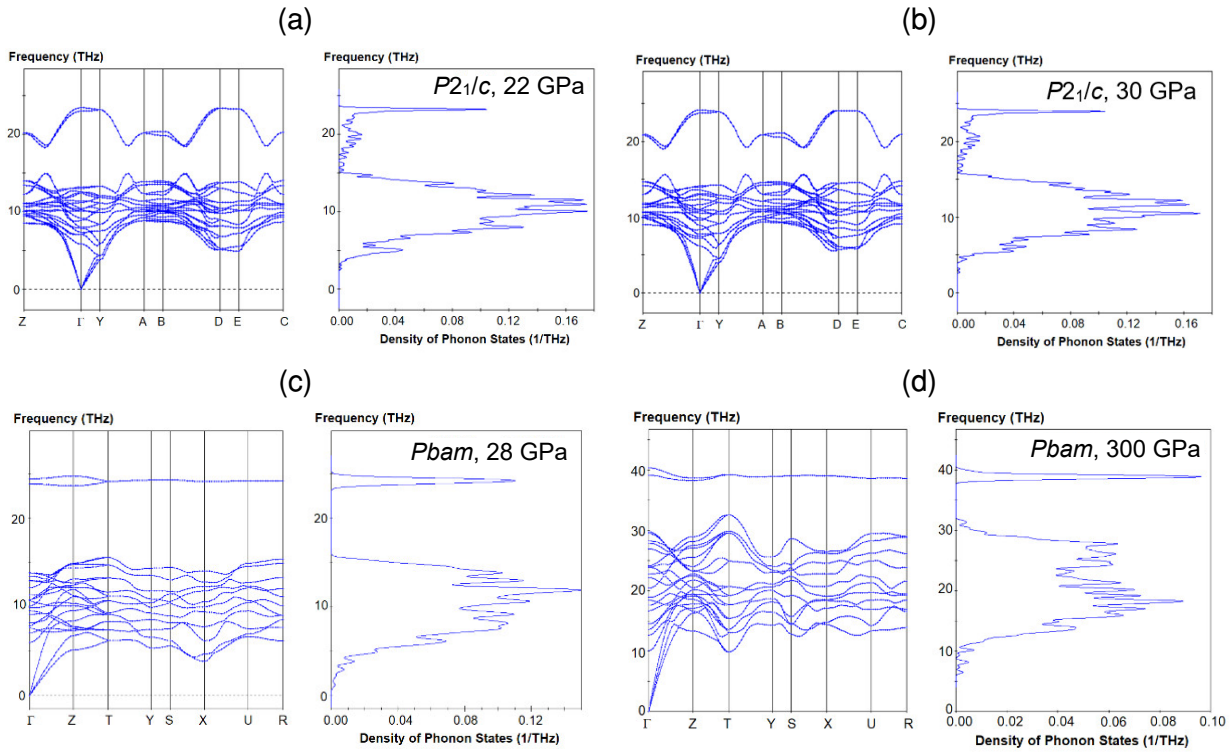

Figure S2. Phonon dispersion curves and the phonon density of states for the various structures with different pressures: (a) the $P2_1/c$ structure at 22 GPa, (b) the $P2_1/c$ structure at 30 GPa, (c) the *Pbam* structure at 28 GPa, and (d) the *Pbam* structure at 300 GPa.

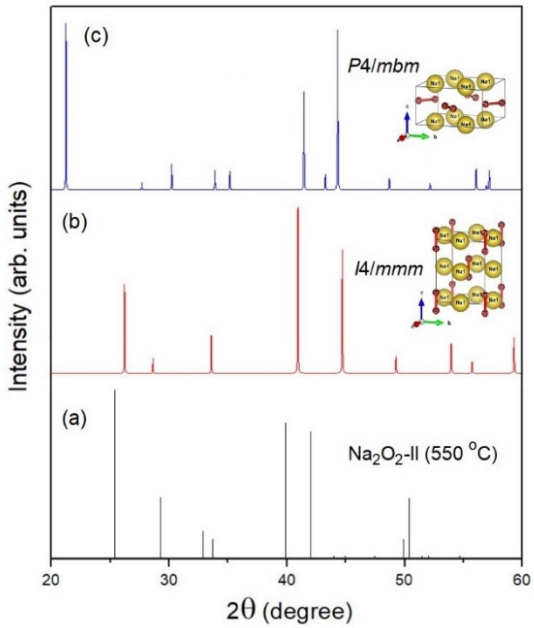

Figure S3. Simulated XRD pattern of the crystal structures: (a) Na_2O_2-II at 550°C and ambient pressure obtained from the Tallman's experiment [6] and (b) - (c) are the *I*4/*mmm* and *P*4/*mbm* structures at 0 K and ambient pressure obtained from the AIRSS searches.

