High-Pressure Synthesis, Electron Energy-Loss Spectroscopy Investigations, and Single Crystal Structure Determination of a Spinel-Type Gallium Oxonitride $Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$

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Received December 14, 2008. Revised Manuscript Received February 10, 2009

Under high-pressure/high-temperature conditions of 5 GPa and 1250 °C, the cubic phase $Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$ ($\square$ = vacancy) was synthesized in a Walker-type multianvil apparatus. For the first time, the crystal structure of a gallium oxonitride was determined on the basis of single crystal X-ray diffraction data. The cubic spinel-type gallium oxonitride crystallizes in the space group $Fd\bar{3}m$ (No. 227) with a lattice parameter $a_0 = 827.8(2)$ pm. The combination of energy-dispersive X-ray spectroscopy (EDS) with electron energy-loss spectroscopy (EELS) allowed the quantification of nitrogen and oxygen for structural refinement. In the literature dealing with oxonitrides, crystal defects in spinel-type materials are handled with different models, mainly the approximation of a constant anion model. The present results indicate that this model is questionable, and one should also take into account a model with both cation and anion vacancies. Furthermore, a linear relationship between the lattice parameters and the ratio N/O in the gallium oxonitrides is questionable.

Introduction

The spinel structure was termed after naturally common compounds ($MgAl_2O_4$, spinel) of composition XY_2O_4, crystallizing in the cubic system with space group $Fd\bar{3}m$ (No. 227). Thirty-two oxide anions per unit cell form a face-centered cubic structure, containing tetrahedrally and octahedrally coordinated vacancies.

Already known from minerals, crystallizing into a defect spinel-type structure, the occurrence of vacancies is a common feature of the crystal structure, which allows charge neutrality to be maintained in case of different oxidation states of incorporated cations.

Spinel-type materials can have magnetic properties and high hardness (γ-Si_3N_4 [1,2]) or may be potentially new cathode materials for solid state lithium batteries, such as the defect spinel $Li_{8n/(n+4)}Mn_{8/(n+4)}O_4$.[3] In the system AlN-$Al_2O_3$, a defect spinel-type material with mixed anion sites, designated as alon, forms at high temperatures above 1700 °C.[4] From the discovery of the first defect spinel γ-alon[5] up to now, the material was established as security “glass”, not only in a window function to protect pilots in cockpits but also to protect instrumentations, due to the extraordinary mechanical and optical properties.[6]

In contrast to the well-known phase diagram of the binary phase system Al_2O_3 and AlN,[6] the knowledge on the respective phases in the system Ga_2O_3 and GaN is fragmentary. The first compound in the system Ga−O−N was mentioned by Verdier and Marchand in 1976 in an article about the reaction of ammonia on gallium oxide, where a phase with the composition $Ga_{1-x/3}\square_{x/3}N_{1-x}O_x$ with $x \sim 0.1$ was isolated at low temperature conditions.[7] In 1979, Grekov and Demidov attempted the first synthesis to achieve gallium oxonitride phases[8] by the pyrolysis of the complex $GaCl_3 \cdot NH_3$, leading to amorphous films with variable nitrogen/oxygen ratios. In the following years, several publications and patents on gallium oxonitrides as passivation films and insulating layers were presented by Shiota and Nishizawa.[9−11] Although neither the crystal structure nor the

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10.1021/cm803371k CCC: $40.75 © 2009 American Chemical Society
Published on Web 04/21/2009

Table 1. Exemplary Result of All EELS Measurements, Displayed from One Single Crystal of the Spinel Gallium Oxonitride Phase as Representative for All Other Measurements

meas. no.	1	2	3	4	5	6	7	8	9	10	11	12
N/O	0.30 ± 0.067	0.29 ± 0.061	0.31 ± 0.070	0.30 ± 0.072	0.18 ± 0.051	0.32 ± 0.069	0.20 ± 0.046	0.21 ± 0.052	0.27 ± 0.062	0.17 ± 0.046	0.16 ± 0.043	0.24 ± 0.053

