Electronic Supplementary Information (ESI):

Theoretical aspects in structural distortion and the electronic properties of lithium peroxide under high pressure

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Table S1. Structural parameters of Li_2O_2 for the $P6_3/mmc$, $P2_1$, $P2_1/c$, and $P2_1/c$† structures at the different pressures.

Pressure (GPa)	Structure	Lattice parameter ($P6_3/mmc$: a = b ≠ c, α = β = 90⁰, γ = 120⁰) ($P2_1$, $P2_1/c$: a ≠ b ≠ c, α = γ = 90⁰, β ≠ 90⁰)				Atom	Site	Atomic coordinates		
		a (Å)	b (Å)	c (Å)	β (degree)			x	y	z
0	$P6_3/mmc$	3.1858	3.1858	7.7182	90.0000	Li(1)	2a	0.00000	0.00000	0.00000
						Li(2)	2c	0.33333	0.66667	0.25000
						O(1)	4f	0.33333	0.66667	0.64950
10	$P6_3/mmc$	3.0767	3.0767	7.4208	90.0000	Li(1)	2a	0.00000	0.00000	0.00000
						Li(2)	2c	0.33333	0.66667	0.25000
						O(1)	4f	0.33333	0.66667	0.64645
11	$P6_3/mmc$	3.0694	3.0694	7.3780	90.0000	Li(1)	2a	0.00000	0.00000	0.00000
						Li(2)	2c	0.33333	0.66667	0.25000
						O(1)	4f	0.33333	0.66667	0.64568
39	$P6_3/mmc$	2.9020	2.9020	6.9536	90.0000	Li(1)	2a	0.00000	0.00000	0.00000
						Li(2)	2c	0.33333	0.66667	0.25000
						O(1)	4f	0.33333	0.66667	0.64135
40	$P6_3/mmc$	2.8987	2.8987	6.9332	90.0000	Li(1)	2a	0.00000	0.00000	0.00000
						Li(2)	2c	0.33333	0.66667	0.25000
						O(1)	4f	0.33333	0.66667	0.64091
75	$P6_3/mmc$	2.7781	2.7781	6.6468	90.0000	Li(1)	2a	0.00000	0.00000	0.00000
						Li(2)	2c	0.33333	0.66667	0.25000
						O(1)	4f	0.33333	0.66667	0.63816
75	$P2_1$	2.5695	2.5942	6.4767	91.8505	Li(1)	2a	0.84403	0.72368	0.11400
						Li(2)	2a	0.65603	0.51017	0.38600
						O(1)	2a	0.34300	0.21666	0.15252
						O(2)	2a	0.15705	0.01719	0.34747
75	$P2_1/c$	2.5695	2.5941	7.0454	113.2454	Li	4e	0.45790	0.89333	-0.13599
						O	4e	-0.00463	0.40036	-0.09748
75	$P2_1/c$†	6.4771	2.5941	6.8903	158.1169	Li	4e	0.72995	0.60668	0.09399
						O	4e	0.19042	1.09963	-0.40707
136	$P2_1$	2.4424	2.4876	6.1569	89.7118	Li(1)	2a	0.85698	0.72372	0.11396
						Li(2)	2a	0.64303	0.51011	0.38604
						O(1)	2a	0.35399	0.22011	0.14973
						O(2)	2a	0.14603	0.01376	0.35026
136	$P2_1/c$	2.4423	2.4877	6.6119	111.3833	Li	4e	0.47094	0.89325	-0.13607
						O	4e	0.00379	0.39687	-0.10025
136	$P2_1/c$†	6.1570	2.4877	6.6353	158.4040	Li	4e	0.74306	0.60677	0.10702
						O	4e	0.20427	1.10314	-0.39600
150	$P2_1$	2.4197	2.4701	6.1009	89.2687	Li(1)	2a	0.85965	0.72409	0.11390
						Li(2)	2a	0.64037	0.50973	0.38611
						O(1)	2a	0.35608	0.22093	0.14924
						O(2)	2a	0.14394	0.01296	0.35076
150	$P2_1/c$	2.4194	2.4703	6.5333	110.9788	Li	4e	0.47361	0.89276	-0.13616
						O	4e	0.00547	0.39595	-0.10074
150	$P2_1/c$ (similar)‖	6.1008	2.4703	6.5333	158.2667	Li	4e	0.52639	0.60724	0.89023
						O	4e	0.99453	0.10405	0.39379
150	$P2_1/c$†	6.1009	2.4703	6.5926	158.4716	Li	4e	0.74587	0.60726	0.10975
						O	4e	0.20690	1.10404	-0.39386
300	$P2_1/c$	2.2464	2.3473	5.9562	107.5213	Li	4e	0.49472	0.88747	-0.13824
						O	4e	0.01976	0.38790	-0.10386
500	$P2_1/c$	2.1174	2.2416	5.5723	105.4396	Li	4e	0.49349	0.61747	1.14122
						O	4e	0.96991	0.11908	1.10491

†Reference 10

‖Structural parameters obtained by using COMPSTRU programme proposed by Flor *et al*[38].

Table S2. Mulliken charges of the Li and O atoms for the $P6_3/mmc$, $P2_1$, and $P2_1/c$ structures of Li_2O_2 at the different pressures. The charge spilling parameters for the $P6_3/mmc$, $P2_1$, and $P2_1/c$ structures are in the ranges of 0.80-0.83 %, 0.85-0.88 %, and 0.89-1.06 %, respectively. The effective ionic valences is calculated by using the difference between the formal ionic charge and the Mulliken charge on the anion species in the crystal proposed by Segall *et al.* [34]

