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# High pressure–high temperature synthesis and elasticity of the cubic nitride spinel $\gamma$ -Si<sub>3</sub>N<sub>4</sub>

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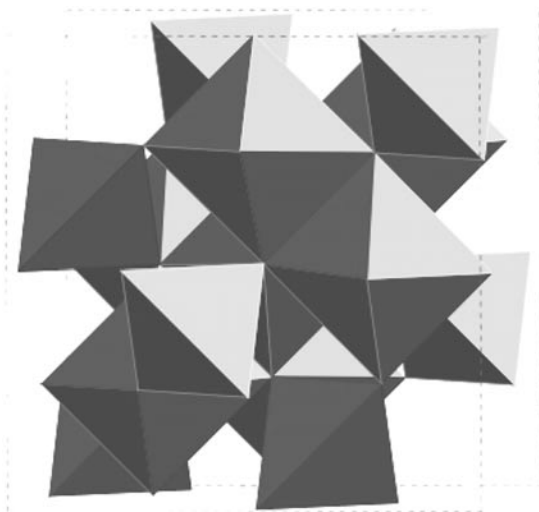
## Abstract

The compressional behaviour of a new dense form of silicon nitride with the cubic spinel structure is studied by energy dispersive x-ray diffraction, following *in situ* synthesis from the low pressure form by laser heating in the diamond anvil cell, combined with theoretical density functional calculations (LDA and GGA). The unit cell dimension and the ambient temperature bulk modulus and its pressure derivative are determined to be  $V_0 = 8.29(\pm 0.03) \text{ \AA}^3/\text{atom}$ ,  $K_0 = 308(\pm 5) \text{ GPa}$  and  $K'_0 = 4 \pm (0.2)$ , in excellent agreement with theoretical calculations within the LDA and GGA. The calculated shear modulus is two to three times those of corresponding oxide spinels, and there is a substantial Cauchy violation, indicating a material with strong covalent bonding that is likely to be extremely hard.

## 1. Introduction

Dense nitride structures of group III and group IV elements (Al, Si, Ga) are well known technological materials, with high mechanical strength and hardness and useful semiconducting properties [1–3]. Recently, new forms of the nitrides Si<sub>3</sub>N<sub>4</sub> and Ge<sub>3</sub>N<sub>4</sub> have been identified in high pressure–high temperature synthesis experiments. These new polymorphs have the dense spinel structure with Si and Ge atoms in octahedral as well as tetrahedral coordination to nitrogen, and nitrogen is four coordinated [4, 5] (figure 1). The spinel ( $\gamma$ -) structured Ge<sub>3</sub>N<sub>4</sub> phase was synthesized in a large volume high pressure apparatus following its initial identification in a diamond anvil cell (DAC) experiment, and its crystal structure was determined by Rietveld analysis of the powder diffraction pattern [4]. In an independent study,  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> was synthesized from reaction between elemental Si and the N<sub>2</sub> pressure medium in a laser heated DAC experiment, and recovered to ambient conditions [5].

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**Figure 1.** Structure of  $\gamma$ - $\text{Si}_3\text{N}_4$  showing the linked  $\text{SiN}_4$  tetrahedral and  $\text{SiN}_6$  octahedral units. The Si atoms are at the centres of the polyhedra.