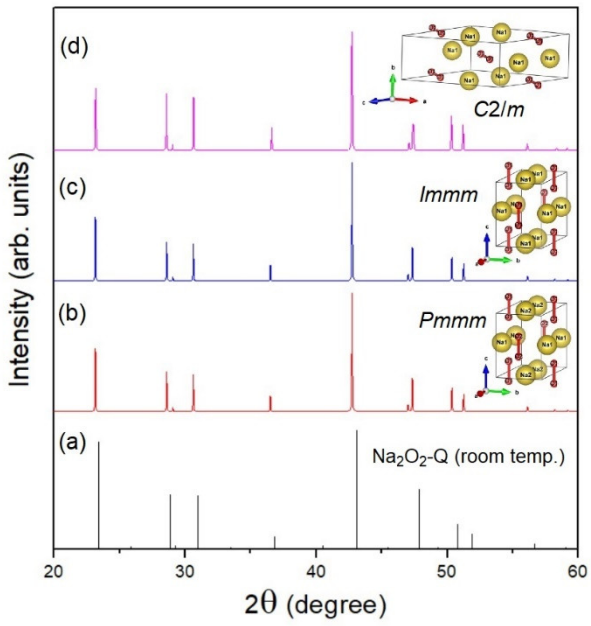

Figure S4. Simulated XRD pattern of the crystal structures: (a) Na_2O_2-Q at room temperature and ambient pressure obtained from the Tallman's experiment [6] and (b) - (d) are the *Pmmm*, *Immm*, and *C*2/*m* structures at 0 K and ambient pressure obtained from the AIRSS searches, respectively.

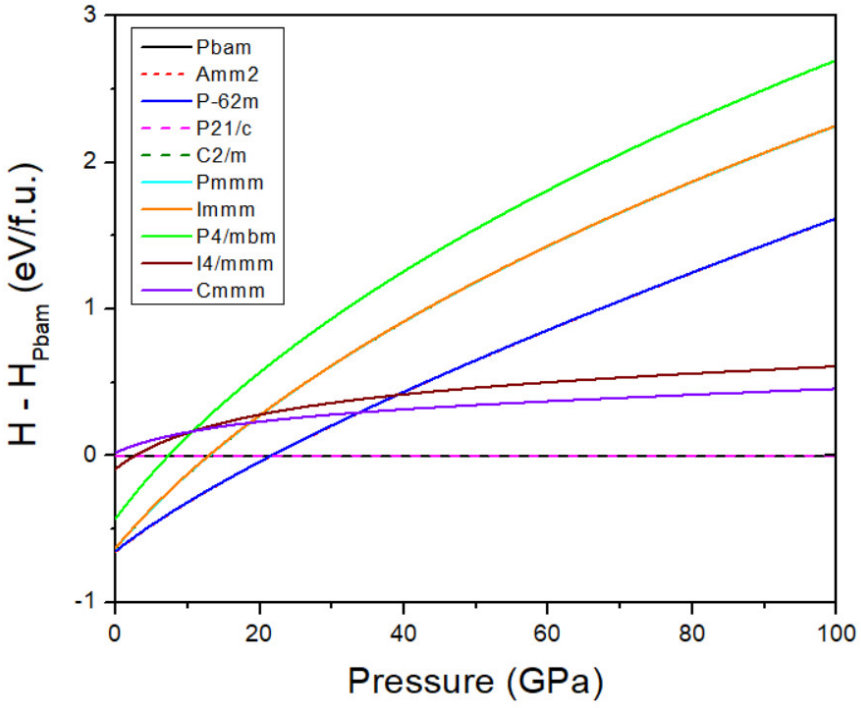

Figure S5. Relative enthalpy of the various structures that obtained from the AIRSS searches with respect to the *Pbam* structure in the pressure range of 0-100 GPa.

