

Spinel-Structured Gallium Oxynitride (Ga₃O₃N) Synthesis and Characterization: An Experimental and Theoretical Study

Emmanuel Soignard,^{*,†} Denis Machon,[‡] Paul F. McMillan,^{*,‡,§} Jianjun Dong,^{||} Bin Xu,^{||} and Kurt Leinenweber[⊥]

Departments of Geological Sciences and of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, Department of Chemistry, University College London, U.K., Royal Institute of Great Britain, London, U.K., and Physics Department, Auburn University, Auburn, Alabama 36849

Received June 8, 2005. Revised Manuscript Received August 17, 2005

Recently the new family of spinel-structured nitrides and oxynitrides of group 14 elements (Si, Ge, Sn) has been explored using high-pressure synthesis techniques. The solid-state compounds have high hardness, and they are semiconducting materials that are predicted to have a wide direct band gap. Here we have prepared the corresponding gallium oxynitride spinel with ideal formula Ga₃O₃N. The synthesis conditions and stability of the new phase were predicted using first-principles calculations, and the experimental study was realized using a combination of laser-heated diamond anvil cell and multianvil high-pressure, high-temperature synthesis techniques. Chemical analysis and X-ray structure refinement indicate that the new phase contains vacancies on the octahedrally coordinated Ga sites, to give an experimental stoichiometry of Ga_{2.8}N_{0.64}O_{3.24}. The Raman spectrum consists of broad bands and resembles the phonon density of states, due to N/O disorder on the anion sites. Optical excitation of the sample with 325 nm laser light at room temperature results in strong photoluminescence between 400 and 750 nm.

Introduction

Semiconducting materials with a wide band gap are of interest for applications in high-temperature electronics and in optoelectronic devices, particularly when the gap is direct. The oxides and nitrides of gallium are wide-gap semiconductors that give rise to materials that are useful in the blue to UV range at short wavelength. The cubic (sphalerite) and hexagonal (wurtzite) forms of GaN have band gap energies of 3.3 eV¹ and 3.4 eV,² respectively. When alloyed with In and Al, hexagonal GaN-based materials with a direct gap have been developed for use in light-emitting diodes and lasers at wavelengths extending from the blue to the ultraviolet range.³ The thermodynamically stable β -Ga₂O₃ polymorph has a direct gap of 4.7 eV, and it has also been proposed for development as a solid-state LED material for UV applications.⁴ The group 13 oxynitride materials have other useful properties related to their electronic structure. α -Ga₂O₃ with the corundum structure is conveniently alloyed with Al₂O₃ to provide selective reduction catalysts for gaseous NO_x,⁵ and various other Ga₂O₃ phases have been

proposed as gas sensors and in nanoscale structures as electron emitters and magnetic memory materials.⁶ Within the Al₂O₃–AlN system, several important Al_xO_yN_z ceramic alloys and compounds are known. At high AlN contents, layered forms based on hexagonal/cubic intergrowths are present. As the Al₂O₃ content is increased, cubic spinel-structured materials begin to appear. A large family of defect spinels (γ -Al₂O₃, Al_xO_yN_z) contain vacancies on both cation and anion sites.⁷ A stoichiometric oxynitride spinel-structured compound is obtained at the Al₃O₃N composition, in which Al³⁺ ions are present on the octahedral and tetrahedral sites and O²⁻ and N³⁻ occupy tetrahedral anion sites.^{8,9}

Among the related nitride compounds Si₃N₄ and Ge₃N₄, high-pressure synthesis has recently resulted in formation of a new class of spinel structures that contain Si⁴⁺ and Ge⁴⁺ cations on both tetrahedral and octahedral sites.^{10–14} The new solid-state compounds are recoverable to ambient conditions, and they possess high hardness and low compressibility, comparable with those of materials such as Al₂O₃–corundum.⁷ The new group 14 nitride spinels are also

* To whom correspondence should be addressed. E-mail: esoignar@usa.net (E.S.); p.f.mcmillan@ucl.ac.uk (P.F.M.).

[†] Department of Geological Sciences, Arizona State University.

[‡] University College London.

[§] Royal Institute of Great Britain.

^{||} Auburn University.

[⊥] Department of Chemistry and Biochemistry, Arizona State University.

- (1) Okumura, H.; Ohta, K.; Ando, K.; Ruhle, W. W.; Nagatomo, T.; Yoshida, S. *Solid-State Electron.* **1997**, *41*, 201.
- (2) Maruska, H. P.; Tietjen, J. J. *Appl. Phys. Lett.* **1969**, *15*, 327.
- (3) Mohammad, S. N.; Salvador, A. A.; Morkoc, H. *Proc. IEEE* **1995**, *83*, 1306.
- (4) Tippins, H. H. *Phys. Rev.* **1965**, *140*, A316.
- (5) Haneda, M.; Kintaichi, Y.; Shimada, H.; Hamada, H. *Chem. Lett.* **1998**, 181.

(6) Aubay, E.; Gourier, D. *J. Phys. Chem.* **1992**, *96*, 5513.

(7) Corbin, N. D. *J. Eur. Ceram. Soc.* **1989**, *5*, 143.

(8) Willems, H. X.; Dewith, G.; Metsellar, R.; Helmholdt, R. B.; Petersen, K. K. *J. Mater. Sci. Lett.* **1993**, *12*, 1470.

(9) Dravid, V. P.; Sutliff, J. A.; Westwood, A. D.; Notis, M. R.; Lyman, C. E. *Philos. Mag. A* **1990**, *61*, 417.

(10) Serghiou, G.; Mieke, G.; Tschauner, O.; Zerr, A.; Boehler, R. *J. Chem. Phys.* **1999**, *111*, 4659.

(11) Leinenweber, K.; O'Keeffe, M.; Somayazulu, M.; Hubert, H.; McMillan, P. F.; Wolf, G. W. *Chem.—Eur. J.* **1999**, *5*, 3076.

(12) He, H.; Sekine, T.; Kobayashi, T.; Kimoto, K. *J. Appl. Phys.* **2001**, *90*, 4403.

(13) Zerr, A.; Mieke, G.; Serghiou, G.; Schwarz, M.; Kroke, E.; Riedel, R.; Fuess, H.; Kroll, P.; Boehler, R. *Nature* **1999**, *400*, 340.

(14) Soignard, E.; McMillan, P. F.; Leinenweber, K. *Chem. Mater.* **2004**, *16*, 5344.

predicted to be wide direct band semiconductors, with band gaps calculated to lie within the range 2.2–4.0 eV.^{15,16} The analogous spinel-structured compound Sn_3N_4 has also been made at ambient pressure,^{17,18} raising the possibility of future preparation of γ -(Si,Ge)₃N₄ films via metastable synthesis routes, such as chemical vapor deposition, to yield materials compatible with optoelectronics applications, for example.