phases of the gallium oxonitride layers were clearly defined in these publications, the usefulness and effectiveness of gallium oxonitride as an optical and electrical material; as well as the importance of its manufacturing was pointed out. In the 1990s, several efforts and approaches to synthesize gallium oxonitrides were made.[12−17] In addition to descriptions of amorphous gallium oxonitride phases, some authors reported about crystalline phases. In 2000, Wolter et al. found a cubic phase with the general formula $Ga_{(x+2)}N_{3x}O_{3-3x}$.[18] During the following years, interface intermediates between pure gallium oxide and gallium nitride or small oxidized regions on pure GaN layers were reported.[19−21] Furthermore, Puchinger et al. described small gallium oxonitride areas as an impurity in small surface areas on a thin film of GaN, which had been derived from a liquid precursor by chemical solution deposition (CSD).[22] The compound was characterized via HRTEM-SAED (high-resolution transmission electron microscopy−selected area electron diffraction), coupled with EEL (electron energy loss) spectroscopy and Auger spectroscopy, proposing a composition of $Ga_{2.8}O_{3.5}N_{0.5}$ with a lattice parameter of $a_0 = 820.0(7)$ pm. Shortly after that, Lowther et al. calculated the theoretical lattice parameter of a hypothetical cubic spinel phase of the composition Ga_3O_3N at $a_0 = 820(7)$ pm.[23] In 2005, McMillan's group in London and our joint cooperation group published the high-pressure/high-temperature synthesis of well-characterized crystalline gallium oxonitride phases for the first time.[24,25] Both studies presented spinel-type phases with lattice parameters a_0 of 826.4(1) pm[24] and 828.1(2) pm,[25] respectively. While Soignard et al. used a mixture of α/β-Ga_2O_3 and w-GaN in a molar ratio of 1:1, we used an amorphous to nanocrystalline gallium oxonitride ceramic, obtained by the pyrolysis of a precursor $[Ga(O^tBu)_2NMe_2]_2$, with a mean N/O ratio of 0.86 as starting material. Both strategies produced spinel-type samples, which were characterized by X-ray powder diffraction. The stability field of this spinel phase was systematically investigated by reactions between hexagonal GaN (99.9%, Alfa Aesar, Karlsruhe, Germany) and monoclinic β-Ga_2O_3 (99.9+%, Sigma Aldrich, Munich, Germany) with different molar ratios under specific high-pressure/high-temperature conditions.[26] One of these experiments, with the starting molar ratio of GaN:Ga_2O_3 = 9:1, resulted in a highly crystalline sample, from which, for the first time, the isolation of single crystals of spinel-type gallium oxonitride became possible. Here we report about the synthesis, compositional analysis, and single crystal structure determination of a gallium oxonitride spinel. The results lead to new insights concerning the constant anion model and the constant cation model, which are mainly used to describe crystal defects in spinel-type γ-alon. Furthermore, the linear relationship between the lattice parameter and the ratio N/O in all investigated gallium oxonitrides is discussed.

Experimental Section

To synthesize the gallium oxonitride spinel, hexagonal GaN and monoclinic β-Ga_2O_3 were mixed thoroughly and filled into a hexagonal boron nitride crucible (Henze BNP GmbH, HeBoSint S10, Kempten, Germany). The boron nitride crucible was positioned into the center of an 18/11-assembly, which was compressed by eight tungsten carbide cubes (TSM-10 Ceratizit, Reutte, Austria). The assembly was compressed to 5 GPa in 2 h, using a multianvil device, based on a Walker-type module, and a 1000 t press (both devices from the company Voggenreiter, Mainleus, Germany). A detailed description of the preparation of the assembly can be found in references 27−29.

The sample was heated up to 1250 °C (cylindrical graphite furnace) in 10 min, kept there for 15 min, and cooled down to 850 °C in 25 min at constant pressure. Afterward, the sample was quenched to room temperature by switching off the resistivity heating, followed by a decompression period of 6 h.

A crystalline product could be separated from the surrounding boron nitride of the crucible. Small colorless, air-resistant crystals of the reaction product were isolated from the bulk sample and tested on a Buerger camera. An energy dispersive X-ray spectroscopic investigation (Jeol JFM-6500F, HP Ge-type detector, Jeol, Ltd., Tokyo, Japan) of these crystals confirmed the presence of gallium, oxygen, and nitrogen.

Spectroscopic (EDS, EELS) and Transmission Electron Microscopic (TEM) Investigations. To verify the crystal structure of the examined particles and to single out the spinel, selected area diffraction patterns (SAD) were recorded before any other analysis.