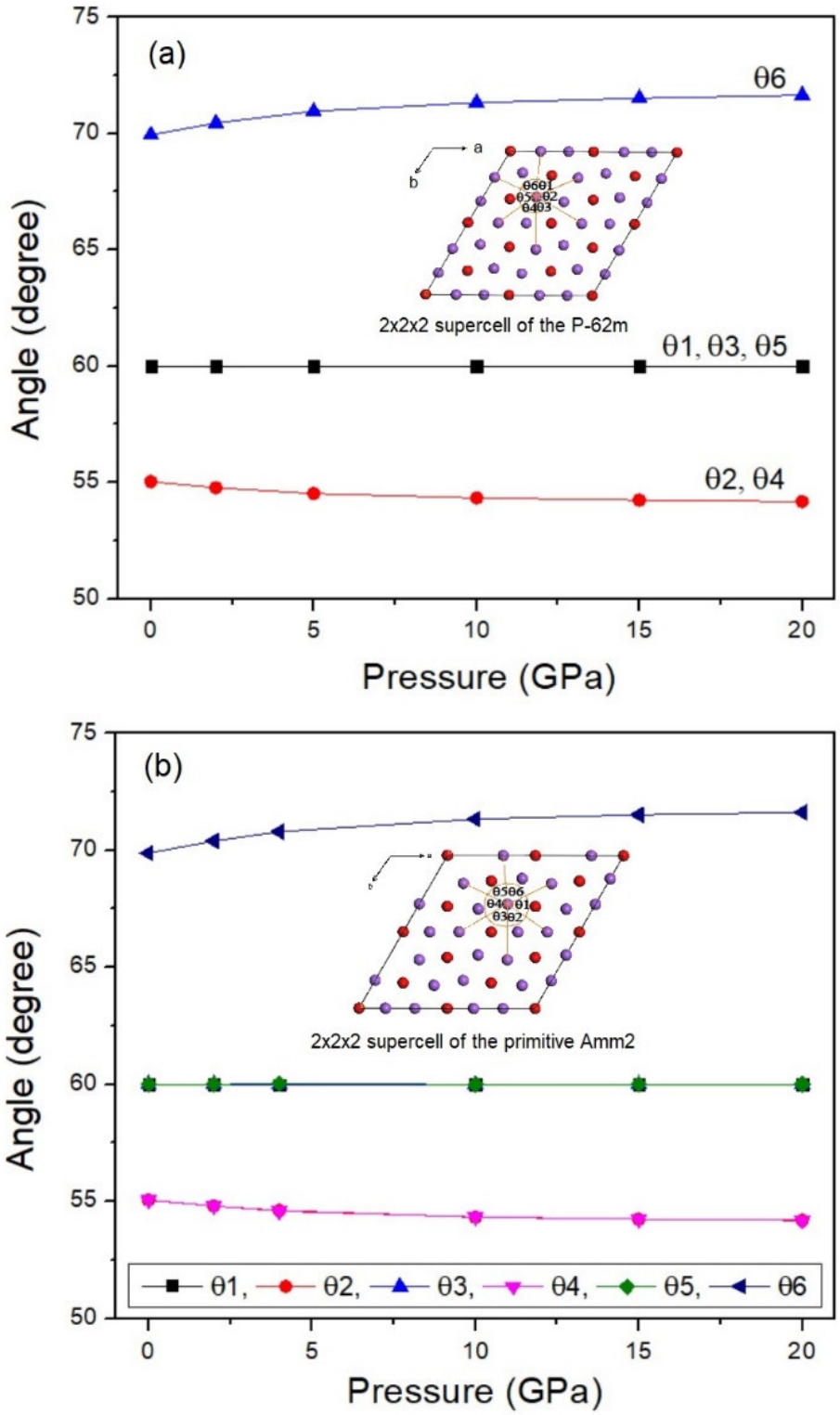

Figure S6. Plot of the angles in the same hexagonal Na layer of (a) 2×2×2 supercell of the *P*-62*m* structure and (b) 2×2×2 supercell of the primitive *Amm*2 structure *versus* pressure from 0 to 20 GPa.

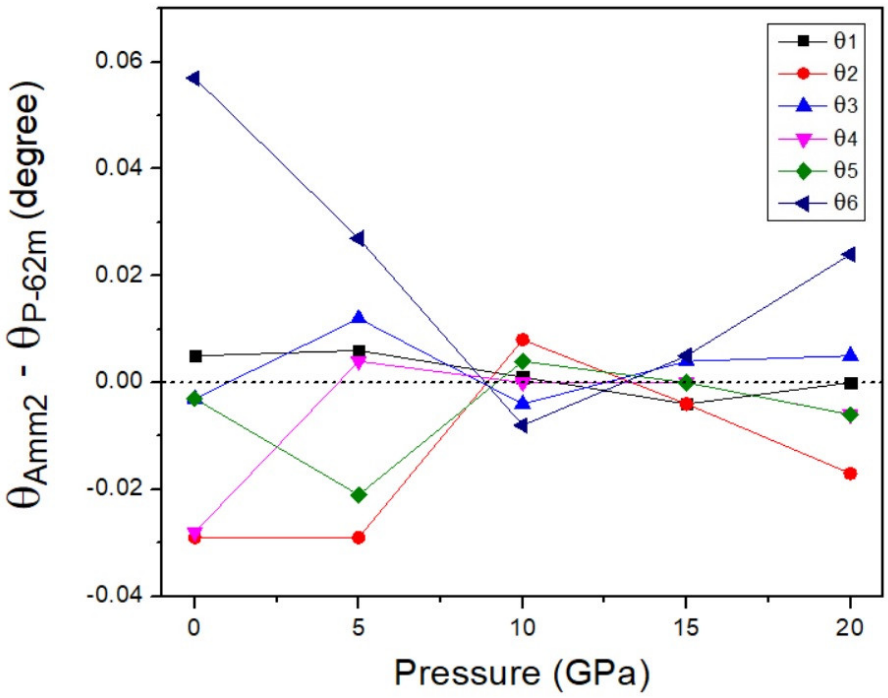

Figure S7. Plot of the differences in the angles between the Amm2 and the P-62m structures at different pressures.