Gallium oxynitride ($\text{Ga}_3\text{O}_3\text{N}$) has been predicted to form a new spinel-structured compound within the Ga_2O_3 –GaN system, with potentially useful electronic properties.^{19,20} It is predicted to be a direct wide band gap semiconductor, comparable with GaN.²⁰ There has previously been an experimental report of a cubic gallium oxynitride phase with composition close to $\text{Ga}_{2.8}\text{O}_{3.5}\text{N}_{0.5}$ that formed metastably during GaN thin film synthesis from chemical precursors.^{21,22} Here, we used a combination of high-pressure, high-temperature (high- P,T) techniques to establish the formation and stability of spinel-structured $\text{Ga}_3\text{O}_3\text{N}$ from $\text{Ga}_2\text{O}_3 + \text{GaN}$ mixtures, and to determine the chemical composition, structure, and properties of the resulting materials. We combined our experiments with a first-principles theoretical study of the formation energetics, stability, and electronic properties of the $\text{Ga}_3\text{O}_3\text{N}$ spinel-structured phase.

In our experimental study, we used laser-heated diamond anvil cell (LH-DAC) techniques combined with in situ synchrotron X-ray diffraction and optical spectroscopy to initially establish the synthesis parameters and recovery of the new phase. We then carried out high- P,T synthesis and recovery experiments in a multianvil device. We characterized the chemical composition, structure, and optical properties of the new compound by electron microprobe analysis, Rietveld refinement of the X-ray powder diffraction pattern, Raman scattering, and photoluminescence spectroscopy. Furthermore, we investigated the optimal synthesis pressure and temperature conditions on the basis of the first-principles total energy calculations and equilibrium statistical models. Our calculated electronic band structure and phonon spectra based on the ideal spinel structure are consistent with our experimental results for the newly synthesized gallium oxynitride samples.

Experimental and Theoretical Techniques

Theoretical Methodologies. We studied the properties of spinel-structured gallium oxynitrides on the basis of first-principles density functional theory (DFT), implemented by the VASP code.^{23–26} The

many-electron exchange-correlation interaction was approximated within the local density approximation (LDA). For parts of the study that were associated with small energy differences, we compared our LDA results with calculations using the generalized gradient approximation (GGA). To improve numerical efficiency, core electrons were approximated with ultrasoft pseudopotentials (US-PPs), and only the s and p valence electrons for these elements and the semicore 3d electrons in Ga were treated explicitly. The wave functions of the valence and semicore electrons were expanded using a plane wave basis, with a kinetic energy cutoff set at 396 eV. Results for Ga–O–N phases relevant to the synthesis of the spinel-structured $\text{Ga}_3\text{O}_3\text{N}$ oxynitrides and the stability and properties of that compound are described below.

High-Pressure, High-Temperature Experiments. We initially investigated the synthesis of Ga_2O_3 –GaN materials using laser-heated DAC techniques. Starting materials were a mixture of Ga_2O_3 (99.99%, containing a mixture of $\alpha + \beta$ phases) and GaN (99.99%, Alfa Aesar) in a 1:1 molar ratio. The powders were ground, pressed together, and then loaded into cylindrical diamond cells with N_2 pressure medium along with ruby chips for pressure measurement. The samples were heated using a Nd^{3+} :YLF laser incident from both sides.²⁷ In situ X-ray diffraction measurements during and following the synthesis attempts were performed at beamline 13 ID-D of the Advanced Photon Source, Argonne National Laboratory (APS). Following laser heating, the samples were recovered for laboratory-based spectroscopy studies.

High-pressure, high-temperature syntheses were carried out using a Walker-type multianvil press in the high-pressure facility at Arizona State University,²⁸ using assemblies with a WC cube truncation of 8 mm. Samples were loaded into various capsule materials, including BN, MgO, and Pt. The last of these provided the best containment environment. A MgO sleeve was placed around the Pt capsule and surrounded by a graphite furnace that was insulated from the sample environment by a ZrO_2 sleeve.

Powder X-ray diffraction patterns of the recovered samples were obtained using a D5000 powder X-ray diffractometer (Cu $K\alpha$), and chemical compositions were determined by wavelength-dispersive electron microprobe analysis using a JEOL JXA-8600 instrument. The accelerating voltage was 15 kV; the beam current was 10 nA with a focused 3 μm beam. Raman spectra were obtained using a custom-built microbeam Raman spectrometer at University College London, based on an Acton 300i spectrograph and Kaiser notch filters, and 488.0/514.5 nm Ar^+ laser illumination.²⁹ Room-temperature photoluminescence data were obtained with a Renishaw microbeam optical system, using 325 nm laser excitation.

Results and Discussion

Theoretical Study of the Synthesis, Structure, and Stability of $\text{Ga}_3\text{O}_3\text{N}$ Spinel. We performed ab initio calculations of the atomic structures and energetic properties within the $\text{Ga}_3\text{O}_3\text{N}$ system to understand the formation and thermodynamic stability of the spinel-structured phase. The ideal spinel crystal has an A_3X_4 stoichiometry (A and X represent cations and anions, respectively) with two molecular equivalents per primitive unit cell corresponding to the fcc structure. Assuming a Ga:O:N ratio of 3:3:1 that corresponds to the ideal stoichiometry, a solid of n $\text{Ga}_3\text{O}_3\text{N}$ molecular units contains n tetrahedrally coordinated Ga atoms

- (15) Mo, S. D.; Ouyang, L.; Ching, W. Y.; Tanaka, I.; Koyama, Y.; Riedel, R. *Phys. Rev. Lett.* **1999**, *83*, 5046.
 (16) Dong, J.; Sankey, O. F.; Deb, S. K.; McMillan, P. F. *Phys. Rev. B* **2000**, *61*, 11979.
 (17) Scotti, N.; Kockelmann, W.; Senker, J.; Trassel, S.; Jacobs, H. Z. *Anorg. Allg. Chem.* **1999**, *625*, 1435.
 (18) Shemkunas, M. P.; Wolf, G. H.; Leinenweber, K.; Petuskey, W. T. *J. Am. Ceram. Soc.* **2002**, *85*, 101.
 (19) Kroll, P. *Phys. Rev. B*, in press.
 (20) Lowther, J. E.; Wagner, T.; Kinski, I.; Riedel, R. *J. Alloys Compd.* **2004**, *376*, 1.
 (21) Wolter, S. D.; DeLuca, J. M.; Mohny, S. E.; Kern, R. S.; Kuo, C. P. *Thin Solid Films* **2000**, *371*, 153.
 (22) Puchinger, M.; Kisailus, D. J.; Lange, F. F.; Wagner, T. *J. Cryst. Growth* **2002**, *245*, 219.
 (23) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.
 (24) Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1996**, *6*, 15.
 (25) Kresse, G.; Hafner, J. *Phys. Rev. B* **1994**, *49*, 14251.

- (26) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558.
 (27) Shen, G. Y.; Rivers, M. L.; Wang, Y. B.; Sutton, S. R. *Rev. Sci. Instrum.* **2001**, *72*, 1273.
 (28) Walker, D. *Am. Mineral.* **1991**, *76*, 1092.
 (29) Soignard, E.; McMillan, P. F. *Chem. Mater.* **2004**, *16*, 3533.

