

Pressure-induced transformations in α - and β -Ge₃N₄: in situ studies by synchrotron X-ray diffraction

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Abstract

Metastable high-pressure transformations in germanium nitride (α - and β -Ge₃N₄ polymorphs) have been studied by energy- and angle-dispersive synchrotron X-ray diffraction at high pressures in a diamond anvil cell. Between $P = 22$ and 25 GPa, the phenacite-structured β -Ge₃N₄ phase ($P6_3/m$) undergoes a 7% reduction in unit-cell volume. The densification is primarily concerned with the a -axis parameter, in a plane normal to the hexagonal c -axis. Based on results of previous LDA calculations and Raman spectroscopic studies, we propose that the structural collapse is due to transformation into a new metastable polymorph (δ -Ge₃N₄) that has a unit-cell symmetry based upon $P3$, that is related to the low-pressure β -Ge₃N₄ phase by concerted displacements of N atoms away from special symmetry sites in the plane normal to the c -axis. No such transformation occurs for α -Ge₃N₄, due to the different stacking of linked GeN₄ layers. All three polymorphs (α -, β - and δ -Ge₃N₄) are based on tetrahedrally coordinated Ge atoms, unlike the spinel-structured γ -Ge₃N₄ phase, that contains octahedrally coordinated Ge⁴⁺. Experimentally determined bulk modulus values for α -Ge₃N₄ ($K_0 = 165(10)$ GPa, $K_0' = 3.7(4)$) and β -Ge₃N₄ ($K_0 = 185(7)$ GPa, $K_0' = 4.4(5)$) are in excellent agreement with theoretical predictions. The bulk modulus for the new δ -Ge₃N₄ polymorph is only determined above the β - δ transition pressure ($P = 24$ GPa); $K = 161(20)$ GPa, assuming $K' = 4$. Above 45 GPa, both α - and δ -Ge₃N₄ polymorphs become amorphous, as determined by X-ray diffraction and Raman scattering.

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1. Introduction

There has been renewed interest in studies of the polymorphism in Si and Ge nitrides since the discovery of new dense phases formed under high-pressure–high-temperature conditions [1–3]. Si₃N₄ and Ge₃N₄ show identical polymorphism at low pressure. Each compound gives rise to a trigonal α -phase ($P6_3$, with $Z = 4$) (Fig. 1a). This is considered to be a high-temperature form that exists metastably at ambient conditions, that may contain intrinsic defects or even chemical impurities [4,5]. The β -polymorph ($P6_3/m$; $Z = 2$), that is considered to be the thermodynamically stable form at low temperatures, has a structure related to that of phenacite

(BeSi₂O₄) or willemite (Zn₂SiO₄) (Fig. 1b). Recently, a new dense spinel-structured polymorph that is stabilized at high pressure ($P > 10$ –15 GPa) has been described for both nitrides (γ -Si₃N₄, γ -Ge₃N₄) [1–3]. A new spinel-structured binary nitride Sn₃N₄ has also been described recently, following chemical synthesis at low pressure [6]. In the case of Si and Ge nitrides, the γ -phase is obtained by heating the α - or β -forms to $T > 1000$ –1500 K at high pressure, or by reacting the elements (Ge, Si) with N₂ under high P – T conditions. In all cases, the new spinel-structured forms are recovered metastably to ambient conditions upon decompression, and they reveal interesting and potentially useful material properties of high hardness and wide optical bandgaps [7,8]. Powdered forms of the new materials can be obtained in large quantities via shock wave synthesis [9]. Recent work has now shown that new oxynitride “SiAlON” spinels can be formed by high P – T treatment of β' Si_{6–z}Al_zO₂N_{8–z} materials [10], and also that new

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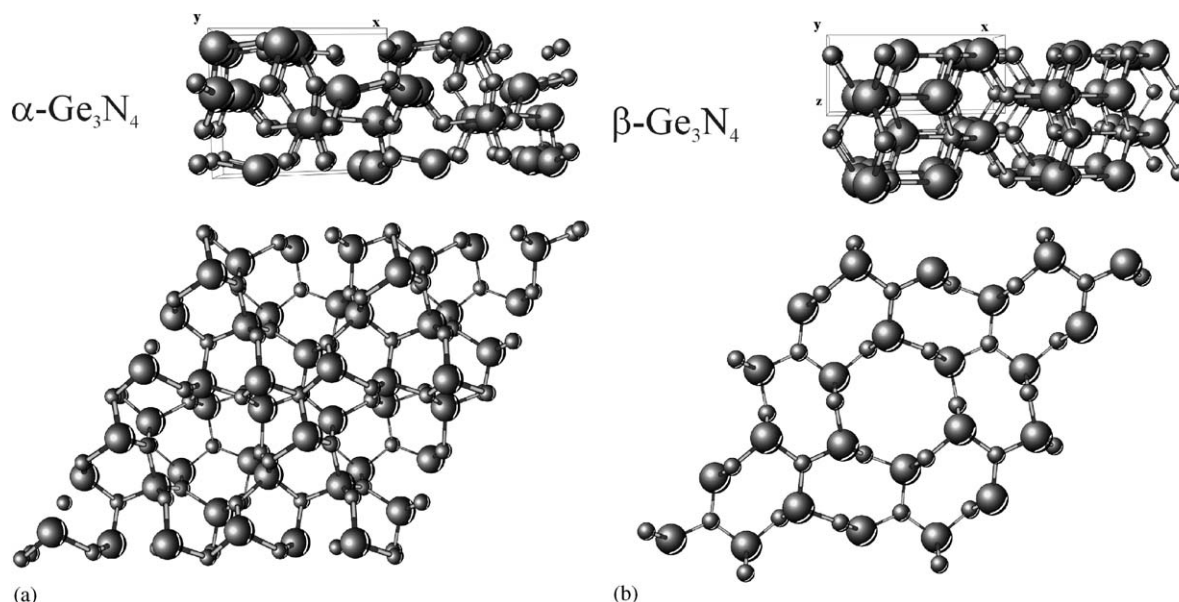


Fig. 1. (a) Projections of the structure of α - Ge_3N_4 and (b) β - Ge_3N_4 . The small spheres represent the N atoms and the large spheres represent the Ge atoms. In each case, the bottom drawing is a projection along the c -axis, and the top drawing is perpendicular to c . The structures of the α - and the β -phases are related as follows: In the β -phase the layers of GeN_4 tetrahedra are connected by three-coordinated N atoms within the plane and form a stacking along with c -axis with a two-layer repeat pattern (i.e., A–B). The α -phase has the same layer pattern, but subsequent layers are rotated by 180° , resulting in a four-layer repeat (i.e., A–B–A'–B'). The channels that are present along the c -axis in the β - Ge_3N_4 structure are thus absent in α - Ge_3N_4 . All the N atoms in β - Ge_3N_4 are in planar triangular coordination to Ge; however, in the α -phase, the N atoms are slightly moved out of the plane of the triangle.

mixed-metal ternary nitride spinels like GeSi_2N_4 can exist. This compound is unusual, in that the “smaller” Si^{4+} cations occupy the octahedral sites, and “larger” Ge^{4+} ions are tetrahedrally coordinated [11,12]. This result can be understood by local bond valence systematics around the anion (N^{3-}) sites within the structure [12].

The α - and β -forms of Si_3N_4 and Ge_3N_4 contain tetrahedrally coordinated Si and Ge, and the nitrogen atoms occupy trigonal planar or near-planar three-coordinated sites. The new high-density spinel structures contain Si and Ge in both octahedral and tetrahedral coordination to nitrogen, and the N atoms are four-coordinated. γ - Ge_3N_4 is the only solid state compound to date that contains Ge in octahedral coordination to nitrogen: γ - Si_3N_4 is only the second example of an SiN_6 -containing material, along with the newly synthesised compound $\text{Ce}_{16}\text{Si}_{15}\text{O}_6\text{N}_{32}$ [13].

Here we have investigated the polymorphism that occurs in β - Ge_3N_4 during metastable compression at ambient temperature, using a combination of energy-dispersive (ED) and high-resolution angle-dispersive (AD) X-ray diffraction of powdered materials. Experiments were carried out at the US National Synchrotron Light Source (Brookhaven, Long Island), at the superconducting wiggler beamline X-17C, and at Daresbury SRS (superconducting wiggler station 9.1). The angular X-ray diffraction studies of the compression pathway were initiated following a recent ab initio (LDA) calculation of the metastable phase relations [14], and

a study of room temperature compression mechanisms in β - Ge_3N_4 by Raman scattering spectroscopy [15].

Our initial studies of this material was motivated by room-temperature compression experiments carried out on β - Ge_3N_4 , that showed a loss of diffraction intensity above $P=17$ – 22 GPa (Fig. 2a). That observation led to the subsequent high-pressure–high-temperature synthesis of γ - Ge_3N_4 spinel [3,16]. That result was confirmed by laboratory high P – T synthesis of γ - Ge_3N_4 using a multi-anvil device, followed by Rietveld analysis of high-resolution laboratory-based X-ray powder diffraction data [3]. In a later ED synchrotron run, we found that diffraction peaks from metastably compressed β - Ge_3N_4 could be followed to $P=40$ GPa, although the character of the pattern changed above $P=20$ GPa (Fig. 2b) [3]. Here, we analyze the variation in unit-cell parameters obtained from these ED synchrotron runs, along with new AD diffraction data. The $V(P)$ plots reveal a large density decrease (5–7%) occurring at $P=20$ – 24 GPa, consistent with the occurrence of a phase transition in metastably compressed β - Ge_3N_4 , that is also indicated by ab initio calculations and Raman spectroscopy [14,15].

