Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information: Anharmonic lattice dynamics of superionic lithium nitride

Gabriel Krenzer[1], Chang-Eun Kim[2], Kasper Tolborg[1], Benjamin J. Morgan[3], and Aron Walsh[1, 4]

[1]Imperial College London, SW7 2BX, London, United Kingdom
[2]Lawrence Livermore National Laboratory, Livermore, CA 94550, United States
[3]University of Bath, BA2 7AY, Bath, United Kingdom
[4]Yonsei University, Seoul, South Korea

October 11, 2021

Study	$a = b$ (Å)	Relative error (%)	c (Å)	Relative error (%)
Present data (α-Li_3N)	3.611	-	3.847	-
Calculated [1]	3.629	0.50	3.855	0.21
Measured [2]	3.648	1.01	3.875	0.72
Measured [3]	3.637	0.72	3.870	0.60
Measured [4]	3.656	1.23	3.868	0.54
Present data (β-Li_3N)	3.518	-	6.266	-
Measured [5]	3.552	0.96	6.311	0.71
Measured [3]	3.555	1.04	6.319	0.85

Table S1: Table of reported lattice parameters of Li_3N.

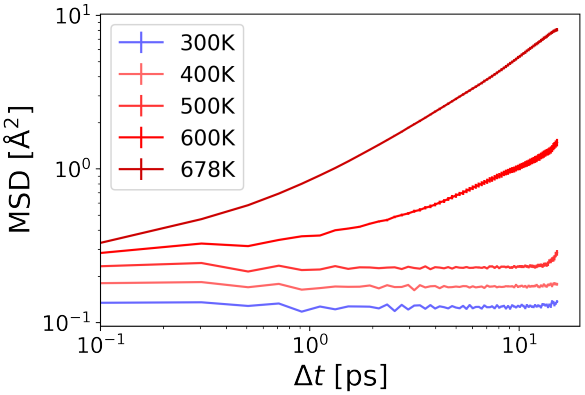


Figure S1: Calculated mean square displacements for α-Li_3N at $300 - 678\,K$. On a log-log plot the diffusive regime corresponds to the sloping linear portion.

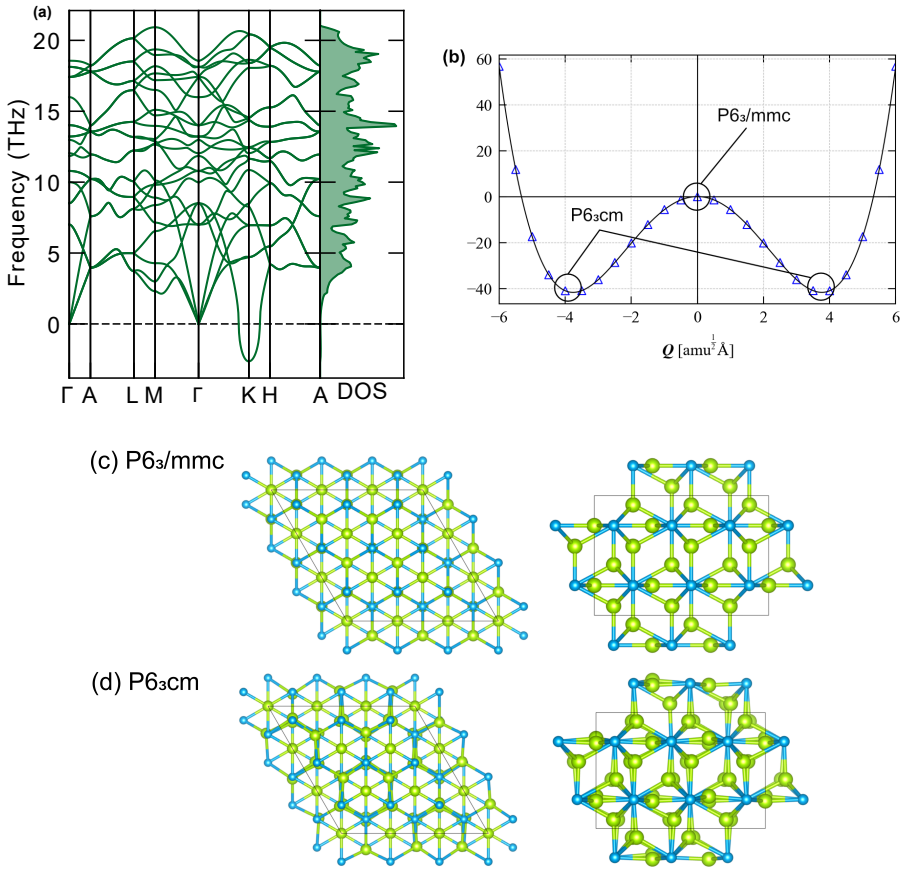


Figure S2: Harmonic lattice dynamics of β-Li_3N. (a) Phonon dispersion and total phonon DOS; (b) PES of the imaginary mode at the K-point; left and right snapshots in (c) and (d) are taken through the ab and bc planes, respectively.

