

# High-Pressure Synthesis of a Gallium Oxonitride with a Spinel-Type Structure

Isabel Kinski<sup>a</sup>, Gerhard Miehe<sup>c</sup>, Gunter Heymann<sup>b</sup>, Ralf Theissmann<sup>c</sup>, Ralf Riedel<sup>a</sup>, and Hubert Huppertz<sup>b</sup>

<sup>a</sup> Institute of Materials Science, Dispersive Solids, Darmstadt University of Technology, D-64287 Darmstadt, Germany

<sup>b</sup> Department Chemie und Biochemie, Ludwig-Maximilians-Universität München, Butenandtstraße 5 – 13 (Haus D), D-81377 München, Germany

<sup>c</sup> Institute of Materials Science, Structure Research, Darmstadt University of Technology, D-64287 Darmstadt, Germany

Reprint requests to Isabel Kinski. E-mail: kinski@materials.tu-darmstadt.de

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The new compound  $\text{Ga}_{2.81}\text{O}_{3.57}\text{N}_{0.43}$  was crystallized under high-pressure / high-temperature conditions in a spinel-type structure from a prestructured gallium oxonitride ceramic, which was obtained from the single-source molecular precursor  $[\text{Ga}(\text{O}^i\text{Bu})_2\text{NMe}_2]_2$  by thermal treatment in an ammonia atmosphere. The optimized precursor-derived gallium oxonitride ceramic remains nanocrystalline up to 600 °C and can be transformed at 7 GPa and 1100 °C into the crystalline phase  $\text{Ga}_{2.81}\text{O}_{3.57}\text{N}_{0.43}$ . The structure, homogeneity, and nitrogen to oxygen ratio were determined using TEM coupled with an electron energy loss spectrometer (EELS) and an energy dispersive X-ray (EDX) spectrometer. For phase analysis and structure confirmation, X-ray powder diffraction data were measured.

**Key words:** High-Pressure, Gallium Oxonitride, Spinel Structure Type

## Introduction

Ceramics and single crystalline phases in the solid solution system  $\text{GaN-Ga}_2\text{O}_3$  have been scarcely investigated, even though the system promises a high potential for industrially relevant properties as suggested by the analogous phases in the well-investigated system  $\text{AlN-Al}_2\text{O}_3$  designated as *alon* phases. Recently, we reported on a new approach to the formation of bulk gallium oxonitride *via* a pyrolysis process [1]. A new synthetic pathway, using molecular precursors with gallium atoms simultaneously bound to nitrogen and oxygen atoms, led to nanocrystalline gallium oxonitride ceramics at 350 °C with variable N/O ratios of 0.86 to 2.1 controlled by the chemical composition of the molecular precursor. Because of their composition and nanocrystallinity, these ceramics are ideal starting materials for high-pressure / high-temperature experiments to form highly crystalline gallium oxonitride phases.

For a theoretical ideal phase composition of  $\text{Ga}_3\text{O}_3\text{N}$  with a spinel structure, Lowther *et al.* calculated a lattice parameter of  $a_0 = 8.20 \pm 0.07$  Å [2].

According to other theoretical simulations, the end member phases wurtzite-type GaN and monoclinic  $\beta\text{-Ga}_2\text{O}_3$  tend to form from solid solutions resulting in a phase separation [3]. This situation and the fact that networks built-up from Ga–O–Ga and Ga–N–Ga units have seldom been reported in literature and were never found with a high degree of crystallinity, makes the synthesis of new crystalline phases in the system  $\text{GaN-Ga}_2\text{O}_3$  a challenge. The most promising starting materials are not the already existing crystalline end member phases GaN and  $\text{Ga}_2\text{O}_3$ , using a solid state reaction, but new nanocrystalline gallium oxonitride ceramics. This approach provides a method that bypasses the formation of the stable end members GaN with wurtzite-type structure and monoclinic  $\beta\text{-Ga}_2\text{O}_3$ . Another ambient-pressure approach for the synthesis of GaN, which uses  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  as starting material, was used by Jung *et al.* [4]. It was modified in our group providing a spinel-type structure gallium oxonitride with a low degree of crystallinity displayed in the powder X-ray diffraction pattern in Fig. 1. From elemental analysis the chemical formula was calculated to  $\text{Ga}_{2.7}\text{N}_{3.66}\text{O}_{0.34}$ , but the degree of crystallinity could

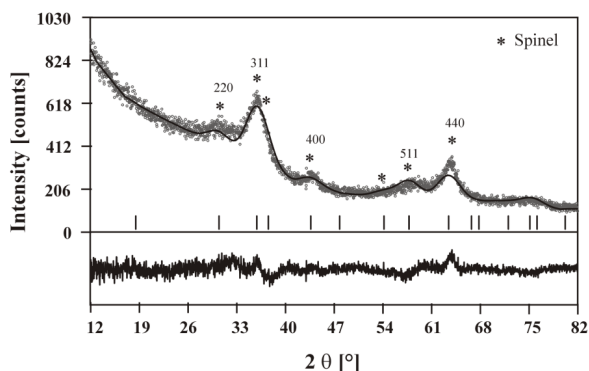


Fig. 1. Observed powder X-ray diffraction pattern ( $\text{Cu-K}\alpha_1$ ) of a spinel-type gallium oxonitride with a low degree of crystallinity synthesized by pyrolysis using  $\text{Ga}(\text{NO}_3)_3 \cdot x \text{H}_2\text{O}$  as starting material.