Following our initial experimental observations, Dong et al. [14] performed ab initio density functional calculations within the LDA to examine the polymorphism that might occur within β - Ge_3N_4 compressed at low T . They concluded that metastable phase transitions should be expected within the pressure range $P=20$ – 30 GPa, involving N atom displacements away

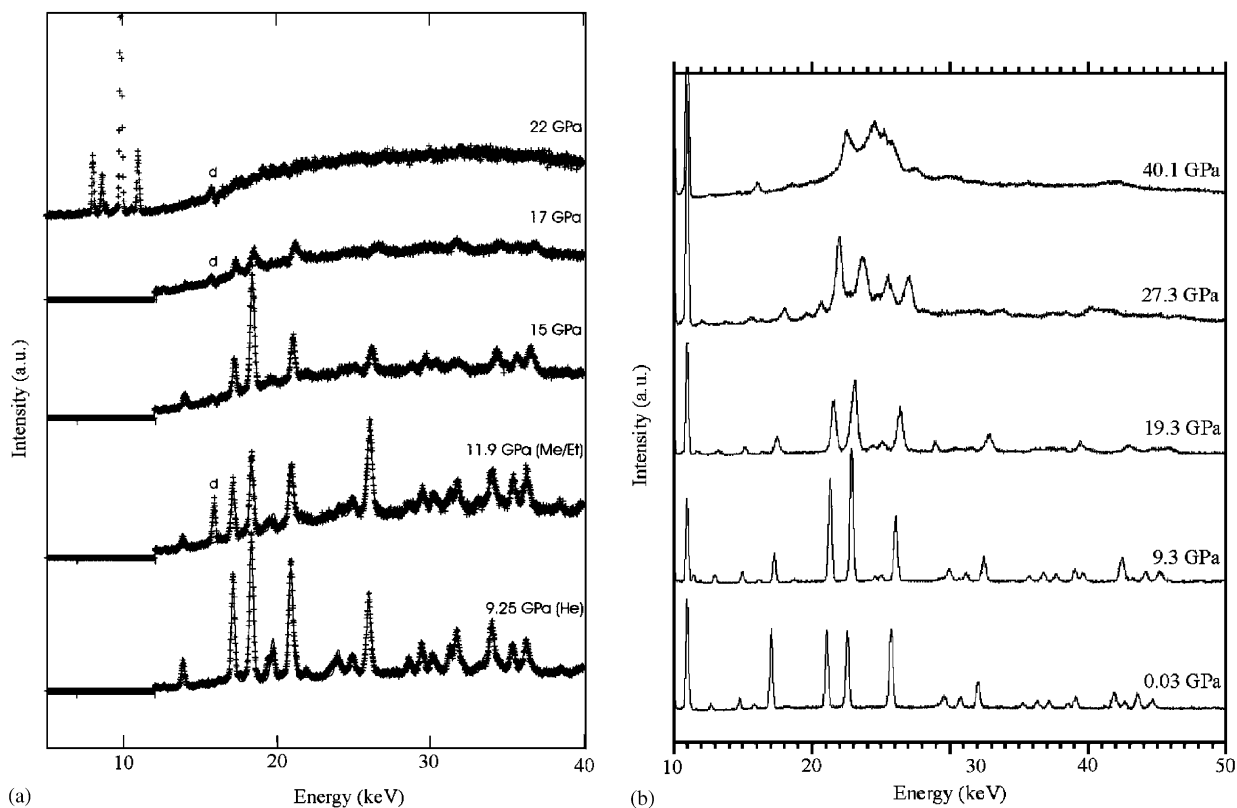


Fig. 2. (a) Energy dispersive X-ray diffraction patterns of β - Ge_3N_4 during compression, collected at Brookhaven NSLS (X-17C). The diffraction angle was 15° (2θ). The intense sharp peaks near 10 keV correspond to Ge fluorescence lines: they have been removed from all but the 22 GPa spectrum for clarity, but they appear unchanged in all spectra. The small peak marked “d” is due to the diamond anvils. (b) ED XRD patterns of β - Ge_3N_4 upon compression. These data were collected during a subsequent visit to Brookhaven NSLS (X-17C) [3]. The diffraction angle was $2\theta = 12^\circ$. Here, crystalline diffraction patterns could be obtained up to 40 GPa, although the peaks became broadened at high pressure.

from special symmetry positions within the $P6_3/m$ structure. The results were first analyzed in terms of displacement patterns considering all unit cells in phase; i.e., Γ point ($q=0$) instabilities. Two second-order phase transitions were predicted to occur, at 20 and 28 GPa, that reduced the symmetry first from $P6_3/m$ to $P\bar{6}$, and then to $P3$ (Fig. 3). The $E(V)$ curve showed inflection points at these pressures. We recently studied the metastable transitions in β - Ge_3N_4 by Raman scattering spectroscopy. The data confirm that a phase transition occurs at $P=20$ GPa. The number of peaks observed at pressures above the transition greatly exceeds that expected for the $P\bar{6}$ structure, but they correspond generally to those predicted for the $P3$ structure. We concluded that the $P6_3/m$ - $P3$ transition had occurred directly in a first-order manner, bypassing the predicted intermediate $P\bar{6}$ phase. In the theoretical study, it had already been recognized that the $P6_3/m$ - $P3$ transition could occur directly via a first-order process, at a predicted transition pressure $P_{\text{tr}} \sim 23$ GPa, because the calculated energy barrier for the first order β - δ transition was small, on the order of 0.01 eV/atom (10.6 kJ/mol) (Fig. 3). The transition pressure corresponds to the common tangent between the minima on

the calculated $E(V)$ curve. We have termed the new “post-phenacite” phase δ - Ge_3N_4 , to distinguish it from previously known α -, β - and γ -polymorphs [15].

In the present work, we have continued our investigation of the metastable compressional behavior of both β - and α - Ge_3N_4 polymorphs, using synchrotron X-ray diffraction techniques in the diamond anvil cell, using three different pressure-transmitting media (He, Ar and 4:1 methanol-ethanol mixtures). We report analyses of the ED data to obtain unit-cell volumes for pure β - Ge_3N_4 , and to demonstrate the onset of the phase transition. The AD technique gives much higher resolution than energy-dispersive studies, so that accurate cell parameters can be determined as a function of pressure through the transition. We carried out the AD study using a mixture of α - and β - Ge_3N_4 phases, allowing their compressional behavior to be compared. The behavior of the β - Ge_3N_4 polymorph in the mixture is calibrated against the refined data for the pure phase obtained in our previous runs, and is shown to be identical. The AD XRD method permits the diffraction features from the α - and β - Ge_3N_4 phases to be clearly identified and distinguished within the sample, so that their cell parameters can be refined independently. The

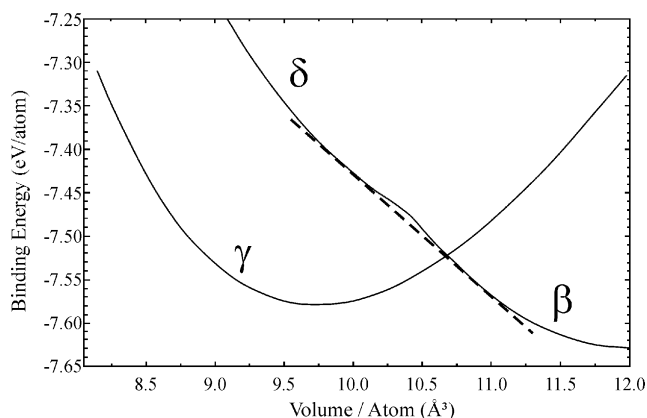


Fig. 3. Diagram reconstructed from Dong et al. [14], showing the binding energies of the β - and γ (spinel)-forms of Ge_3N_4 as a function of volume (on a per atom basis). The curve for $\beta\text{-Ge}_3\text{N}_4$ deviates from the expected parabolic behavior due to the concerted displacement of N atoms from their trigonal planar sites. In the original work it was suggested that the polymorph should undergo a sequence of two second-order phase transitions to cause the symmetry to change from $P6_3/m-P6-P3$. However, the $P6_3/m-P3$ transformation could also occur via a first-order transition, at the common tangent to the minima in the $E(V)$ curve, to give a new high pressure $\delta\text{-Ge}_3\text{N}_4$ polymorph. This is the case indicated by a recent Raman scattering study of the phase transition [15]. The slope of the common tangent connecting the two extrema generated by changes in curvature of the $E(V)$ relation gives a calculated value $P_{\text{theory}}=23$ GPa for the $\beta\text{-}\delta$ transition pressure [14].

AD technique also permits to identify occasional diffraction features that result from random crystallites still present in samples at high pressure. The crystallites are not part of the diffraction from the bulk of the sample, although they are incorporated into the ED XRD patterns. This discrimination is important in studying the onset of amorphization in the Ge_3N_4 materials at very high pressure.

