Electronic Supplementary Information (ESI):

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

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Figure S6. Partial density of states (PDOS) of Li and O for the P63/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. ................................................................. S9-S11
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Figure S8. Electron density maps of various structures of Li$_2$O$_2$ projected onto (020) plane of: (a) the *P6_3mmc* 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.

Figure S9. ELFs for various structures of Li$_2$O$_2$ projected onto (020) plane of: (a) the *P6_3mmc* 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.

Figure S10. Crystal structures of Li$_2$O$_2$ for three phases at the different pressures. (a) the *P6_3mmc* 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.
Table S1. Structural parameters of Li$_2$O$_2$ for the $P6/mmc$, $P2_1$, $P2_1/c$, and $P2_1/c^\dagger$ structures at the different pressures.

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>Structure</th>
<th>Lattice parameter (P$6/mmc$: $a = b = c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$) (P$2_1$, P$2_1/c$: $a \neq b \neq c$, $\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$)</th>
<th>Atom</th>
<th>Site</th>
<th>Atomic coordinates</th>
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<tr>
<td></td>
<td></td>
<td>a (Å) b (Å) c (Å) $\beta$ (degree)</td>
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<td>0</td>
<td>$P6/mmc$</td>
<td>3.1858 3.1858 7.7182 90.0000</td>
<td>Li(1)</td>
<td>2a</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Li(2)</td>
<td>2c</td>
<td>0.33333</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O(1)</td>
<td>4f</td>
<td>0.33333</td>
</tr>
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<td>Li(1)</td>
<td>2a</td>
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<tr>
<td></td>
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<td>Li(2)</td>
<td>2c</td>
<td>0.33333</td>
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<tr>
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<td>O(1)</td>
<td>4f</td>
<td>0.33333</td>
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<td>$P6/mmc$</td>
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<td>Li(2)</td>
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<tr>
<td>39</td>
<td>$P6/mmc$</td>
<td>2.9020 2.9020 6.9536 90.0000</td>
<td>Li(1)</td>
<td>2a</td>
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<td>2c</td>
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<td>Li(1)</td>
<td>2a</td>
<td>0.00000</td>
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<tr>
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<td>Li(2)</td>
<td>2c</td>
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<tr>
<td>75</td>
<td>$P6/mmc$</td>
<td>2.7781 2.7781 6.6468 90.0000</td>
<td>Li(1)</td>
<td>2a</td>
<td>0.00000</td>
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<td>Li(2)</td>
<td>2c</td>
<td>0.33333</td>
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<tr>
<td>75</td>
<td>$P2_1$</td>
<td>2.5695 2.5942 6.4767 91.8505</td>
<td>O(1)</td>
<td>4f</td>
<td>0.33333</td>
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<td>Li(1)</td>
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<td>O(1)</td>
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<td>Li</td>
<td>4e</td>
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</tr>
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<td>75</td>
<td>$P2_1/c$</td>
<td>2.5695 2.5941 7.0454 113.2454</td>
<td>O(1)</td>
<td>4f</td>
<td>0.72995</td>
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<td>Li</td>
<td>4e</td>
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<td>Li(2)</td>
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<td>$P2_1$</td>
<td>2.4424 2.4876 6.1569 89.7118</td>
<td>O(1)</td>
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<td>Li</td>
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<td>2a</td>
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<td>Li</td>
<td>4e</td>
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<td>136</td>
<td>$P2_1/c^\dagger$</td>
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<td>O(1)</td>
<td>2a</td>
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<td>Li(1)</td>
<td>2a</td>
<td>0.64037</td>
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<td>Li(2)</td>
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<td>$P2_1$</td>
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<td>O(1)</td>
<td>2a</td>
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<td>Li</td>
<td>4e</td>
<td>0.47361</td>
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<tr>
<td>150</td>
<td>$P2_1/c$</td>
<td>2.4194 2.4703 6.5333 110.9788</td>
<td>O(1)</td>
<td>2a</td>
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<td>Li</td>
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<td>0.52639</td>
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<tr>
<td>150</td>
<td>$P2_1/c^\dagger$</td>
<td>6.1008 2.4703 6.5333 158.2667</td>
<td>O(1)</td>
<td>2a</td>
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<td>Li</td>
<td>4e</td>
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<td>300</td>
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<td>2.1174 2.2416 5.5723 105.4396</td>
<td>O(1)</td>
<td>2a</td>
<td>0.49349</td>
</tr>
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</table>