Pressure (GPa)	Structure	Mulliken charge (*e*)								Effective ionic * valences ($\|e\|$)
		Li(1)	Li(2)	Li(3)	Li(4)	O(1)	O(2)	O(3)	O(4)	
0	$P6_3/mmc$	0.99	0.99	0.77	0.77	-0.88	-0.88	-0.88	-0.88	0.12
0†	$P6_3/mmc$†	0.99	0.99	0.77	0.77	-0.88	-0.88	-0.88	-0.88	0.12
4	$P6_3/mmc$	1.00	1.00	0.77	0.77	-0.88	-0.88	-0.88	-0.88	0.12
6	$P6_3/mmc$	1.00	1.00	0.77	0.77	-0.88	-0.88	-0.88	-0.88	0.12
8	$P6_3/mmc$	1.01	1.01	0.77	0.77	-0.89	-0.89	-0.89	-0.89	0.11
10	$P6_3/mmc$	1.01	1.01	0.77	0.77	-0.89	-0.89	-0.89	-0.89	0.11
11	$P6_3/mmc$	1.01	1.01	0.77	0.77	-0.89	-0.89	-0.89	-0.89	0.11
12	$P6_3/mmc$	1.02	1.02	0.77	0.77	-0.89	-0.89	-0.89	-0.89	0.11
15	$P6_3/mmc$	1.02	1.02	0.77	0.77	-0.89	-0.89	-0.89	-0.89	0.11
20	$P6_3/mmc$	1.03	1.03	0.77	0.77	-0.90	-0.90	-0.90	-0.90	0.10
25	$P6_3/mmc$	1.04	1.04	0.76	0.76	-0.90	-0.90	-0.90	-0.90	0.10
30	$P6_3/mmc$	1.05	1.05	0.76	0.76	-0.91	-0.91	-0.91	-0.91	0.09
35	$P6_3/mmc$	1.06	1.06	0.76	0.76	-0.91	-0.91	-0.91	-0.91	0.09
39	$P6_3/mmc$	1.06	1.06	0.76	0.76	-0.91	-0.91	-0.91	-0.91	0.09
40	$P6_3/mmc$	1.06	1.06	0.76	0.76	-0.91	-0.91	-0.91	-0.91	0.09
41	$P6_3/mmc$	1.07	1.07	0.76	0.76	-0.91	-0.91	-0.91	-0.91	0.09
45	$P6_3/mmc$	1.07	1.07	0.76	0.76	-0.92	-0.92	-0.92	-0.92	0.08
50	$P6_3/mmc$	1.08	1.08	0.76	0.76	-0.92	-0.92	-0.92	-0.92	0.08
55	$P6_3/mmc$	1.08	1.08	0.76	0.76	-0.92	-0.92	-0.92	-0.92	0.08
60	$P6_3/mmc$	1.09	1.09	0.76	0.76	-0.92	-0.92	-0.92	-0.92	0.08
65	$P6_3/mmc$	1.10	1.10	0.76	0.76	-0.93	-0.93	-0.93	-0.93	0.07
70	$P6_3/mmc$	1.10	1.10	0.75	0.75	-0.93	-0.93	-0.93	-0.93	0.07
75	$P6_3/mmc$	1.11	1.11	0.75	0.75	-0.93	-0.93	-0.93	-0.93	0.07
75	$P2_1$	0.90	0.90	0.90	0.90	-0.90	-0.90	-0.90	-0.90	0.10
135	$P2_1$	0.92	0.92	0.92	0.92	-0.92	-0.92	-0.92	-0.92	0.08
136	$P2_1/c$	0.92	0.92	0.92	0.92	-0.92	-0.92	-0.92	-0.92	0.08
150	$P2_1/c$	0.92	0.92	0.92	0.92	-0.92	-0.92	-0.92	-0.92	0.08
300	$P2_1/c$	0.94	0.94	0.94	0.94	-0.94	-0.94	-0.94	-0.94	0.06
500	$P2_1/c$	0.95	0.95	0.95	0.95	-0.95	-0.95	-0.95	-0.95	0.05

†Reference 10

*Reference 34

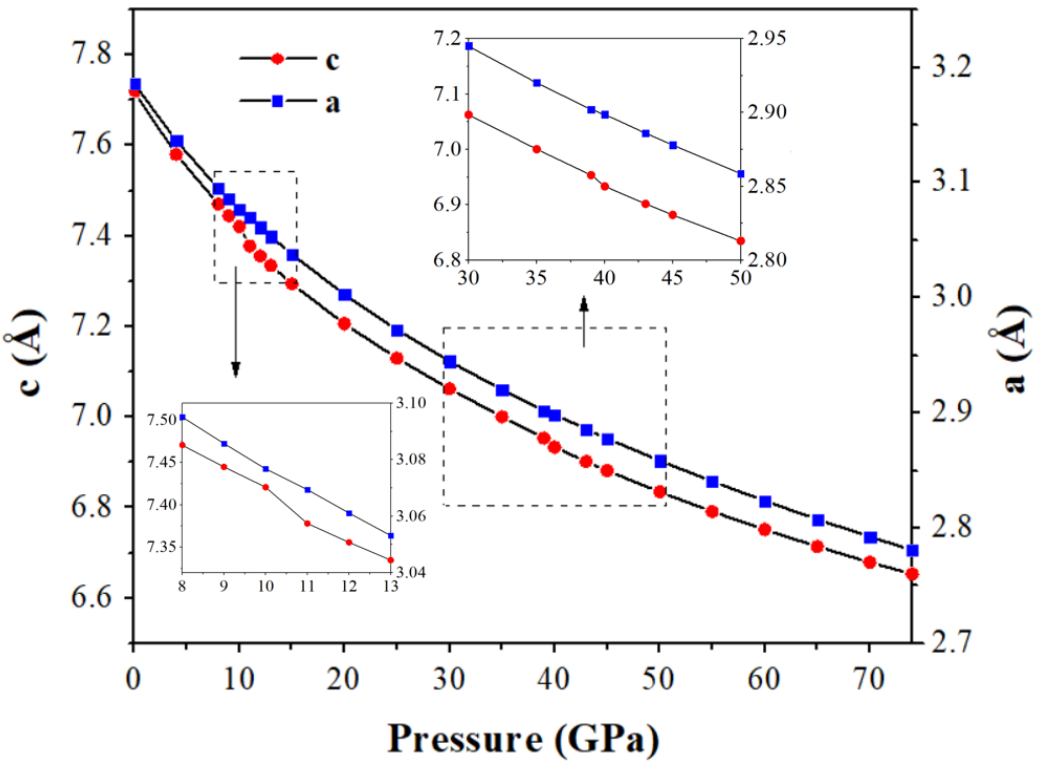


Figure S1. Plot of the lattice constants (*a* and *c*) *versus* pressure (0-74 GPa). Insets represent the enlargement in the rectangular dashed lines.