2. Experimental

The Ge_3N_4 samples used in the experiments were originally obtained from Aldrich[®] (44,755-2) in >99.99% chemical purity. X-ray diffraction indicated that a mixture of α - and β - Ge_3N_4 phases (approximately 1:2) was present (Fig. 4). That material was used for the AD diffraction experiments carried out at SRS Daresbury. Samples of nearly pure $\beta\text{-Ge}_3\text{N}_4$ polymorph (usually containing 1–3% of elemental Ge) for the Brookhaven ED runs were obtained by treating the mixture at 8 GPa and 900°C in a multi-anvil device. For all AD runs and one later series of ED runs, aliquots of the germanium nitride samples were pressed into discs ($\sim 2\text{--}3\ \mu\text{m}$ thick, 40 μm across), and loaded into the sample chambers of (a) Mao-Bell (Brookhaven runs) or (b) cylindrical diamond anvil cells (Daresbury). In early Brookhaven runs, the $\beta\text{-Ge}_3\text{N}_4$ sample was loaded as a

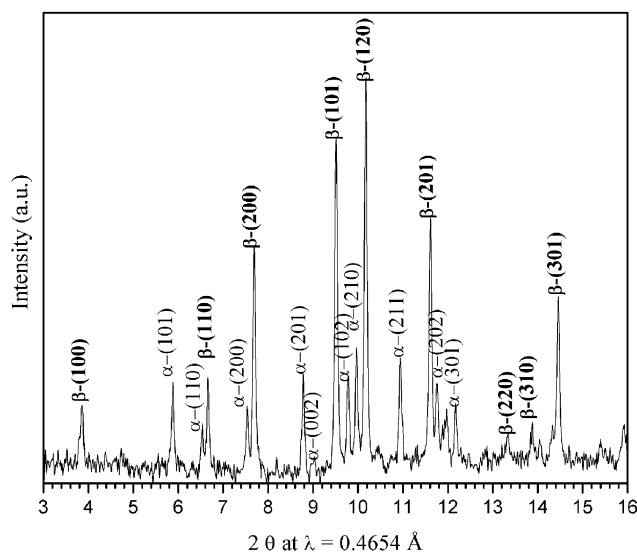


Fig. 4. X-ray diffraction pattern of the germanium nitride starting material used in the AD study, taken at the SRS 9.1 beamline station outside the DAC. The sample consisted of a 2:1 mixture of $\alpha\text{-Ge}_3\text{N}_4$ and $\beta\text{-Ge}_3\text{N}_4$. Peaks for the two phases are indexed in the pattern.

powder with sintered grains into the sample chamber of the DAC. For the first series of ED runs, He was loaded under pressure as a pressure medium, using the gas loading apparatus at the Geophysical Laboratory (Washington, DC). A second set of loadings were carried out using 4:1 methanol:ethanol mixture. A final series of ED experiments were carried out in Ar, loaded cryogenically into the cell. Further details of the DAC loading for the Brookhaven runs were described previously [1–3]. For the Daresbury runs, the diamonds had 300 μm culet diamonds. A 250 μm -thick tungsten gasket was pre-indented to 30 μm . Tungsten was used as a gasket material for its strong X-ray absorption, thus minimizing the diffraction from the gasket that might interfere with the sample diffraction pattern in the AD experiment. Furthermore, tungsten is a *bcc* structured metal that shows only a single strong diffraction line. In most experiments, the sample signal was strong and no signal from the gasket was observed (Figs. 5 and 6). At higher pressures, the sample signal became much weaker, but the gasket line did not interfere with the diffraction pattern of the sample, in the region of interest (Fig. 6).

The pressure medium used in the AD runs was a 4:1 methanol/ethanol mixture that remains fluid and provides a hydrostatic environment to approximately 10 GPa. Although it solidifies above this pressure, it remains much softer than the ceramic nitrides studied here, so that non-hydrostatic effects induced by the pressure medium are not expected to influence the results. In our previous ED runs at Brookhaven, data were collected using He, Ar, and 4:1 methanol/ethanol

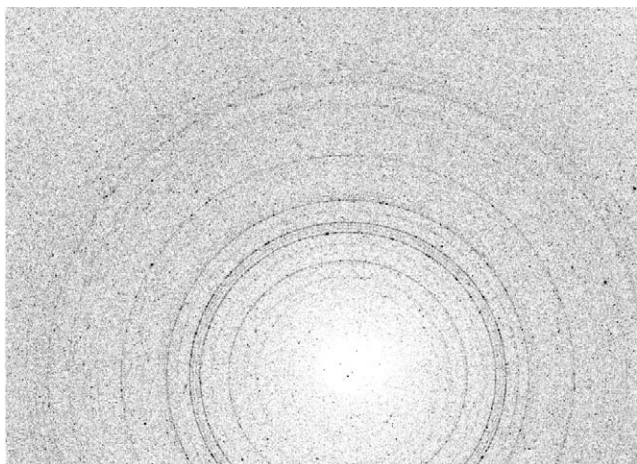


Fig. 5. A typical 2D angle-dispersive diffraction pattern obtained for germanium nitride samples at high pressure in the DAC. The pattern shown here was obtained at $P=12$ GPa, where both α - and β - Ge_3N_4 are present as crystalline phases. The diffraction rings are due to both polymorphs. The diffraction rings for the α - Ge_3N_4 phase are slightly less “spotty”, indicating that phase has a smaller grain size, and is distributed homogeneously throughout the sample.

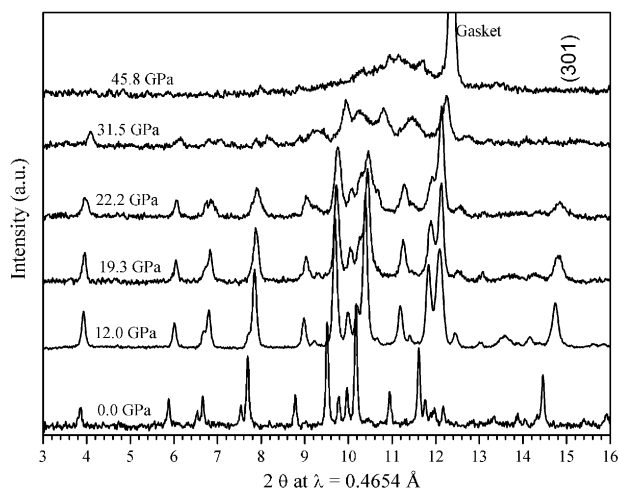


Fig. 6. Integrated 1-D X-ray diffraction patterns of germanium nitride in the diamond anvil cell upon increasing pressure from room pressure up to $P=46$ GPa. The strong peak just above 12° is due to the tungsten gasket. Up to $P=32$ GPa, all peaks can be indexed to the crystalline α - or β - δ - Ge_3N_4 polymorphs. The diffraction peaks of the crystalline phases broaden with increasing pressure to finally show an amorphous pattern at the highest pressures (see text and Fig. 9).

mixture as pressure media. No systematic differences in behavior of the samples or derived compressibility values could be distinguished between data obtained using different pressure media, or between “pure” and “mixed-phase” (β - + α -phase) samples.

Pressure was measured by ruby fluorescence, using several grains distributed throughout the cell. The pressure gradient within the medium never exceeded

10% of the average pressure, and was generally less than 5%, as determined by recording pressures from several different ruby grains within the sample chamber, even at the highest pressures. In fact, in such experiments on polycrystalline samples, the main deviations from a hydrostatic pressurization environment occur because of grain–grain contacts. In a multi-phase assemblage, such as that studied here, a phase transition occurring in one phase can be detected in the mechanical response of the other phase. In fact, the high resolution of the AD XRD data permitted us to observe such subtle effects in the α -/ β - Ge_3N_4 mixture studied here, and this observation is discussed within the text.

Angle-dispersive X-ray diffraction patterns were obtained using monochromatic radiation ($\lambda = 0.4654 \text{ \AA}$) at beamline 9.1 at the UK synchrotron radiation source (SRS) at Daresbury. The X rays incident on the sample were collimated and defined by a $75 \mu\text{m}$ diameter pinhole placed in front of the cell. Diffraction patterns were collected using an image plate detector. Integration of the 2-D data was performed using the software EDIPUS, that was made available to us by R.J. Nelmes and M. McMahon (University of Edinburgh). This software package was developed by the Edinburgh group for integration of 2-D AD XRD data sets, and it has been used extensively in their many crystallographic studies of materials at high pressure [17,18]. A typical 2-D data set for a polycrystalline sample taken within the cell is shown in Fig. 5. The patterns were first corrected for the spatial distortion of the image plate and image plate reader and then integrated around the rings. The resulting 1-D spectra were calibrated using the integrated pattern of a Zr foil standard collected in the same conditions (Fig. 6).