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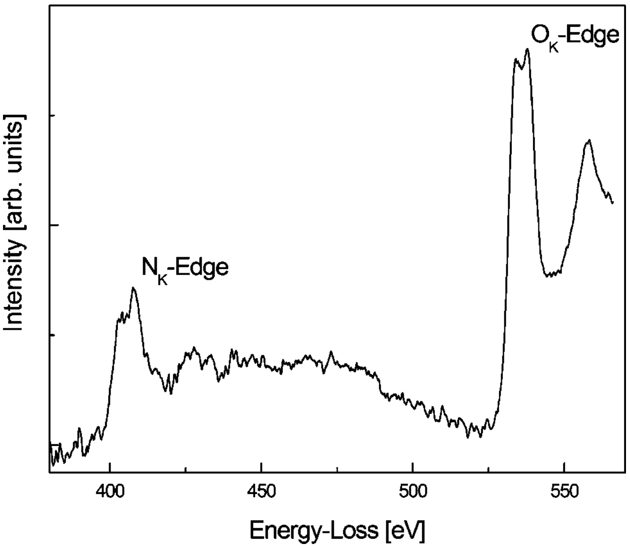

Figure 1. Typical EEL spectrum from a selected area of a single crystal of the cubic spinel phase $Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$.

For a quantitative analysis of the elemental composition of the specific particle, the combination of energy-dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) provides a powerful approach for the characterization. The crucial point is the resolution of the used beam, because adjacent GaN and Ga_2O_3 particles will lead to the elements gallium, oxygen, and nitrogen, if the beam width is too broad. Therefore, it should be emphasized that only with a narrow beam resolution and a careful choice of neighborless crystals a measurement without overlapping particles is guaranteed. So, the simultaneous use of EDS and EEL spectroscopy allows nitrogen and oxygen to be quantified in the matrix and their distribution in the microstructure to be characterized.

The homogeneity and the nitrogen to oxygen ratio of the synthesized spinel-type gallium oxonitride phase were determined through a transmission electron microscope (FEI CM12 operated at 120 kV, equipped with a LaB_6 cathode), coupled with an electron energy loss spectrometer (Gatan DigiPeels 766 parallel electron spectrometer, attached to the FEI CM12) and an energy dispersive X-ray (EDAX Genesis 2000) spectrometer. Several series of spectra were taken from small crystals of the reaction product. In detail, different areas of one as well as various particles, showing the spinel structure, were examined. The spinel structure of all analyzed particles was confirmed by selective area electron diffraction patterns (SAED). To avoid the loss of nitrogen during the investigation, caused by a heating process through the interaction of highly accelerated electrons with the sample (ionization), we used a double tilt liquid nitrogen cooling stage (Gatan, Model 613) for the sample holder. In former measurements, a nitrogen loss could be observed during beam radiation in high vacuum.

Table 1 gives a survey over the results of 12 measurements on one single crystal of the spinel gallium oxonitride phase. Each value represents a different position at the crystal. These measurements yield a mean value of $\overline{\mathrm{N/O}} = 0.25 \pm 0.06$, representative for this single crystal. Figure 1 shows a representative EELS measurement, recorded on a single crystal. All further measurements on different crystals led to similar results, definitely confirming a considerable amount of nitrogen in the examined spinel-type gallium oxonitride crystals of our high-pressure sample. The ideal composition of a defect free spinel gallium oxonitride is Ga_3O_3N, which means the highest possible amount of nitrogen. Taking into account the determined value of $\overline{\mathrm{N/O}} = 0.25 \pm 0.06$, the molar ratio of oxygen: nitrogen is 3.20:0.80. As a result of the fact that charge neutrality in the colorless spinel must be guaranteed, the total composition of the spinel gallium oxonitride crystal averages to $Ga_{2.93}(O_{3.20}N_{0.80})$, based on the preliminary acceptance of a filled anion model (see below).

Crystal Structure Analysis. The powder diffraction pattern of the reaction product was collected with a Stoe Stadi P diffractometer, using monochromatized Cu Kα_1 ($\lambda = 154.051$ pm) radiation. Figure 2 illustrates the result of a Rietveld refinement, showing reflections of the starting material hexagonal gallium nitride (w-GaN) and reflections of the cubic spinel phase. The reflections of the latter were indexed on the basis of a cubic unit cell, leading to a refined lattice parameter of $a_0 = 828.0(1)$ pm (FullProf,[30,31] Table 1). The lattice parameters, determined from the powder ($a_0 = 828.0(1)$ pm) and the single crystal data ($a_0 = 827.8(2)$ pm), agree well.

