Synthesis and Structure Refinement of the Spinel, γ-Ge_3N_4

K. Leinenweber,* M. O'Keeffe, M. Somayazulu, H. Hubert,
P. F. McMillan, and G. H. Wolf[a]

Abstract: γ-Ge_3N_4 is formed from α- or β-Ge_3N_4 at pressures greater than 12 GPa and temperatures above 1000 °C. It has the spinel structure, symmetry $Fd\bar{3}m$, and lattice parameter $a = 8.2125(1)$ Å. Germanium has both tetrahedral [Ge–N = 1.879(2) Å] and octahedral [Ge–N = 1.996(1) Å] coordination to nitrogen. The difference between the octahedral and tetrahedral bond lengths in this nitride is close to that expected from systematics, which were largely derived from oxides.

Keywords: germanium • high-pressure chemistry • nitrides • spinel phases

Introduction

Whereas the Group IV metal oxides exhibit a very rich structural polymorphism, with a range of metal atom coordination numbers, nitrides of silicon and germanium have been previously known to exist only in the α and β forms. Both of these structures are based on a framework of corner-linked MN_4 tetrahedra. These compounds are of considerable interest, since they have useful properties of high hardness and thermal resistance. The β structure in particular has been proposed as a model for a potential superhard form of C_3N_4,[1] which has resulted in a great deal of research on this composition.

This study was undertaken to search for further polymorphism in these compounds. Ge_3N_4 is a good candidate for this because transitions to higher Ge coordination states might occur at accessible pressures, similar to the situation in oxides in which germanium easily changes from four to six coordination.

A recent study on silicon nitride in a diamond cell[2] indicates a spinel, high-pressure phase for this compound. The same group has also synthesized the spinel phase of Ge_3N_4.[2] The current study provides verification and new information on the Ge_3N_4 spinel through in situ X-ray diffraction in the diamond anvil cell, and Rietveld refinement of recovered samples.

Results and Discussion

In our studies of Ge_3N_4, diamond cell and multiple anvil high-pressure experiments were performed (see Experimental Section for details). Signs of phase transition were seen first in experiments in a diamond anvil cell. A sequence of energy dispersive X-ray diffraction spectra taken of β-Ge_3N_4 at room temperature and pressures up to 40 GPa show major changes in the spectra (Figure 1). From ambient pressure to approximately 15 GPa, the diffraction peaks of the β phase remain sharp; however, at and above 19 GPa there is a marked peak broadening and decrease in intensity of the crystalline pattern. This indicates a significant disruption of the structure, such as loss of planarity of the NGe_3 groups. The unit-cell volume also decreases anomalously as the pattern weakens.

Results of a heating experiment in a diamond cell at 24 GPa are shown in Figure 2. Transformation to a new crystalline phase begins at temperatures as low as 400 °C. With increasing temperature, the diffraction pattern of the new phase sharpens, indicating a general coarsening and/or annealing of the crystals of the high-pressure phase. The new phase is retained on cooling the sample back to room temperature and on decompression to ambient pressure (Figure 2). The diffraction lines of the new phase, though broad, are consistent with a cubic spinel structure for the high-pressure phase. Following the α and β nomenclature for the two previously known phases of Ge_3N_4, we will use the term γ-Ge_3N_4 to refer to this new phase.

Following the discovery of this material in the diamond anvil cell, well-crystallized samples of up to 100 milligrams were synthesized in a multiple anvil apparatus at pressures over 12 GPa and temperatures of 1000–1200 °C. These conditions appear to be near the phase boundary between

---

[a] Prof. K. Leinenweber, Prof. M. O'Keeffe, Dr. M. Somayazulu,
Dr. H. Hubert, Prof. P. F. McMillan, Prof. G. H. Wolf
Department of Chemistry and Biochemistry, Arizona State University,
Tempe AZ 85287-1604 (USA)
Fax: (+1) 480-965-0474
E-mail: aokdl@asu.edu