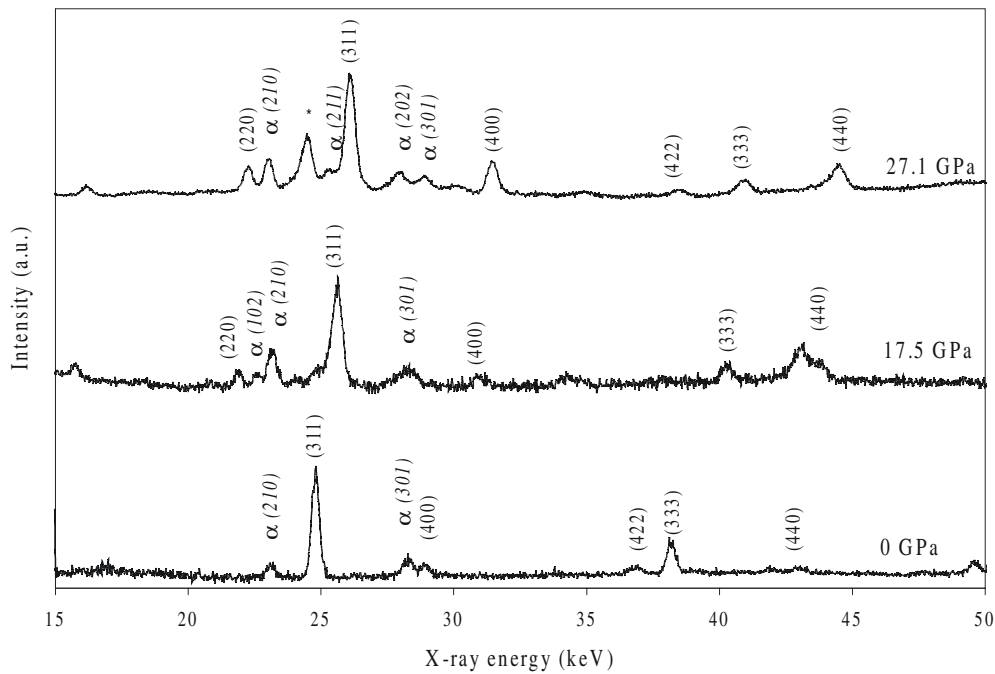
The phase was identified by electron diffraction in a transmission electron microscope, and by Raman spectroscopy. More recently, cubic silicon nitride has been obtained in shock wave and multi-anvil experiments [6–8].  $\gamma$ - $\text{Ge}_3\text{N}_4$  has also been synthesized from laser heating  $\text{Ge} + \text{N}_2$  [9]. In this study, we have obtained the cubic  $\gamma$ -spinel phase of  $\text{Si}_3\text{N}_4$  by laser heating the low pressure  $\alpha$ -form of silicon nitride in the DAC, and have studied the new phase by energy dispersive (synchrotron) x-ray diffraction during compression to 35 GPa and decompression to ambient conditions. The results permit the determination of the zero-pressure bulk modulus, its pressure derivative and the cell volume.

## 2. Experiment

Commercially obtained  $\alpha$ - $\text{Si}_3\text{N}_4$  was loaded into a ‘cylindrical’ design diamond cell for double-sided laser heating studies, with bevelled diamond anvils having  $250 \mu\text{m}$  outer culets. The sample chamber was formed by drilling a  $160 \mu\text{m}$  hole in a Re gasket. Pure nitrogen was used as the pressure transmitting fluid. The pressure was measured using the ruby fluorescence scale [9] ( $d\lambda/dP = 0.365 \text{ nm GPa}^{-1}$ ). Samples were loaded with  $\sim 1\%$  amorphous B powder to efficiently absorb the heating laser energy, and were pressurized to approximately 20 GPa. Laser heating was achieved with  $\sim 15$ – $30 \text{ W}$  of  $1064 \text{ nm}$  radiation from a Nd:YAG laser. Energy dispersive x-ray diffraction patterns were collected at the superconducting wiggler beam line station X17-B1 of the National Synchrotron Light Source (NSLS). Data were collected at a diffracting angle of  $2\theta = 12.0000^\circ$ .

## 3. Results and discussion

In figure 2, we plot selected energy dispersive x-ray diffraction patterns for  $\gamma$ - $\text{Si}_3\text{N}_4$  as a function of pressure, both on decompression and further compression following synthesis at  $P \sim 20 \text{ GPa}$ . Before laser heating, the pattern showed only peaks of  $\alpha$ - $\text{Si}_3\text{N}_4$ . Following laser heating, a new set of peaks corresponding to the (220), (311), (400), (333) and (440)



**Figure 2.** Changes in the energy dispersive x-ray diffraction pattern of Si<sub>3</sub>N<sub>4</sub> as a function of decreasing pressure following synthesis in the laser heated DAC at  $\sim 27$  GPa. Note that relative peak intensities cannot be interpreted quantitatively in this energy dispersive experiment, because they depend upon both the grain size distribution and orientation within the recrystallized region of the sample, as well as the x-ray sampling geometry and the beam profile through the DAC. Peaks due to unreacted  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> starting material are observed in all of the spectra, corresponding to regions that were not laser heated but were sampled by the x-ray beam. The peak marked with \* in the 27.1 GPa spectrum can not be identified: it does not correspond to any peaks of the gasket or pressure-transmitting medium, nor to any known Si<sub>3</sub>N<sub>4</sub> phase.

