# Solid Solutions and Ternary Compound Formation among $Ge_3N_4$−$Si_3N_4$ Nitride Spinels Synthesized at High Pressure and High Temperature

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Following the discovery of spinel structured silicon and germanium nitrides, we investigated the possibility of intermediate compositions or even solid solution in that new system. The multianvil syntheses were performed at 23 GPa and above 2000 °C. The synthesis products from a wide range of mixtures of low-pressure phases of $Si_3N_4$ and $Ge_3N_4$ gave rise to ternary silicon germanium nitride with the spinel structure. The results showed a complete solid solution between the two end members at the experimental conditions. The structure refinement also showed a strong site preference of silicon and germanium. The silicon atoms preferentially fill the octahedral sites and the germanium atoms preferentially fill the tetrahedral sites. Both $\gamma$-$Si_3N_4$ and $\gamma$-$Ge_3N_4$ were predicted to be wide band gap semiconductors. Therefore, the complete solid solution between those two end members could give rise to a new family of tunable wide band gap semiconductors.

## Introduction

Nitride spinels formed by the group 14 elements ($Si_3N_4$, $Ge_3N_4$, $Sn_3N_4$) provide a new class of solid-state materials with potentially useful mechanical and optoelectronic properties.[1−4] They possess low compressibility and high hardness, comparable with corundum and silicon carbide used in cutting and grinding applications.[2,4−6] They are predicted to form a new family of wide direct gap semiconductors[1,7−10] that are comparable with the wurtzite-stuctured (Ga, Al, In)-nitrides that were recently developed to provide new green/blue-UV LEDs and solid-state laser diodes.[11,12] The spinel nitrides were first prepared under high-pressure, high-temperature conditions by transformation of low-pressure compounds (α-, β-, $Si_3N_4$, $Ge_3N_4$) or by reaction between the elements (Si, Ge + $N_2$)[1−3,5,13] or by metastable synthesis from chemical precursors ($Sn_3N_4$).[14] The possibility of high-throughput synthesis of powdered materials has been demonstrated using shock techniques by Sekine et al.[4] Synthesis and recovery of "SiAlON" spinel oxynitrides has been reported recently with $O^{2-}$ or $N^{3-}$ occupying the anion sites within the spinel structure.[15,16] Substitution among cation sites in oxide spinels is often used to "tune" their properties. Here, we present new results on the synthesis and characterization of $(Si, Ge)_3N_4$ spinel solid solutions and intermediate compounds prepared at high pressure and recovered to ambient conditions.

The spinel structure type is taken by a wide range of main group and transition-metal oxides, halides, and chalcogenides. It gives rise to several technologically important classes of materials, including the magnetic ferrites $M_{1-x}Zn_xFe_2O_4$ (M = Mg, Ni, Co, Fe, Mn) that are used for information storage, $Cu_xZn_{1-x}Cr_2Se_4$ spinels that are currently being investigated for their CMR

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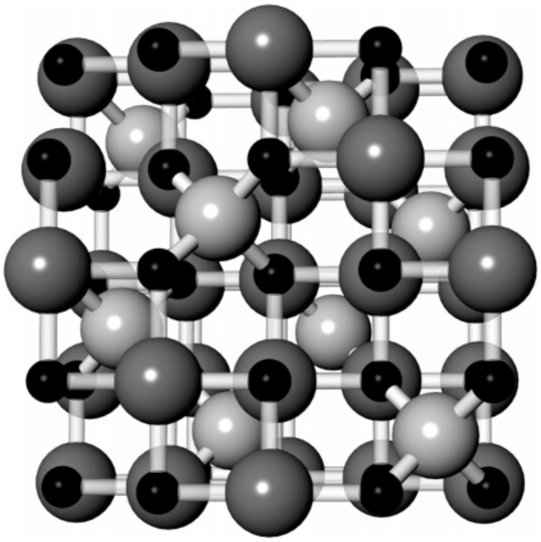

**Figure 1.** Representation of the spinel structure with the composition $AB_2X_4$. The light gray spheres represent the atoms in the tetrahedral 8a sites. The dark gray spheres represent the atoms in the 16 d octahedral site. Finally, the black spheres represent the atoms in the 32 e sites, atoms X. If the spinel is normal, the light gray spheres are A atoms and the dark gray spheres are B atoms. If the spinel is inverse, the light gray spheres represent B atoms and half of the dark gray spheres stands for A atoms and the other half represents B atoms.