Single crystal intensity data were collected at room temperature from a colorless crystal (dimensions: $0.025 \times 0.025 \times 0.020$ mm^3), using an Enraf-Nonius Kappa CCD with graded multilayer X-ray optics (Mo Kα radiation, $\lambda = 71.073$ pm). According to the Laue symmetry $m\bar{3}m$ and systematic extinctions $h + k = 2n$, $h + l$, $k + l = 2n$, $0kl$ with $k + l = 4n$ and k, $l = 2n$, and $h00$ with $h = 4n$, the cubic space group $Fd\bar{3}m$ (No. 227) was derived, which was suitable for structure solution (direct methods) and refinement. However, the starting positional parameters were taken from the structural refinement of $Ga_{2.81}O_{3.57}N_{0.43}$[24] to adjust our results to the previously published data. Ga1 occupies the Wyckoff site $8a$ ($^1/_8$,$^1/_8$,$^1/_8$), Ga2 the position $16d$ ($^1/_2$,$^1/_2$,$^1/_2$), and the oxygen and nitrogen anions are at $32e$ (origin choice 2). As the differentiation between oxygen and nitrogen on the mixed Wyckoff site $32e$ is impossible from X-ray data, the results of the above-reported EELS measurements were used to restrain the ratio of $\overline{\mathrm{N/O}} = 0.25 \pm 0.06$ in the structural refinement. The refinement of the occupancy parameter of the tetrahedrally coordinated gallium site (Ga1, $8a$) showed full occupation within two standard deviations so that full occupancy was assumed in the final cycles. In contrast, the octahedral gallium site (Ga2, $16d$) exhibited a site occupation deficiency of about 10% in all steps of the refinement. To maintain charge neutrality, the negative charge resulting from the occupancy of the anionic site was set equal to the sum of positive charges from Ga1 and Ga2. The final least-squares cycles resulted in a total occupation of 95.4(4)% for the anionic site. From these data, the nominal composition is $Ga_{2.79}(O_{3.05}N_{0.76})$, which implies vacancies on the cationic and on the anionic part of the structure. All relevant details of the data collections and evaluations are summed up in Table 2. Structure solution and parameter refinement with anisotropic displacement parameters for all atoms (full-matrix least-squares against F^2) were performed by the SHELX-97 software suite.[32,33] The final difference Fourier synthesis did not reveal any significant residual peaks (see Table 2). Additionally, the positional parameters, occupancy factors (Table 3), anisotropic displacement parameters (Table 4), interatomic distances, and angles (Table 5) are listed.

Further details of the crystal structure investigation can be obtained in the Supporting Information or from the Fachinformationszentrum (FIZ) Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-419664.

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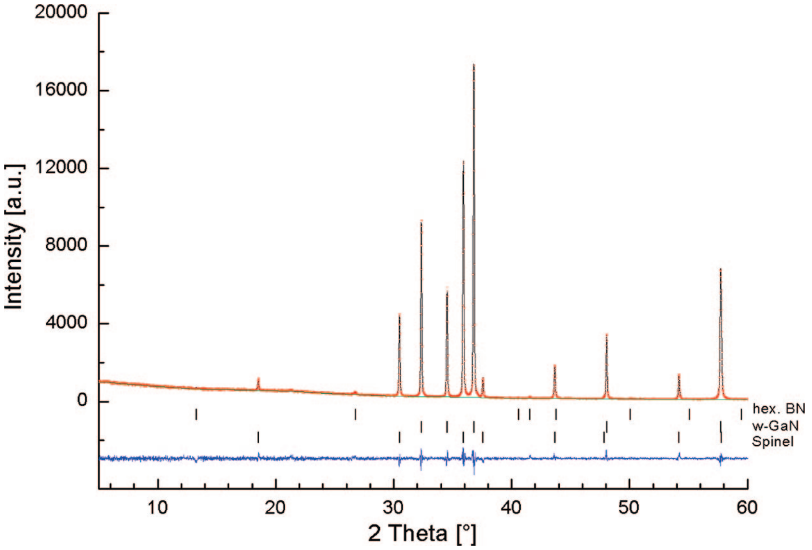

Figure 2. Rietveld refinement of the powder diffraction pattern of the reaction product, including the cubic spinel phase $Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$, w-GaN, and hexagonal BN from the capsule material.

Table 2. Crystal Data and Structure Refinement for $Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$

empirical formula	$Ga_{2.79}(O_{3.05}N_{0.76})$
molar mass, g·mol^{-1}	254
crystal system	cubic
space group	$Fd\bar{3}m$ (No. 227)
powder diffractometer	Stoe Stadi P
radiation	Cu Kα_1 (λ = 154.051 pm)
Powder Diffraction Data	
a, pm	828.0(1)
volume, nm^3	0.5682(1)
Single Crystal Data	
single crystal diffractometer	Enraf-Nonius Kappa CCD
radiation	Mo Kα (λ = 71.073 pm)
a, pm	827.8(1)
volume, nm^3	0.5673(2)
formula units per cell	$Z = 8$
temperature, K	293(2)
calculated density, g·cm^{-3}	5.95
crystal size, mm^3	0.025 × 0.025 × 0.020
detector distance, mm	40.0
irradiation/exposure, s	110
absorption coefficient, mm^{-1}	26.13
absorption correction	semiempirical
F(000), e	930
θ range, deg	4.3−32.3
range in *hkl*	±12, ±8, ±7
total no. reflections	171
independent reflections	69 (R_{int} = 0.0138)
reflections with $I \geq 2\sigma(I)$	62 (R_σ = 0.0152)
parameters/restraints	10/1
goodness-of-fit (F^2)	1.153
final *R* indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0171$ $wR_2 = 0.0516$
R indices (all data)	$R_1 = 0.0191$ $wR_2 = 0.0528$
larg. diff. peak and hole, e·Å^{-3}	0.94/−0.75

