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Short Communication

Elastic Behavior of γ-Li$_3$N under Pressure

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Abstract

The elastic properties of γ-Li$_3$N have been studied for the first time by first-principles method. Three independent elastic constants, aggregate elastic moduli (B, G, E), Poisson's ratio (υ) and Debye temperature Θ_D are calculated as a function of pressure from 37.12 ($\beta \rightarrow \gamma$ transition value) to 200 GPa and the implications of the results are discussed.

Keywords: Li$_3$N; γ-phase; Elastic properties; Debye temperature.

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1. Introduction

Lithium nitride is appealing as a superionic conductor, which determines its use as an electrolytic solution in lithium cells and as a material for hydrogen storage [1]. Li$_3$N has multiphase states, three main structures having been identified now [2]. It crystallizes in a hexagonal structure, α-Li$_3$N, with a space group *P6/mmm* at ambient conditions at equilibrium pressure. The existence of high-pressure β- and γ-phases was confirmed in experiments and their behaviour at high pressure studied by different workers [1-5]. At ~0.5-0.6 GPa α-Li$_3$N is observed to transform into a second layered hexagonal structure β-Li$_3$N ($P6_3/mmc$). B-Li$_3$N is metastable at ambient pressure and is typically found mixed with α-Li$_3$N phase. With increasing pressure a further phase transition to a cubic structure (γ-Li$_3$N) $Fm\overline{3}m$ at 27.6 GPa is found [6]. It is proved by Lazicki *et al.* [2] that β−Li$_3$N indeed transforms to γ-Li$_3$N, but in the pressure range of 36–45 GPa. Recently S. Cui *et al.* [7] proved that the transformation pressure of $\alpha \rightarrow \beta$ is 1.5 GPa and the β-Li$_3$N transforms into a cubic structure γ-Li$_3$N at 38.8 GPa. The γ-Li$_3$N phase is uncommonly

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stable up to at least 200 GPa and quite compressible in this pressure regime, making it a good candidate for an internal pressure standard. The unit cell dimension of γ-Li_3N is a = 4.976 Å [2]. In technological applications the cubic Li_3N can be used as possible electrolyte material for lithium-based batteries and hydrogen storage material.

The electronic properties of γ-Li_3N have been studied by Gordienko [8] but there is no work available on elastic properties. But we know that knowledge of the elastic constants C_{ij} is essential for many practical applications related to the mechanical properties of materials, e.g. load deflection, sound velocities, internal strain, thermo-elastic stress. The elastic constant data help us to analyze the thermodynamic and thermo-elastic properties of ionic solids at high temperatures. For this reason, the present work has been undertaken for a detailed calculation of elastic properties of γ-Li_3N as a function of pressure from 37.12 to 200 GPa.

2. Computational Details

The first-principles *ab-initio* calculations are performed using the CASTEP code [9] in the framework of density functional theory with generalized gradient approximation (GGA) in the scheme of PBE exchange-correlation functional [10]. The electron-ion interactions are represented by ultra-soft Vanderbilt-type pseudopotentials for Li ($1s^2$ $2s^1$) and N ($2s^2$ $2p^3$) [11]. The valence electron wavefunctions are expanded in a plane wave basis set with a kinetic energy cut-off of 300 eV and $6 \times 6 \times 6$ Monkhorst-Pack grid for sampling the Brillouin zone. The elastic constants are calculated by the stress-strain method. Geometry optimization is conducted using convergence thresholds of 10^{-8} eV/atom for the total energy and 0.01 eV/Å for the maximum force.

3. Results and Discussions

3.1. *Structural properties*

The geometry optimization as a function of normal stress has been performed by minimizing the total energy of γ-Li_3N (having a cubic structure, $Fm\bar{3}m$). The optimized lattice constant at ambient pressure is 4.570 Å (Table 1) which is in fair agreement with the experimental value [2]. The transition pressure from $\beta \rightarrow \gamma$ phase has been found to be 37.12 GPa. The lattice parameter continues to decrease as a function of pressure from 37.12 to 200 GPa but there is an obvious volume drop at the transition (not shown).