reflections of the  $Fd-3m$  cell of  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> (spinel phase) appeared. Peaks due to  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> were still present in untransformed regions of the sample. As reported previously [5], the spinel-structured  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> phase was recovered upon decompression to ambient. Spectra taken *in situ* both during decompression to ambient and during further compression to 35 GPa permitted the volume to be calculated as a function of pressure. The spectrum collected in the DAC at room pressure in two separate runs gave the ambient pressure cell edge as  $a_0 = 7.742 \pm 0.009$  Å, leading to an ambient pressure volume  $V_0 = 8.286 \pm 0.030$  Å<sup>3</sup>/atom. The variation of cell volume with pressure is shown in figure 3. In order to obtain a best fit estimate of the bulk modulus and its pressure derivative, we used a measure of the negative Eulerian strain,  $f_v$  [10, 11]:

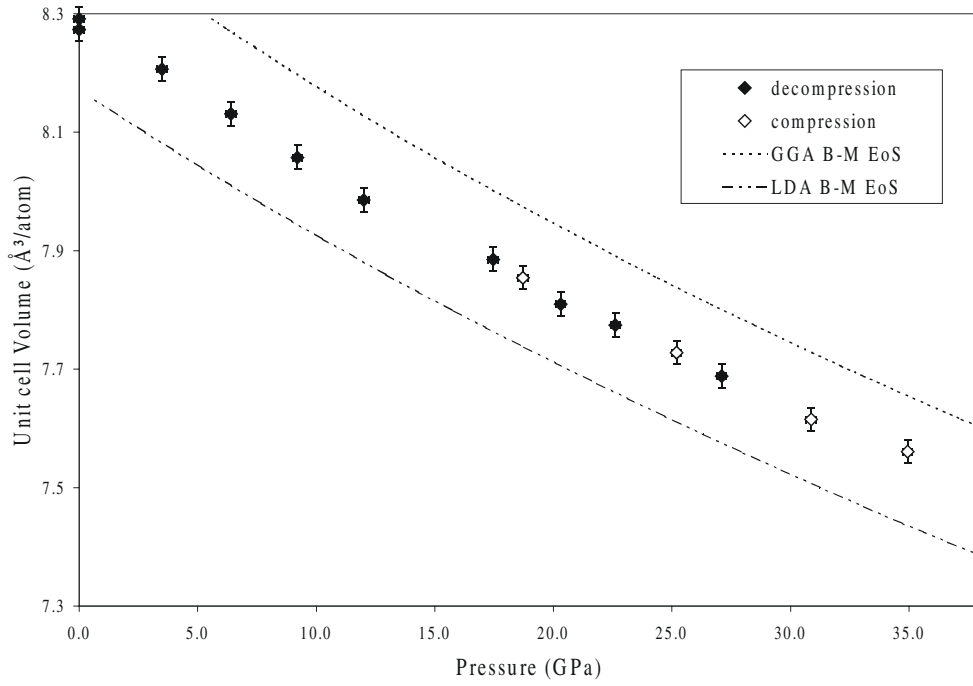
$$f_v = 1/2[(V/V_0)^{-2/3} - 1]$$

and a normalized pressure,  $F$ ,

$$F = P[3f_v(1 + 2f_v)^{2.5}]^{-1}.$$

The Birch–Murnaghan EoS (to third order) is written in terms of  $f_v$  and  $F$  as