Results and Discussion

The new gallium oxonitride phase $Ga_{2.79}(O_{3.05}N_{0.76})$ crystallizes into a defective spinel-type structure (Figure 3) with a lattice parameter of $a_0 = 827.8(2)$ pm (single crystal data).

Table 6 and Figure 4 show a comparison of the lattice parameters of γ-Ga_2O_3 [34,35] with all known gallium oxonitrides, arranged in the order of increasing ratio of $\overline{N/O}$.

Table 3. Atomic Coordinates, Isotropic Equivalent Displacement Parameters U_{eq} (in Å^2), and Site Occupancy Factors for $Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})^a$

atom	Wyckoff position	*x*	*y*	*z*	U_{eq}	S.O.F.
Ga1	8*a*	$^1/_8$	$^1/_8$	$^1/_8$	0.0075(3)	1
Ga2	16*d*	$^1/_2$	$^1/_2$	$^1/_2$	0.0114(3)	0.895(4)
O	32*e*	0.2569(2)	*x*	*x*	0.0083(7)	0.763(3)
N	32*e*	0.2569(2)	*x*	*x*	0.0083(7)	0.191(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Anisotropic Displacement Parameters U_{ij} (in Å^2) for $Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ga1	0.0075(3)	U_{11}	U_{11}	0	0	0
Ga2	0.0114(3)	U_{11}	U_{11}	−0.0017(2)	U_{23}	U_{23}
O/N	0.0083(7)	U_{11}	U_{11}	−0.0005(6)	U_{23}	U_{23}

Table 5. Interatomic Distances (in pm) and Angles (in deg) Calculated with the Single Crystal Lattice Parameters of $Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$ with Standard Deviations in Parentheses

Ga1−O/N	189.1(3)	4×
Ga2−O/N	201.4(2)	6×
O/N−Ga1−O/N	109.5	
O/N−Ga2−O/N	180	
O/N−Ga2−O/N	86.71(9)	
O/N−Ga2−O/N	93.29(9)	

Additionally, the results of a GGA (generalized gradient approximation) and LDA (local density approximation) calculation of Kroll et al. [36,37] are shown in Table 6 and Figure 4. The value of 820(7) pm from ref. 23 for a hypothetical Ga_3O_3N is not shown in the graphic because of its high standard deviation. As expected, the typical GGA and LDA calculations over- and underestimate the experimentally determined values (all calculations are based on the constant anion model (see below)). With the exception

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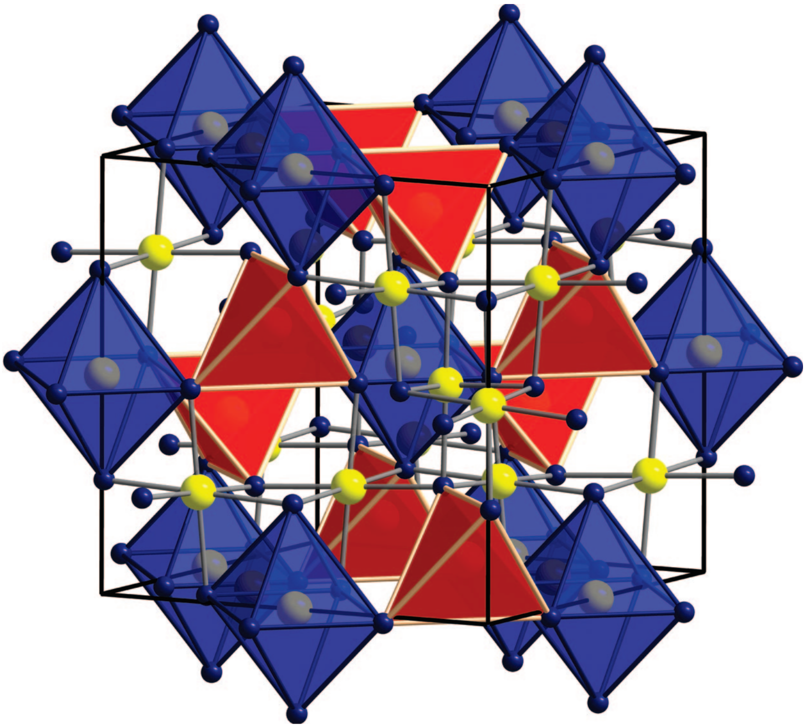

Figure 3. Crystal structure of spinel-type gallium oxonitride. The tetrahedra and octahedra are displayed as light (red) and dark (blue) polyhedra, respectively.

