Supplementary Information: Anharmonic lattice
dynamics of superionic lithium nitride

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<table>
<thead>
<tr>
<th>Study</th>
<th>a = b (Å)</th>
<th>Relative error (%)</th>
<th>c (Å)</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present data (α-Li₃N)</td>
<td>3.611</td>
<td>-</td>
<td>3.847</td>
<td>-</td>
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<tr>
<td>Calculated [1]</td>
<td>3.629</td>
<td>0.50</td>
<td>3.855</td>
<td>0.21</td>
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<tr>
<td>Measured [2]</td>
<td>3.648</td>
<td>1.01</td>
<td>3.875</td>
<td>0.72</td>
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<tr>
<td>Measured [3]</td>
<td>3.637</td>
<td>0.72</td>
<td>3.870</td>
<td>0.60</td>
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<tr>
<td>Measured [4]</td>
<td>3.656</td>
<td>1.23</td>
<td>3.868</td>
<td>0.54</td>
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<tr>
<td>Present data (β-Li₃N)</td>
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<td>-</td>
<td>6.266</td>
<td>-</td>
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<tr>
<td>Measured [5]</td>
<td>3.552</td>
<td>0.96</td>
<td>6.311</td>
<td>0.71</td>
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<tr>
<td>Measured [3]</td>
<td>3.555</td>
<td>1.04</td>
<td>6.319</td>
<td>0.85</td>
</tr>
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</table>

Table S1: Table of reported lattice parameters of Li₃N.
Figure S1: Calculated mean square displacements for $\alpha$-Li$_3$N at 300 – 678 K. On a log-log plot the diffusive regime corresponds to the sloping linear portion.
Figure S2: Harmonic lattice dynamics of $\beta$-Li$_3$N. (a) Phonon dispersion and total phonon DOS; (b) PES of the imaginary mode at the K-point; left and right snapshots in (c) and (d) are taken through the $ab$ and $bc$ planes, respectively.
An imaginary mode is observed in the phonon dispersion of $\beta$-Li$_3$N at the K-point and is shown in Figure S2(a). The energy barrier between the two wells of the PES shown in Figure S2(b) is 40.95 meV. It corresponds to a thermal energy of 475.2 K, which is beyond the stability range of the $\beta$-phase according to the calculated phase diagram shown in (manuscript) and neutron powder diffraction data [3]. This could mean that $\beta$-Li$_3$N takes $P6_3cm$ symmetry instead of the accepted $P6_3/mmc$ symmetry. The structures corresponding to the $P6_3/mmc$ and $P6_3cm$ phases are shown in Figures S2(c) and S2(d). No diffraction data showing uncertainties on the Li positions could be found. $\beta$-Li$_3$N is usually synthesised at high pressure, which might be the reason why the reported $P6_3cm$ phase was not reported in the literature. It is important to note, however, that the $P6_3/mmc$ phase could also be stabilized by phonon-phonon interactions meaning that the $P6_3cm$ is never stable. The direct conversion between energy barrier and temperature alone is not enough to confirm that the $P6_3cm$ phase really exists over the stability range of $\beta$-Li$_3$N, hence the above discussion should be taken lightly. Further experimental investigations, or temperature-dependent lattice dynamics calculations including phonon-phonon interactions are necessary.
Figure S4: Renormalised phonon dispersion of α-Li$_3$N computed at 300 K, 400 K, 500 K, 600 K, and 678 K. The breakdown of all the modes can be observed at 678 K.
References