("colossal magnetoresistance") properties,[17,18] and $Li_xMn_2O_4$ compounds that are being developed for battery applications.[19] However, no spinels based on the nitride ($N^{3-}$) anion had been prepared prior to 1999. That situation changed dramatically with near-simultaneous reports of spinel formation among the group 14 nitrides, $Si_3N_4$, $Ge_3N_4$, and $Sn_3N_4$, from three independent research groups.[1−3,14]

The spinel structure contains cations in octahedral and tetrahedral sites (Figure 1). The ideal stoichiometry is $AB_2X_4$, where A cations are tetrahedral and B cations are octahedral, to give rise to a "normal" spinel. Another possibility is that both A and B cations occupy octahedral sites, and one-half of the B cations become tetrahedral, giving rise to "inverse" spinels. Spinel-structured compounds can have varying degrees of tetrahedral/octahedral site occupancy, depending upon the temperature and pressure of synthesis. This includes the type mineral $MgAl_2O_4$, that is partly inverse with $Al^{3+}$ cations partially occupying both octahedral and tetrahedral sites. Cation exchange between the sites occurs rapidly at high temperature, and the normal-inverse character of the spinel can be quenched to various degrees, dependent upon the cooling rate. The kinetics of such cation hopping between tetrahedral and octahedral sites is a critical parameter for $Li^+$ battery applications among $Li_xMn_2O_4$ spinels.[19] The occurrence of the spinel structure is important for geophysics. The earth's upper mantle is largely composed of a $(Mg_{0.9}Fe_{0.1})_4SiO_4$ solid solution that has the olivine structure. Under the high-pressure, high-temperature conditions attained within the earth, such Mg−Fe olivine gives rise in two stages to a silicate with the spinel structure, thus causing observable increase in seismic velocities at 410 and 520 km depth.[20]

Our synthesis of $Ge_3N_4$ spinel arose from an investigation of the high-pressure compressibility of the low-pressure compound $\beta$-$Ge_3N_4$, that has a structure analogous to phenacite ($Be_2SiO_4$) or willemite ($Zn_2SiO_4$); it was observed that the crystalline diffraction peaks intensity greatly decreased in the pressure range $P >$ 15−17 GPa.[2,13,21,22] Subsequent heating experiments within the high-$P$ range resulted in crystallization of a new $Ge_3N_4$ polymorph with the spinel structure.[2,13] The new $\gamma$-$Ge_3N_4$ phase was later synthesized in a multi-anvil device, and its structure was determined by Rietveld refinement of X-ray powder diffraction data. In an independent study, Zerr et al. had prepared the new spinel-structured phase, $\gamma$-$Si_3N_4$, via high-pressure, high-temperature synthesis from the elements ($Si + N_2$) in a laser-heated diamond anvil cell.[1] Serghiou et al. also prepared the $\gamma$-$Ge_3N_4$ phase by a similar route.[3] In a further independent study, spinel-structured $Sn_3N_4$ was obtained metastably at ambient pressure from chemical precursors.[14] Sekine et al. later reported the formation of $\gamma$-$Si_3N_4$ and $\gamma$-$Ge_3N_4$ spinel by shock wave synthesis from nitride ceramic powders.[4] The results of these pioneering studies were all reported within a few months of each other, so that the field of nitride spinels opened up rapidly. This has caused a new area in solid-state materials chemistry exploration.[5,7,23−30] The new spinel-structured materials contain group 14 cations ($Si^{4+}$, $Ge^{4+}$, $Sn^{4+}$) on both tetrahedral and octahedral sites.