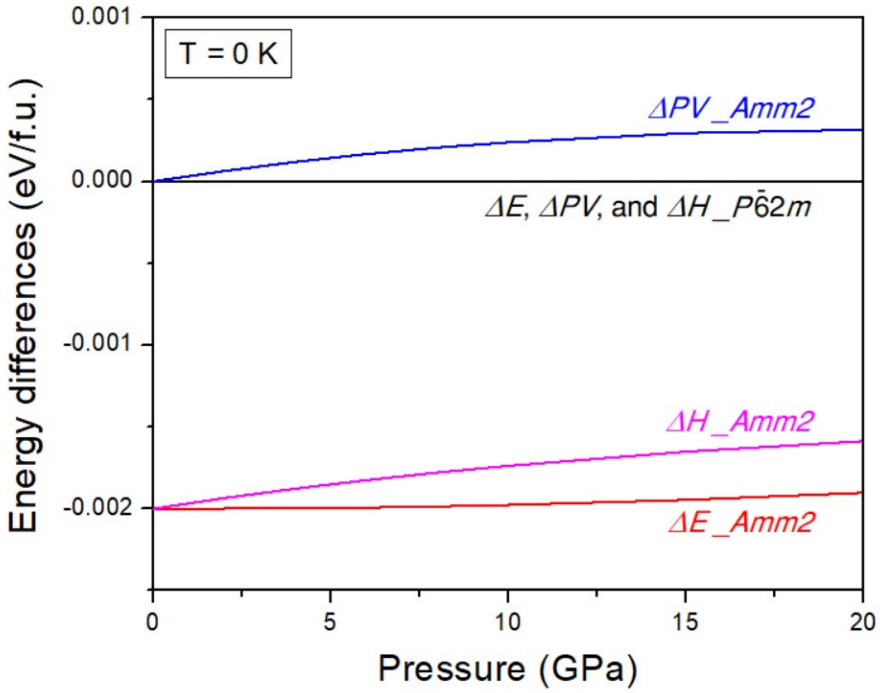

Figure S8. Plot of total energy (*E*), enthalpy (*H*), and work done (*PV*) of the *Amm*2 structure with respect to the *P*-62*m* structure *versus* pressure.

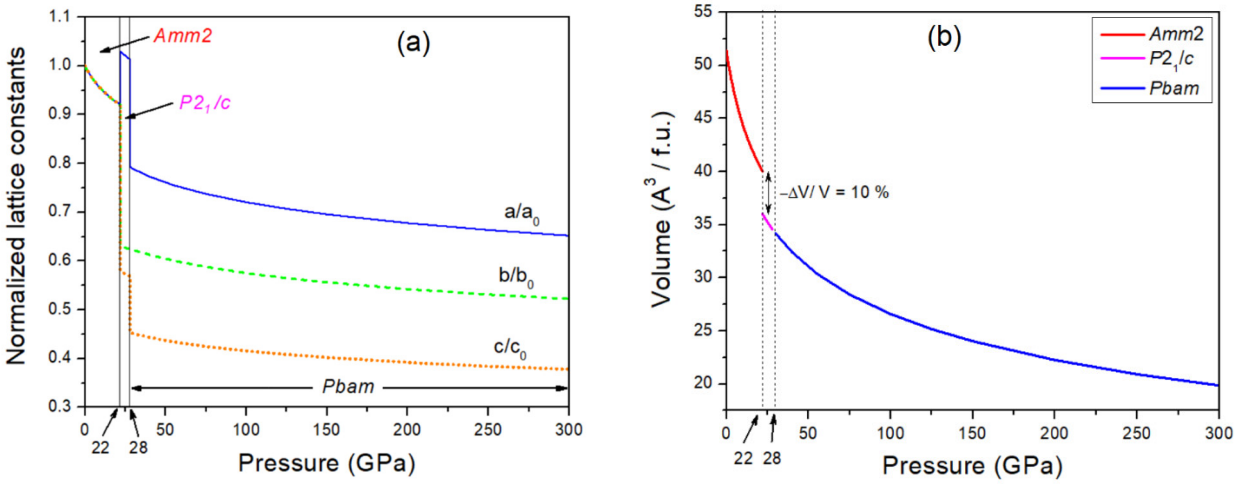

Figure S9. (a) Plot of the normalized lattice constants *versus* pressure ranging from 0 to 300 GPa. The a_0, b_0, and c_0 are the lattice constants at 0 GPa of the *Amm*2 structure. (b) The volume change of the three structure of Na_2O_2 at the pressure range of 0-300 GPa: the *Amm*2, the *P*2$_1$/*c*, and the *Pbam* structures.