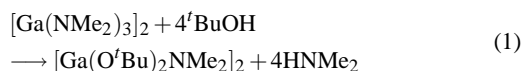
not be improved by optimization of the pyrolysis or annealing parameters. This emphasizes the necessity of a high-pressure / high-temperature approach with appropriate starting materials to reach phases with high crystallinity in the system  $\text{GaN-Ga}_2\text{O}_3$ .

## Experimental Section

### Synthesis

**General:** All reactions and operations were carried out under inert conditions with rigorous exclusion of oxygen and moisture. All solvents were dried and distilled from Na/K alloy prior to use.

**Synthesis of the precursor:** Lithium dimethylamide ( $\text{LiNMe}_2$ ) and bis[tris(dimethylamino)gallane] ( $[\text{Ga}(\text{NMe}_2)_3]_2$ ) were synthesized following the literature procedures [5, 6].  $[\text{Ga}(\text{O}^i\text{Bu})_2\text{NMe}_2]_2$  was synthesized by a modified reaction procedure according to eq. (1) [7].



**Synthesis of gallium oxonitride ceramics:** The nanocrystalline ceramic was prepared from the molecular precursor in ammonia atmosphere at elevated temperatures in quartz glass Schlenk tubes *via* a pyrolysis process as reported in reference [1]. Therefore, the precursor  $[\text{Ga}(\text{O}^i\text{Bu})_2\text{NMe}_2]_2$  was distributed in an  $\text{Al}_2\text{O}_3$  boat placed in the hottest zone of a furnace within a quartz glass Schlenk tube. The pyrolysis was performed in dry ammonia with a heating rate of  $100^\circ\text{C/h}$  up to the holding temperature of  $350^\circ\text{C}$ . The maximum temperature was kept constant for two hours with subsequent cooling to ambient temperatures.

**Experiments under HP / HT conditions:** For the high-pressure / high-temperature treatment, the gallium oxonitride

ceramic was filled into a molybdenum capsule (outside diameter: 2.35 mm; wall thickness: 0.25 mm), which was inserted the other way round in a second molybdenum capsule (inner diameter: 2.45 mm) under argon into a glove box. To prevent a reaction between the molybdenum capsules and the graphite furnace, the sample capsule was loaded into a 3.66 mm outside diameter, 0.33 mm wall thickness, and 6.0 mm length hexagonal boron nitride cylinder that was sealed by a BN plate. This arrangement was placed into the center of a cylindrical resistance heater (graphite) that had a variable (stepped) wall thickness in order to minimize the thermal gradient along the sample. Details of the construction of the assembly can be found in references [8–11].  $\text{MgO}$  rods filled the space at the top and at the bottom of the sample. A cylindrical zirconia sleeve, surrounding the furnace, provided thermal insulation. As pressure medium a  $\text{Cr}_2\text{O}_3$  doped  $\text{MgO}$  octahedron (Ceramic Substrates & Components LTD., Isle of Wight) with an edge length of 18 mm was used. A hole was drilled into the octahedron, the cylindrical assembly positioned inside and contacted with a molybdenum ring at the top and a molybdenum plate at the bottom. The experimental temperature was monitored using a  $\text{Pt/Pt}_{87}\text{Rh}_{13}$  thermocouple that was inserted axially into the octahedral assembly, the hot junction in contact with the boron nitride cylinder. Eight tungsten carbide cubes, separated by pyrophyllite gaskets (Plansee, Reutte, TSM10, edge length: 32 mm), with a truncation of 11 mm were used to compress the octahedron (“18/11 assembly” in conventional terminology) *via* a modified Walker-style split-cylinder multianvil apparatus.

For the reaction the assembly was compressed within 3 h to 7.0 GPa and heated up to  $1100^\circ\text{C}$  in the following 10 min. After holding this temperature for 10 min, the sample was quenched to room temperature. After decompression, the recovered experimental octahedron was broken apart in a glove box and the sample carefully separated from the surrounding molybdenum metal.

**Characterization methods:** Transmission electron microscopy and electron energy loss spectroscopy were performed on a Jeol JEM 3010 microscope operated at 300 kV with an  $\text{LaB}_6$  filament and post column energy filter (Gatan imaging filter (GIF)). The spatial resolution for the elemental analysis is about 2 nm. In order to determine the structure of the crystalline high-pressure phase a Philips CM20 microscope with  $\text{LaB}_6$  cathode operated at 200 kV and equipped with an energy-dispersive X-ray (EDX) system (Voyager, HPGe-detector) was used. For selected-area electron diffraction (SAED) the camera length was calibrated through an external Au-standard.