The $\gamma$-$Si_3N_4$ and $\gamma$-$Ge_3N_4$ compounds have interesting and potentially useful mechanical properties.[6,31] They possess low-compressibility and high-hardness values that are comparable with hard oxide and carbide ceramics such as corundum and silicon carbide, developed for polishing, cutting, and grinding applications.[6] Research is now under way to prepare bulk quantities of the dense nitride materials and to test their high-temperature stability and performance under operating conditions.[4,27] Both materials are also predicted to be wide band gap semiconductors, useful for high-$T$ electronics, with direct band gaps occurring in the range $E_{gap} \sim 2-4$ eV.[1,7,8]

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Solid-solution formation among oxide spinels, with various cation substitutions occurring on the octahedral and tetrahedral sites, is well-known. It is used to "tune" the desired properties of spinel materials, for example, among magnetic ferrites $M_{1-x}Zn_xFe_2O_4$ and $Cu_xZn_{1-x}Cr_2Se_4$ CMR materials. Solid-solution formation also occurs among silicate and germanate spinels synthesized at high pressure (e.g., $Mg_2SiO_4-Fe_2SiO_4$ and $Ni_2GeO_4-Mg_2SiO_4$).[32] It seemed likely that mixing of $Si^{4+}/Ge^{4+}$ on octahedral or tetrahedral sites would occur among $Si_3N_4-Ge_3N_4$ spinels, synthesized under high-pressure conditions, resulting in potential tuning of the mechanical and optoelectronic properties.[7−10,23,33,34] Any strong cation site preferences would result in cation ordering among and between the sites and cause formation of intermediate ordered compounds, such as $Si_2GeN_4$ or $Ge_2SiN_4$. The possibility of solid-solution formation and the likely existence of such intermediate ternary spinel nitride compounds have been examined theoretically and by preliminary laser-heated diamond anvil cell experiments: however, the results and predictions are contradictory.[35] Here, we have used high *P*−*T* synthesis techniques to obtain thermally equilibrated bulk samples of $Si_3N_4-Ge_3N_4$ spinels, recovered to ambient *P* and *T* for characterization of their structures and their mechanical and optical properties.

## Experimental Section

The samples were synthesized using a Walker-type cylindrical multianvil press using an 8/3 assembly contained inside eight tungsten carbide cubes.[36,37] The assembly was compacted by an oil pressure of 5000 psi (515 metric tons), corresponding to a pressure developed within the samples of ~23 GPa. The samples were then resistively heated to temperatures of 2000−2300 °C for times ranging between 10 min and 2 h. The starting materials used were mixtures of the low-pressure phases α-$Si_3N_4$ and α- + β-$Ge_3N_4$. The samples were ground to fine powders and then pressed into graphite capsules, to provide a sufficiently reducing atmosphere and nonreactive container during high *P*−*T* treatment. The graphite transformed into diamond during the high *P*−*T* experiments. It was surrounded by Re foil that acts as the resistively heated furnace material. The Re furnace is surrounded by a thermally insulating $LaCrO_3$ sleeve. The assembly is then placed inside a $MgAl_2O_4$/MgO octahedron which acts as a pressure-transmitting medium. The temperature was recorded using a type C thermocouple placed next to the sample. The structural nature of samples after quench/recovery was determined by powder X-ray diffraction (Siemens D5000) using CuKα radiation. Aliquots of the samples were preserved to determine their composition via electron microprobe analysis (Si/Ge ratio and absolute N content). For all samples synthesized in graphite capsules, the measured oxygen content of the samples remained <3 at. %.The recovered samples were also studied using Raman spectroscopy, using an exciting wavelength of 514.53 nm. The laser power was maintained below ~5 mW to prevent $N_2$ loss from or oxidation of the samples.[38]