The energy-dispersive data were obtained at the US NSLS facility at Brookhaven, Long Island, at station X-17C. The initial data sets were collected, using He or 4:1 MeOH/EtOH pressure medium, at a scattering angle $2\theta = 15^\circ$ (Fig. 2a). The third data set was collected at a scattering angle $2\theta = 12^\circ$, using an Ar pressure medium (Fig. 2b) [3,19]. The ED data were fitted using the LeBail extraction technique. The background due to Compton scattering from the diamonds was subtracted manually, then lattice parameters and peak shapes were refined [3]. In the LeBail extraction procedure, the structure is not considered explicitly, but peaks are placed at each of the diffracting energies and the peak intensity and shape are fitted at that position. This allows lattice parameters to be extracted with good precision when structural information cannot easily be obtained, as is the case in ED studies, and it eliminates the need for the arbitrary removal of spurious peaks, because of the high degree of redundancy of the fit for high-symmetry materials (i.e., generally >15 peaks were reliably fit in the present study, for only two lattice parameters (a and c), that were combined to yield the volume).

3. Results and discussion

The combined $V(P)$ data for β - Ge_3N_4 from all data sets are shown in Fig. 7. The first two ED runs were performed in helium (9–14 GPa) and in 4:1 methanol–ethanol pressure media (0.5–26 GPa). In the MeOH–EtOH runs, no sharp peaks were observed above 17 GPa because of a combination of small sample size and low density (the sample was not pressed into a pellet, but used as sintered grains) and an extreme weakening of the spectrum compared with the Compton background (Fig. 2a). In a subsequent run using a pelletized sample of pure β - Ge_3N_4 in an argon pressure medium, diffraction peaks were observed up to 40 GPa (Fig. 2b). In that run, there was a rapid decrease in volume (~ 5 –7%) between $P=22$ and 23 GPa (Fig. 7a). The volume drop indicates the occurrence of a large structural change in the material, and it is most likely associated with a phase transition. Due to the weakening of the ED spectrum above 15–17 GPa, coupled with the possible presence of spurious reflections from untransformed regions of the sample, the detailed behavior of c and a parameters throughout the transition could not be resolved from the data.

In order to study the phase transition in greater detail, we performed the experiment using high-resolution angular dispersive experiments (Figs. 5 and 6). Refined $V(P)$ values from the AD data set for β - Ge_3N_4 are combined with the ED data in Fig. 7. Both the low-pressure compressional data and the occurrence of a phase transition associated with a 5–7% volume drop between 22 and 24 GPa were reproduced in both types of experiment, using three different pressure-transmitting media, for all samples.

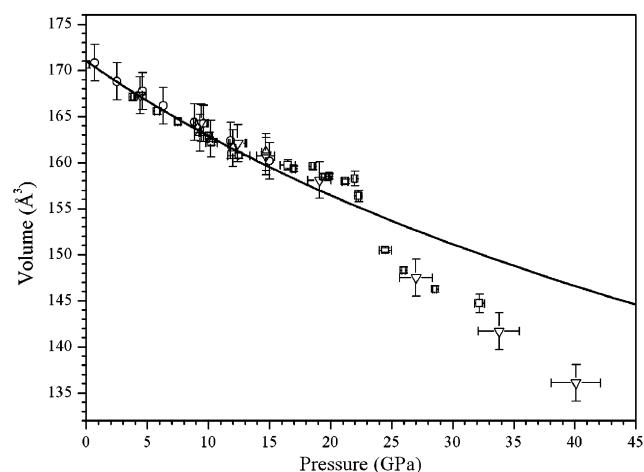


Fig. 7. Unit-cell volumes of β - Ge_3N_4 as a function of pressure, using data taken from a compilation of ED and AD runs, for three pressure-transmitting media (He: triangles; MeOH/EtOH: circles—ED and squares—AD; and Ar: inverted triangles), and for pure β - Ge_3N_4 (ED) and “mixed phase” α/β - Ge_3N_4 (AD) samples. The solid line shows the $V(P)$ relation determined from fitting the data below the phase transition region to a third-order Birch–Murnaghan equation of state.

The AD experiments were carried out for a mixture of α - and β - Ge_3N_4 . Because of the differences in space group symmetry and lattice parameters between the two structures, and also the high resolution of the AD technique, peaks from the α - and β -phases were clearly distinguished within both the 2-D and the integrated 1-D diffraction patterns (Figs. 4–6), and the lattice parameters of the two phases could be fitted independently. In particular, the fitting procedure systematically rejected any peak overlap between both phases in order to prevent any wrong assignments and resulting error in the fit. Comparison of the β - Ge_3N_4 data between the AD and ED studies allowed us to determine that no changes in the $V(P)$ behavior occurred because of the mixed-phase nature of the sample. The AD study of the mixed-phase sample allowed us to compare the compressional behavior of α - and β - Ge_3N_4 .

We begin with a discussion of α - Ge_3N_4 . The variation in the unit-cell volume of α - Ge_3N_4 as a function of pressure is presented in Fig. 8. Below $P=15$ GPa, the $V(P)$ data show a regular decrease that can be fitted by a third-order Birch–Murnaghan equation of state. To obtain values for the zero pressure bulk modulus (K_0) and its pressure derivative K' , we used normalized pressure (f) and Eulerian strain (f) variables defined by

$$f = \frac{1}{2} \left[\left(\frac{V}{V_0} \right)^{-2/3} - 1 \right]$$

and

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

We excluded points above 15 GPa from the fit, because the $V(P)$ relation behaves anomalously in this region

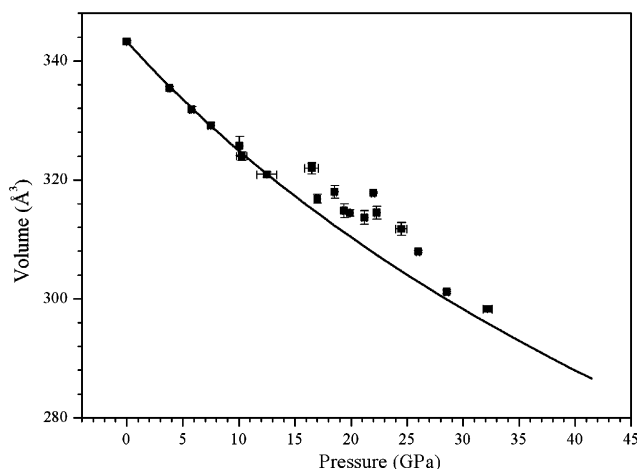


Fig. 8. Unit-cell volumes of α - Ge_3N_4 as a function of pressure, using data taken from the AD runs, using the “mixed phase” α/β - Ge_3N_4 sample, in a 4:1 MeOH/EtOH pressure-transmitting medium. The solid line shows the $V(P)$ relation determined from fitting the data below 15 GPa to a third-order Birch–Murnaghan equation of state.

(see below). The F - f plot is nearly a horizontal line, indicating that K' must lie close to 4 (note that the error bars become larger to lower pressure, as the volume approaches the V_o value that acts as the reference in the normalised plot) (Fig. 10a). In a first estimate, we assumed $K_0' = 4$ (thus truncating the Birch–Murnaghan EoS at second order): this yielded $K_0 = 163(2)$ GPa. A least squares fit to the data set yielded $K_0 = 165(10)$ GPa, for a fitted value of $K_0' = 3.7(4)$. These values are in

Table 1

Experimental and theoretical (LDA) bulk moduli (K) and pressure derivatives (K') for the α -, β -, γ - and δ -phases of germanium nitride

Phase	Measured K (GPa)	Measured K'	Theoretical K (GPa) ¹¹	Calculated K' ¹¹
α -Ge ₃ N ₄	165(10) ^a	3.7(4) ^a	178	2.1
β -Ge ₃ N ₄	185(7)	4.4(5)	185	3.7
δ -Ge ₃ N ₄	161(20) ^b	4 ^c	—	—
γ -Ge ₃ N ₄	296(4) ²	4.0	240	4.5

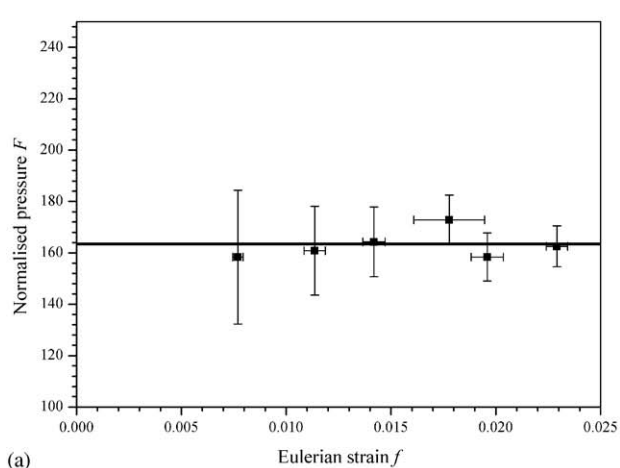
^a K_o , K_o' at $P = 1$ atm.

^b K at $P = 25$ GPa.