3.2. *Single crystal elastic constants*

The elastic constants of a material describe its response to an applied stress, or conversely, the stress required to maintain a given deformation. To determine the elastic constants from first-principles usually involve setting either the stress or the strain to a finite value.

The calculated elastic constants and bulk modulus B for γ-Li_3N at ambient condition are shown in Table 1 along with the available data for other phases of Li_3N as well.

Table 1. Lattice parameter (in Å), Elastic constants C_{ij} (in GPa) and Bulk modulus B (in GPa) of Li_3N at ambient pressure.

Phase	a	c	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B	Ref.
α -phase	3.664	3.932	122.8	24.6	5.4	129.5	16.6	63	[12]
β-phase	3.579	6.360	131.8	28.8	8.7	180.4	37.1	67	[12]
γ-phase	4.570	-	288.5	151.8	-	-	199.7	84	This
	4.976	-	-	-	-	-	-	78	[2] Expt
	4.772	-	-	-	-	-	-	77	[8]
	4.870	-	-	-	-	-	-	77	[1]

The calculated elastic constants C_{ij} for γ-Li_3N as a function of pressure are shown in Fig. 1. It shows that all the elastic constants of γ-Li_3N increase with pressure but by different rates. Unfortunately, there are no experimental data for comparison. The mechanical stability in a cubic crystal under isotropic pressure is judged using the following condition [13]:

$$\tilde{C}_{44} > 0, \qquad \tilde{C}_{11} > |\tilde{C}_{12}|, \qquad \tilde{C}_{11} + 2\tilde{C}_{12} > 0 \tag{1}$$

where, $\tilde{C}_{\alpha\alpha} = C_{\alpha\alpha} - P \ (\alpha = 1, 4), \quad \tilde{C}_{12} = C_{12} + P.$

It is obvious from Fig. 1 that C_{11}, C_{12}, and C_{44} increase monotonically with increasing pressure, and the elastic constants under pressure are consistent with Eq. (1), indicating that Li_3N should be stable under the pressure from 37.12 to 200 GPa.

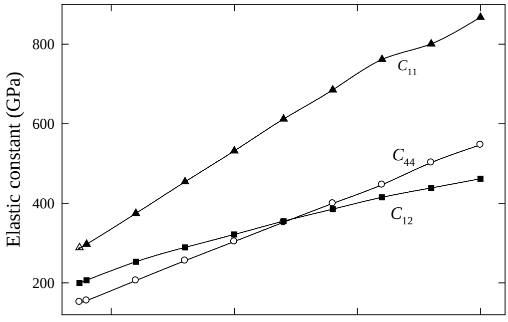

Fig. 1. Calculated elastic constants of γ-Li_3N as a function of pressure.

3.3. *Debye temperature and elastic properties of polycrystalline aggregate*

One popular method for calculating the Debye temperature θ_D is from elastic constant data, since it may be estimated from the average sound velocity v_m, via the following equation [14]:

$$\Theta_D = \frac{h}{k}\left[\frac{3n}{4\pi}\left(\frac{N_A \rho}{M}\right)\right]^{\frac{1}{3}} v_m \tag{2}$$

where h is Planck's constant, k is Boltzmann's constant, M is molecular weight, N_A is Avogadro's number, n is the number of atoms per formula unit, ρ is the density. The average wave velocity v_m is calculated approximately from compressional and shear wave velocity, which are obtained from Hill's equation [15]. Hill [15] proved that the Voigt and Reuss equations represent upper and lower limits of the true polycrystalline constants. He showed that the polycrystalline moduli are the arithmetic mean values of the Voigt and Reuss moduli, and are thus given by $B_H \equiv B = ½(B_R + B_V)$ and $G_H \equiv G = ½(G_R + G_V)$. The polycrystalline Young's modulus (E) and the Poisson's ratio (υ) are then calculated using the relationships $E = 9BG/(3B + G)$ and $\upsilon = (3B - 2G)/(6B + 2G)$.

Fig. 2 represents the variation of sound velocities of γ-Li_3N as a function of pressure. Both the longitudinal and transverse sound velocities increase as the pressure is increased.