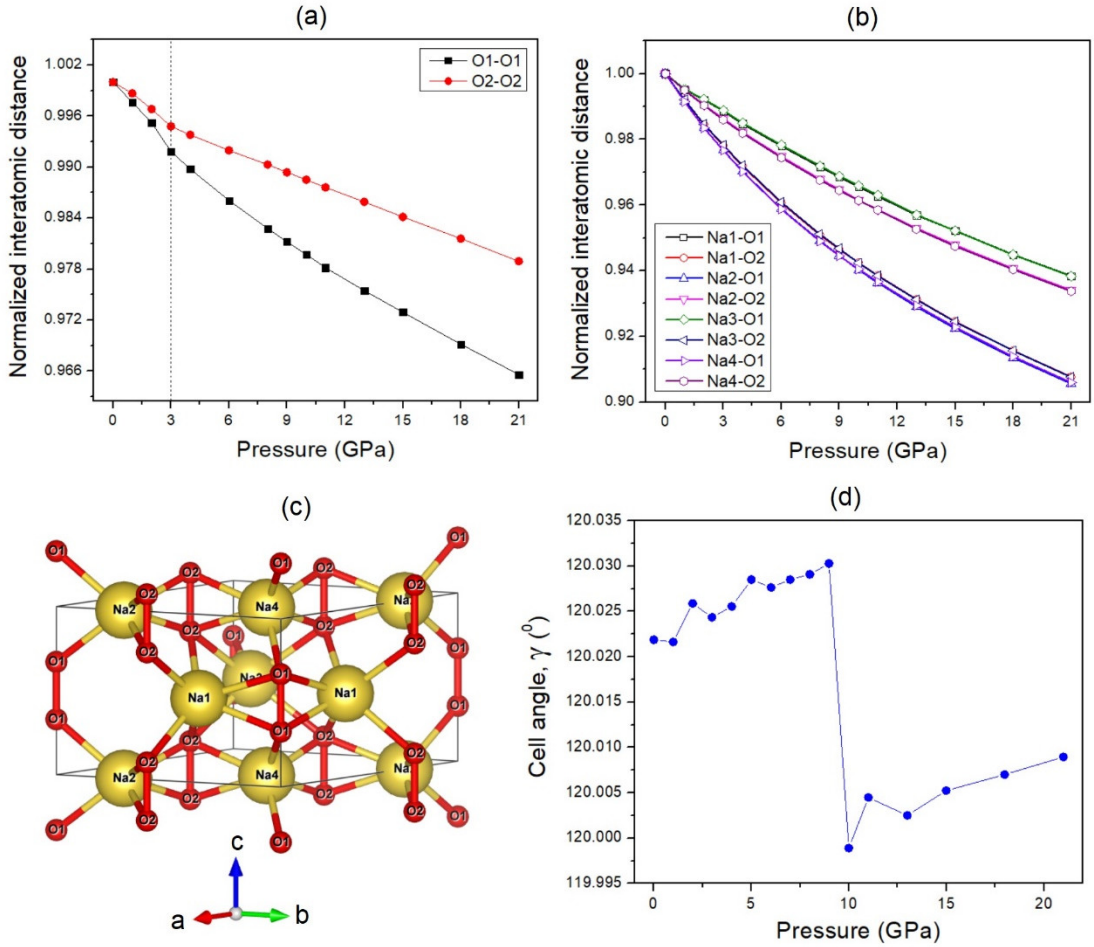

Figure S10. (a) and (b) are the plots of normalized interatomic distances *versus* pressure for the O-O and Na-O in the *Amm*2 structure as (c), respectively. (d) Plot of the cell angle (γ) of the primitive *Amm*2 structure *versus* pressure from 0 to 21 GPa.