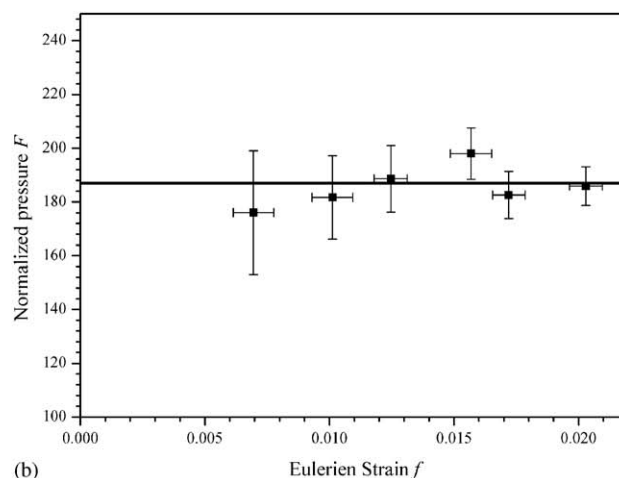
^c Assumed value.

excellent agreement with theoretical predictions [14] (Table 1). Substantial broadening of the α -Ge₃N₄ diffraction peaks was observed above $P = 30$ GPa, and the diffraction peaks of α -Ge₃N₄ can no longer be distinguished from a broad amorphous above $P \sim 35$ –40 GPa (Figs. 6 and 9).

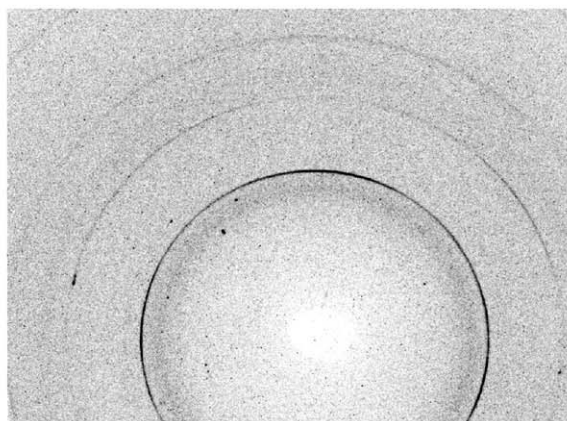
The $V(P)$ data for α -Ge₃N₄ exhibit a slight “upward bulge” in the 15–25 GPa region, indicating volumes that are slightly larger (1–2%) than the normal compressibility trend. We can suggest several possible origins for this feature. First, it could be thought to be due to “stiffening” of the methanol–ethanol pressure medium above 10 GPa. However, this is unlikely because the onset of the “upturn” in $V(P)$ occurs approximately 5 GPa above the solidification of the pressure medium (see also discussion below for β -Ge₃N₄). Second, a structural transformation might occur within the α -Ge₃N₄ phase, which could be analogous to the β - δ phase transition described for β -Ge₃N₄ (below). However, the mechanical weakening and subsequent “hardening” visible in Fig. 8 bring the $V(P)$ relation back to the low pressure trend by 25 GPa: also, the a/c



(a)



(b)



(c)

Fig. 9. AD (2-D) diffraction pattern of a Ge₃N₄ sample compressed to $P = 47$ GPa. Diffraction from the sample is now characterized by diffuse amorphous rings, indicating “pressure-induced amorphization” has occurred. Only weak spots indicate the presence of a few remaining grains of crystalline material. The strong sharp ring observed in the pattern is due to the tungsten gasket.

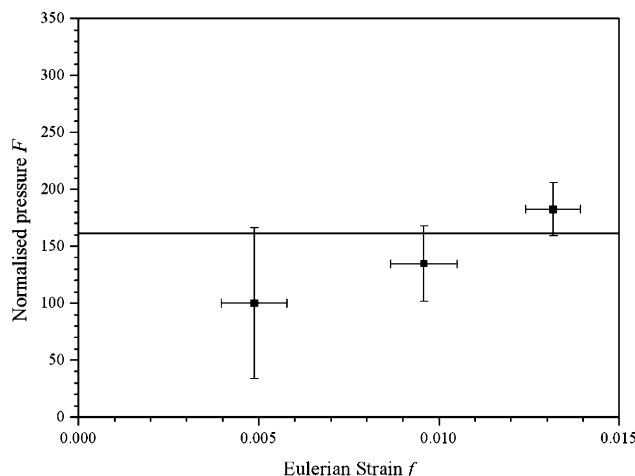


Fig. 10. Normalized pressure (F) versus Eulerian strain (f) relations for (a) α - Ge_3N_4 ; (b) β - Ge_3N_4 ; (c) δ - Ge_3N_4 . These fits permit estimation of the bulk modulus (K_0 , or $K_{25 \text{ GPa}}$, for δ - Ge_3N_4), and its pressure derivative (K') for the Ge_3N_4 polymorphs (see Table 1).

ratio does not show the same behavior across the transformation region as does that for β/δ - Ge_3N_4 (see also below). However, the observation of the anomalous $V(P)$ data indicate that the high-pressure behavior of α - Ge_3N_4 might require further investigation. Our preferred interpretation is that the α - Ge_3N_4 sample is sensitive to the β - δ transition occurring within the β - Ge_3N_4 sample, in which it is embedded as a minority component. There is a 5–7% volume reduction associated with the β/δ phase transformation, along with an onset of mechanical weakening within the β - Ge_3N_4 polymorph above $P=15$ GPa. The α - Ge_3N_4 phase will thus experience a reduction in external (pressure) constraints, and may relax its volume to a larger value than expected from the intrinsic compressibility relation. When the first-order β - δ transition is completed within the “matrix” majority phase, the α - Ge_3N_4 polymorph will again experience the full pressure from the external pressurization medium, and its $V(P)$ relation returns to the low-pressure curve (Fig. 8).

The variations with pressure of the β - Ge_3N_4 cell volume and lattice parameters are quite different to those recorded for α - Ge_3N_4 (Figs. 7, 8). A previous study by Raman spectroscopy clearly indicated that a phase transition occurs within the sample at $P=20$ – 22 GPa, and that some mechanical weakening associated with phonon mode broadening and loss of Raman intensity may be present above $P=15$ GPa [15]. This is consistent with results of previous ab initio (LDA) calculations, that indicate that a sequence of $P6_3/m-P6-P3$, or a direct first-order $P6_3/m-P3$ transition, might occur in the 20–25 GPa range. The Raman spectroscopic results indicated that the latter possibility was more likely, during ambient temperature compression [14,15]. The changes observed in the X-ray diffraction patterns

and the $V(P)$ plots, from both the ED and AD XRD studies, confirm the occurrence of a phase transition that is associated with a 5–7% volume decrease, above $P=22$ GPa. There is a smooth decrease in the cell volume up to $P=15$ GPa, that permits the bulk modulus of the low pressure β - Ge_3N_4 polymorph to be estimated. A reduced variable F - f plot was constructed, as for α - Ge_3N_4 , using the determined $V(P)$ data and the zero-pressure volume V_0 (Fig. 10b). The second-order Birch–Murnaghan solution with $K'=4$ is shown as a horizontal line on the plot. This assumption gave $K_0=187(6)$ GPa. A third-order Birch–Murnaghan fit gave $K_0=185(10)$ GPa, for a fitted $K'_0=4.4(5)$. These values are again in excellent agreement with ab initio calculations [14,20,21] (Table 1). Between 21 and 23 GPa, there is a large (5–7%) drop in the volume, that is not observed for the α - Ge_3N_4 phase (Figs. 7 and 8). This volume drop occurs for both the ED data obtained for the pure β - Ge_3N_4 phase, and in the AD runs on the mixed α - and β -containing sample (Fig. 7). During a recent Raman study of metastably compressed β - Ge_3N_4 , we observed a large number of new peaks appearing in the spectrum above $P=21$ GPa, that signalled a phase transition occurring into a newly-described δ - Ge_3N_4 polymorph [15]. From the observed Raman data compared with predictions from our previous theoretical studies, we concluded that the high-pressure phase had $P3$ symmetry, with a structure related to β - Ge_3N_4 by small displacements of the N atoms [14,15]. We propose that the volume drop observed for β - Ge_3N_4 here is associated with the β - δ phase transition.

The predicted X-ray diffraction pattern for the δ - Ge_3N_4 phase differs only slightly from that of β - Ge_3N_4 (Fig. 11). The main difference is the increased intensity of the (111) reflection, near $2\theta=11.4^\circ$ (at $\lambda=0.4654 \text{ \AA}$). However, that peak coincides with a

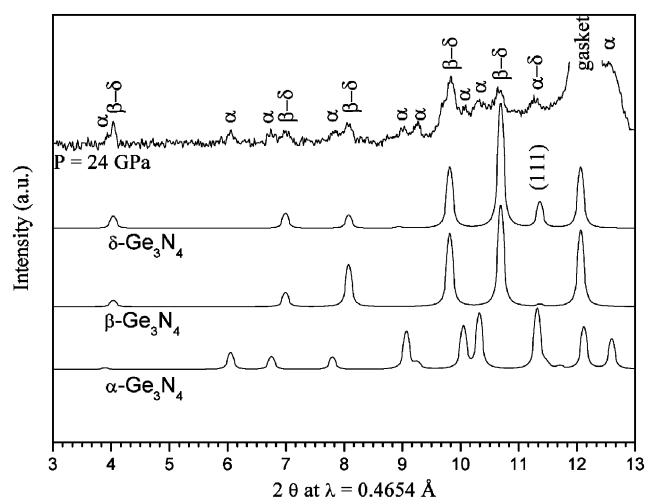


Fig. 11. Calculated X-ray diffraction patterns of α -, β - ($P6_3/m$) and δ - Ge_3N_4 ($P3$) at 24–25 GPa, compared with an observed pattern in the same pressure range.