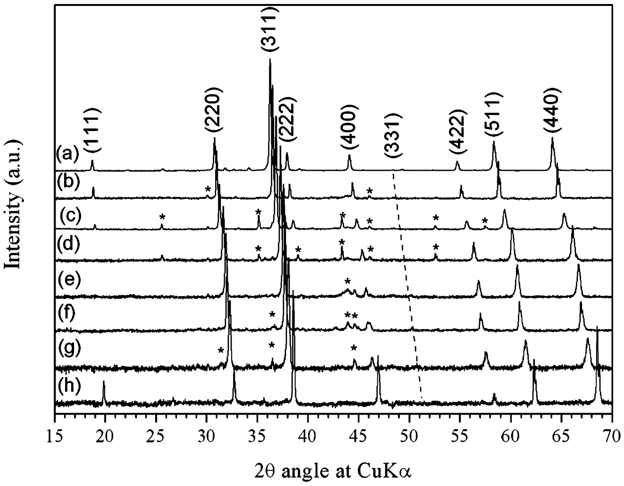

**Figure 2.** X-ray diffraction patterns of the sample synthesized from mixtures of low-pressure $Si_3N_4$ and $Ge_3N_4$ phases. Pattern (a) is that of γ-$Ge_3N_4$ previously published by Leinenweber et al.[2] Patten (b) is that of BB239, (c) BB242, (d) BB236, (e) BB240, (f) BB234, (g) BB241, (h) BB250 which is γ-$Si_3N_4$. The background of the X-ray diffraction patterns was subtracted to clarify the figure. The peaks indicated with ∗ do not correspond to the spinel pattern or the starting material except in the γ-$Ge_3N_4$ pattern (a) where the extra peaks are from the starting material.

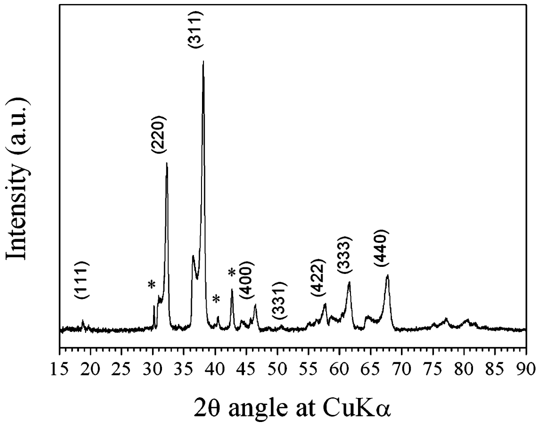

**Figure 3.** X-ray diffraction pattern of a mixture of 2 $Si_3N_4$ + 1 $Ge_3N_4$ heated at 1500 °C and 23 GPa for 2 h. The pattern clearly shows a shoulder on the left-hand side of all the peaks. The peak shape is characteristic of an incomplete reaction between the two starting materials. However, none of the starting low-pressure phases of silicon nitride and germanium nitride are observed. The pattern is that of spinels with a range of compositions.

## Results and Discussion

X-ray diffraction and electron microprobe analysis indicated that samples recovered from the high *P*−*T* synthesis runs corresponded to single-phase (Ge,Si)-nitride spinels, with bulk compositions identical to those of the starting mixtures (Figure 2, Table 1). None of the samples show any remaining trace of the starting low-pressure phases.

One experiment performed at 1500 °C showed evidence that an equilibrium spinel was not obtained during the run duration (Figure 3). The spinel peaks in that case were broadened and asymmetric, indicating inhomogeneity in the sample. To fully equilibrate the Si/Ge distribution within the spinel samples, we performed all further experiments at higher temperatures, typically above 2000 °C.