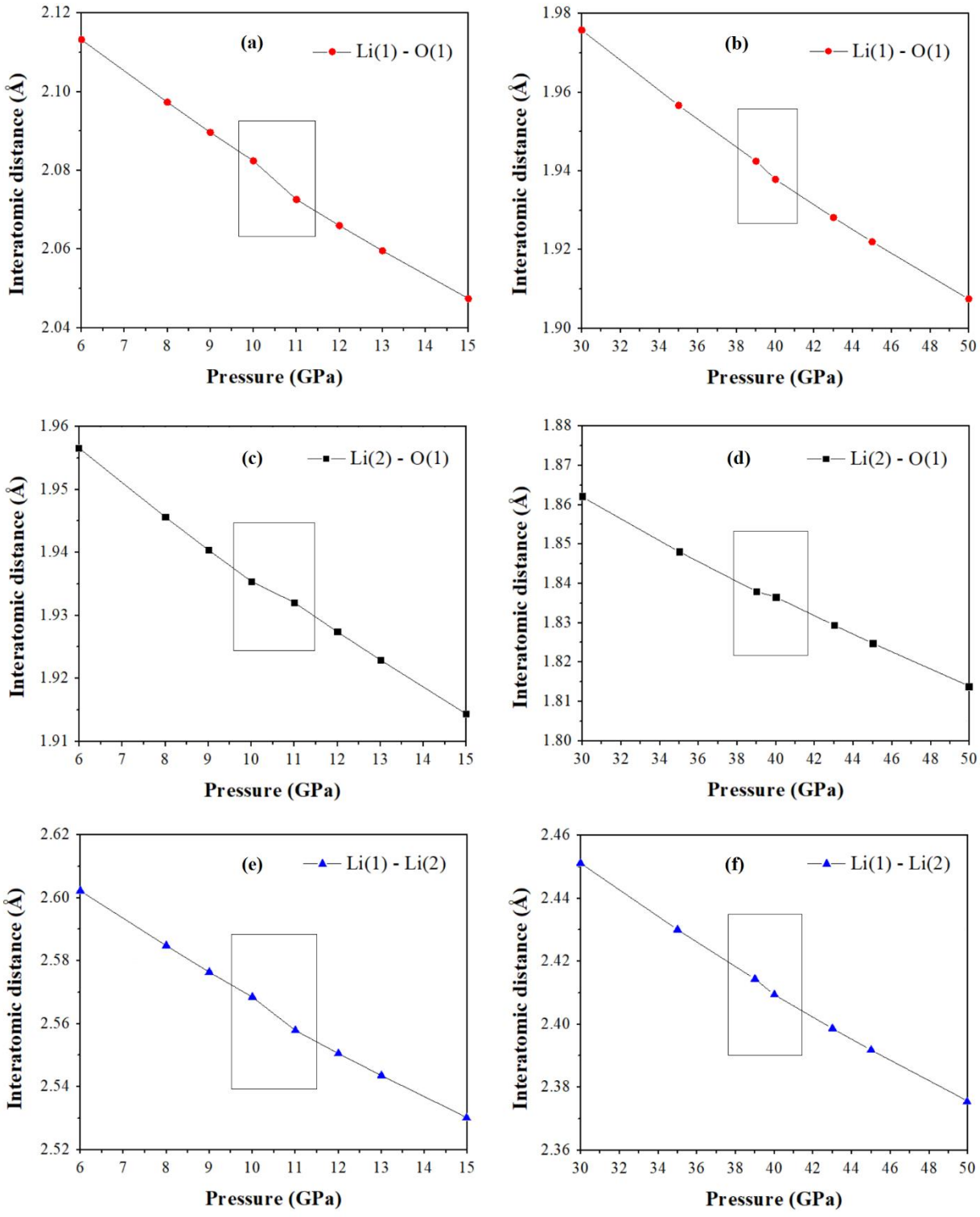


Figure S2. (a)-(b), (c)-(d), and (e)-(f) represent the interatomic distances of the Li(1)-O(1), Li(2)-O(1), and Li(1)-Li(2) in the pressure ranges of 6-15 GPa and 30-50 GPa, respectively. The rectangular solid lines mark the abnormal change of the interatomic distances in the pressure ranges of 10-11 GPa and 39-40 GPa.