Table 1. Parameters of the Third-Order Birch–Murnaghan Equations of States of Three Unit-Cell-Based Atomic Models of the Spinel-Structured Ga₃O₃N That Have the Lowest Energy Calculated within the LDA^a

model	E_0 (eV/Ga ₃ O ₃ N)	V_0 (Å ³ /Ga ₃ O ₃ N)	a_0 (Å)	B_0 (GPa)	B_0
I	-48.109 (0.000)	69.5424	8.2246	210	4.13
II	-47.966 (0.143)	69.6928	8.2305	208	4.17
III	-47.854 (0.255)	69.6181	8.2275	209	4.14

^a Model I is found to be the minimal energy configuration, and models II and III occur at 143 and 255 meV/Ga₃O₃N (13.8 and 24.6 kJ/mol) higher energy, respectively, above the ground state. The three models have comparable equilibrium volumes and bulk moduli.

(labeled as ^{IV}Ga), 2*n* octahedrally coordinated Ga atoms (^{VI}Ga), 3*n* O atoms, and *n* N atoms. The Gibbs free energy of formation of the oxynitride from a mixture containing the corresponding oxide and nitride is defined as

$$\Delta G_{\text{formation}}(T,P) = G_{\text{Ga}_3\text{O}_3\text{N}}(T,P) - [G_{\text{Ga}_2\text{O}_3}(T,P) + G_{\text{GaN}}(T,P)] \quad (1)$$

Here *G* represents the Gibbs free energy for each molecular unit, and a negative $\Delta G_{\text{formation}}$ corresponds to a driving force for the formation of the oxynitride. Because the oxynitride spinel can have O or N atoms distributed among the anion sites, it is likely that there will be a large configurational entropy term contained within $\Delta G_{\text{formation}}$. A complete statistical model of the Gibbs free energy of Ga₃O₃N material that might contain such oxygen/nitrogen compositional disorder requires calculating a very large number of atomic configurations using supercell models. In the first stage of our theoretical investigation, we performed the ab initio energetic calculations with a limited number of atomic configurations using (pseudo) face-centered-cubic unit-cell models. We interpreted our data using a simplified model that breaks the Gibbs energy into two terms:

$$G_{\text{Ga}_3\text{O}_3\text{N}}(T,P) = H_{\text{ground}}(P) + G_{\text{alloy}}(T,P) \quad (2)$$

Here H_{ground} is the temperature-independent enthalpy of the ground-state (lowest energy) configuration, which allows us to gain insights into the energetically favored local coordination states and their O/N ordering, and to study pressure effects on the Gibbs free energy of formation. The temperature effects are then described by the second term, G_{alloy} , which models the contributions related to the O/N disorder. In this study, we ignored the entropy contributions due to lattice vibrations.

We first studied the pressure effects on formation of Ga₃O₃N by setting $T = 0$ K; the Gibbs free energy of formation $\Delta G_{\text{formation}}$ is thus identical to the enthalpy of formation $\Delta H(P) = \Delta E + P\Delta V$. We first carried out a search for the lowest energy *unit-cell* configuration of the spinel-structured Ga₃O₃N. Among the $8!(6!2!) = 28$ possible configurations, there are three crystallographically distinct O/N arrangements for (Ga₃O₃N)₂. We used the LDA to calculate lattice parameters at $P = 1$ atm and also the $V(P)$ relations for these three models: the calculated third-order Birch–Murnaghan equations of state parameters for each of these three unit-cell models are listed in Table 1. The configuration labeled as model I has a rhombohedral sym-

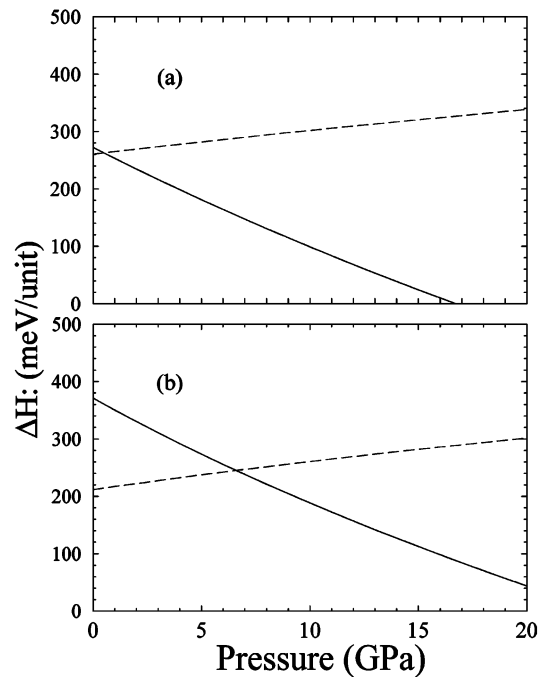


Figure 1. LDA-calculated formation enthalpy ΔH (i.e., Gibbs free energy of formation $\Delta G_{\text{formation}}$ at zero temperature) as a function of pressure using (a) LDA methods and (b) the GGA approach. The calculated positive ΔH suggests an endothermic formation. The solid plots are calculated assuming the oxynitrides are synthesized from β -Ga₂O₃ and wurtzite GaN, and the dashed plots are calculated assuming the oxynitrides are synthesized from α -Ga₂O₃ and wurtzite GaN. The solid plot and the dashed plot cross at the pressure of the β -to- α phase transition in Ga₂O₃ (predicted to be 0.5 and 6.6 GPa by LDA and GGA methods, respectively).

metry ($R\bar{3}m$). This has the lowest equilibrium energy, and it is considered to provide the ground-state configuration of Ga₃O₃N in our theoretical study. The rhombohedral distortion from the ideal cubic structure is very small; i.e., the angles between the pseudocubic lattice vectors are 89.33° within the equilibrium configuration. The calculated equilibrium volume and the bulk modulus of this ground-state configuration compare favorably with the experimental measurements (see below). At zero pressure, our LDA calculations predict an endothermic enthalpy of formation, with $\Delta H = +272$ meV per Ga₃O₃N unit (26.2 kJ/mol) with respect to Ga₂O₃ (monoclinic β phase) + GaN (hexagonal wurtzite structure). The LDA calculations predict a negative $d\Delta H/dP$ slope (solid line in Figure 1a), so the Gibbs free energy of formation becomes negative at $P > 17$ GPa. However, Ga₂O₃ does not remain in the monoclinic β phase at high pressure. According to our (static) LDA calculations, a β -to- α phase transition in Ga₂O₃ takes place at $P \approx 0.5$ GPa. Most importantly, the slope of $d\Delta H/dP$ becomes *positive* when Ga₂O₃ is in the α phase (dashed line plot, Figure 1a). The experimental phase transition has been reported to occur between 0.1 MPa and 4.4 GPa;^{30,31} however, a direct transition pressure was not recorded in those studies.³² Recently, Tu et al. have reported a β -to- α phase transition in Ga₂O₃ at 13.3 GPa.³³ However, there is some uncertainty in the nature of the starting material used in that work, and

(30) Foster, L. M.; Stumpf, H. C. *J. Am. Chem. Soc.* **1951**, 73, 1590.