© WILEY-VCH Verlag GmbH, D-69451 Weinheim, 1999

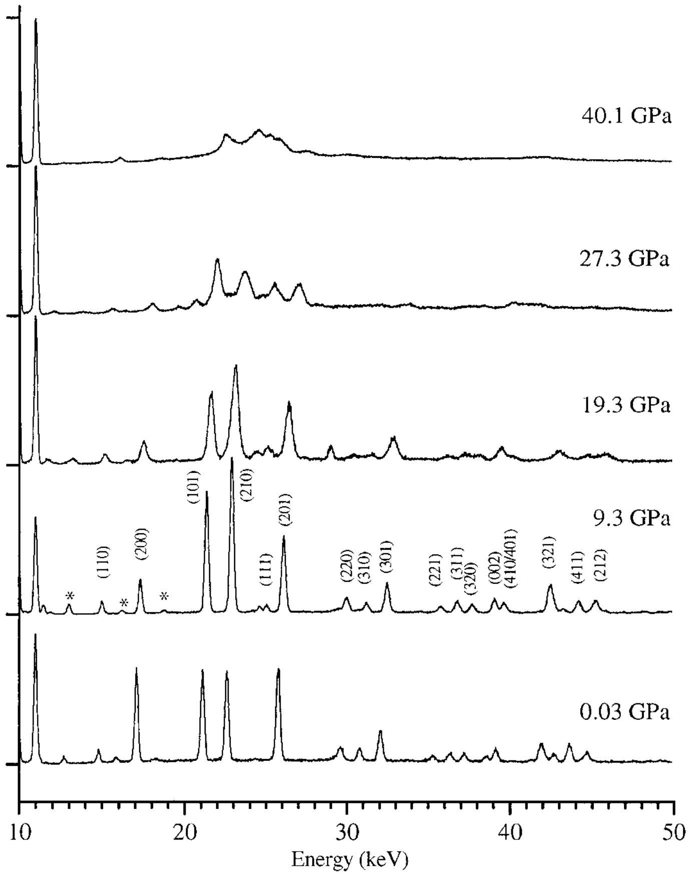

Figure 1. Variation of the X-ray diffraction spectrum of β-Ge_3N_4 with pressure, at room temperature. The sample is well-crystallized up to 19 GPa, then a marked peak broadening and decrease of peak intensities is observed. The spectra are normalized to the germanium fluorescence line, which is located near 11 keV.

β- and γ-Ge_3N_4. Also, no intermediate phases were observed (such as olivine) in any of the runs; this includes runs performed close to the phase boundary, from which mixtures of β and γ were obtained.

Rietveld refinement of the spinel phase with the program GSAS[3] gives a good fit to the diffraction spectrum, with $R_{wp} = 4.8\,\%$, $\chi^2 = 3.0$, and the crystallographic R-factor = 2.2 % (Figure 3). Refined structural parameters are listed in Table 1. The spinel structure has four- and six-coordinate cation sites, and it is of interest to compare bond lengths in these two different environments. The Brown–Altermatt bond-length/bond-strength correlation[4] predicts that for a given cation, the change in bond length for change in coordination number from Z_1 to Z_2 will be $\delta d = 0.37\ln(Z_2/Z_1)$ Å. In the case of $Z_1 = 4$, $Z_2 = 6$, $\delta d = 0.150$ Å. This is closely obeyed in silicon and germanium oxides in which Si or Ge are four (^{iv}Si, ^{iv}Ge) and six (^{vi}Si, ^{vi}Ge) coordinate (see Table 2).

There are far fewer examples of multiple coordinations among the nitrides. Recently $Ce_{16}Si_{15}O_6N_{32}$ with six-coordinate Si was described.[5] The ^{vi}Si–N bond length reported (2.105 Å) is about 0.37 Å longer than the ^{iv}Si–N bond length in Si_3N_4 (i.e., more than 0.2 Å longer than expected). There is a precedence for unusually stretched bonds (e.g., in La_2O_3),[6] and it is conceivable that this is an example.