$$F = K_0[1 - 3/2(4 - K'_0)f_v].$$



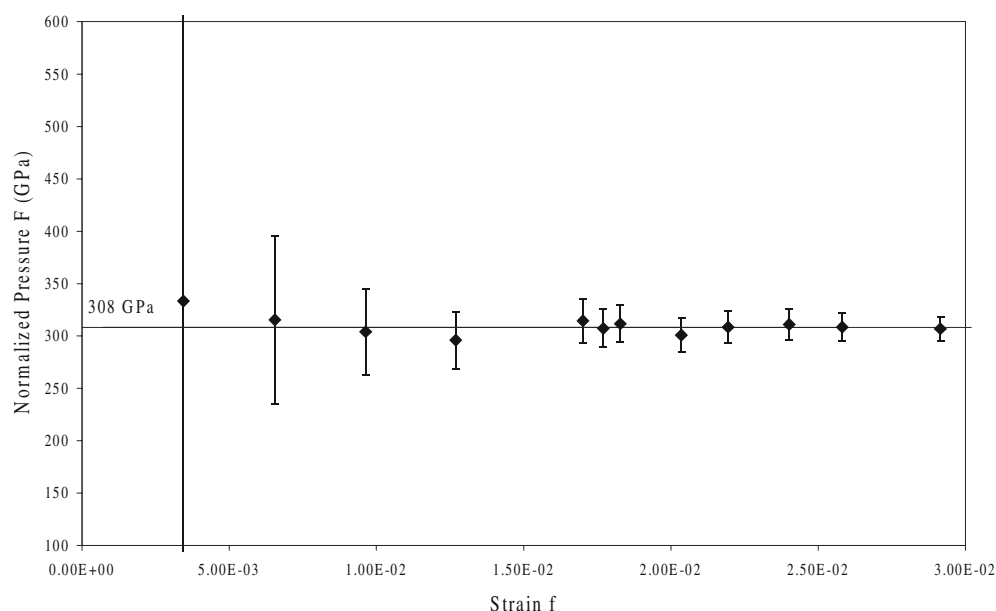
**Figure 3.** Pressure dependence of the unit cell volume in  $\text{Si}_3\text{N}_4$  measured between 0 and 35 GPa at room temperature. The open diamonds are data collected during compression and the filled symbols correspond to data collected during decompression. The dash-dotted line is the EoS calculated from a Birch–Murnaghan fit to data calculated within the LDA, and the dotted line is a fit to calculated points within the GGA. The theoretical points bracket the experimental data.

**Table 1.** Summary of high pressure parameters of  $\gamma\text{-Si}_3\text{N}_4$  obtained from a Birch–Murnaghan equation of state analysis of experimental and theoretical data points.

	$V_0$ ( $\text{\AA}^3/\text{atom}$ )	$K$ (GPa)	$K'$
Experiment	8.29(3)	308(5)	4.0(2)
Theory (LDA)	8.142	308	3.9
Theory (GGA)	8.450	284	3.9

The parameters  $K_0$  and  $K'_0$  are readily extracted from the intercept and slope in a linear plot of  $F$  versus  $f_v$  (figure 4). A least squares best fit to our data yields  $K_0 = 308(\pm 5)$  GPa and  $K'_0 = 4.0(\pm 0.2)$  (table 1).

We have also calculated the structure, compressibility and elastic moduli of spinel  $\text{Si}_3\text{N}_4$ . The calculations are based on density functional theory (DFT), and are performed with the VASP code [12], using ultra-soft pseudopotentials and a planewave basis set. A Ceperley–Alder form of the local exchange/correlation energy in the local density approximation (LDA) is adopted. The planewave cutoff is chosen as 25.6 Ryd, and the numerical integration of the Brillouin zone is carried out over a discrete  $4 \times 4 \times 4$  Monkhorst–Pack  $k$ -grid. Since spinel crystals are cubic, the theoretical structure optimization is straightforward. For a given unit cell volume, the lattice constant is fixed while internal coordinates of Si and N atoms are optimized through a conjugate gradient technique until the minimum LDA total energy at that volume is reached. The high symmetry of the spinel structure is taken into account and



**Figure 4.** Reduced variable  $F-f_v$  plot using data shown in figure 3. A linear least squares best fit gave  $K_0 = 308(5)$  GPa and  $K'_0 = 4.0(2)$ .