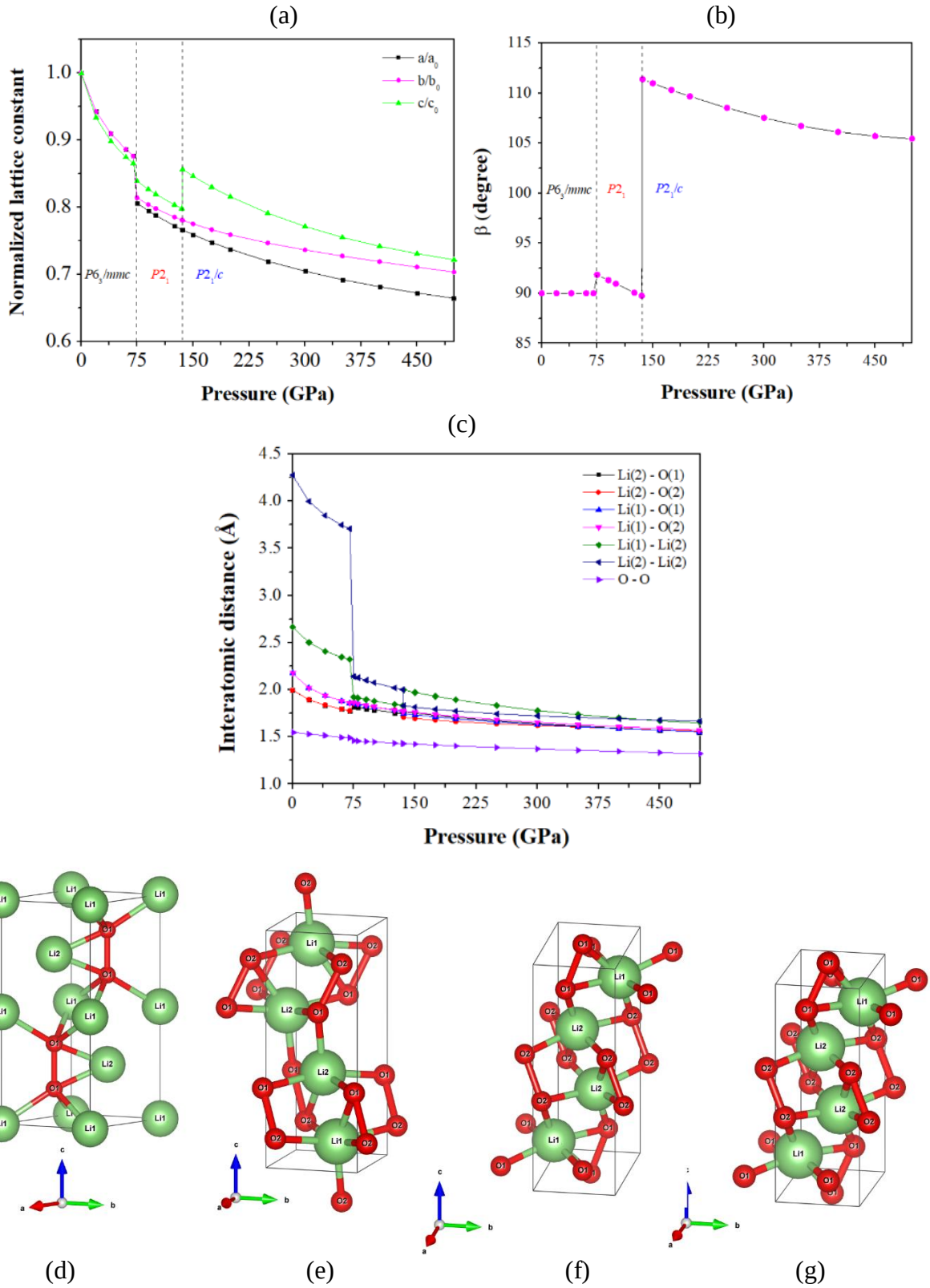


Figure S3. (a) Plot of the normalized lattice constants *versus* pressure, (b) Plot of the β *versus* pressure, (c) Plot of the interatomic distance *versus* pressure, (d) the $P6_3/mmc$ structure at 0 GPa, (e) the $P2_1$ structure at 75 GPa, (f) the $P2_1/c$ structure at 150 GPa, and (g) the $P2_1/c$ structure at 500 GPa.

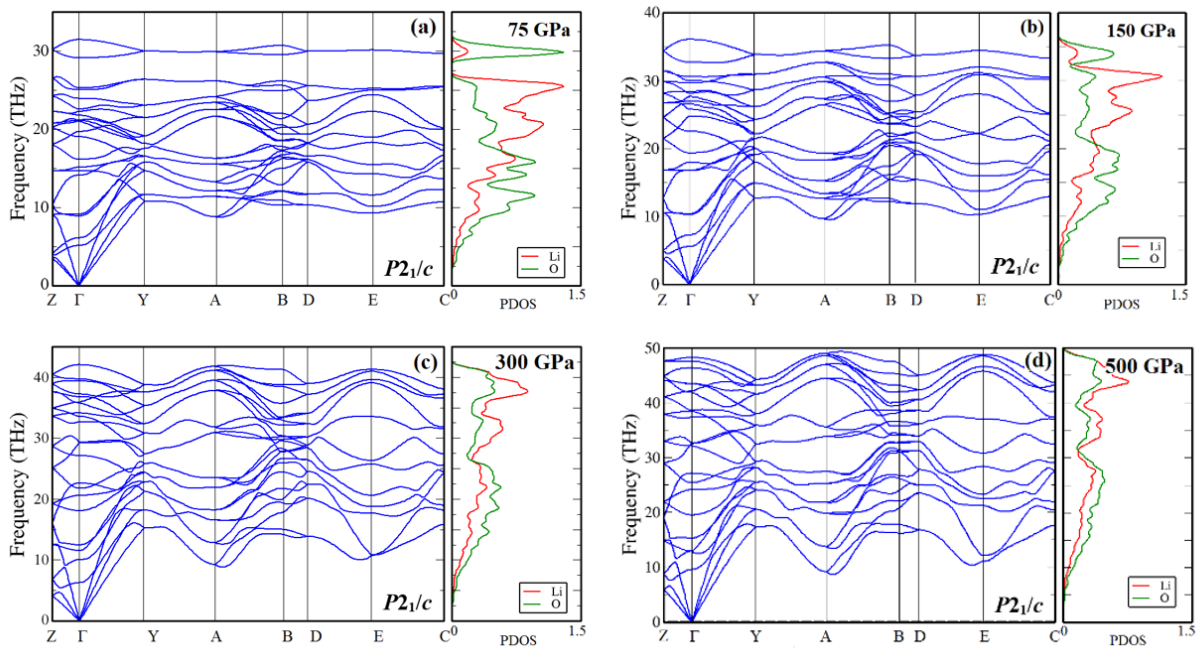


Figure S4. Phonon dispersion curves and partial phonon density of states (PDOSs) for the $P2_1/c$ structure at pressures of: (a)-(d) 75, 150, 300, and 500 GPa, respectively.