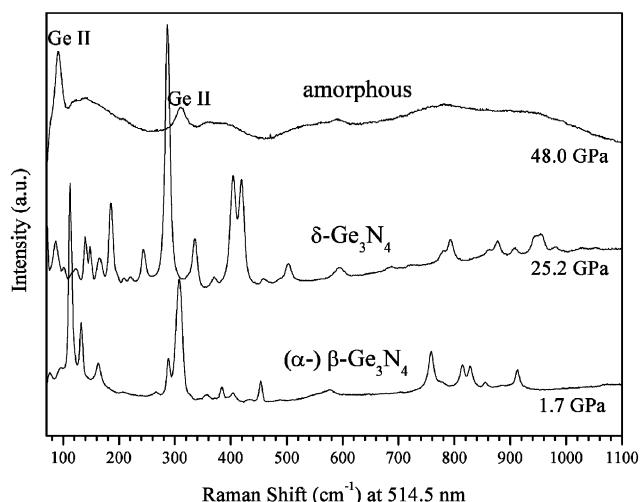


Fig. 12. Raman spectra of Ge_3N_4 at high pressure. The low-pressure spectrum contains peaks mainly from the β -phases, but some features from the α -phase are present, along with a peak near 300 cm^{-1} due to elemental Ge (this disappears above 8–10 GPa due to the Ge-I/II transition) because of the very weak scattering from the metallic Ge-II. The pattern at $P=25$ GPa is quite different and contains many more Raman peaks, due to the transformation into the $\delta\text{-Ge}_3\text{N}_4$ phase [15]. The pattern obtained at 48 GPa indicates complete amorphization of the sample, because of the broad bands observed in the spectrum. The sharp crystalline features present at low wavenumber are attributed to the high-pressure phase of elemental germanium (Ge-II), that was present as an impurity within the starting material. The Ge-II lines now appear strong, because of the broadening and weakening of the amorphous Ge_3N_4 pattern.

reflection from the $\alpha\text{-Ge}_3\text{N}_4$ phase present within the sample studied by angle-dispersive techniques (Fig. 11). However, by 25 GPa, the Raman spectra show clearly that the $\beta\text{-Ge}_3\text{N}_4$ sample has transformed completely into $\delta\text{-Ge}_3\text{N}_4$ (Fig. 12). The X-ray pattern then consists of peaks from $\delta\text{-Ge}_3\text{N}_4$, most of which are common to reflections of the pressure $\beta\text{-Ge}_3\text{N}_4$ phase, but one of which coincides with a peak of $\alpha\text{-Ge}_3\text{N}_4$, that coexists with the $\delta\text{-Ge}_3\text{N}_4$ in the sample that does not undergo any analogous phase transition (Fig. 11).

Just below the transition, beginning at $P\sim 15$ GPa, the $V(P)$ data for $\beta\text{-Ge}_3\text{N}_4$ show a slight upward deviation from the compressibility curve. A similar effect was observed for $\alpha\text{-Ge}_3\text{N}_4$. This effect is not due to the pressure medium, because it was observed in ED and AD data for samples pressurized in MeOH/EtOH and in argon, for pure $\beta\text{-Ge}_3\text{N}_4$ and the $\alpha\text{-}\beta$ mixture. The difference with the $\alpha\text{-Ge}_3\text{N}_4$ data is that here the data do not return to the $V(P)$ curve of the low-pressure phase, following the transformation region. We propose that this is associated with mechanical weakening within the $\beta\text{-Ge}_3\text{N}_4$ sample premonitory to the $\beta\text{-}\delta$ transition. Although the $\beta\text{-}\delta$ ($P6_3/m\text{-}P3$) phase transformation is formally first order, it is closely linked to soft vibrational modes within the $\beta\text{-Ge}_3\text{N}_4$ sample, that begin to be manifested at lower pressure [14,15]. In the Raman

spectroscopic study, broadening and loss of intensity in Raman peaks began to be observed at $P\sim 15$ GPa, well below the transition [15]. This will result in a larger K' than expected within the $\beta\text{-Ge}_3\text{N}_4$ phase.

As the $\beta\text{-}\delta$ transition begins to occur, certain regions of the sample will occupy a 5–7% smaller volume than before. This will result in a positive volume relaxation in surrounding regions, that correspond to untransformed α - or $\beta\text{-Ge}_3\text{N}_4$. Once the transition is completed, above $P=24$ GPa, the $V(P)$ relation of the $\alpha\text{-Ge}_3\text{N}_4$ sample returns to that observed at low pressure. The $V(P)$ relation of the other phase corresponds to that of the $\delta\text{-Ge}_3\text{N}_4$ polymorph.

Using the data points between 24 and 37 GPa, we have fit the $V(P)$ data using a second-order Birch–Murnaghan EoS formalism, assuming $K'=4$, to obtain a bulk modulus estimate for the $\delta\text{-Ge}_3\text{N}_4$ polymorph as $K=161(20)$ GPa (note: this is a bulk modulus referred to a reference volume point at 24 GPa, i.e., $K_{24\text{ GPa}}$, rather than “ K_0 ”) (Fig. 10c). It is not strictly correct to extrapolate this value down to ambient pressure, nor to extrapolate that for $\beta\text{-Ge}_3\text{N}_4$ up to above the $\beta\text{-}\delta$ transition; although the transition is first order in nature, it is only slightly so, and mode softening that affects the compressibility occurs within the two phases, that cannot exist much above or below the transition pressure [14,15]. We do note that the bulk modulus of the high-pressure $\delta\text{-Ge}_3\text{N}_4$ phase is 15% smaller than that of the low-pressure $\beta\text{-Ge}_3\text{N}_4$ phase, close to that of the $\alpha\text{-Ge}_3\text{N}_4$ polymorph. Usually, we expect high-pressure, higher-density phases to have lower compressibility than their low-pressure, low-density counterparts. However, the $\delta\text{-Ge}_3\text{N}_4$ form is derived from $\beta\text{-Ge}_3\text{N}_4$ by relaxation of the N atom positions away from their special positions within the phenacite structure: this gives rise to additional degrees of freedom for structural relaxation during compression, and it is normal that the compressibility should be greater, and similar to that of $\alpha\text{-Ge}_3\text{N}_4$.

In order to record further crystallographic details and better define the nature of the phase transition, we also refined the a - and c -axis lattice parameters for the α -, β -, and $\delta\text{-Ge}_3\text{N}_4$ polymorphs, from our high-resolution AD data (Fig. 13). The $\alpha\text{-Ge}_3\text{N}_4$ data show a monotonic decrease with increasing pressure. The $c(P)$ values do show a small anomaly in the vicinity of the $\beta\text{-}\delta$ transformation; this can be analyzed as discussed above for the $V(P)$ relations. The data for $\beta\text{-Ge}_3\text{N}_4$ reveal a 2.5% reduction in the a -axis parameter at the transition pressure, that does not occur in the c dimension (Fig. 13b). This implies that the $\beta\text{-}\delta$ transition is associated with a contraction in the a -axis, or in the plane normal to c , that is consistent with the structural mechanism for the transformation suggested by the atomic displacement patterns obtained from ab initio calculations [14]. Both the a and c parameters

