Cubic Lithium Nitride to 200 GPa

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This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48, and funded by SSAAP and SEGRF
Acknowledgements

- Members of High Pressure Group at LLNL: Hyunchae Cynn, William Evans, Magnus Lipp, Bruce Baer, Valentin Iota, Jae-Hyun Klepeis, Ken Visbeck, Brian Maddox, Geun Woo Lee, Zsolt Jenei

- HPCAT (sector 16 of the APS) at which all experiments were performed; we thank Maddury Somayazulu and Micheal Hu for technical assistance and scientific input.

- Andy McMahan (LLNL), Deepa Kasinathan (UCD) and Jan Kunes (UCD) for help with theoretical aspects
OUTLINE

Background

Results from
  • X-Ray Diffraction
  • X-Ray Raman Scattering
  • Total energy DFT calculations

Conclusions
Li$_3$N (previously known info)

- Two low pressure phases had been observed:
  - $\alpha$ phase is a superionic conductor via hopping of Li$^{1+}$ ions within Li$_2$N layers, in which N ions exist in 3- ionic state.
  - $\beta$ phase is metastable at 0 GPa, stable up to < 35 GPa.
  - high pressure cubic phase was predicted by theory.

Technological applications:
- possible electrolyte material for lithium-based batteries
- possible hydrogen storage material

Thrust of this research:
Determine structure, equation of state, stability of any novel high pressure phase.
X-Ray Diffraction Results

- mixed phase at 0 GPa
- transition to transparent cubic phase between 35 and 45 GPa
- signal from argon pressure medium and rhenium gasket obscure the details
γ-Li3N – a new cubic phase

- Pattern well understood as a combination of Cu and Li3N in cubic Fm3m phase.
- Peak broadening at 200 GPa very minimal even under non-hydrostatic conditions – very little internal stresses/strains.

- Cubic Li3N takes on simple rocksalt structure, with Li1+ ions tetrahedrally coordinated with 4 nitrogen ions in all tetrahedral holes in lattice.

Rietveld-refined XRD structure data
Inelastic X-Ray (Raman) Scattering

• Yields the same information as XAS, but experiment can be done with hard x-rays—(becomes possible to examine k-edges of low-Z materials in bulk)

Experimental set-up (16IDD, HPCAT, APS)

x-ray transparent Be gasket

incident beam energy scanned from 380 – 430 eV above elastic scattering energy (9.6870 eV) to probe nitrogen k-edge

\[E_i - E_j \approx 10 \text{ keV}\]

\[\Delta E = E_i - E_j\]
The x-ray raman spectra can be understood as transitions to low-lying conduction states with nitrogen p character – differences between the XRS and PDOS are indications of the presence of core-hole interactions (excitons) and non-dipole allowed transitions.
Equation of State

- cubic phase of Li$_3$N remains very compressible up to 200 GPa (maximum pressure achieved in this experiment)

- $B_0$, $V_0$ from fit to non-hydrostatic higher-pressure data agree well with results from fit to lower-pressure hydrostatic data.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>$V_0$ (Å$^3$/atom)</th>
<th>$B_0$ (GPa)</th>
<th>$B_0'$</th>
<th>$B_0$ collapse</th>
<th>$V_0$ collapse</th>
<th>Transition pressure (GPa)</th>
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<tbody>
<tr>
<td><strong>Experiment (this work)</strong></td>
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<tr>
<td>P6$_3$/mmc</td>
<td>8.6 ± 0.2</td>
<td>71 ± 19</td>
<td>3.9 ± 0.9</td>
<td>8 ± 0.5%</td>
<td>40 ± 5</td>
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<tr>
<td>Fm3m</td>
<td>7.7 ± 0.2</td>
<td>78 ± 13</td>
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<td><strong>Theory (this work)</strong></td>
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<td>P6$_3$/mmc</td>
<td>8.61 ± 0.02</td>
<td>68 ± 3</td>
<td>3.6 ± 0.1</td>
<td>6.7%</td>
<td>40.4</td>
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<tr>
<td>Fm3m</td>
<td>7.79 ± 0.02</td>
<td>73.1 ± 0.8</td>
<td>3.85 ± 0.01</td>
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<td><strong>Experiment (Ho, et al)</strong></td>
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<td>(PRB 59, 6083 (1999))</td>
<td>P6$_3$/mmc</td>
<td>8.76</td>
<td>74 ± 6</td>
<td>3.7 ± 0.7</td>
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<td>(PRB 59, 6083 (1999))</td>
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<td>78.17</td>
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<td>P4$_3$m</td>
<td>7.02</td>
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γ-Li$_3$N is a good candidate for an internal pressure indicator for ultra-high pressure applications

- simple cubic crystal structure
- stable up to at least 200 GPa with minimal peak broadening even under non-hydrostatic conditions
- compressibility compares well with other common pressure standards
- low-Z composition makes it particularly suitable for low-Z applications

Possible problem: reactivity, especially at high pressures, is unknown.

Equation of state data was then fit to modified 3rd order Birch-Murnaghan equation:

\[
P = \begin{cases}
p_r - \frac{1}{2} (3B_r - 5P_r) \left[ 1 - \left( \frac{V}{V_r} \right)^{-\frac{2}{3}} \right] + \frac{9}{8} B_r \left( B'_r - 4 + \frac{35P_r}{9B_r} \right) \left[ 1 - \left( \frac{V}{V_r} \right)^{-\frac{2}{3}} \right]^2 \\
\end{cases}
\left( \frac{V}{V_r} \right)^{-\frac{5}{3}}
\]

Bulk Modulus of γ-phase and comparison to common pressure indicators*

\[
B = -V \frac{\partial P}{\partial V}
\]

DFT Calculation Results

Equation of State

- Total energy calculations yield $V_0, B_0, B_0'$ consistent with experiment – Li$_3$N is well described by theoretical model.

- Widening of the band gap indicates insulating cubic phase, explains color change from opaque to transparent across hexagonal-cubic phase transition.

Comparison with experimental results

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Predicted Metallization

\( P = 40 \text{ GPa} \)
(transition to cubic phase)

\( P \sim 760 \text{ GPa} \)
43% of unit cell volume at transition
(maximum band gap)

\( P \sim 7.9 \text{ TPa} \)
16% of unit cell volume at transition.
(metallization)
Conclusions

The high pressure cubic phase of Li$_3$N identified in this study has several interesting properties including:

- Structural transition similar to graphite-diamond and hexagonal-cubic boron nitride
- Unusually high phase stability at megabar pressures
- High compressibility on the order of standard pressure indicators used in diamond anvil cell research
- Metallization at ultra-high gigabar pressures, on the order of closed-shell wide-gap insulators Ne, MgO and NaCl which metallize at 134 TPa, 20.7 TPa, & 0.455 TPa, respectively