†Reference 10

lStructural parameters obtained by using COMPSTRU programme proposed by Flor et al.\textsuperscript{8}.
Table S2. Mulliken charges of the Li and O atoms for the $P6_3/mmc$, $P2_1$, and $P2_1/c$ structures of Li$_2$O$_2$ 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 ($|e|$) |
|---------------|-----------|-----------------------|-----------------------------------|
| 0             | P63/mmc   | Li(1) 0.99 Li(2) 0.99 Li(3) 0.77 Li(4) 0.77 O(1) -0.88 O(2) -0.88 O(3) -0.88 O(4) -0.88 | 0.12 |
| 0'            | P63/mmc+  | Li(1) 0.99 Li(2) 0.99 Li(3) 0.77 Li(4) 0.77 O(1) -0.88 O(2) -0.88 O(3) -0.88 O(4) -0.88 | 0.12 |
| 4             | P63/mmc   | Li(1) 1.00 Li(2) 1.00 Li(3) 0.77 Li(4) 0.77 O(1) -0.88 O(2) -0.88 O(3) -0.88 O(4) -0.88 | 0.12 |
| 6             | P63/mmc   | Li(1) 1.00 Li(2) 1.00 Li(3) 0.77 Li(4) 0.77 O(1) -0.88 O(2) -0.88 O(3) -0.88 O(4) -0.88 | 0.12 |
| 8             | P63/mmc   | Li(1) 1.01 Li(2) 1.01 Li(3) 0.77 Li(4) 0.77 O(1) -0.89 O(2) -0.89 O(3) -0.89 O(4) -0.89 | 0.11 |
| 10            | P63/mmc   | Li(1) 1.01 Li(2) 1.01 Li(3) 0.77 Li(4) 0.77 O(1) -0.89 O(2) -0.89 O(3) -0.89 O(4) -0.89 | 0.11 |
| 11            | P63/mmc   | Li(1) 1.01 Li(2) 1.01 Li(3) 0.77 Li(4) 0.77 O(1) -0.89 O(2) -0.89 O(3) -0.89 O(4) -0.89 | 0.11 |
| 12            | P63/mmc   | Li(1) 1.02 Li(2) 1.02 Li(3) 0.77 Li(4) 0.77 O(1) -0.89 O(2) -0.89 O(3) -0.89 O(4) -0.89 | 0.11 |
| 15            | P63/mmc   | Li(1) 1.02 Li(2) 1.02 Li(3) 0.77 Li(4) 0.77 O(1) -0.89 O(2) -0.89 O(3) -0.89 O(4) -0.89 | 0.11 |
| 20            | P63/mmc   | Li(1) 1.03 Li(2) 1.03 Li(3) 0.77 Li(4) 0.77 O(1) -0.90 O(2) -0.90 O(3) -0.90 O(4) -0.90 | 0.10 |
| 25            | P63/mmc   | Li(1) 1.04 Li(2) 1.04 Li(3) 0.76 Li(4) 0.76 O(1) -0.90 O(2) -0.90 O(3) -0.90 O(4) -0.90 | 0.10 |
| 30            | P63/mmc   | Li(1) 1.05 Li(2) 1.05 Li(3) 0.76 Li(4) 0.76 O(1) -0.91 O(2) -0.91 O(3) -0.91 O(4) -0.91 | 0.09 |
| 35            | P63/mmc   | Li(1) 1.06 Li(2) 1.06 Li(3) 0.76 Li(4) 0.76 O(1) -0.91 O(2) -0.91 O(3) -0.91 O(4) -0.91 | 0.09 |
| 39            | P63/mmc   | Li(1) 1.06 Li(2) 1.06 Li(3) 0.76 Li(4) 0.76 O(1) -0.91 O(2) -0.91 O(3) -0.91 O(4) -0.91 | 0.09 |
| 40            | P63/mmc   | Li(1) 1.06 Li(2) 1.06 Li(3) 0.76 Li(4) 0.76 O(1) -0.91 O(2) -0.91 O(3) -0.91 O(4) -0.91 | 0.09 |