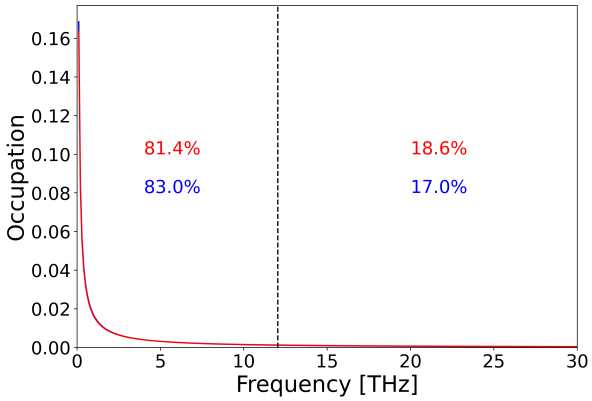
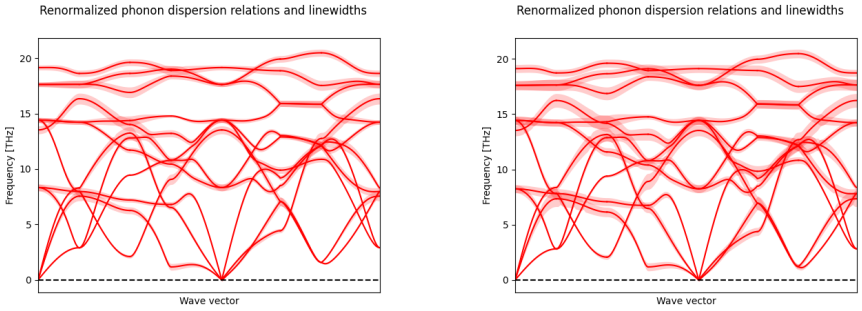


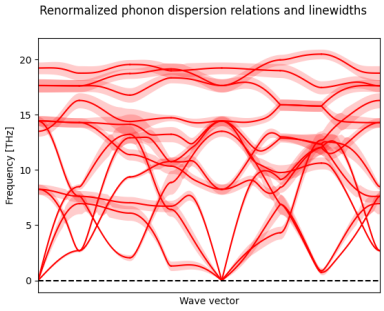
Figure S3: Bose-Einstein distribution of phonon quasiparticles with respect to frequency at 298 K (blue), and at 678 K (red). The fraction of phonon occupying states below and above $\omega_{\mathrm{av}} = 12.04$ THz is also highlighted.

An imaginary mode is observed in the phonon dispersion of β-Li_3N 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 β-phase according to the calculated phase diagram shown in (manuscript) and neutron powder diffraction data [3]. This could mean that β-Li_3N 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. β-Li_3N 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 β-Li_3N, hence the above discussion should be taken lightly. Further experimental investigations, or temperature-dependent lattice dynamics calculations including phonon-phonon interactions are necessary.

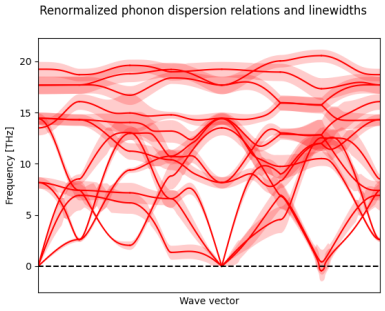


(a) 300K

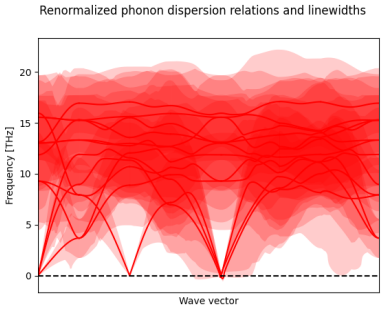
(b) 400K



(c) 500K



(d) 600K



(e) 678K

Figure S4: Renormalised phonon dispersion of α-Li_3N 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

[1] Zhao, Y., Tian, X., Xue, W. & Gao, T. The structure, dynamical and thermodynamic properties of α-Li_3N: a first-principles study. *Solid state communications* **149**, 2130–2134 (2009).

[2] Rabenau, A. & Schulz, H. Re-evaluation of the lithium nitride structure. *Journal of the Less Common Metals* **50**, 155–159 (1976).

[3] Huq, A., Richardson, J. W., Maxey, E. R., Chandra, D. & Chien, W.-M. Structural studies of Li_3N using neutron powder diffraction. *Journal of alloys and compounds* **436**, 256–260 (2007).

[4] Tapia-Ruiz, N. *et al.* Low dimensional nanostructures of fast ion conducting lithium nitride. *Nature communications* **11**, 1–8 (2020).

[5] Beister, H. J., Haag, S., Kniep, R., Strössner, K. & Syassen, K. Phase transformations of lithium nitride under pressure. *Angewandte Chemie International Edition in English* **27**, 1101–1103 (1988).