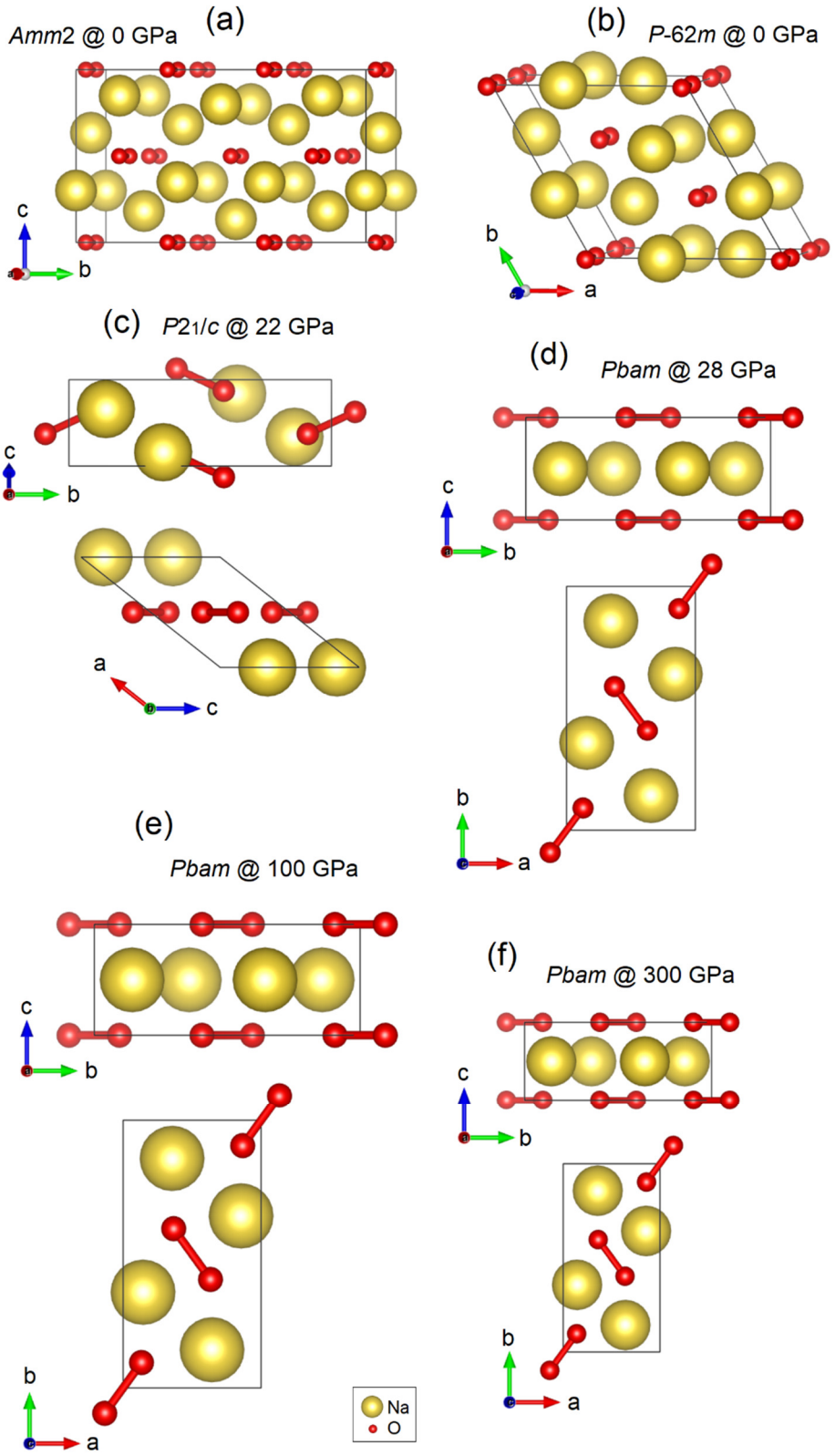

Figure S11. The peroxide group alignment in each phase of Na_2O_2: (a) the *Amm*2 structure at 0 GPa, (b) the *P*-62*m* structure at 0 GPa, (c) the *P*2$_1$/*c* structure at 22 GPa, (d) the *Pbam* structure at 28 GPa, (e) the *Pbam* structure at 100 GPa, and (f) the *Pbam* structure at 300 GPa.