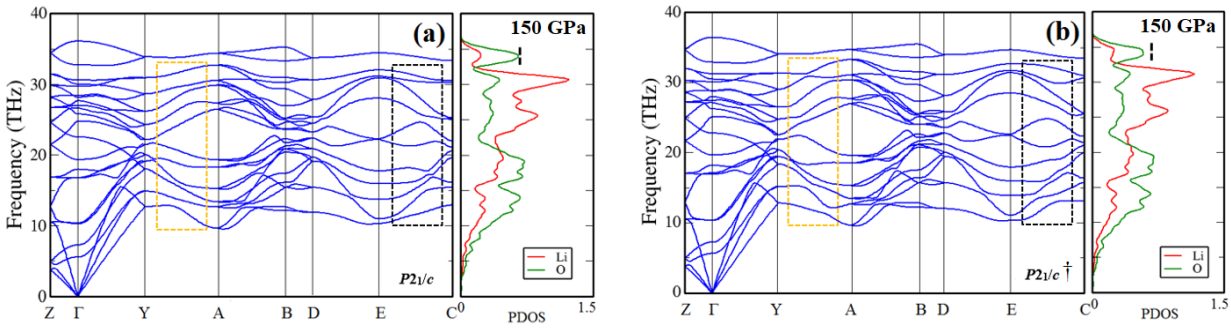
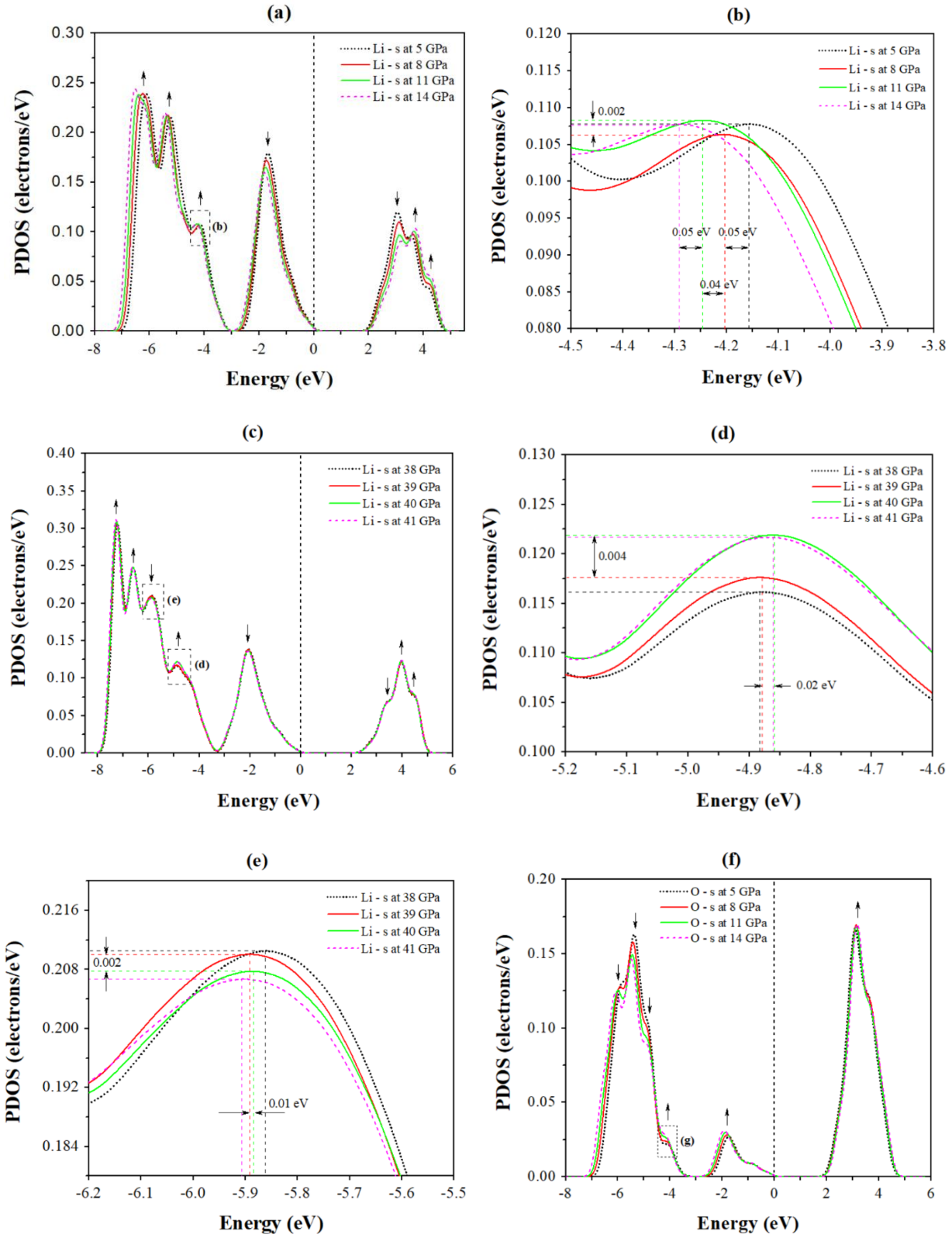
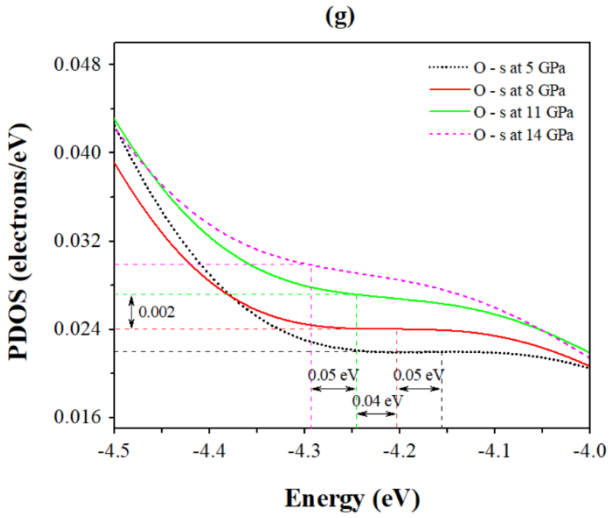
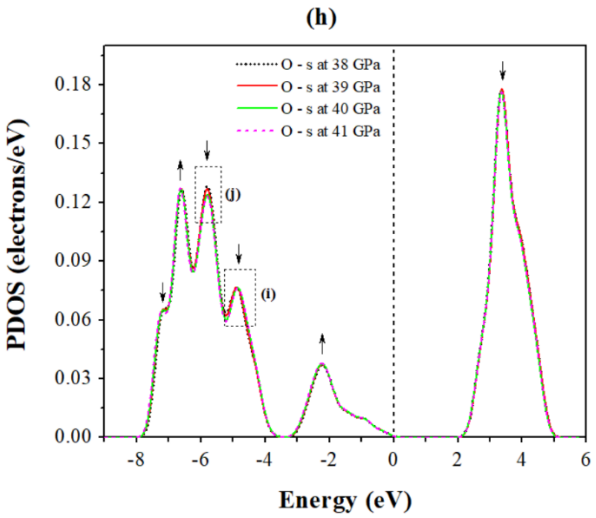


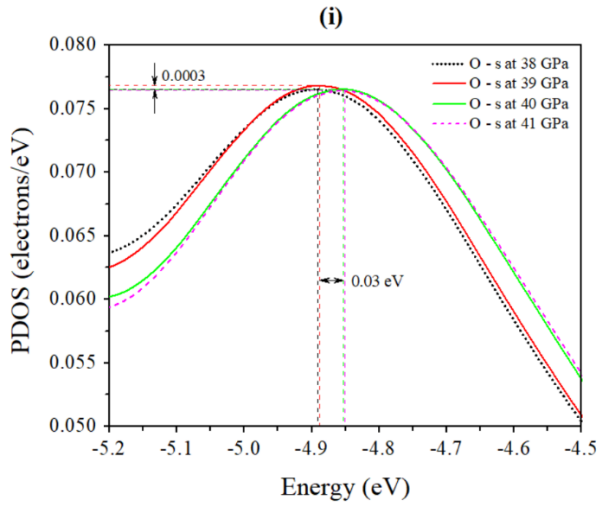
Figure S5. Phonon dispersion curves and partial phonon density of states (PDOSs) for two structures of Li_2O_2 at 150 GPa: (a) the $P2_1/c$ structure, and (b) the $P2_1/c^{\dagger}$ structure. The yellow and black rectangular dashed lines represent the differences between the $P2_1/c$ and $P2_1/c^{\dagger}$ structure in the Y-A and E-C paths, respectively. The vertical dashed lines mark the peak of the highest frequency phonon modes in the $P2_1/c$ structures.