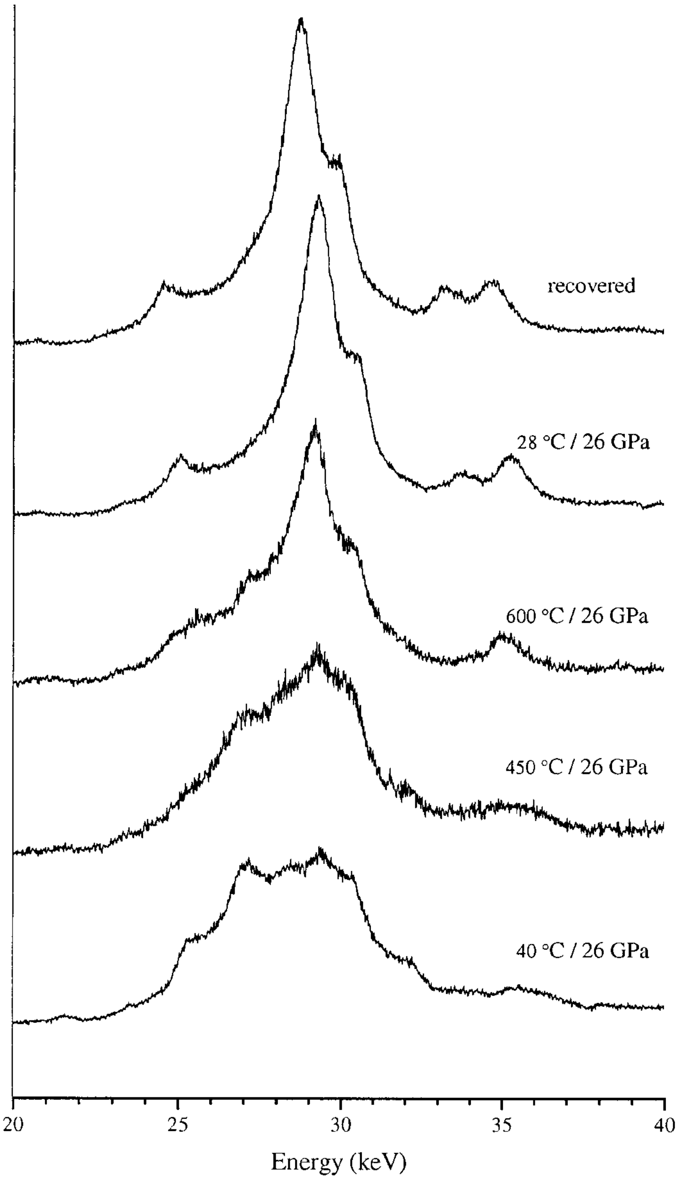

Figure 2. X-ray diffraction spectra of Ge_3N_4 during a heating experiment at 26 GPa. The highly broadened spectrum from the β phase is replaced by the spinel spectrum between 450 and 600 °C. The spinel phase can be recovered to ambient pressure, as shown in the top spectrum.

For γ-Ge_3N_4, it is found that both the ^{iv}Ge–N bond length, 1.879(2) Å, and the ^{vi}Ge–N bond length, 1.996(1) Å, are very similar to those predicted from bond valences (Table 2).[7–13] The difference between octahedral and tetrahedral bond lengths, 0.12 Å, is close to the value of 0.15 Å predicted above.

There are examples of high-pressure oxide spinels M_2SiO_4 (M = Fe, Co, and Ni). In each case the ^{iv}Si–O bond length is about 0.03 Å longer than expected, but the ^{vi}M–O are equal to the expected[6] value to within 0.004 Å. We note that in γ-Ge_3N_4, the tetrahedral Ge–N bond lengths are about 0.045 Å longer than in β-Ge_3N_4, so that it may be a recurrent theme in high-pressure spinels that tetrahedral bonds are slightly stretched.