Table 6. Comparison of the Lattice Parameters (pm) of γ-Ga_2O_3 and Gallium Oxonitrides in the Spinel-Type Structure

phase	ratio N/O	lattice param. *a*, pm	references
γ-Ga_2O_3		822; 823.8(6), 822.43 (GGA); 807.48 (LDA)	34−37
$Ga_{22}O_{30}N_2$	0.06	827.14 (GGA); 812.01 (LDA)	36 and 37
$Ga_{2.81}O_{3.57}N_{0.43}$	0.12	826.4(1)	24
$Ga_{2.8}O_{3.5}N_{0.5}$	0.14	820.0(7)	22
$Ga_{23}O_{27}N_5$	0.185	829.81 (GGA); 814.88 (LDA)	36 and 37
$Ga_{2.8}O_{3.24}N_{0.64}$	0.20	828.1(2)	25
$Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$	0.25 ± 0.06	827.8(2) (single cryst.)	this work
$Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$	0.25 ± 0.06	828.0(1) (powder)	this work
Ga_3O_3N	0.33	820(7); 832.61 (GGA); 817.63 (LDA)	23, 36, and 37

of the value published by Puchinger et al. ($Ga_{2.8}O_{3.5}N_{0.5}$: $a_0 = 820.0(7)$ pm, determined on a thin film [22]), all other experimental values can be found on or near a straight line plotted in Figure 4, which depends approximately linearly on the ratio N/O. It is obvious that the lattice parameters, determined in this work (827.8(2) and 828.0(1) pm for single crystal and powder XRD data, respectively), show slightly smaller values as would be expected from the extrapolation of the plotted line. A possible explanation for that requires a closer look at the structure.

On the basis of the structure refinement of the single crystal data, the bond length between the tetrahedral gallium site (Ga1) and the mixed occupied anionic position comes to 189.1(3) pm, and the corresponding value for Ga2 is 201.4(2) pm. Interestingly, the structure refinement showed a not fully occupied octahedral site 16*d* (Ga2). Soignard et al. obtained similar results during their Rietveld refinement of the phase $Ga_{2.8}O_{3.24}N_{0.64}$.[25] In the beginning of their refinement of the powder pattern, the occupancies of the tetrahedral and octahedral gallium sites were refined freely. Similar to our results, they observed that the occupancy of the tetrahedral site remained very close to unity. In contrast, the octahedrally coordinated gallium site was determined to be 0.90(4), resulting in the composition $Ga_{2.8}O_{3.24}N_{0.64}$ by keeping charge neutrality. This behavior is nearly identical to our results from single crystal data, where the tetrahedrally coordinated

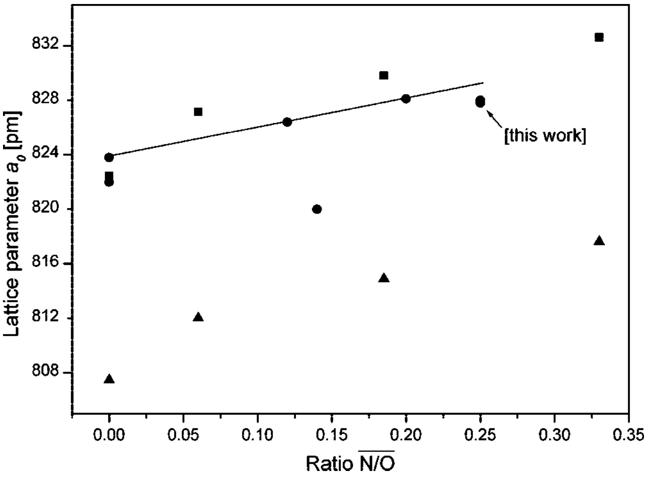

Figure 4. Lattice parameters of γ-Ga_2O_3 and cubic spinel-type gallium oxonitrides as a function of the ratio N/O (data see Table 6). The circles (●) stand for the experimental collected data, the triangles (▲) encode LDA results, and the squares (■) represent lattice parameters calculated via GGA.

site is fully occupied and the occupancy of the octahedral site comes to 0.895(4).