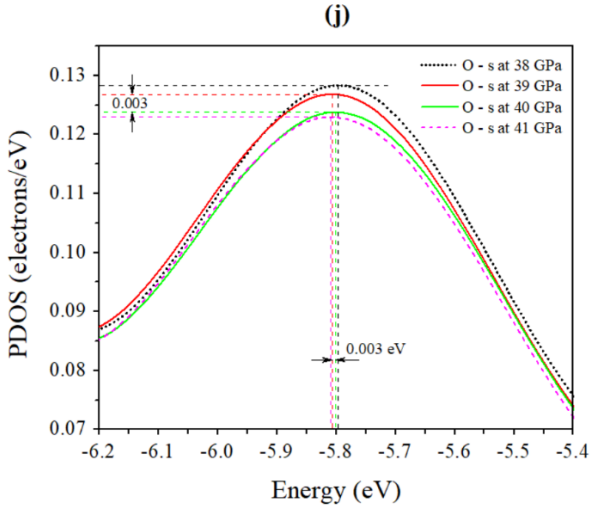
Figure S6. Partial density of states (PDOSs) of Li and O for the $P6_3/mmc$ structure at 5, 8, 11, 14, 38, 39, 40, and 41 GPa: (a)-(e) for the s-states of Li, (f)-(j) for the s-states of O, and (k)-(r) for the p-states of O. The arrows represent the trends of changes with increasing pressure. The vertical dashed lines represent the Fermi level.

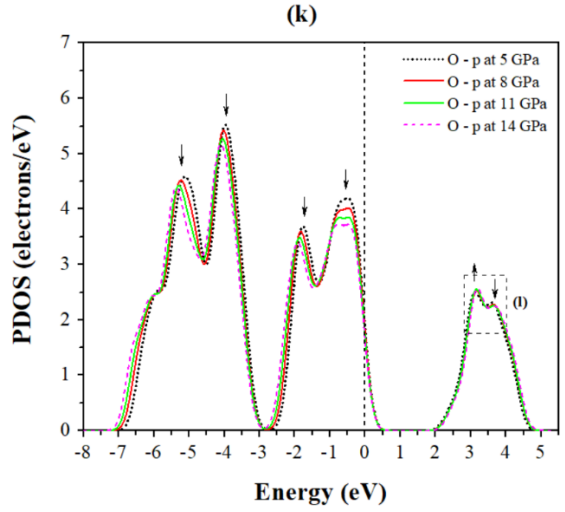


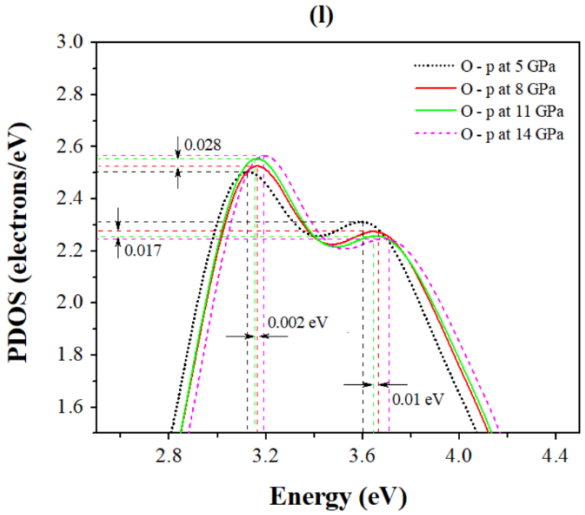

(g)
O - s at 5 GPa
O - s at 8 GPa
O - s at 11 GPa
O - s at 14 GPa
0.002
0.05 eV
0.05 eV
0.04 eV
PDOS (electrons/eV)
Energy (eV)

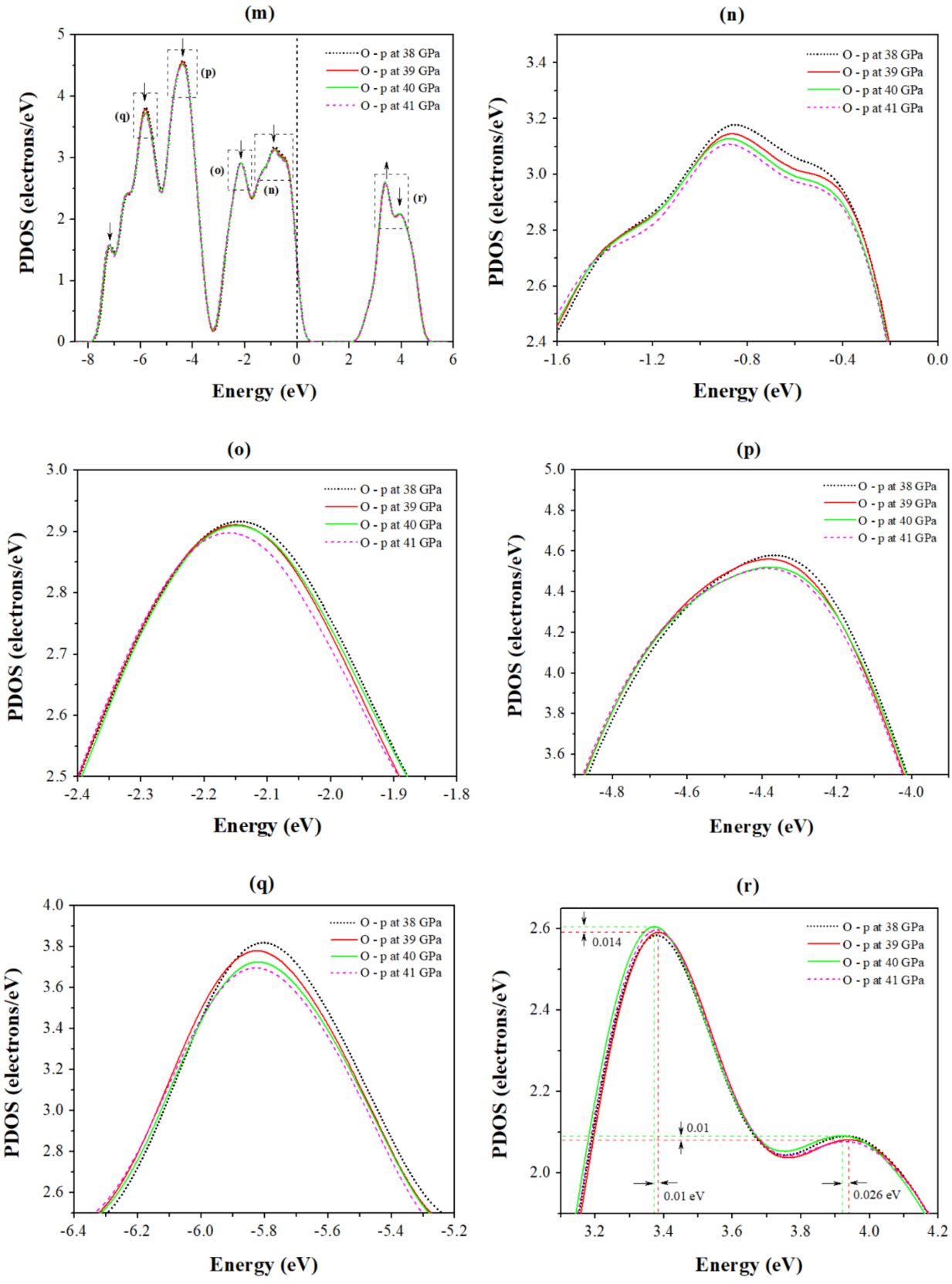

(h)
O - s at 38 GPa
O - s at 39 GPa
O - s at 40 GPa
O - s at 41 GPa
(j)
(i)
PDOS (electrons/eV)
Energy (eV)