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**Table 1. Nominal Germanium and Silicon Ratio in the Starting Mixture and Measured Values in the Product from Electron Microprobe for Each of the Multianvil Syntheses from Mixtures of $Si_3N_4$ and $Ge_3N_4$**

| | starting material | | product | | synthes is conditions | | |
|---|---|---|---|---|---|---|---|
| | Si | Ge | Si | Ge | P (GPa) | T (°C) | duration (min) |
| BB241 | 0.800(20) | 0.200(20) | 0.822(10) | 0.178(10) | 23(2) | 2000(10) | 35 |
| BB234 | 0.667(15) | 0.333(15) | 0.653(10) | 0.347(10) | 23(2) | 2000(10) | 18 |
| BB240 | 0.667(15) | 0.333(15) | 0.606(10) | 0.395(10) | 23(2) | 2000(10) | 20 |
| BB236 | 0.500(15) | 0.500(15) | 0.476(10) | 0.524(10) | 23(2) | 2000(10) | 20 |
| BB242 | 0.333(15) | 0.667(15) | 0.278(10) | 0.722(10) | 23(2) | 2000(10) | 60 |
| BB239 | 0.200(20) | 0.800(20) | 0.125(10) | 0.875(10) | 23(2) | 2000(10) | 20 |

**Table 2. Results from the Rietveld Refinement of Each of the Synthesis Run Products**[a]

| | Si 16d | Si 8a | Ge 8a | Ge 16d | U | a | wRp (%) | Rp (%) | $\chi^2$ |
|---|---|---|---|---|---|---|---|---|---|
| Si3N4 | 1 | 1 | | | 0.2596(8) | 7.7381(2) | | 5.42 | 2.7 |
| BB241 | 1 | 0.467 | 0.533 | | 0.2577(5) | 7.8349(5) | 5.8 | 4.6 | 1.3 |
| BB234 | 0.979 | | 1 | 0.021 | 0.2599(8) | 7.9031(5) | 3.0 | 2.2 | 2.1 |
| BB240 | 0.908 | | 1 | 0.092 | 0.2579(6) | 7.9307(4) | 7.0 | 5.6 | 1.9 |
| BB236 | 0.714 | | 1 | 0.286 | 0.2568(9) | 7.9919(5) | 7.8 | 6.0 | 2.0 |
| BB242 | 0.417 | | 1 | 0.583 | 0.2590(8) | 8.0840(9) | 6.8 | 5.1 | 0.7 |
| BB239 | 0.188 | | 1 | 0.812 | 0.2634(1) | 8.1532(8) | 6.8 | 5.4 | 1.9 |
| Ge3N4 | | | 1 | 1 | 0.2577(1) | 8.2125(1) | 4.8 | 2.2 | 3.0 |

[a] The atom in the 16 d sites are octahedrally coordinated to N and the atoms in 8A sites are tetrahedrally coordinated to N.

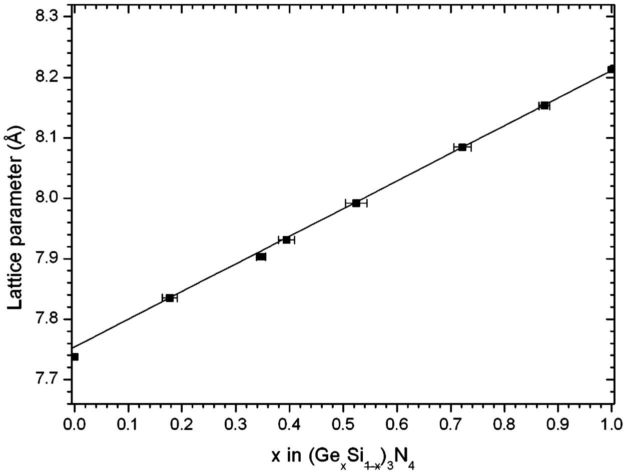

**Figure 4.** Lattice parameter of the spinel nitride materials as a function of composition. The lattice parameters are aligned on a straight line except for one point at the composition the closest to $GeSi_2N_4$ (0.3473 Si and 0.6527 Ge).