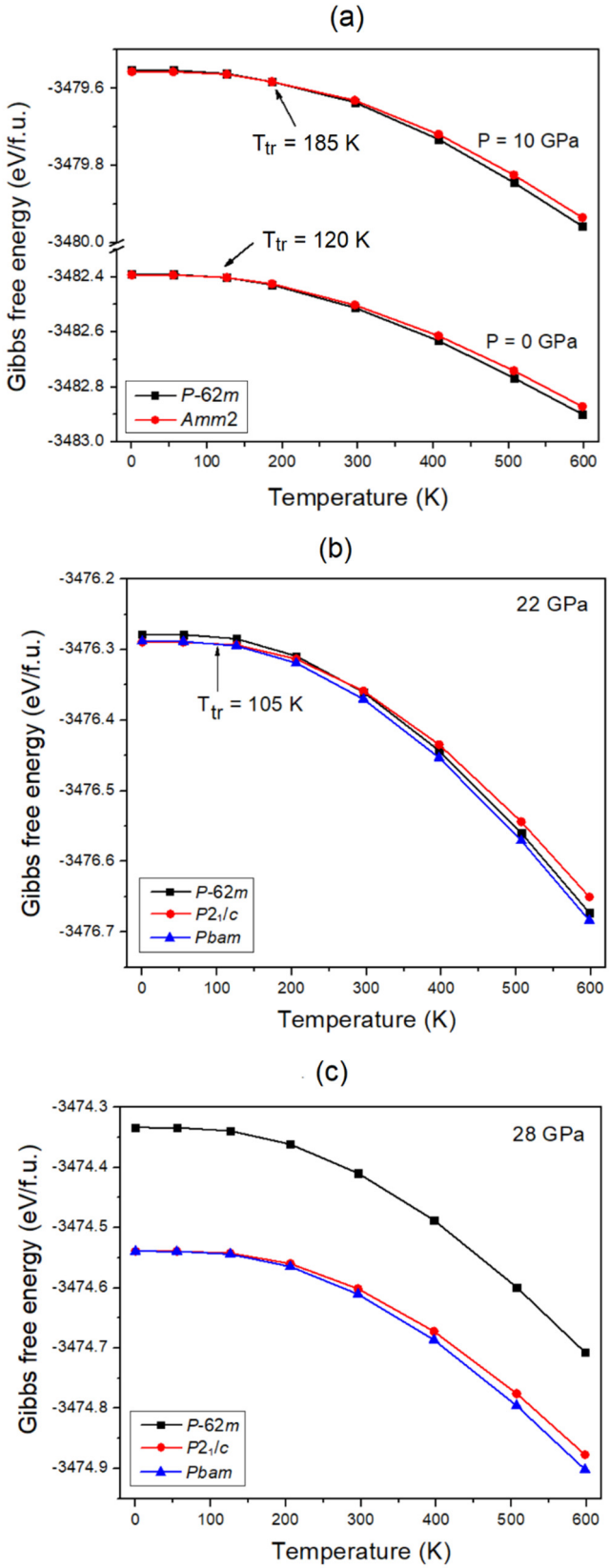

Figure S12. Plot of Gibbs free energy *versus* temperature for the structures at different pressures: (a) 0 and 10 GPa, (b) 22 GPa, and (c) 28 GPa.

WP		Atom	Atomic Displacements			
			u_x	u_y	u_z	|u|
3f	(x,0,0)	Na2	0.0020	0.0000	0.0000	0.0124
2e	(0,0,z)	O1	0.0000	0.0000	0.0010	0.0045
3g	(x,0,1/2)	Na1	-0.0190	0.0000	0.0000	0.1182
4h	(1/3,2/3,z)	O2	0.0000	0.0000	-0.0010	0.0045

NOTE: u_x, u_y and u_z are given in relative units. |u| is the absolute distance given in Å

Available from: http://www.cryst.ehu.es/cgi-bin/cryst/programs/nph-compstru

Figure S13. Comparison of the atomic displacement between the Tallman's and Föppl's structures using the COMPSTRU program.[7]

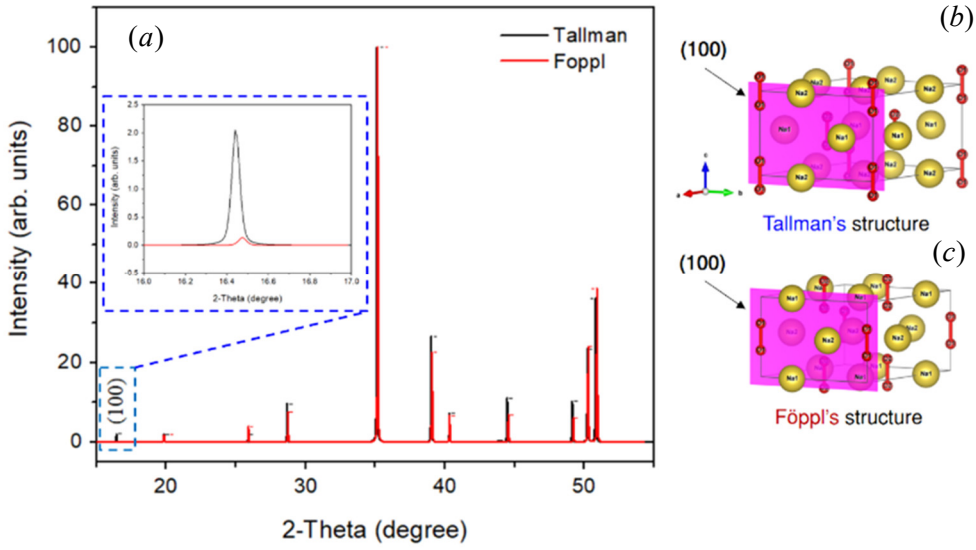

Figure R14. (a) Simulated XRD pattern of the Tallman's and Föppl's structures, (b) – (c) the (100) plane of the Tallman's and Foppl's structures.

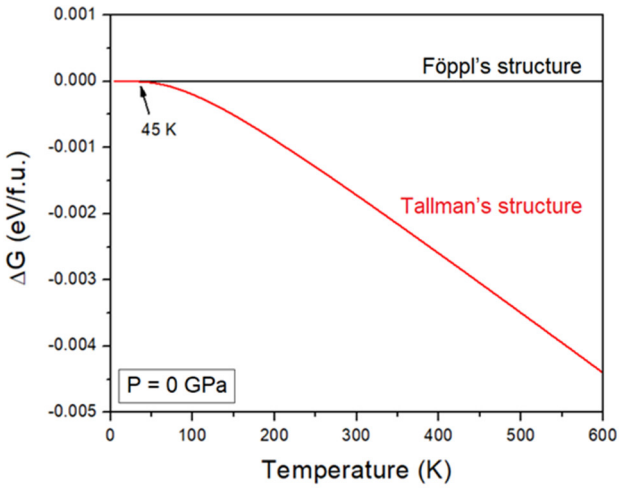

Figure S15. Relative Gibbs free energy (ΔG) of the *P*-62*m* structure between the Tallman's and the Föppl's structures as a function of temperature at ambient pressure.