(31) Remeika, J. P.; Marezio, M. *Appl. Phys. Lett.* **1966**, 8, 87.

(32) Machon, D.; McMillan, P. F.; Xu, B.; Dong, J. *Phys. Rev. B*, submitted for publication.

Table 2. Analysis of Local Coordination Ordering Schemes within the Three Unit-Cell Models of the Spinel-Structured Ga₃O₃N in Terms of the Ratio of Various Types of AX₄ Tetrahedral and AX₆ Octahedral Units (%)

model	tetrahedral Ga			octahedral Ga		
	^{IV} GaO ₄	^{IV} GaO ₃ N	^{IV} GaO ₂ N ₂	^{VI} GaO ₆	^{VI} GaO ₅ N	^{VI} GaO ₄ N ₂
I		100		25		75
II		100			50	50
III	50		50		50	50

we have recently repeated the study: we find that the β - α transition occurs at $P = 22$ GPa.³² It is obvious that the nature of the Ga₂O₃ starting material, and how it transforms under high- P,T conditions, will affect the energetics of the high-pressure synthesis experiment.

Within the present study, we repeated our calculations within the GGA (Figure 1b). The GGA calculations predict a phase transition pressure for Ga₂O₃ of 6.6 GPa. The GGA formation enthalpy for the Ga₃O₃N synthesis reaction is predicted as +370 meV (35.6 kJ/mol) at $P = 1$ atm, and this value is reduced to its minimum of +245 meV (23.6 kJ/mol) at the Ga₂O₃ transition pressure. Despite the quantitative differences between the two sets of calculations, the GGA results agree qualitatively with the findings from the LDA calculations. Both the LDA and GGA studies predict that the optimal pressure for synthesizing the spinel-structured Ga₃O₃N from Ga₂O₃ + GaN mixtures is around that of the β -to- α phase transition in Ga₂O₃ ($P \approx 6.6$ GPa, according to GGA calculations).

Next, we investigated the temperature effects on the stability of the oxynitride system. A simple ideal solution model has been previously adopted to estimate the effects of O/N disorder in spinel-structured oxynitrides.^{19,34} Such a simple statistical model is valid only in the cases where all the atomic configurations have very similar energies, and it approximates the additional Gibbs free energy term with a contribution due to the alloy disorder with a pure entropic term:

$$G_{\text{alloy}}(T,P) = -4k_{\text{B}}T[x \ln x + (1-x) \ln(1-x)]$$

(here the factor 4 is due to the presence of four possible different anion sites in the molecular unit that are assumed to be equally accessible). It is known that such simple models can significantly underestimate the alloy formation temperature if some of the atomic configurations are energetically inaccessible at the temperature of the experiment. To obtain a better estimate of the entropic contribution to the Gibbs free energy that is more relevant to our experimental results, we studied the correlation between the energetic properties of the oxynitride materials and their local atomic ordering schemes among the three unit-cell models (Table 2). The spinel structure is described as a packing of AX₄ tetrahedra and AX₆ octahedra present in a 1:2 ratio. In the case of Ga₃O₃N, there are five possible types of AX₄ tetrahedra, i.e., ^{IV}GaO₄, ^{IV}GaO₃N, ^{IV}GaO₂N₂, ^{IV}GaON₃, and ^{IV}GaN₄. Similarly, there exist seven types of AX₆ octahedra: ^{VI}GaO₆,

^{VI}GaO₅N, ^{VI}GaO₄N₂, ^{VI}GaO₃N₃, ^{VI}GaO₂N₄, ^{VI}GaON₅, and ^{VI}GaN₆. The distribution of various types of AX₄ and AX₆ units within the three models studied is listed in Table 2. No ^{IV}GaON₃, ^{IV}GaN₄, ^{VI}GaON₅, or ^{VI}GaN₆ species were considered to simplify the statistical analysis; such N-rich AX₄ or AX₆ species are expected to have low concentration because the average O:N ratio is 3:1. The LDA calculations show a clear energetic preference for the structure containing ^{IV}GaO₃N sites over those with the combination 50% ^{IV}GaO₄ + 50% ^{IV}GaO₂N₂ and the 25% ^{VI}GaO₆ + 75% ^{VI}GaO₄N₂ combination over that with 50% ^{VI}GaO₅N + 50% ^{VI}GaO₄N₂.

We then constructed a three-energy-level model to investigate the consequences of this anion site ordering on the formation energetics of the oxynitride spinel, using the ground-state energies of the three lowest energy models found above (Table 1):

$$\Delta G_{\text{formation}}(T,P) = \Delta H(P) - \frac{1}{2}k_{\text{B}}T \ln[4 + 12e^{-2\Delta\epsilon_1/k_{\text{B}}T} + 12e^{-2\Delta\epsilon_2/k_{\text{B}}T}]$$

Here $\Delta H(P)$ is the static formation enthalpy as discussed above, the values 4, 12, and 12 are the degeneracies of the levels corresponding to each model, and $\Delta\epsilon_1$ and $\Delta\epsilon_2$ are the energies of the two “excited” states (i.e., models II and III) compared to the ground-state energy (as listed in column 2 of Table 1). At a given pressure, the alloy formation temperature corresponds to that at which $\Delta G_{\text{formation}}$ becomes zero. On the basis of our LDA calculations, this condition occurs at $T_{\text{alloy}} = 2800$ K. That result means that, according to our model, a stoichiometric Ga₃O₃N spinel phase would become thermodynamically stabilized with respect to other ordering schemes and could be synthesized from Ga₂O₃ + GaN mixtures above $P \approx 6$ –7 GPa and $T = 2800$ K. This temperature estimate is considerably higher than that used experimentally to synthesize an oxynitride spinel-structured material from the component oxides and nitrides (synthesis temperatures as low as 1200 °C at 5 GPa; see below). The main reasons for the discrepancy are that the oxynitride materials obtained experimentally contain vacancies on the Ga³⁺ and perhaps also on the anion sites and the O:N ratio obtained is larger than the ideal stoichiometry that was modeled. Both considerations will have a large effect on the relative energies of ground-state and experimentally accessible “excited-state” models. Also, it is not yet clear that it is justified to exclude high-N-content environments such as ^VGaON₃, ^{IV}GaN₄, ^{VI}GaON₅, or ^{VI}GaN₆ on purely statistical grounds from the thermodynamic treatment. Such species could have special stability due to local bonding environments, including bond valence constraints.³⁵ That will have to be tested in future investigations of local coordinations in Ga_xO_yN_z materials using appropriate experimental probes of the local structural environments (e.g., X-ray absorption spectroscopy/EXAFS, NMR, etc.).

Laser-Heated Diamond Anvil Cell Studies of Ga₂O₃–GaN Mixtures. We began our experimental studies of the

(33) Tu, B. Z.; Cui, Q. L.; Xu, P.; Wang, X.; Gao, W.; Wang, C. X.; Liu, J.; Zou, G. T. *J. Phys.: Condens. Matter* **2002**, *14*, 10627.