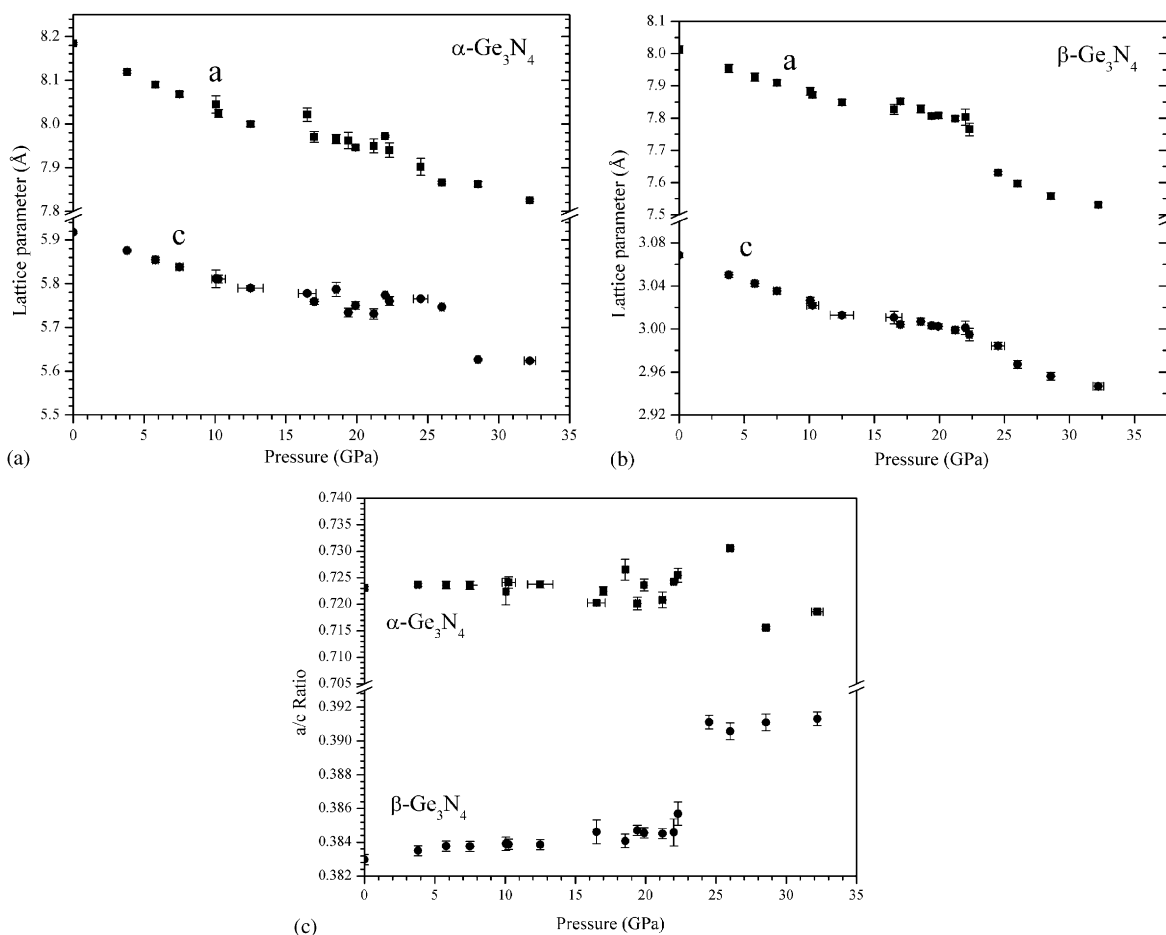


Fig. 13. (a) α - Ge_3N_4 lattice parameters as a function of pressure. Both the a -axis (full squares) and the c -axis (full circles) parameters decrease steadily as the pressure is increased. (b) β - Ge_3N_4 lattice parameter as a function of pressure, the a -axis (squares) shows a rapid decrease between 21 and 23 GPa associated with the β - δ transition, whereas the c -axis (full circles) decreases steadily with little change in this region as pressure increases; (c) cla ratio as a function of pressure for α - Ge_3N_4 (full squares) and β - Ge_3N_4 (full circles); the β - Ge_3N_4 cla ratio data show a jump at the transition pressure.

exhibit a slight “upturn” between 15 and 25 GPa, as has been discussed previously for the $V(P)$ data. To eliminate such “global” effects, we have plotted the a/c ratios for the α - and β -phases as a function of pressure through the transition region (Fig. 13c). That for the α - Ge_3N_4 polymorph carries across the transition without change: that for β - Ge_3N_4 jumps abruptly from 0.383 to 0.391 at the β - δ transition (i.e., $\sim 2\%$ change), marking the collapse in structural constraints normal to the c -axis.

The $V(P)$ and unit-cell axis data for metastably compressed β - Ge_3N_4 are consistent with the occurrence of a β - δ phase transition, as was recently observed by Raman spectroscopy [15]. In our previous theoretical study, it had been proposed that a sequence of second-order displacive phase transitions driven by zone center soft modes involving displacements of the N atoms away from special symmetry sites could occur within the structure, in a symmetry sequence $P6_3/m-P\bar{6}-P3$ [14]. In the experimental Raman scattering study, however, it was concluded that the $P6_3/m-P3$ (i.e., β - δ) transition

occurred directly, due to the number of peaks observed above the phase transition pressure. The phase transition was thus determined to be first order in character, because it was associated with greater than a single order parameter. However, it is likely that vibrational mode softening occurs within the β - Ge_3N_4 phase prior to the phase transition, reminiscent of the underlying second-order nature of the phase transition predicted at $q=0$ and $T=0$ K, that results in mechanical weakening of the sample at pressures below the phase transition, above $P=12$ –15 GPa. No soft vibrational modes were observed in the Raman study, but these are expected to be spectroscopically inactive [14]. In the Raman spectroscopic study, the characteristic peaks of the β - Ge_3N_4 phase did begin to broaden above 10–12 GPa, indicating the presence of dynamical disordering or mechanical weakening within the sample, prior to the phase transition at 20–22 GPa [15].

The X-ray data are thus consistent with the occurrence of a first-order β - δ phase transition in Ge_3N_4

upon compression. The $V(P)$ jump is completed within 2–3 GPa of the transition pressure, rather than spread out over 8–10 GPa, as would occur if two sequential second-order displacive phase changes were present instead. We conclude that the transition is first order in nature, in agreement with the Raman scattering study.

In the theoretical work, the soft modes were initially investigated at the Brillouin zone centre (Γ point). However, a previous calculation on related β - Si_3N_4 using empirically derived force constants had suggested that mode instabilities might also occur away from $q=0$, but parallel to the c -axis (i.e., along 00ζ) [22]. In subsequent LDA calculations, Dong et al. showed that no such (00ζ) mode softening occurred for β - Ge_3N_4 [14]. In our own Raman scattering study, most of the modes observed at high pressure could be accounted for within the $P3$ symmetry predicted for δ - Ge_3N_4 . However, a family of additional weak peaks were observed in the spectrum, that indicated the presence of a larger true unit-cell than expected, within perhaps a “disordered” or “incommensurate” structure, involving condensation of phonon modes away from the Γ point, or the involvement of some order–disorder process during pressurisation.

In the present study, we observed a large decrease in the a -axis parameter of Ge_3N_4 at the β – δ transition, but not in the c -parameter (Fig. 13). This result indicates that the β – δ transition is associated with structural collapse in the plane normal to c , associated with N atom displacements in the a – b plane, as predicted by theory. Before and after the transition the c/a ratio is constant, indicating that a transition between structurally distinct polymorphs has occurred, and the data confirm that the transition occurs over a narrow pressure range. The α - Ge_3N_4 phase, that was studied simultaneously within the same pressure chamber, does not show any such changes in the a and c parameters over the same pressure range, indicating that the β – δ transition only occurs within the phenacite-structured polymorph. This polymorph contains channel-like voids extending parallel to the c -axis: these voids are absent within the α - Ge_3N_4 polymorph (Fig. 1). It is the presence of those voids that allows the N atoms to move away from their initial symmetric positions in the β - Ge_3N_4 structure [14]. In the α -phase, a similar set of movements would require substantial bond breaking and displacements of Ge and N atoms to occur, although it is not impossible. This possibility should be investigated further theoretically.

The diffraction peaks of both (α - and β/δ -) Ge_3N_4 polymorphs become broadened and weakened above $P=24$ GPa (Fig. 6). This was also observed in our previous ED studies (Fig. 2b) [3,19]. For example, the distinctive (301) reflection of β/δ - Ge_3N_4 near $14.5^\circ 2\theta$ ($\lambda = 0.4654 \text{ \AA}$) is no longer distinguished from the

background by the time the pressure has reached 31.5 GPa (Fig. 6). These results indicate that disordering occurs in the atomic positions within the high-pressure phase. At very high pressures, only an “amorphous” diffraction pattern is observed in the 2-D and integrated 1-D patterns at 45.8 GPa (Figs. 6, 10). This is consistent with the broad amorphous bands observed in the Raman spectrum at the same pressure (Fig. 12). It is readily seen from the 2-D AD image (Fig. 10) that weak crystalline peaks though to be present in the ED spectra above 40 GPa (Fig. 2b) result only from several small crystallites present within the sample, and that most of the sample is characterized by diffuse amorphous diffraction rings. The results indicate that, above 35–40 GPa, both α - and β/δ - Ge_3N_4 polymorphs have become so disordered on an atomic scale that they have lost all structural and vibrational coherence: i.e., “pressure-induced amorphization” has occurred [23,24]. This disorder cannot involve Ge or N diffusional processes because of the low temperature; however, local bonding rearrangements can occur, while the atoms remain close to their original positions.

A mechanism for the amorphisation phenomenon is suggested from the theoretical results. Dong et al. found that five-fold coordinated Ge environments would appear within the δ - Ge_3N_4 structure at very high densities, formed in a displacive manner via close approach of three-coordinated bridging N atoms to adjacent GeN_4 tetrahedra [14]. By $P=35$ GPa, the volume of the δ - Ge_3N_4 phase is tending toward that of spinel-structured γ - Ge_3N_4 (Fig. 14), although the metastably compressed tetrahedrally coordinated polymorph has become highly metastable with respect to the stable high-density spinel phase (Fig. 2). The spinel polymorph contains 2/3 of its Ge atoms in octahedral

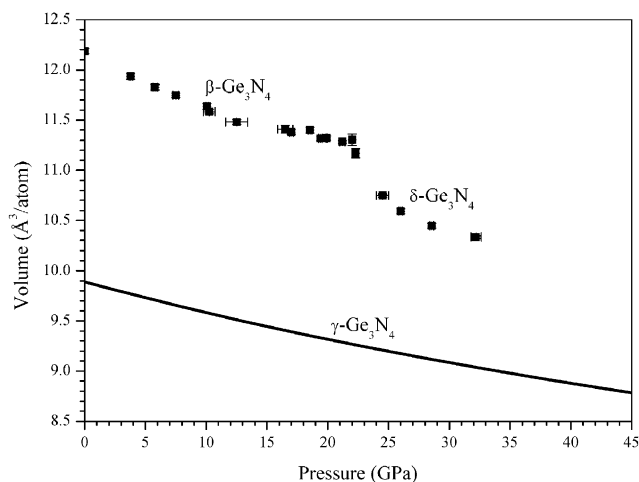


Fig. 14. $V(P)$ diagram comparing the relative volumes of the β -, δ - and γ -phases of Ge_3N_4 . The units are given on a per atom basis in order to allow a useful comparison between the volumes of phases with different number of formula units per cell.

coordination (GeN_6 species) as well as 1/3 tetrahedrally coordinated GeN_4 groups, and its formation from the low-pressure polymorphs involves a major structural reorganization that involves a high activation energy barrier (0.08 eV/atom: 85 kJ/mol) (Fig. 3). This is why the tetrahedrally coordinated polymorphs can be compressed metastably at ambient temperature. We can understand the occurrence of Ge_3N_4 amorphization in terms of development of local coordination instabilities developed within the low-pressure structures at high density. Formation of five-fold coordinated GeN_5 groups (or, equivalently, formation of NGe_4 polyhedra) will result in lengthened and weakened Ge–N bonds, lowering the energy barriers towards structural relaxation within the sample towards the more stable dense form. However, the low (ambient) temperature of the compression experiments precluded the nucleation and growth of the stable high-pressure crystalline phase ($\gamma\text{-Ge}_3\text{N}_4$): the result is an amorphous form of Ge_3N_4 .