Finally, we mention some aspects of the phenacite to spinel transition. This transition is known for several other compositions, such as Zn_2GeO_4 and $LiAlGeO_4$,[13] and always has a very large negative volume change, close to 20 %. In the

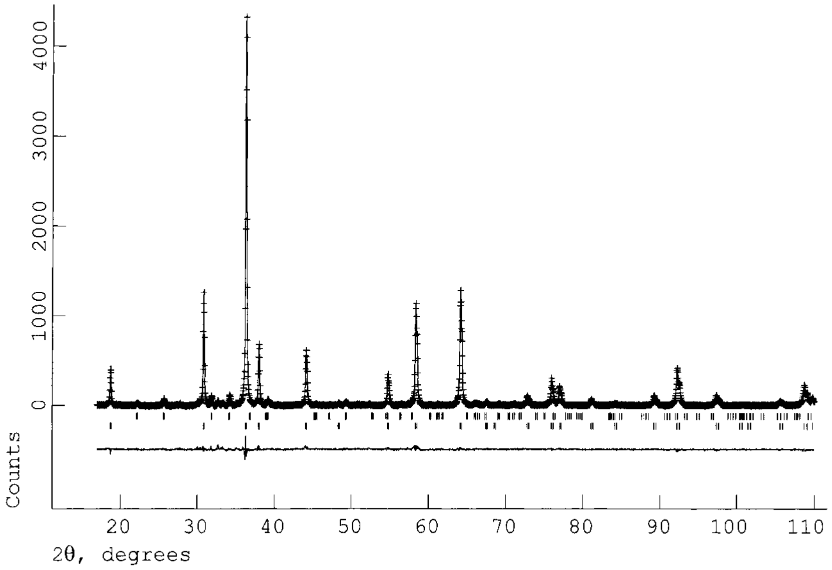

Figure 3. Refined powder X-ray spectrum of Ge_3N_4 spinel, which was used to derive the structure parameters reported here. The data is shown as crosses, and the fit is shown with a solid line. The difference curve is displayed underneath the spectrum. The lower row of tick marks shows the spinel peak positions; the sample also included 6 wt% of residual β-Ge_3N_4, represented by the upper set of tick marks.

Table 1. Refined structural parameters for γ-Ge_3N_4 (space group: $Fd\bar{3}m$ (No. 227), $a = 8.2125(1)$ Å).

	x	y	z	$100 \times U_{iso}$ [Å^2]
Ge(1)	0.125	0.125	0.125	2.93(4)
Ge(2)	0.5	0.5	0.5	2.62(3)
N	0.2577(1)	0.2577(1)	0.2577(1)	1.82(7)

Table 2. Bond lengths in selected silicon and germanium (T) oxides and nitrides (X).

	^{iv}T–X	^{vi}T–X	Reference
$K_2Si_4O_9$	1.622	1.778	[7]
$BaSi_4O_9$	1.626	1.771	[8]
bond valence for Si–O	1.624	1.774	[9]
$K_2Ge_4O_9$	1.762	1.887	[10]
$BaGe_4O_9$	1.750	1.877	[11]
bond valence for Ge–O	1.748	1.898	[9]
β-Si_3N_4	1.734	–	[12]
$Ce_{16}Si_{15}O_6N_{32}$	–	2.105	[13]
bond valence for Si–N	1.770	1.920	[9]
β-Ge_3N_4	1.834	–	[12]
γ-Ge_3N_4	1.879	1.996	this work
bond valence for Ge–N	1.880	2.030	[9]

current case of Ge_3N_4, the volume decrease (measured at ambient pressure) is 19.4%. High-pressure spinels can also be produced from olivines, as in the case of the mineral Mg_2SiO_4,[14] with volume reductions of about 10%. Although it also seems plausible for a phenacite phase to transform to an olivine, it is interesting that this transition has not been observed in any compound to date. There is another class of compounds with tetrahedral cations in the sulfides and selenides, such as $CaAl_2S_4$, $HgAl_2S_4$, $ZnAl_2Se_4$, $CdAl_2Se_4$, and $HgAl_2Se_4$, that also transform directly to spinels without any olivine intermediates, with volume decreases around 12%.[15]

Experimental Section

The starting material for these experiments was a commercially available sample (Alpha/Aesar), consisting of a mixture of β-Ge_3N_4 and α-Ge_3N_4 in a 80:20 ratio and a small amount of elemental germanium.