| 41            | P63/mmc   | Li(1) 1.07 Li(2) 1.07 Li(3) 0.76 Li(4) 0.76 O(1) -0.91 O(2) -0.91 O(3) -0.91 O(4) -0.91 | 0.09 |
| 45            | P63/mmc   | Li(1) 1.07 Li(2) 1.07 Li(3) 0.76 Li(4) 0.76 O(1) -0.92 O(2) -0.92 O(3) -0.92 O(4) -0.92 | 0.08 |
| 50            | P63/mmc   | Li(1) 1.08 Li(2) 1.08 Li(3) 0.76 Li(4) 0.76 O(1) -0.92 O(2) -0.92 O(3) -0.92 O(4) -0.92 | 0.08 |
| 55            | P63/mmc   | Li(1) 1.08 Li(2) 1.08 Li(3) 0.76 Li(4) 0.76 O(1) -0.92 O(2) -0.92 O(3) -0.92 O(4) -0.92 | 0.08 |
| 60            | P63/mmc   | Li(1) 1.09 Li(2) 1.09 Li(3) 0.76 Li(4) 0.76 O(1) -0.92 O(2) -0.92 O(3) -0.92 O(4) -0.92 | 0.08 |
| 65            | P63/mmc   | Li(1) 1.10 Li(2) 1.10 Li(3) 0.76 Li(4) 0.76 O(1) -0.93 O(2) -0.93 O(3) -0.93 O(4) -0.93 | 0.07 |
| 70            | P63/mmc   | Li(1) 1.10 Li(2) 1.10 Li(3) 0.75 Li(4) 0.75 O(1) -0.93 O(2) -0.93 O(3) -0.93 O(4) -0.93 | 0.07 |
| 75            | P63/mmc   | Li(1) 1.11 Li(2) 1.11 Li(3) 0.75 Li(4) 0.75 O(1) -0.93 O(2) -0.93 O(3) -0.93 O(4) -0.93 | 0.07 |
| 75            | P2_1      | Li(1) 0.90 Li(2) 0.90 Li(3) 0.90 Li(4) 0.90 O(1) -0.90 O(2) -0.90 O(3) -0.90 O(4) -0.90 | 0.10 |
| 135           | P2_1      | Li(1) 0.92 Li(2) 0.92 Li(3) 0.92 Li(4) 0.92 O(1) -0.92 O(2) -0.92 O(3) -0.92 O(4) -0.92 | 0.08 |
| 136           | P2_1/c    | Li(1) 0.92 Li(2) 0.92 Li(3) 0.92 Li(4) 0.92 O(1) -0.92 O(2) -0.92 O(3) -0.92 O(4) -0.92 | 0.08 |
| 150           | P2_1/c    | Li(1) 0.92 Li(2) 0.92 Li(3) 0.92 Li(4) 0.92 O(1) -0.92 O(2) -0.92 O(3) -0.92 O(4) -0.92 | 0.08 |
| 300           | P2_1/c    | Li(1) 0.94 Li(2) 0.94 Li(3) 0.94 Li(4) 0.94 O(1) -0.94 O(2) -0.94 O(3) -0.94 O(4) -0.94 | 0.06 |
| 500           | P2_1/c    | Li(1) 0.95 Li(2) 0.95 Li(3) 0.95 Li(4) 0.95 O(1) -0.95 O(2) -0.95 O(3) -0.95 O(4) -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 $\beta$ 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$_2$O$_2$ 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.
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$_2$O$_2$ 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. ELF for various structures of Li$_2$O$_2$ 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$_2$O$_2$ 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.