(34) Fang, C. M.; Metselaar, R.; Hintzen, H. T.; de With, G. *J. Am. Ceram. Soc.* **2001**, *84*, 2633.

(35) Dong, J.; Deslippe, J.; Sankey, O. F.; Soignard, E.; McMillan, P. F. *Phys. Rev. B* **2003**, *67*, 094104.

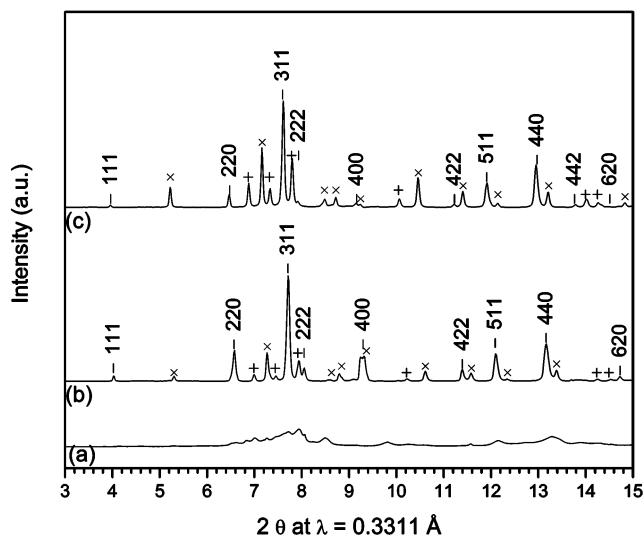


Figure 2. Synchrotron X-ray diffraction patterns in the diamond anvil cell of the $\text{Ga}_2\text{O}_3 + \text{GaN}$ mixture (a) at 10.5 GPa before heating, (b) at 10.5 GPa after laser heating to 1700 °C, and (c) after pressure release. The patterns were collected at a wavelength $\lambda = 0.3311 \text{ \AA}$. The vertical tick marks indicate the position of the spinel peaks at, respectively, 10.5 GPa and room pressure. The “+” and “x” symbols, respectively, identify the GaN and $\alpha\text{-Ga}_2\text{O}_3$ peaks.

synthesis of gallium oxynitride spinel-structured materials using laser-heating techniques in the diamond anvil cell. In Figure 2, we present in situ synchrotron X-ray diffraction patterns of a stoichiometric $\text{Ga}_2\text{O}_3\text{-GaN}$ sample taken before and after laser heating in the DAC at 10.5 GPa and following decompression to ambient P . Before heating, the pattern consists of broad peaks due to Ga_2O_3 and GaN that have been mechanically strained by compression. Following heating, a new series of peaks appear due to a new oxynitride phase formed by reaction among the end members. The new phase is readily identified as a spinel-structured $\text{Ga}_x\text{O}_y\text{N}_z$ compound, by comparison with the X-ray diffraction pattern of cubic $\gamma\text{-Ge}_3\text{N}_4$ at similar pressures.¹¹ X-ray diffraction peaks due to $\beta\text{-Ga}_2\text{O}_3$ and wurtzite-structured GaN are also present within the pattern, following all of the heating experiments at high pressure. All of the peaks are sharpened, due to relaxation of mechanical strains during the laser-heating experiment.

The results of the LH-DAC studies indicated that full transformation/recovery of the new cubic spinel-structured $\text{Ga}_x\text{O}_y\text{N}_z$ phase could never be completed during these runs, even during/after experiments carried out to peak temperatures well in excess of 2000 °C. Those observations led us to carry out a series of multianvil synthesis experiments, described below.

The peaks assigned to the new spinel-structured $\text{Ga}_x\text{O}_y\text{N}_z$ compound formed during the LH-DAC runs were fitted to a cubic lattice, with $a_0 = 8.160 \text{ \AA}$ at 10.5 GPa. Following recovery to room pressure and temperature, the lattice parameter relaxed to $a_0 = 8.280 \text{ \AA}$, which is close to the value observed by Puchinger et al. for a metastable $\text{Ga}_{2.8}\text{O}_{3.5}\text{N}_{0.5}$ cubic material formed during precursor-based synthesis of GaN films²² and also to that calculated for spinel-structured $\text{Ga}_3\text{O}_3\text{N}$.^{19,20} The results of the synchrotron-based X-ray diffraction studies following LH-DAC synthesis and during decompression allow us to estimate a bulk modulus

Table 3. Details of the Multianvil Synthesis Runs Using a Range of Capsule Materials and Experimental Temperatures^a

run number	pressure (GPa)	temp (°C)	duration (min)	capsule material	run product
R403	5	1500	120	BN	spinel + GaN + $\beta\text{-Ga}_2\text{O}_3$ + Ga
R404	5	1500	110	MgO	spinel + GaN + Ga
R405	5	1500	120	Pt	GaN + $\alpha\text{-Ga}_2\text{O}_3$ + spinel
R407	5	1500	60	Pt	GaN + $\alpha\text{-Ga}_2\text{O}_3$ + spinel
R440	5	1200	120	Pt	GaN + $\alpha\text{-Ga}_2\text{O}_3$
BB296	5	1700	40	Pt	spinel (+ GaN + $\alpha\text{-Ga}_2\text{O}_3$)

^a The run products are detailed in the far right column.

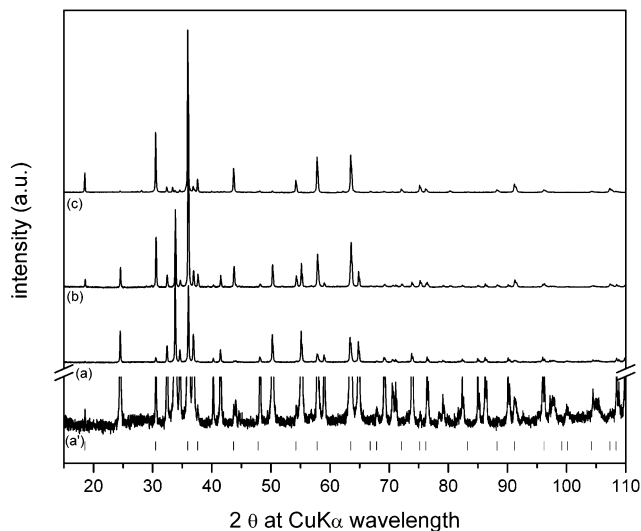


Figure 3. X-ray diffraction pattern of the multianvil samples synthesized at 5 GPa and 1200 °C (a), 1500 °C (b), and 1700 °C (c). The (a') spectrum is a zoom on the low-intensity part of spectrum (c) showing that a small amount of the spinel phase is synthesized. The vertical ticks indicate the spinel peak position. The patterns were collected using a Cu $K\alpha$ wavelength on a D5000 spectrometer with a position-sensitive detector.

of $B_0 = 234 \text{ GPa}$ for the new gallium oxynitride phase, which is comparable with that for $\gamma\text{-Ge}_3\text{N}_4$.¹¹

Multianvil Synthesis Experiments. High-pressure, high-temperature synthesis experiments of the new $\text{Ga}_x\text{O}_y\text{N}_z$ material were carried out at 5 GPa and 1500–1700 °C, using a welded Pt capsule to isolate the sample from the pressure-transmitting/furnace assembly (Table 3). Samples synthesized at 1700 °C showed a diffraction pattern that was dominated by the new phase, whereas synthesis runs at 1500 °C showed the presence of $\beta\text{-Ga}_2\text{O}_3 + \text{GaN}$ phases. These represent either unreacted starting materials, due to sluggish reaction kinetics, or phases formed during metastable back-transformation during decompression. The results of the 1200 °C synthesis run are dominated by the starting materials; however, weak peaks due to the $\text{Ga}_x\text{O}_y\text{N}_z$ spinel are present in the diffraction pattern of the recovered material, indicating that the synthesis is thermodynamically favored under these P, T conditions, but is kinetically hindered (Figure 3).