Analysis of the X-ray diffraction patterns shows that, for all compositions examined in the system $Si_3N_4-Ge_3N_4$, the product was a single-spinel nitride phase (Figure 2). This result was confirmed by electron microprobe analysis, which showed the samples to be chemically homogeneous. The composition of the product spinel was identical with the bulk starting composition, to within analytic and weighing errors. Continuous solid-solution formation was thus achieved between $\gamma$-$Si_3N_4$ and $\gamma$-$Ge_3N_4$ spinel end members during the high $P-T$ synthesis conditions, involving mixing of the $Si^{4+}$ and $Ge^{4+}$ cations on octahedral and tetrahedral sites, that was maintained during sample recovery to ambient conditions. The lattice parameter of the cubic $\gamma$-$(Si,Ge)_3N_4$ spinel solid solution is plotted as a function of Si/Ge ratio in Figure 4. The value for $\gamma$-$Ge_3N_4$ is 8.2125 Å, much larger than that for silicon nitride spinel ($a_0$ = 7.7376(1) Å). Between the two end members, the lattice parameter shows a linear variation with composition, according to Vegard's law.

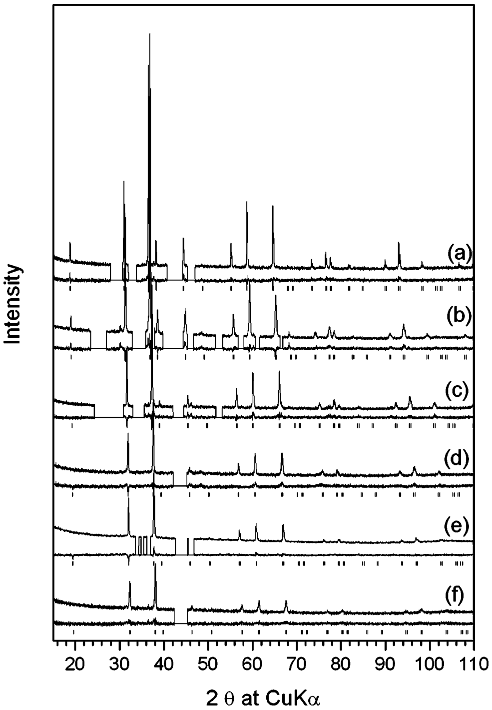

**Figure 5.** X-ray diffraction of the spinel with the difference curve from the Rietveld refinement. The difference curves are on the same scale as the X-ray diffraction patterns. The patterns were scaled to have approximately the same amount of counts for the background. To get a better refinement, we blanked out the regions of the patterns with peaks that are not part of the spinel pattern. These regions appear as steps in the patterns.

We refined the powder X-ray diffraction data for each of the spinel compositions via the Rietveld method using GSAS.[39,40] The results are presented in Figure 5, and details of the refinements are summarized in Table 2. Rietveld refinement of the X-ray diffraction data indicates that, for Si-rich compositions, the Si atoms are preferentially located in the octahedral sites, and the Ge atoms occupy the tetrahedral positions. Refinement of X-ray patterns for samples with composition near $SiGe_2N_4$ showed that the Si atoms are only present in

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octahedral sites, whereas the Ge atoms occupy all of the tetrahedral sites and are partially distributed among the octahedral sites (Table 2). The ternary nitride spinel formed at the $GeSi_2N_4$ composition is thus a normal, rather than an inverse, spinel. That result is consistent with preliminary results from our laser-heated diamond anvil cell experiments[35] and with ab initio calculations reported by Dong et al.[7] Within the solid-solution series, the octahedral sites are first filled with Si atoms, and then by Ge atoms as the Ge/Si ratio increases. Likewise, the tetrahedral sites are first filled with Ge, and then by Si atoms, as the $Si_3N_4$ content becomes large.