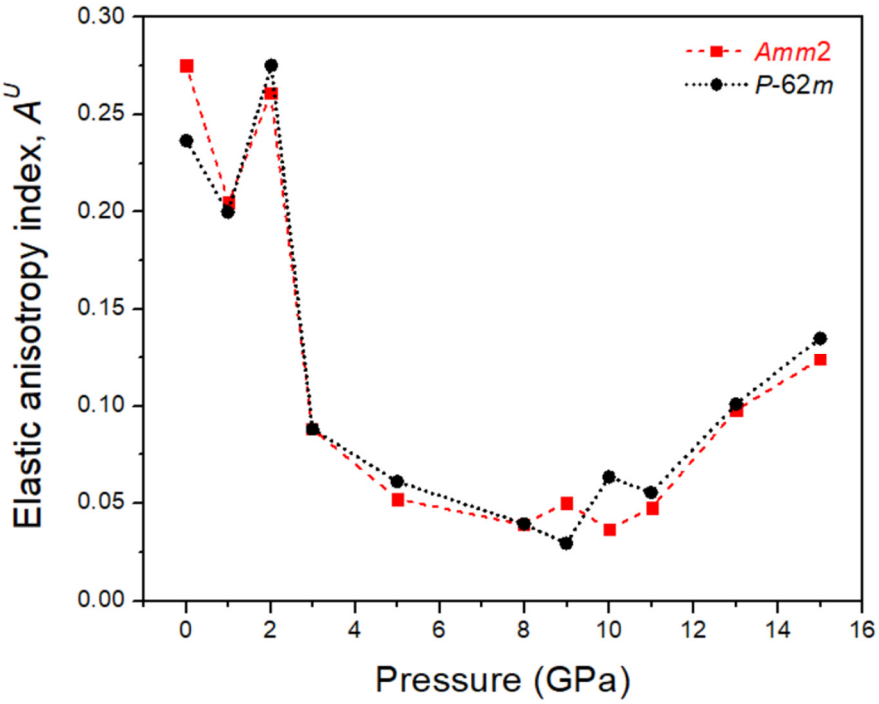

Figure S16. Plot of the universal elastic anisotropy index (A^U) for the *P*-62*m* and the *Amm*2 structures *versus* pressure from 0 to 15 GPa.

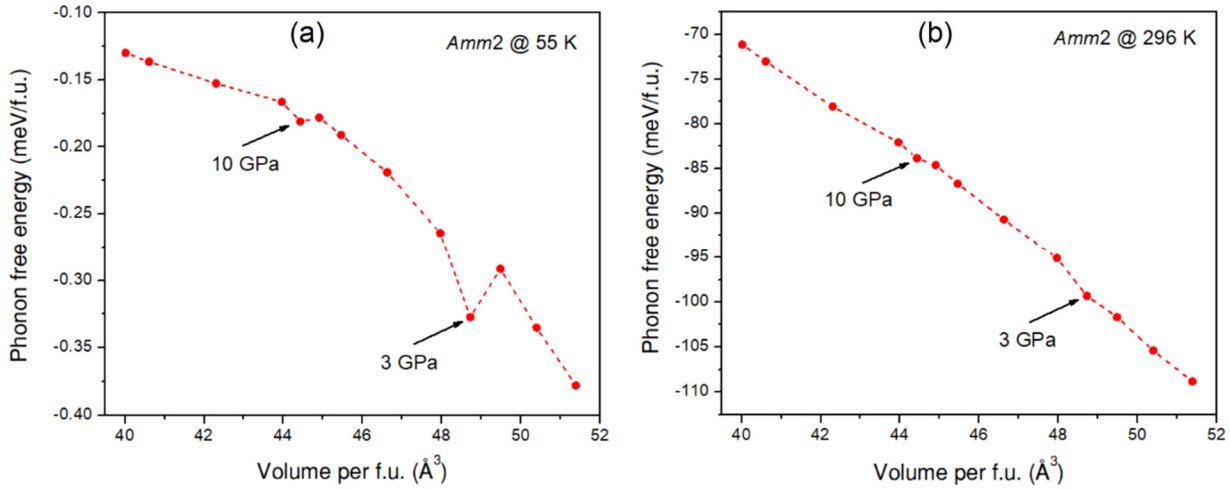

Figure S17. Plot of the phonon free energy for the *Amm*2 structure *versus* volume at the different temperatures: (a) 55 K and (b) 296 K.

References

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