Zerr has recently reported a new phase of Si_3N_4 , that appears upon metastable compression of $\beta\text{-Si}_3\text{N}_4$ at ambient temperature, that he has termed the “ $\delta\text{-Si}_3\text{N}_4$ ” polymorph, and has proposed is a “post-spinel” polymorph [25]. It is useful to examine the possible connection between this new form of Si_3N_4 , and the new $\delta\text{-Ge}_3\text{N}_4$ polymorph described here. Zerr has proposed that the new $\delta\text{-Si}_3\text{N}_4$ phase corresponds to a “post-spinel” structure, that thus necessarily contains high-coordinate Si atoms [2,26]. However, the Raman spectra presented by Zerr for $\delta\text{-Si}_3\text{N}_4$ are similar in form to those obtained in our recent study for the post-phenacite phase $\delta\text{-Ge}_3\text{N}_4$. Examination of the published diffraction data indicates that all but two of the peaks could be assigned to a Si_3N_4 polymorph with the $\delta\text{-Ge}_3\text{N}_4$ structure, that has a similar diffraction signature to the $\beta\text{-Si}_3\text{N}_4$ phase (Fig. 11). We conclude that Zerr might in fact observe the occurrence of a $\beta\text{-}\delta$ polymorphic phase transition in Si_3N_4 , analogous to that described here for Ge_3N_4 . The new $\delta\text{-Si}_3\text{N}_4$ polymorph would then be isostructural with $\delta\text{-Ge}_3\text{N}_4$, and it would thus correspond to a “post-phenacite” rather than a “post-spinel” structure, and contain only four-coordinated Si atoms.

5. Conclusion

We have confirmed by analysis of energy-dispersive and high-resolution angle-dispersive synchrotron X-ray diffraction studies that $\beta\text{-Ge}_3\text{N}_4$ undergoes a metastable phase transition at approximately 22 GPa, into a new polymorph termed “ $\delta\text{-Ge}_3\text{N}_4$ ”. The phase transition is characterized by a reduction of approximately 5–7% in the cell volume, and it is associated with a discontinuity in the compressional behavior of the *a*-axis but not the *c*-axis parameter. The results are consistent with theoretical predictions by Dong [14] as well as with a

recent Raman spectroscopic study [15]. The transformation involves a first-order $P6_3/m\text{-}P3$ phase transition. The high-pressure $\delta\text{-Ge}_3\text{N}_4$ polymorph is derived structurally from $\beta\text{-Ge}_3\text{N}_4$, and the two are related by small cooperative displacements of the N atoms. Both phases contain Ge in tetrahedral coordination to nitrogen. It is likely that a newly described $\delta\text{-Si}_3\text{N}_4$ polymorph is analogous to $\delta\text{-Ge}_3\text{N}_4$, based upon comparison of the X-ray diffraction and Raman data with those of Ge_3N_4 . The $\beta\text{-}\delta$ transition does not occur for $\alpha\text{-Ge}_3\text{N}_4$, because of the different crystal stacking of GeN_4 -connected layers. However, both $\alpha\text{-}$ and $\beta/\delta\text{-Ge}_3\text{N}_4$ exhibit pressure-induced amorphization at $P > 30\text{--}35$ GPa, because of Ge–N bond lengthening and weakening associated with incipient formation of GeN_5 (NGe_4) species in the structures, lowering the activation energy barriers to exploration of highly-coordinated configurations.

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References

- [1] G. Serghiou, G. Miehe, O. Tschauer, A. Zerr, R. Boehler, *J. Chem. Phys.* 111 (1999) 4659.
- [2] A. Zerr, G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fueß, P. Kroll, R. Boehler, *Nature* 400 (1999) 340.
- [3] K. Leinenweber, M. O’Keeffe, M. Somayazulu, H. Hubert, P.F. McMillan, G.W. Wolf, *Chem. Eur. J.* 5 (1999) 3076.
- [4] S. Wild, P. Grieson, K.H. Jack, *Spec. Ceram.* 5 (1972) 385.
- [5] S.N. Ruddlesden, P. Popper, *Acta Crystallogr.* 11 (1958) 465.
- [6] N. Scotti, W. Kockelmann, J. Senker, S. Traßel, H. Jacobs, *Z. Anorg. Allg. Chem.* 625 (1999) 1435.
- [7] A. Zerr, M. Kempf, M. Schwarz, E. Krobe, M. Göken, R. Riedel, *J. Am. Ceram. Soc.* 85 (2002) 86.
- [8] E. Soignard, M. Somayazulu, J. Dong, O.F. Sankey, P.F. McMillan, *J. Phys.: Condens. Matter* 13 (2001) 557.
- [9] T. Sekine, H. He, T. Kobayashi, M. Zhang, F. Xu, *Appl. Phys. Lett.* 76 (2000) 3706.
- [10] T. Sekine, H. He, T. Kobayashi, M. Tansho, K. Kimoto, *Chem. Phys. Lett.* 344 (2001) 395; M. Schwarz, A. Zerr, E. Kroke, et al., *Angew. Chem. Int. Ed.* 41 (2002) 789.
- [11] E. Soignard, M.S. Somayazulu, H.-K. Mao, J. Dong, O.F. Sankey, P.F. McMillan, *Solid State Commun.* 120 (2001) 237.
- [12] J. Dong, J. Deslippe, O.F. Sankey, E. Soignard, P.F. McMillan, *Phys. Rev. B* 67 (2003) 094104.
- [13] K. Köllisch, W. Schnick, *Angew. Chem. Int. Ed.* 38 (1999) 357.

- [14] J. Dong, O.F. Sankey, S.K. Deb, P.F. McMillan, *Phys. Rev. B* 61 (2000) 11979.
- [15] P.F. McMillan, S.K. Deb, J. Dong, *J. Raman Spectrosc.* 34 (2003) 567–577.
- [16] P.F. McMillan, in: R.J. Hemley, G.L. Chiarotti, M. Bernasconi, L. Ulvi (Eds.), *High Pressure Phenomena, Proceedings of the International School of Physics “Enrico Fermi” Course CXLVII*, IOS Press, Amsterdam, 2001, p. 477.
- [17] R.O. Piltz, M.I. McMahon, J. Crain, P.D. Hatton, R.J. Nelmes, R.J. Cernik, G. Bushnell-Wye, *Rev. Sci. Instrum.* 63 (1992) 700.
- [18] R.J. Nelmes, M.I. McMahon, J.S. Loveday, S. Rekh, *Phys. Rev. Lett.* 88 (2002) 155503.
- [19] M.S. Somayazulu, K. Leinenweber, H. Hubert, P.F. McMillan, G.W. Wolf, in: M.H. Manghnani, H. Nellis, M.F. Nicol (Eds.), *AIRAPT-17*, University Press, Hyderabad, India, 1999, p. 663.
- [20] J.E. Lowther, *Phys. Rev. B* 62 (2000) 5.
- [21] W.Y. Ching, S.-D. Mo, I. Tanaka, M. Yoshiya, *Phys. Rev. B* 63 (2001) 064102.
- [22] A.P. Mirgorodsky, M.I. Baraton, P. Quintard, *Phys. Rev. B* 48 (1993) 13326.
- [23] E.G. Ponyatovsky, O.I. Barkalov, *Mater. Sci. Rep.* 8 (1992) 147.
- [24] P. F. McMillan, in: R. J. Hemley, G. L. Chiarotti, M. Bernasconi, L. Ulvi (Eds.), *High Pressure Phenomena, Proceedings of the International School of Physics “Enrico Fermi” Course CXLVII*, IOS Press, Amsterdam, 2001, p. 511; A.K. Arora, in: R. J. Hemley, G. L. Chiarotti, M. Bernasconi, L. Ulvi (Eds.), *High Pressure Phenomena, Proceedings of the International School of Physics “Enrico Fermi” Course CXLVII*, IOS Press, Amsterdam, 2001, p.546.
- [25] A. Zerr, *Phys. Status Solidi B-Basic Res.* 227 (2001) R4.
- [26] P. Kroll, J. von Appen, *Phys. Status Solidi B-Basic Res.* 226 (2001) R6.