Chemical and Structural Characterization of the New Spinel-Structured $\text{Ga}_3\text{O}_3\text{N}$ Phase. Figure 4 shows an optical micrograph of a sectioned sample recovered from a multianvil synthesis experiment from a stoichiometric mixture of $\text{Ga}_2\text{O}_3 + \text{GaN}$ at 5 GPa and 1700 °C. The bright outer ring is due to the Pt capsule. An inner ring of white material contains mostly Ga_2O_3 , which we believe occurs mainly due to thermal decomposition of the GaN starting material ($\text{GaN} \rightarrow \text{Ga} + \text{N}_2$) and subsequent escape of N_2

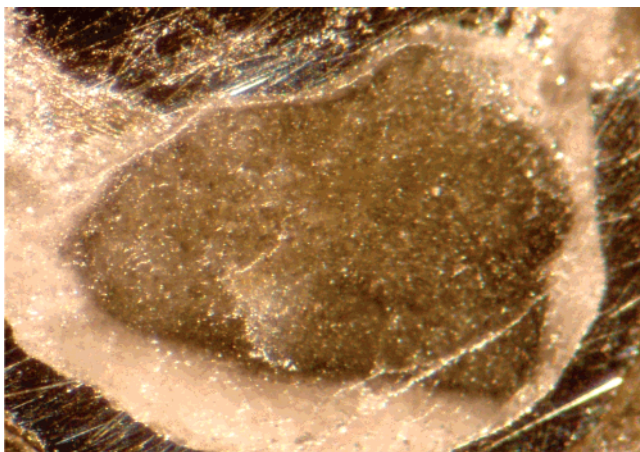


Figure 4. Optical micrograph of a sectioned sample recovered from a multianvil synthesis run. The shiny dark gray part is the platinum capsule. The white part is the unreacted Ga_2O_3 . The brown material is the gallium oxynitride phase.

Table 4. Electron Microprobe Analysis Using GaN Ga K α for the Ga Standard, Al_2O_3 O K α for the O Standard, and BN N K α for the N Standard^a

O wt %	N wt %	Ga wt %	total wt %	O atom %	N atom %	Ga atom %
18.65	3.29	75.13	97.07	47.05	9.47	43.49
18.24	2.68	76.54	97.46	46.93	7.89	45.18
18.19	2.91	76.03	97.13	46.68	8.54	44.78
18.74	3.02	76.58	97.34	47.13	8.67	44.2
18.51	3.68	76.02	97.21	46.09	10.47	43.44
18.59	3.47	75.75	97.81	46.54	9.93	43.53
18.9	3.38	75.37	97.65	47.18	9.65	43.17
18.87	3.33	75.83	98.03	47.09	9.48	43.42
18.64	3.73	75.36	97.73	46.37	10.6	43.03
19.12	3.37	75.30	97.79	47.5	9.57	42.93
19.11	3.59	74.80	97.50	47.33	10.16	42.51
18.7(3)	3.3(3)	75.7(6)		46.9(5)	9.5(8)	43.6(8)

^a The last line presents the mean and standard deviation for each column.

from the capsule. The central part of the sample is homogeneous and is brown in color. Backscattered electron imaging during the electron probe microanalysis revealed light gray grains along with occasional darker gray grains within the primary gallium oxynitride matrix, due to GaN and Ga_2O_3 , respectively, as expected from the X-ray diffraction study. Electron probe microanalysis of the matrix material gave an average composition of $\text{Ga}_{43.6(8)}\text{O}_{46.9(5)}\text{N}_{9.5(8)}$, with a N:O ratio of 0.20(1) (Table 4). This formulation would imply vacancies present on the anion sites relative to the ideal spinel structure and a Ga oxidation state slightly below +3. However, electron probe analysis of such samples can underestimate the quantity of light elements present. Here we have used the crystallographic data to provide additional constraints on the sample composition.

The structure of the new gallium oxynitride spinel was deduced from X-ray studies of the most phase pure samples recovered from multianvil synthesis runs ($P = 5$ GPa, $T = 1700$ °C). The powder X-ray diffraction data were analyzed using the Rietveld refinement technique. From the refinement, it was determined that the sample contained 14.5% wurtzite-structured GaN and 2.0% β - Ga_2O_3 , in addition to the majority (83.5%) gallium oxynitride spinel phase. The diffraction pattern of the $\text{Ga}_x\text{O}_y\text{N}_z$ phase was refined within the cubic spinel structure (space group $Fd\bar{3}m$), using the GSAS program.^{36,37} To begin the refinement, the N:O ratio

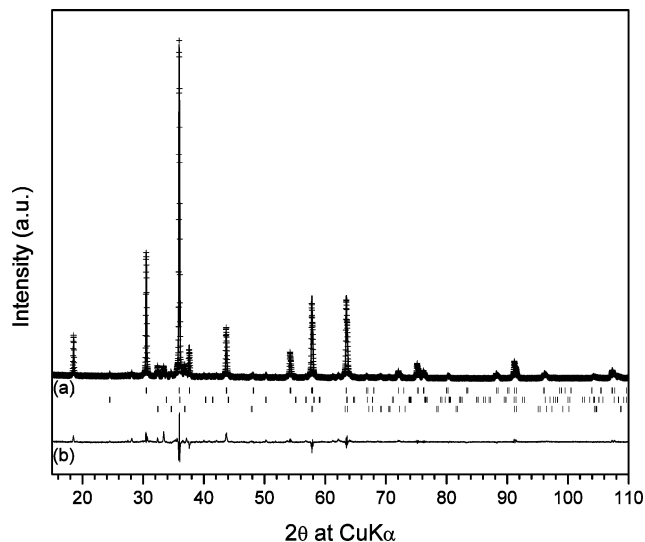


Figure 5. Refined powder X-ray diffraction pattern of cubic spinel-structured gallium oxynitride that was used to derive the experimental structure parameters reported here. The experimental data points are shown as plus signs, and the fit to the data is shown with a solid gray line (a). The difference curve (b) is displayed underneath the spectrum. The upper row of tick marks shows the reflections (2θ values) for the spinel phase, the sample also including 2% residual Ga_2O_3 is indicated by the middle row of tick marks, and 14.5% GaN is represented by the lower row of tick marks.