only 10 irreducible  $k$ -points are explicitly computed in the structure optimization. By fitting the calculated energy versus volume data points to a third-order Birch–Murnaghan EoS, the LDA calculations yield  $K_0 = 308$  GPa (assuming  $K'_0 = 4.0$ ) and  $V_0 = 8.142 \text{ \AA}^3/\text{atom}$ . The same calculation within the generalized gradient approximation (GGA, Perdew-91 functional) yields  $K_0 = 284$  GPa and  $V_0 = 8.450 \text{ \AA}^3/\text{atom}$  (table 1). Compared with our experimental result (measured at 300 K), the LDA underestimates  $V_0$  by approximately 1.7%, but gives a value for  $K_0$  that is in agreement with experiment, within the error. The GGA overestimates  $V_0$  by about 2.0% and underestimates  $K_0$  by 7.8%. This level of agreement with experimental results is typical of DFT calculations. Our results are also consistent with recent theoretical results of Mo *et al* [13] (LDA and atomic-like basis sets) and Zerr *et al* [5] (LDA/GGA and planewave basis sets).

**Table 2.** LDA calculated elasticity constants of nitride and oxide spinels, compared with experimental data for the oxides.

	$C_{11}$ (GPa)	$C_{12}$ (GPa)	$C_{44}$ (GPa)	$K_0$ (GPa)	$G_0$ (GPa)	Cauchy violation: $C_{44}/C_{12}$
$\gamma$ -Ge <sub>3</sub> N <sub>4</sub>	395.1	165.4	234.5	242.0 <sup>a</sup>	176.2	1.42
$\gamma$ -Si <sub>3</sub> N <sub>4</sub>	532.6	191.2	341.0	305.0 <sup>a</sup>	258.3	1.78
MgAl <sub>2</sub> O <sub>4</sub>	266.2	148.0	148.6	187.4 <sup>a</sup>	103.0	1.00
$\gamma$ -Mg <sub>2</sub> SiO <sub>4</sub>	333.7	111.0	140.0	185.2 <sup>a</sup>	127.8	1.26
Expt						
MgAl <sub>2</sub> O <sub>4</sub> [16]	282.9	154.8	155.4	197.9	108.5	1.00
$\gamma$ -Mg <sub>2</sub> SiO <sub>4</sub> [17]	327	126	112	184	119	0.89

<sup>a</sup> Bulk modulus estimated from elasticity calculations:  $K_0 = (C_{11} + 2C_{12})/3$ .

**Table 3.** Summary of bulk moduli determined experimentally for Ge<sub>3</sub>N<sub>4</sub> and Si<sub>3</sub>N<sub>4</sub> polymorphs.

	$V_0$ (Å <sup>3</sup> /atom)	$K$ (GPa)	$K'$
$\alpha$ -Si <sub>3</sub> N <sub>4</sub> [20]	10.429	228.5	4.0 <sup>a</sup>
$\beta$ -Si <sub>3</sub> N <sub>4</sub> [21]	10.411	270	4.0 <sup>a</sup>
$\gamma$ -Si <sub>3</sub> N <sub>4</sub>	8.286	308	4.0
$\alpha$ -Ge <sub>3</sub> N <sub>4</sub> <sup>a</sup> [19]	12.321	178	2.1
$\beta$ -Ge <sub>3</sub> N <sub>4</sub> [4]	12.308	218	4.0 <sup>a</sup>
$\gamma$ -Ge <sub>3</sub> N <sub>4</sub> [22]	9.891	296	4.0

<sup>a</sup> Assumed values for  $K$  and  $K'$ .

The hardness of a material is more closely correlated with the shear modulus than the bulk modulus [14]. We have calculated the elastic constants with LDA-DF theory. First, the total energy of the LDA equilibrium structure is calculated. Then, the unit cell models are ‘deformed’ along each of the three Cartesian axes by several small, finite amounts. Total energies at each ‘deformed’ point are calculated, and the results fitted to quadratic functions to obtain the elastic coefficients. In cubic systems like spinel, only three independent elastic constants,  $C_{11}$ ,  $C_{12}$  and  $C_{44}$ , are necessary to describe the elastic behaviour of the material. The shear modulus was estimated using both the Hashin formulation:

$$G_1^* = G_1 + 3(5/(G_2 - G_1) - 4\beta_1)^{-1}$$

and the Shtrikman formula:

$$G_2^* = G_2 + 3(5/(G_1 - G_2) - 6\beta_2)^{-1}.$$

Here,  $G_1 = (C_{11} - C_{12})/2$ , the tetragonal shear modulus,  $G_2 = C_{44}$ , the rhombohedral shear modulus,  $K_0 = (C_{11} + 2C_{12})/3$ , the bulk modulus,  $\beta_1 = -3(K_0 + 2G_1)/\{5G_1(3K_0 + 4G_1)\}$  and  $\beta_2 = -3(K_0 + 2G_2)/\{5G_2(3K_0 + 4G_2)\}$  [14]. The shear modulus reported here is an average:  $G_0 = (G_1^* + G_2^*)/2$ . Our LDA calculations (table 2) indicate a very high shear modulus of cubic spinel  $\gamma$ -Si<sub>3</sub>N<sub>4</sub>,  $G_0 = 258$  GPa, between 2 and 2.5 times the value for the isoelectronic oxide spinels MgAl<sub>2</sub>O<sub>4</sub> and  $\gamma$ -Mg<sub>2</sub>SiO<sub>4</sub> [16, 17]. The related spinel  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub> compound has a calculated shear modulus of 176 GPa. Based upon comparison between theoretical and experimental elastic constants for the oxide spinels (table 2), it is unlikely that our calculated (LDA) shear moduli are in error by more than 5–7%. From the correlation between Vickers hardness and shear modulus presented by Teter [14], we estimate a value of 30 GPa for the hardness of  $\gamma$ -Si<sub>3</sub>N<sub>4</sub>. This is a very high value, placing  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> in the class of ‘hard’ to ‘super-hard’ materials.

The experimentally determined bulk modulus values for the  $\alpha$ -,  $\beta$ - and  $\gamma$ - phases of Ge<sub>3</sub>N<sub>4</sub> and Si<sub>3</sub>N<sub>4</sub> are compared in table 3. As expected, the densely packed spinel-structured phases are much less compressible than the less dense phases that are stable at room pressure. The densification of Si<sub>3</sub>N<sub>4</sub> across the  $\alpha$ - $\gamma$  transition is 20.4%, similar to the  $\beta$ - $\gamma$  transition observed in Ge<sub>3</sub>N<sub>4</sub> [4]. The physical and chemical similarity in the two materials indicates that solid solutions may be formed, as is found in the elements (Si<sub>1-x</sub>Ge<sub>x</sub> alloys) and in spinel-structured Si- and Ge-bearing oxides also prepared at high pressure [18].

Many oxide spinels are known and their compressibilities and shear moduli have been measured. It is interesting to compare the elastic properties of  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> with those of MgAl<sub>2</sub>O<sub>4</sub> ( $K_0 = 198$  GPa;  $G_0 = 109$  GPa) and  $\gamma$ -Mg<sub>2</sub>SiO<sub>4</sub> ( $K_0 = 184$  GPa;  $G_0 = 119$  GPa) [15], which are isoelectronic with the nitride and also contain only first row cations. The bulk moduli and shear moduli for the nitride spinel are much larger ( $K_0$  by 30%, and  $G_0$  by a factor of 2–2.5) than those found for the oxides. This observation may be linked to the stronger bonding in the nitride material, which is nominally based on N<sup>3-</sup> anions and 4+ cations, compared

with O<sup>2-</sup> and average cation charge (8/3)<sup>+</sup> in the oxides. The degree of Cauchy violation ( $C_{44}/C_{12} \neq 1$ ) indicates the deviation from a two-body central force model. There is little or no Cauchy violation ( $C_{44}/C_{12} \approx 1$ ) for oxide spinels indicating nearly ideal ionic behaviour. In contrast, nitride spinels have  $C_{44}/C_{12} = 1.8$  for  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> and 1.4 for  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub>. Such a large value indicates that bonding in the nitrides is much more covalent. This could correlate with the large value of the shear modulus and high hardness in the nitride materials.

#### 4. Conclusion

In conclusion,  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> has been prepared from its low pressure ( $\alpha$ -) phase by laser heating in the diamond anvil cell, and its stability upon decompression is demonstrated by *in situ* synchrotron X-ray diffraction. The new spinel phase was characterized by X-ray diffraction, and the bulk modulus, its pressure derivative and the ambient pressure lattice parameter were obtained from the data. These dense nitride materials likely have high hardness. Theoretical calculations indicate that they may also have useful optoelectronic properties [19].

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