This observation contradicts the usual expectation that smaller $Si^{4+}$ cations should occupy tetrahedral sites and $Ge^{4+}$ ions should occupy the larger octahedral sites.[41,42] However, it is likely that cation site occupancies are determined primarily by local bonding considerations in these nitride spinels.[7] The $N^{3-}$ anions seek to maintain a near-regular tetrahedral arrangement to maintain $sp^3$ hybridization. If Ge atoms were to occupy octahedral sites, the bonding around N atoms would be $[NGe^{vi}{}_3Si^{iv}{}_1]$. Single bond lengths between $Ge^{vi}$-N and $Si^{iv}$-N are 1.98 and 1.76 Å,[7] respectively, so that the local environment around N atoms would be asymmetric. However, placing Si atoms in octahedral coordination and Ge in tetrahedral sites gives an arrangement $[NSi^{vi}{}_3Ge^{iv}{}_1]$, with $Ge^{iv}$-N and $Si^{vi}$-N bonds that are nearly equal (1.85 and 1.88 Å, respectively).[7] Precedents for such an "inverse" view of crystal bonding, involving local bond valence considerations and the importance of cation packing around the anions, have been discussed by O'Keeffe and Hyde.[7,43]

Raman scattering spectroscopy has been used for identification of $\gamma$-$Si_3N_4$ and $\gamma$-$Ge_3N_4$ spinels following high $P-T$ synthesis experiments. We obtained Raman spectra for each of the synthesized compositions in the $Si_3N_4-Ge_3N_4$ system (Figure 6). The peaks display one-mode behavior, as expected for a continuous solid solution with strong coupling of the intra- and intermolecular vibrations ($SiN_4$/$SiN_6$ and $GeN_4$/$GeN_6$ groups). The linear shift in band positions as a function of composition allows four of the five expected peaks to be identified unambiguously (Figure 7). The peaks were assigned using the predicted[8] and measured[44] peak positions and assignment for the germanium nitride end member and following the peak position as a function of composition. The peak positions for $\gamma$-$Si_3N_4$ and $\gamma$-$Ge_3N_4$ spinels have been predicted previously using ab initio calculations.[8,23,45] In general, there is good agreement between experiment and theory. However, the $T_{2g}$ mode predicted by Kroll[23] to occur at 500 $cm^{-1}$ for $\gamma$-$Si_3N_4$ occurs at 729 $cm^{-1}$. A more recent calculation from Fang et al. predicted that mode to occur at 726 $cm^{-1}$.

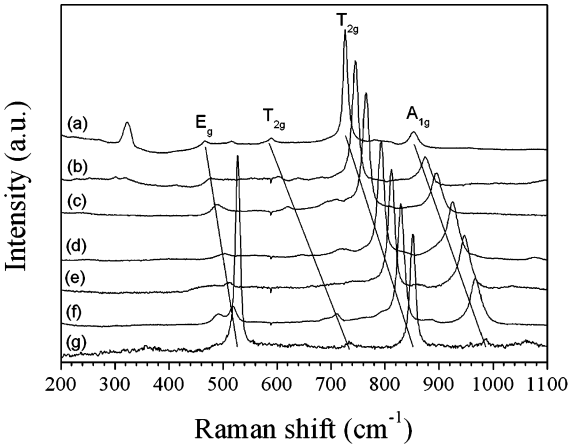

**Figure 6.** Raman spectra of the ternary spinel nitrides and the end members $Si_3N_4$ and $Ge_3N_4$. The spectra were collected using the green line of an $Ar^+$ laser at 514.5 nm. Some low fluorescence background was observed in the spectra. To make the figure easier to read, a straight line was used to fit the background and was subtracted from the patterns. The intensity of the patterns was normalized to have the same intensity for the $T_{2g}$ mode (strong peak between 750 and 850 $cm^{-1}$). Spectrum (a) is that of $\gamma$-$Ge_3N_4$, (b) BB239, (c) BB242, (d) BB236, (e) BB240, (f) BB241, (g) BB250 which is pure $\gamma$-$Si_3N_4$.