These results are in accord to research into the defective spinel γ-Al_2O_3,[38,39] which also shows vacancies at the octahedrally coordinated cationic site. A long-standing controversy has surrounded the question of whether the vacancies occupy the tetrahedral or the octahedral sites in the spinel structure.[40−44] One of the last investigations, based on transmission electron diffraction experiments, claimed that the tetrahedral sites are fully occupied by aluminum and that the vacancies are located only at the octahedral site.[45] Furthermore, theoretical considerations, based on pair-potential calculations, showed that a vacancy prefers the octahedral site more than the tetrahedral site by an average of 3.7 eV per vacancy.[46] In this context, we should not forget that cation vacancies in a nonstoichiometric spinel "$MgAl_2O_4$" are also found at octahedral sites.[47] The first-principles calculations of Kroll et al. also had octahedral vacancies in the lowest energy structure of $Ga_{23}O_{27}N_5$.[36]

As a result of the fact that the here reported gallium oxonitride contains more nitrogen (EELS results) than the above-mentioned compound of Soignard et al., the total composition is necessarily calculated to $Ga_{2.79}O_{3.05}N_{0.76}$. This result leads to vacancies on the cation site (octahedrally coordinated site 16*d*) and on the anion site 32*e*, relative to the ideal spinel structure, leading to the notation $Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$. In analogy, such vacancies must be also invoked for the compound of Soignard et al. This result differs from former models, used in the structural characterization of spinel-type oxonitrides. For example, the ideal structure of γ-alon Al_3O_3N would have a cubic spinel-type structure (space group $Fd\bar{3}m$, No. 227) with oxygen and nitrogen atoms, randomly distributed at the Wyckoff site 32*e,* and the aluminum atoms at the tetrahedral (8*a*) and octahedral (16*d*) sites. The assumption of crystal defects, based on deviations from the ideal composition, led to the introduction of new structure models by Adams et al.,[48] Lejus et al.,[49] and McCauley.[4] The first model, designated as the constant anion model, is based on aluminum vacancies and can be formulated as $Al_{(2+x/3)}\square^{Al}{}_{(3-4x)/12}O_{3-x}N_x$ (Adams et al.), $Al_{(8+x)/3}\square^{Al}{}_{(1-x)/3}O_{4-x}N_x$ (Lejus et al.; all values multiplied by 4/3 to point on the ideal spinel composition AB_2O_4), or $Al_{(64+x)/3}\square^{Al}{}_{(8-x)/3}O_{(32-x)}N_x$ (McCauley, standardized to 32 anions inside the unit cell of the spinel-type structure). The second model of McCauley is the constant cation model, represented by the formula $Al_{24}O_{(72-3x)/2}N_x\square_{[(72-x)/2-32]}$, in which the cationic part of the structure is always fully occupied. Up to now, ab initio calculations between the constant anion and the constant cation model in the alon systems revealed that the constant anion model with vacancies on the Al sites is preferred, whereas a model with oxygen interstitial anions is unlikely.[50] This model was also confirmed by structure refinements, based on XRD and neutron diffraction data.[51] Thus, the alon spinel unit cell has eight aluminum cations in tetrahedral sites and 15 Al and one vacancy in the 16 octahedral sites ($Al_8{}^{[4]}Al_{15}{}^{[6]}\square^{[6]}O_{27}N_5$).[6] The normal spinel composition with eight nitrogen atoms in the formula ($x = 8$) does not exist, whereas alon ($x = 5$) and alon′ (Φ') ($x = 2$) are stable phases.[52]

Kroll et al. calculated the hypothetical structure of a spinel-type gallium oxonitride with the ideal composition γ-Ga_3O_3N and showed that the lowest energy is realized in a regular distribution of the nitrogen atoms in the slightly distorted cubic substructure of the anionic part of the structure.[36] However, the estimation of the enthalpy for the formation of a spinel-type gallium oxonitride is still endothermic, especially when the lowest energy structures of GaN and Ga_2O_3 are used. Thus, the ternary compound is postulated to be formed at elevated temperatures with substantial entropy contributions ΔS. Further calculations on defective spinel-type structures like $Ga_{23}O_{27}N_5$ and $Ga_{22}O_{30}N_2$ (both with the constant anion model) revealed a lower enthalpy of formation (still endothermic) than the calculations of the ideal γ-Ga_3O_3N. The necessary entropy terms are presumably raised by a mixing of oxygen and nitrogen in the anionic part of the structure itself and of the vacancies within the octahedral sites of the structure. Hence, Kroll et al. conclude that at 1000 K all spinel-type phases are thermodynamically unstable with respect to the binary compounds β-Ga_2O_3 and GaN. The necessary temperatures for the formation of Ga_3O_3N, $Ga_{23}O_{27}N_5$, $Ga_{22}O_{30}N_2$, and γ-Ga_2O_3 are 1486, 1370, 1456, and 2400 K, respectively.[36] Accordingly, the formation of defective spinel-type oxonitrides is always more favored than the ideal composition Ga_3O_3N.