(i)
O - s at 38 GPa
O - s at 39 GPa
O - s at 40 GPa
O - s at 41 GPa
0.0003
0.03 eV
PDOS (electrons/eV)
Energy (eV)


(j)
O - s at 38 GPa
O - s at 39 GPa
O - s at 40 GPa
O - s at 41 GPa
0.003
0.003 eV
PDOS (electrons/eV)
Energy (eV)


(k)
O - p at 5 GPa
O - p at 8 GPa
O - p at 11 GPa
O - p at 14 GPa
(l)
PDOS (electrons/eV)
Energy (eV)


(l)
O - p at 5 GPa
O - p at 8 GPa
O - p at 11 GPa
O - p at 14 GPa
0.028
0.017
0.002 eV
0.01 eV
PDOS (electrons/eV)
Energy (eV)


(m)
PDOS (electrons/eV)
Energy (eV)
O - p at 38 GPa
O - p at 39 GPa
O - p at 40 GPa
O - p at 41 GPa
(q)
(p)
(o)
(n)
(r)
(n)
(o)
(p)
(q)
(r)
0.014
0.01
0.01 eV
0.026 eV

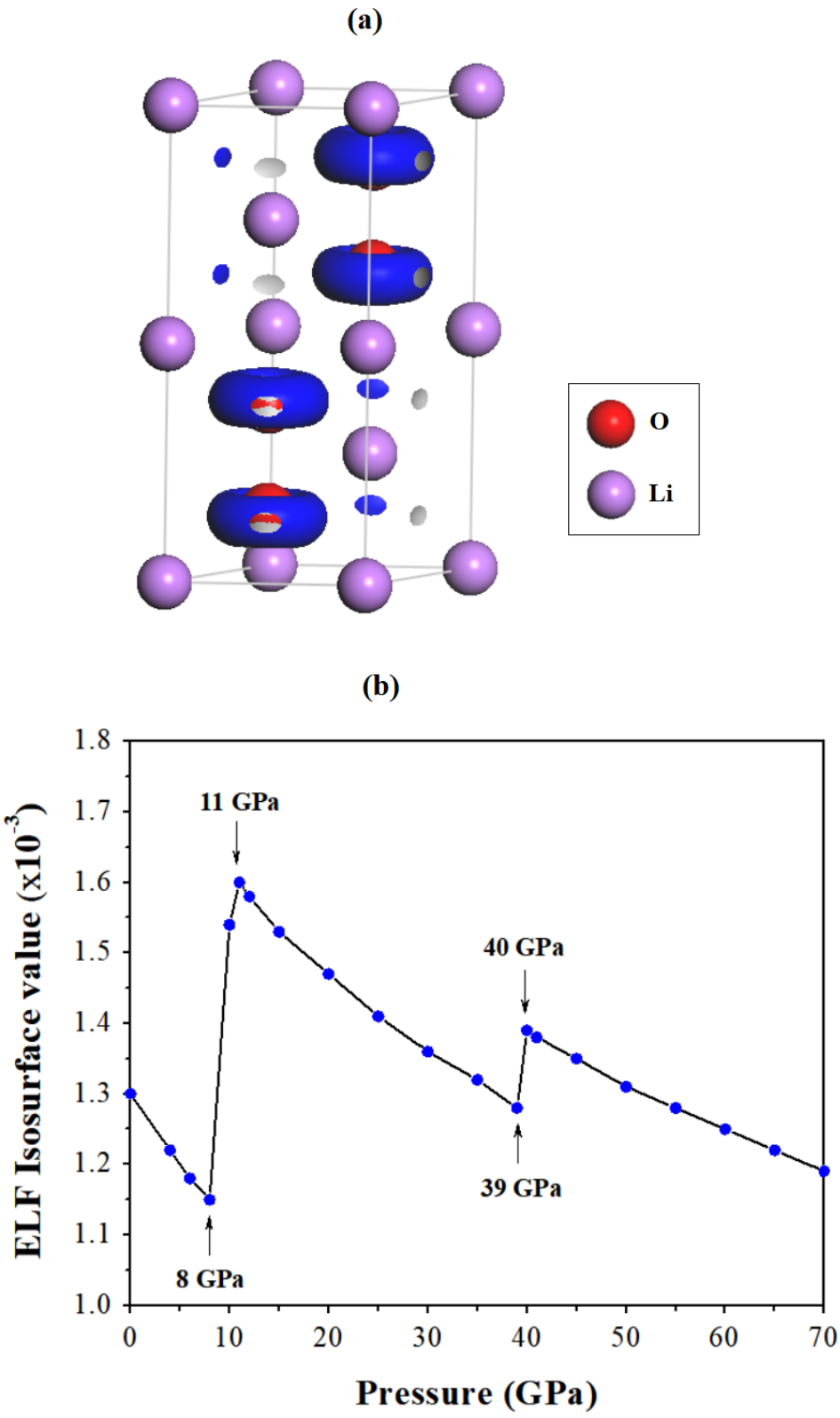


Figure S7. (a) Isosurface of the electron localization functions (ELF) in the $P6_3/mmc$ structure at 40 GPa. (b) Plot of the ELF isosurface value for the $P6_3/mmc$ structure in the pressure range of 0-70 GPa.