Table 5. Results from the Rietveld Refinement of the X-ray Diffraction Pattern Taken on the Sample Synthesized at 5 GPa and 1700 °C^a

atom	x	y	Z	occupancy	U_{iso}
Ga	0.125	0.125	0.125	1.000	0.0216
Ga	0.5	0.5	0.5	0.904	0.0195
O	0.264	0.264	0.264	0.808	0.0100
N	0.264	0.264	0.264	0.162	0.0100

^a The refinement was based on the spinel structure with a starting model placing the O and N atoms at the 0.25 position. We refined the Ga site occupancies and determined the O:N ratio using the electron microprobe data while maintaining the charge balance. The lattice parameter $a_0 = 8.281(2)$ Å, $\chi^2 = 9.35$, $R_{\text{wp}} = 9.64\%$, and $R_p = 7.02\%$.

within the anion sites was fixed at the value determined from the electron microprobe analysis (0.2). In the first stage of the refinement, the occupancies of both tetrahedral and octahedral Ga sites were refined freely. However, the occupancy of the tetrahedral site remained very close to unity, so we assumed the occupancy of Ga atoms in that site to be equal to 1 in further refinement steps. The occupancy of Ga in the octahedral site was then further refined and was determined to be 0.90(4). If we assume a Ga^{3+} oxidation state, the chemical composition of the oxynitride spinel determined by the X-ray analysis is $\text{Ga}_{2.8}\text{N}_{0.64}\text{O}_{3.24}$. The refinement using these parameters resulted in a good fit to the observed diffraction data, $R_{\text{wp}} = 9.57\%$, $\chi^2 = 9.23$, with a crystallographic R factor of 6.91% (Figure 5). The refinement details and refined structural parameters are given in Table 5. We also attempted to refine the predicted rhombohedral structure using the powder pattern. However, the data did not indicate any sign of the distortion and were better refined with the cubic structure which has fewer degrees of freedom.

(36) Toby, B. H. *J. Appl. Crystallogr.* **2001**, *34*, 210.

(37) Larson, A. C.; Von Dreele, R. B. *Los Alamos Natl. Lab., [Rep.] LAUR (U. S.)* **2000**, *86*, 748.

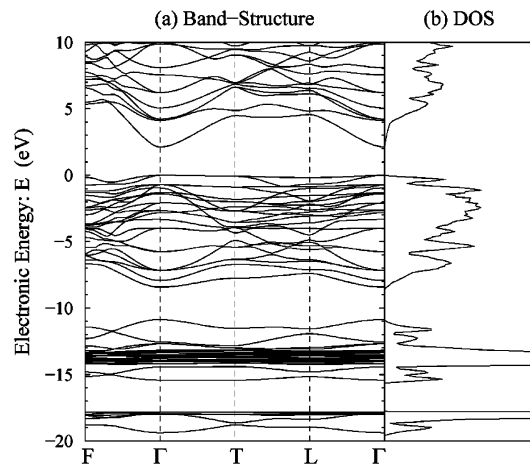


Figure 6. (a) Electronic band structure and (b) electronic density of states for $\text{Ga}_3\text{O}_3\text{N}$ calculated using first-principles (DFT) methods within the LDA.

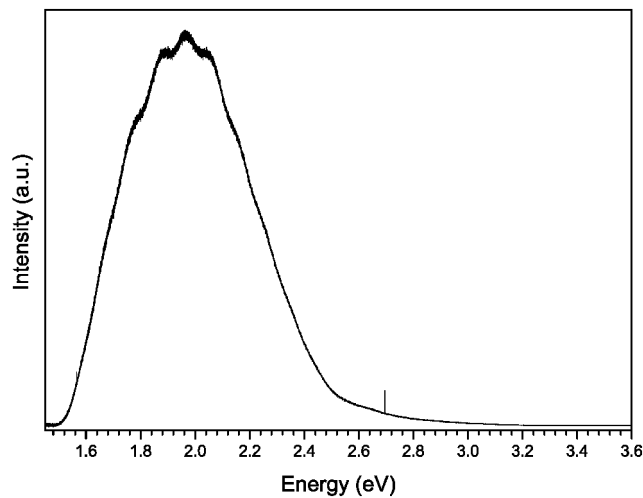


Figure 7. Photoluminescence spectrum of the $\text{Ga}_{2.8}\text{N}_{0.64}\text{O}_{3.24}$ sample obtained via high- P,T synthesis in the multianvil experiments, using UV laser excitation (325 nm).

Electronic Properties. Using ab initio LDA methods, we calculated the electronic band structure within the LDA on the basis of our atomic model of the ground-state configuration of $\text{Ga}_3\text{O}_3\text{N}$ (model I). The LDA-predicted band dispersion is plotted in Figure 6a from the center of the Brillouin zone (the Γ point) along three directions to the F , T , and L points at the zone boundaries. The electronic density of states function is shown in (b). Our calculations indicate that spinel-structured gallium oxynitrides are direct wide band gap semiconductors, with optoelectronic properties that are similar to those of wurtzite- and sphalerite-structured GaN and gallium oxides. Because of well-known limitations of the LDA for such electronic structure calculations, the predicted magnitude of the band gap (2.1 eV) is likely to be underestimated in this study. The same LDA methods underestimate the band gaps of the GaN (wurtzite) and $\beta\text{-Ga}_2\text{O}_3$ phases by 1.3 and 2.3 eV, respectively; we thus expect the experimental band gap of $\text{Ga}_3\text{O}_3\text{N}$ (spinel) to lie around 4 eV. We obtained room-temperature photoluminescence spectra of the $\text{Ga}_{2.8}\text{N}_{0.64}\text{O}_{3.24}$ sample obtained by high- P,T synthesis, using 325 nm laser excitation (Figure 7). The onset of the photoluminescence signal begins just below 2.5 and extends to 1.5 eV. Because the experimentally synthesized material contains a large quantity of defects on the

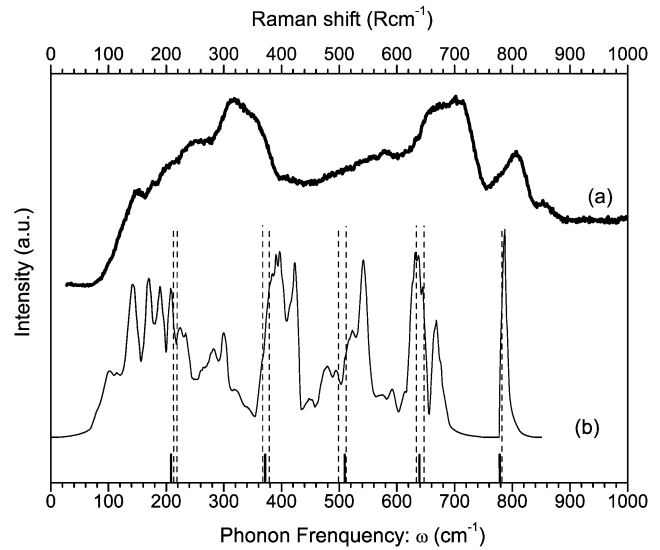


Figure 8. (a) Raman spectrum collected for the $\text{Ga}_{2.8}\text{N}_{0.64}\text{O}_{3.24}$ sample at an excitation wavelength of 514.5 nm. The bold solid lines on the frequency scale below indicate the positions of the Raman bands for the analogous spinel form of $\gamma\text{-Ge}_3\text{N}_4$. (b) Phonon density of states (vDOS) calculated for the $R\bar{3}m$ pseudocubic $\text{Ga}_3\text{O}_3\text{N}$ phase, predicted as “model I” in the enthalpy calculations (Table 1). The dashed lines indicate the Raman-active modes for that phase.