The calculations on γ-alons and on the gallium oxonitrides are always based on the constant anion model with a completely filled anionic part of the structure. This model may not be the only one possible, as already noted by McCauley.[4] Our experimental data lead to the composition $Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$. Therefore, the validity of the approximation of a constant anionic part of the structure is in question. From the existing models, the formation enthalpy of the ternary oxonitride spinels is unfavorable relative to the low-energy structures of the oxides. Up to now, the deficiency in enthalpy can only be balanced with contributions that arise from a mixing of oxygen and nitrogen in the anionic part of the structure. We tend toward the view that this contribution can be additionally enhanced by the assumption of defects on site 32*e*.

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A problem for a reliable calculation of the enthalpy is the fact that a true distribution of oxygen and nitrogen gives a substantial contribution to the configurational entropy. Now, additional vacancies in the anionic part of the structure next to the already included cationic defects on the octahedral site ought to be considered. These noninteger occupations are usually treated by the application of supercells, complicating a computational approach. Nevertheless, with respect to increasing computer power, more calculations are planned in the near future.

An analytical approach concerning the question of ordering oxygen, nitrogen, and the vacancies inside the anionic substructure might be possible via neutron diffraction experiments at a single crystal of acceptable size.

Next to the EELS research, an experimental determination of the specific density of the single crystals would be very desirable, to confirm the reported results by a second independent method. Up to now, this verification through all possible density measurement methods such as Archimedes, pycnometer, and floating method were impossible, because the current size of the single crystals was not sufficient.

Coming back to the discussion of the lattice parameters (see above, Table 6, and Figure 4), we insist on the assumption that the determined vacancies both in the cationic and anionic part of the structure have a noticeable impact on the size of the unit cell, reducing it to a smaller size than expected (see Figure 4). Certainly, $Ga_{2.81}O_{3.57}N_{0.43}$ and $Ga_{2.8}O_{3.24}N_{0.64}$ also have got vacancies, but not to the extent existing in $Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$. Therefore, a linear dependency of the lattice parameter with an increasing ratio N/O is questionable.

Pashchenko et al. [53] already presumed the existence of defects in both the cation and the anion substructure in technologically important mono- and polycrystalline manganese−zinc ferrites, which were used in the magnetic heads of video tape recorders and the transformer cores of color television sets. This assumption was based on an entire collection of experimental results, dealing with chemical inhomogeneities, that determine the quality of the manganese−zinc ferrites.

The complete description of the spinel-type structure requires an additional parameter, designated as the "anion parameter *u*".[54] If the value *u* is equal to 0.25, the anions form a perfect cubic close packed structure, defining regular tetrahedral and octahedral coordinations around the sites 8*a* (point symmetry $\bar{4}3m$) and 16*d* ($m\bar{3}m$), respectively. In our structure refinement, the parameter *u* has a value of 0.2569(2), slightly higher than the ideal value of 0.25. This causes an enlargement of the tetrahedral site at the expense of the octahedral one and a degeneration of the octahedral site symmetry to $.\bar{3}m$ (displacement of the oxygen atoms along the [111] direction).

Conclusion

The data from the single crystal structure refinement of the presented spinel-type gallium oxonitride confirm a fully occupied tetrahedral gallium site and vacancies at the octahedrally coordinated gallium position, coupled with vacancies on the anionic site (Wyckoff position 32*e*). So, the composition of the characterized single crystal comes to $Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$, revealing anionic vacancies in a single crystal structure determination of a spinel-type structure for the first time.

Acknowledgment. The authors gratefully acknowledge the continuous support of this work by Prof. Dr. W. Schnick, Department Chemie and Biochemie of the University of Munich (LMU). Special thanks go to Dr. P. Mayer for collecting the single crystal data and to H.-J. Kleebe (TU Darmstadt) for allowing the use of the TEM facilities. This work was financially supported by the Deutsche Forschungsgemeinschaft HU 966/5-1 and KI 838/3-1. H. Huppertz and R. Riedel are indebted to the Fonds der Chemischen Industrie for financial support.

Supporting Information Available: Crystallographic data in CIF format.

This material is available free of charge via the Internet at http://pubs.acs.org.

CM803371K

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