The high pressure X-ray diffraction experiments were carried out at beam line X-17C of the NSLS at Brookhaven National Laboratory. For experiments in a diamond anvil cell at room temperature, samples were pressurized in a methanol/ethanol 4:1 mixture, sealed with a stainless steel gasket. Pressure was measured by means of the ruby fluorescence technique. Heat experiments with a diamond anvil cell were performed in a resistively heated diamond cell (design after Fei) with a rhenium gasket.

For the multiple anvil synthesis, samples were loaded into sample assemblies of a Walker-style multiple anvil press at ASU. Graphite or Re heaters were used, and the samples were enclosed in Re capsules. In-house X-ray diffraction measurements were performed on a Siemens D5000 diffractometer with a position-sensitive detector.

Acknowledgments

This work was supported by the National Science Foundation Division of Materials Research. Thanks to Sharon Furcone and Heather Lee for the early multiple anvil runs on Ge_3N_4 below 10 GPa. The experiments at the X17C beam line at Brookhaven National Laboratories benefited greatly from the presence of J. Hu at that facility. Two anonymous reviewers provided timely and informative reviews.

---

[1] A. Y. Liu, M. L. Cohen, *Science* **1989**, *245*, 841–842.

[2] A. Zerr, G. Meihe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fuess, P. Kroll, R. Boehler, *Nature* **1999**, *400*, 340–342 ; The Serghiou et al. Ge_3N_4 spinel report is in press in Journal of Solid State Chemistry.

[3] A. C. Larson, R. B. Von Dreele, *GSAS: General Structure Analysis System*, Los Alamos National Laboratory, **1998**.

[4] I. D. Brown, D. Altermatt, *Acta Crystallogr. B* **1985**, *41*, 244–247.

[5] K. Köllisch, W. Schnick, *Angew. Chem.* **1999**, *111*, 368–370; *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 357–359.

[6] M. O'Keeffe, *Struct. Bonding* **1989**, *71*, 161–190.

[7] D. K. Swanson, C. T. Prewitt, *Am. Mineral.* **1983**, *68*, 581–585.

[8] L. W. Finger, R. M. Hazen, B. A. Fursenko, *J. Phys. Chem. Solids* **1995**, *56*, 1389–1393.

[9] N. E. Brese, M. O'Keeffe, *Acta Crystallogr. B* **1991**, *47*, 192–197.

[10] H. Vollenkle, A. Wittmann, *Monatsh. Chem.* **1971**, *102*, 1245–1250.

[11] Y. I. Smolin, *Dokl. Akad. Nauk SSSR* **1968**, *181*, 595–598.

[12] S. Wild, P. Grieveson, K. H. Jack, *Special Ceramics* **1972**, *5*, 355–357. Concordant bond lengths for β-Si_3N_4 were found by using $P6_3$ instead of $P6_3/m$ by R. Grün, *Acta Crystallogr. B*, **1979**, *35*, 800–804.

[13] L. Liu, W. A. Bassett, *Elements, Oxides, Silicates: High-Pressure Phases with Implications for the Earth's Interior*, Oxford, **1986**, pp. 166–169.

[14] A. E. Ringwood, A. Major, *Phys. Earth Planet. Int.* **1970**, *3*, 89–108.

[15] O. Muller, R. Roy, *The Major Ternary Structural Families*, Springer, New York, **1974**.

Received: August 2, 1999 [F1956]

© WILEY-VCH Verlag GmbH, D-69451 Weinheim, 1999