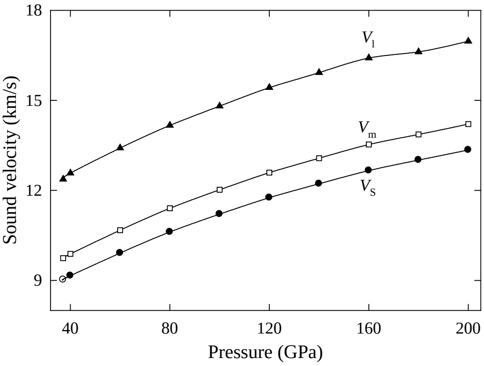

Fig. 2. Longitudinal and transverse sound velocities of γ-Li_3N as a function of pressure.

The aggregate bulk, shear and Young's moduli (B, G, E) and the Poisson's ratio υ are shown in Fig. 3 as a function of pressure. It is seen that both the bulk and shear moduli increase as pressure is increased, but they do so in a different rate, particularly at higher pressure. One of the most widely used malleability indicators of materials is Paugh's ductility index (G/B) [16]. As is known, if $G/B < 0.5$ the material will have a ductile behavior, whereas if $G/B > 0.5$ the material is brittle. We find the G/B ratio for γ-Li_3N is 0.66 at 37.12 GPa which decreases to 0.46 as the pressure increases to 200 GPa. Thus according to this indicator γ-Li_3N starts with a brittle behavior and then moves toward ductility. The Poisson's ratio for the brittle covalent materials is small, whereas for ductile metallic materials it is typically 0.33 [17]. The value of this ratio is 0.22 at 37.12 GPa which increases to 0.3 at 200 GPa. Thus the material would show ductile metallic characteristics near 200 GPa.

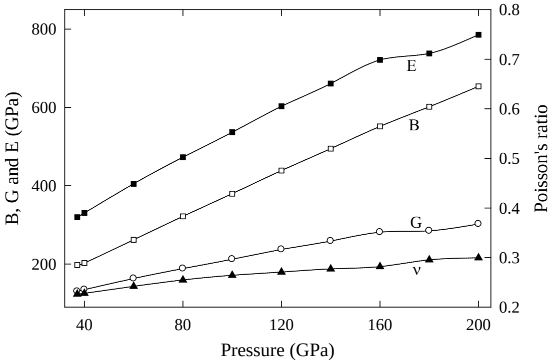

Fig. 3. Bulk, shear, Young's moduli and Poisson's ratio of γ-Li_3N as a function of pressure.

Fig. 4 shows the Debye temperature of γ-Li_3N as a function of pressure which indicates that it increases as the pressure increases. We note further that the value of Θ_D at ambient conditions is 1599 K while it is 755 K and 942 K for α-Li_3N and β-Li_3N [12], respectively.

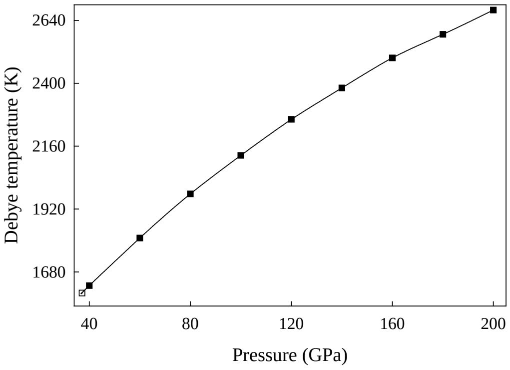

Fig. 4. The Debye temperature Θ_D of γ-Li_3N as a function of pressure.

4. Conclusions

The elastic properties including three independent elastic constants and Debye temperature of γ-Li_3N have been investigated. The mechanical stability of γ-Li_3N has also been investigated for the pressure ranges 37.12−200 GPa. γ-Li_3N is found to exhibit metallic ductile characteristics at higher pressures. The aggregate elastic moduli and Debye temperature are calculated as a function pressure and the implications of the obtained results are discussed. The Debye temperature is found to be quite high in the γ-phase compared to the other two phases of Li_3N.

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