Ga^{3+} sites, and also perhaps on the anion sites, along with O/N disorder, it is unlikely that the photoluminescence feature corresponds to excitations across the band gap. Instead, the observed PL band is likely to arise from defect-related transitions between states mainly within the gap, so that the intrinsic band gap for a stoichiometric ordered material would lie considerably above 2.5 eV, as predicted by theory.

Phonon Spectrum. The Raman spectrum of the new oxynitride spinel phase contains several broad bands (Figure 8), indicating substantial disorder among the O and N atoms on the 32e sites in the spinel structure and/or the presence of cation (Ga^{3+}) or anion vacancies. The broad bands have maxima near 700 and 800 cm^{-1} , and also near 300 cm^{-1} , that correspond generally to the positions of Raman-active modes within the analogous spinel-structured compound $\gamma\text{-Ge}_3\text{N}_4$.³⁸ To aid in the interpretation of our experimentally obtained Raman spectra of $\text{Ga}_x\text{O}_y\text{N}_z$ phases, we calculated the Γ point phonon frequencies of the 14-atom rhombohedral unit cell of $\text{Ga}_3\text{O}_3\text{N}$ (model I structure) using first-principles LDA methods. The same technique was previously used to predict the positions of the Raman-active vibrational modes in $\gamma\text{-Ge}_3\text{N}_4$.^{29,38} The pseudocubic $R\bar{3}m$ model structure for $\text{Ga}_3\text{O}_3\text{N}$ is predicted to have nine Raman-active modes ($4A_{1g} + 5E_g$), with zone-center frequencies calculated at 213, 219, 367, 379, 499, 512, 634, 647, and 782 cm^{-1} . These calculated frequencies are denoted by dashed lines in Figure 8. Within an anion-disordered structure, as expected for the real $\text{Ga}_x\text{O}_y\text{N}_z$ spinel, the predicted zone-center modes act as poles for interpreting the broadened spectra that approach the full vibrational density of states (vDOS). The expected mode frequencies are grouped around the five frequency values (i.e., 216, 373, 506, 640, and 782 cm^{-1}) that are associated

(38) Deb, S. K.; Dong, J.; Hubert, H.; McMillan, P. F.; Sankey, O. F. *Solid State Commun.* **2000**, *114*, 137.

with the ideal spinel structure. By analogy with the Raman spectrum of γ -Ge₃N₄, we expect the lowest frequency peak (216 cm⁻¹) and the two highest frequency peaks (640 and 782 cm⁻¹) to have the strongest intensities, whereas the two intermediate frequency peaks (373 and 506 cm⁻¹) are relatively weak. We cannot yet directly calculate the effects of the O/N disorder on the broadening patterns observed in our Raman spectra. However, it is likely that the observed Raman spectrum provides a first view of the vDOS functions of Ga₃O₃N and also γ -Ge₃N₄ spinels.

To provide a semiquantitative estimation of the widths of the broad peaks, we calculated the full phonon dispersion using a 112-atom supercell model. The Born effective charge induced LO–TO splitting in the ionic compounds are corrected on the basis of the interplanar force constant model proposed by Kunc and Martin.³⁹ As shown in Figure 8, the highest frequency strong Raman peak (i.e., the A_g mode near 782 cm⁻¹) is expected to be the sharpest one. The other strong peak near 640 cm⁻¹ is expected to have a broader width (40–60 cm⁻¹).

Conclusions

We synthesized bulk samples of a new gallium oxynitride spinel-structured phase using high-pressure, high-temperature techniques from Ga₂O₃ + GaN mixtures. We demonstrated that the new material has a cubic spinel structure, or one that might be slightly distorted from cubic symmetry, due to anion site (O/N) ordering. The structure was refined using Rietveld analysis of X-ray powder diffraction data and further interpreted using Raman spectroscopy and electronic structure and phonon calculations.

Synthesis of the gallium oxynitride spinel, with a composition close to Ga₃O₃N, now extends the family of nitride and oxynitride spinel-structured compounds, from γ -(Si,-Ge)₃N₄, Sn₃N₄, cubic SiAlON compounds synthesized at high pressure, and vacancy-containing metastable Al₂O₃ forms and AlON compounds that are already well-known at ambient pressure.

Our theoretical study showed that the most stable structure for Ga₃O₃N corresponds to a rhombohedral distortion of the ideal spinel structure. The formation of Ga₃O₃N is endothermic at ambient pressure and low temperature, and the optimal synthesis pressure is predicted to lie close to that for the β -to- α phase transition in Ga₂O₃ (around 6.6 GPa according to our GGA calculations). The calculated direct band gap energy for a stoichiometric oxynitride spinel was estimated to be around 4 eV. This value is larger than that obtained from photoluminescence data collected on our experimentally synthesized sample, which likely contains Ga³⁺ vacancies and other structural defects. The synthesis of this new Ga–O–N phase makes contact with the important optoelectronic materials known to exist in the (Ga,Al,In)N system that provide light-emitting diodes and solid-state lasers in the blue to UV range. A cubic Ga₃O₃N material similar to the compound synthesized here has recently been prepared in thin film form via chemical precursor techniques.⁴⁰ That result indicates that the new materials could be developed for use within novel optoelectronic devices.

Acknowledgment. This study was supported by U.K. EPSRC Grant GR/R65206 to P.F.M. P.F.M. is a Wolfson-Royal Society Research Fellow acknowledging support from the Research Merit Award scheme. The multianvil experiments were enabled via funding to COMPRES, the Consortium for Materials Properties Research in Earth Sciences, under U.S. NSF Cooperative Agreement EAR 01-35554. Portions of this work were performed at GeoSoilEnviroCARS (Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the U.S. NSF–Earth Sciences (Grant EAR-0217473), Department of Energy–Geosciences (Grant DE-FG02-94ER14466), and State of Illinois. Use of the APS was supported by the U.S. DOE, Basic Energy Sciences, Office of Energy Research, under Contract No. W-31-109-Eng-38. The theoretical work at Auburn University is supported by the U.S. DOE under Contract No. DE-FG02-03ER46060 to J.D.

CM051224P

(39) Kunc, K.; Martin, R. M. *Phys. Rev. Lett.* **1982**, *48*, 406.

(40) Kinski, I.; Miede, G.; Heymann, G.; Theissmann, R.; Riedel, R.; Huppertz, H. *Z. Naturforsch.*, in press.