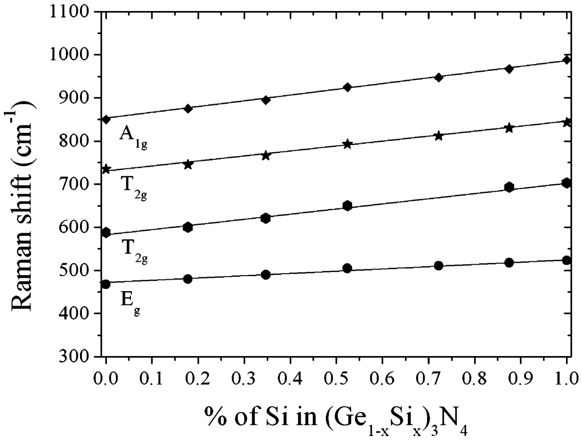

**Figure 7.** Raman shift as a function of composition for four of the spinel modes. The fifth mode at low wavenumber is extremely weak and not observed on most of the spectra. The shift is linear as a function of composition for each of the modes with a positive shift with increasing Si content for all four of the plotted modes.

In a preliminary study of solid solution or intermediate compound formation within $Si_3N_4-Ge_3N_4$ spinels, carried out using the laser-heated diamond anvil cell technique, we concluded that a solvus was present between a $\gamma$-$Ge_3N_4$ end member and a ternary compound close to $Si_2GeN_4$.[35] Ching et al.[9] had predicted that the $Si_2GeN_4$ composition would not correspond to a stable compound within the system and that $Ge_2SiN_4$ instead should be stabilized as a ternary nitride spinel. However, those authors placed $Si^{4+}$ in tetrahedral sites and $Ge^{4+}$ in octahedral locations to carry out the calculations. Our experimental findings suggest that the preferred site occupancies are in fact reversed. Dong et al.[7] used LDA and GGA methods to investigate the Si and Ge site preferences and found that the Si atoms should preferentially occupy octahedral sites and Ge atoms tetrahedral sites, in agreement with experiment. The calculations predicted that a stable ternary compound should be formed at the $Si_2GeN_4$ composition. Dong et al.[7] extended their calculations to consider solid-

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solution behavior at high temperature, using a statistical mechanical model based upon the calculated energy parameters. In that work, two miscibility gaps were predicted to occur between $Si_2GeN_4$ and $Ge_3N_4$ with a consolute temperature $T_{c1} < 1100$ °C and a second between $Si_2GeN_4$ and $Si_3N_4$, $T_{c2} < 600$ °C. The observation of two coexisting spinels with compositions near $Si_2GeN_4$ and $Ge_3N_4$ indicated that the first solvus, but not the second, had been accessed during the high $P-T$ experiments. The laser-heated diamond cell experiments were carried out at approximately 2000 K, measured by thermal emission spectrometry. The observed unmixing into two nitride spinels must have occurred during the quench. The present experiments were carried out within the better-controlled thermal environment of a multianvil apparatus.[36]

Because the structural properties of the spinel nitride solid solution vary linearly with composition, we expect that physical properties such as the band gap also vary in a similar way.[7,8] Further studies should investigate the optical absorption and luminescence characteristics of these $(Si,Ge)_3N_4$ materials that appear to have similar optoelectronic characteristics, including a tunable optical band gap,[46] comparable to the GaN−(In, Al)N solid solutions.[7,8,11,12,47]

## Conclusion

The new experimental results on formation of spinel-structured compounds prepared at high pressure, high temperature within the $Si_3N_4-Ge_3N_4$ system using multianvil synthesis techniques showed that a continuous solid solution is obtained and recovered to ambient $P-T$ conditions. Analysis of the X-ray diffraction intensities indicates that Si atoms first fill octahedral sites and that the Ge atoms preferentially occupy tetrahedral sites within the spinel structure. This initially surprising result can be rationalized on the basis of local valence bonding requirements of the tetrahedral N atoms, around $N^{3-}$ anion sites. The Raman spectroscopic study also showed a linear shift of the modes as a function of composition. The new results indicate that $Si_3N_4-Ge_3N_4$ continuous solid solutions within the newly recognized nitride spinel structure can be synthesized and recovered to ambient conditions, leading to the possibilities of "tuning" physical properties, such as the band gap within this new family of optoelectronic materials.

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