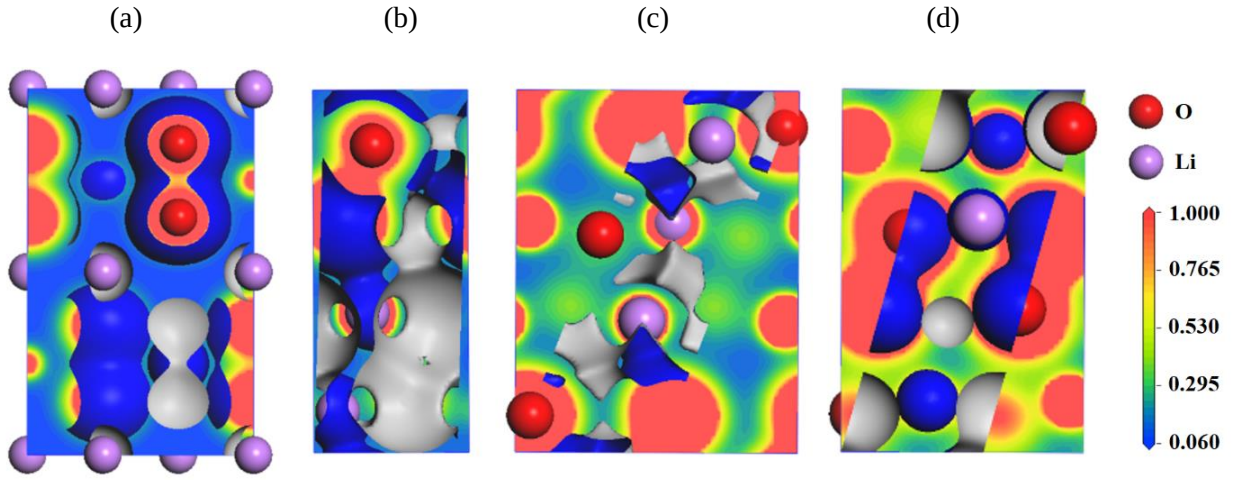


Figure S8. Electron density maps of various structures of Li_2O_2 projected onto (020) plane of: (a) the $P6_3/mmc$ structure at 0 GPa, (b) the $P2_1$ structure at 75 GPa, (c)-(d) the $P2_1/c$ structure at 150 and 500 GPa, respectively. The electron density isosurfaces values of 0.200 for (a, b, c) and 1.412 for (d).

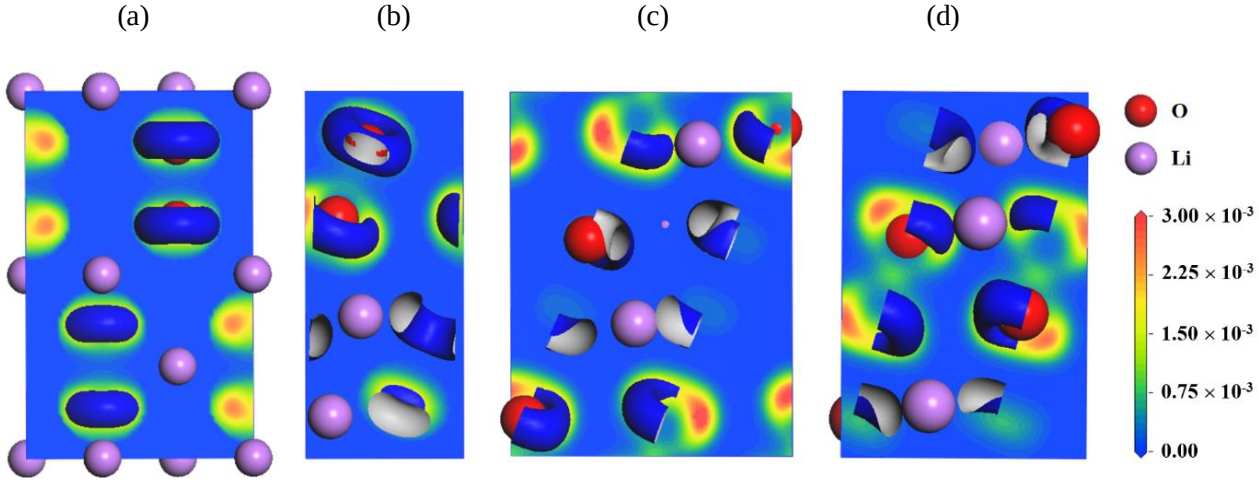


Figure S9. ELFs for various structures of Li_2O_2 projected onto (020) plane of: (a) the $P6_3/mmc$ structure at 0 GPa, (b) the $P2_1$ structure at 75 GPa, (c)-(d) the $P2_1/c$ structure at 150 and 500 GPa, respectively. The ELF isosurface values of 0.001 for (a) and 0.002 for (b, c, d).

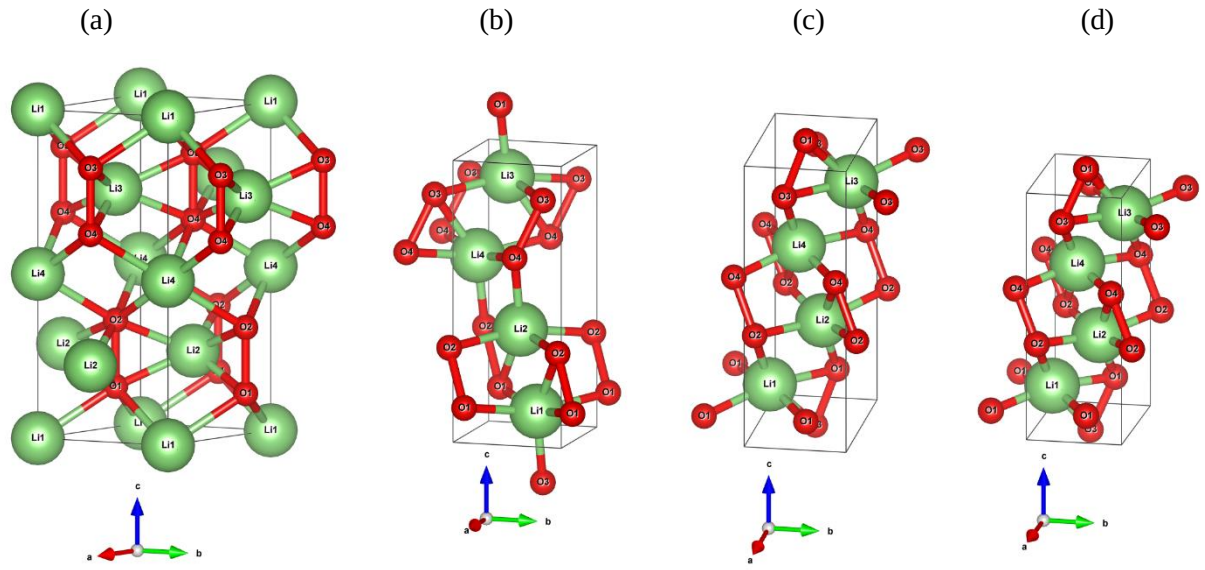


Figure S10. Crystal structures of Li_2O_2 for three phases at the different pressures: (a) the $P6_3/mmc$ structure at 0 GPa, (b) the $P2_1$ structure at 75 GPa, (c)-(d) the $P2_1/c$ structure at 150 and 500 GPa, respectively.