X-ray powder diffraction data were collected with a STOE STADI/P diffractometer equipped with a linear position sensitive detector ( $6^\circ$ ) using transmission geometry ( $\text{Cu-K}\alpha_1$  and  $\text{Mo-K}\alpha_1$  radiation). X-ray powder data were measured from  $5^\circ$  to  $50^\circ$   $2\theta$  with steps of  $0.02^\circ$   $2\theta$  and a counting time

of 120 s per step. For phase analysis and structure refinement the program Winplotr package was used [12]. The morphology of the crystals was visualized using a scanning electron microscope (SEM) (Jeol 6300F).

**Sample preparation:** In order to retrieve the sample after the high-pressure experiment, the octahedron was opened and the molybdenum capsule subsequently cut up in argon inside of a glove box followed by the isolation of the sample. Parts of the sample were ground, suspended in dried isopropanol, and dispersed on a copper grid for the TEM analysis, the other part was used for the XRD investigations. The amounts of molybdenum and  $\gamma\text{-Mo}_2\text{N}$  mixed in the sample depend on the sample preparation varying with the retrieving of the sample by scratching it out of the Mo capsule.

## Results and Discussion

For the high-pressure / high-temperature treatment, the starting material was a nanocrystalline gallium oxonitride ceramic with a mean N/O ratio of 0.86 that was prepared from  $[\text{Ga}(\text{O}^i\text{Bu})_2\text{NMe}_2]_2$  as precursor at 350 °C in ammonia atmosphere. The retrieved transparent crystals displayed a light greenish color in a light optical microscope. In order to get an overview of the homogeneity of the sample and the structural characteristics, EDX spectroscopy was used to distinguish between residual molybdenum particles from the capsule, side products, and newly formed crystallites.

All the crystallites of the new phase exhibited the same high degree of crystallinity and stability in the electron beam during TEM analysis. Fig. 2 shows the selected-area electron diffraction (SAED) pattern indicating a cubic face-centered cell. Extinctions owing to a  $d$  glide plane perpendicular to the 4-fold axis ( $hk0$  present only for  $h+k=4n$ ) indicate space group  $Fd\bar{3}m$  (Nr. 227) leading to a spinel-type structure. Extinctions and pseudo-extinctions within the zone  $[\bar{1}20]$  (Fig. 2) prove this suggestion.

In the following, the general conditions limiting possible reflections due to  $F$ -centering ( $h,k,l$  all even or all odd) have always been presupposed. Zone  $[\bar{1}20]$  is spanned by the reflections 002 and 420. These two reflections are extinct because of the  $d$  glide plane ( $hk0$  present only for  $h+k=4n$ ). However, in the central part of Fig. 2 – which represents the zero order Laue zone – reflections with  $h+k+l \neq 4n$  are generally absent – also if none of the indices is 0 (002 and  $00\bar{2}$  are present as very weak spots owing to multiple diffraction by interaction with FOLZ reflections). This extinction cannot be explained by a crystallographic glide

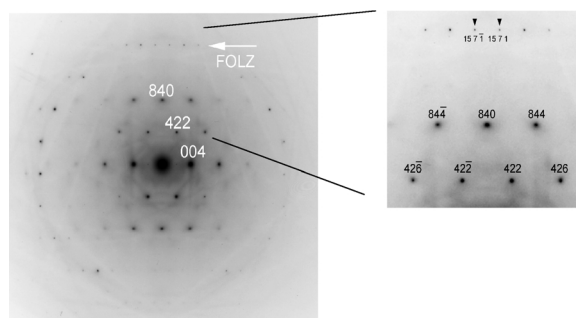


Fig. 2. Electron diffraction pattern of zone  $[\bar{1}20]$  of a gallium oxonitride crystal. The zero order Laue zone (ZOLZ) displays only reflections with all indices even. Because of the anion position at  $x,x,x$  with the special value  $x=1/4$  only reflections with  $h+k+l=4n$  are present (see magnified area on the right sight). The row of reflections marked by an arrow in the 1<sup>st</sup> order Laue zone (FOLZ) indicates, where the missing ZOLZ-reflections should be.

plane. It allows an estimation of the positional parameters of the anion and is interpreted as follows:

In a spinel structure the coordinates of the atomic positions depend on the choice of settings for the origin in the space group  $Fd\bar{3}m$ . We chose the equi-point with point symmetry  $\bar{3}m$  as unit cell origin. The cations occupy Wyckoff positions  $8a$  ( $1/8, 1/8, 1/8$ ) and  $16d$  ( $1/2, 1/2, 1/2$ ) with special conditions on  $hkl$  limiting possible reflections, namely for positions  $8a$  ( $1/8, 1/8, 1/8$ ) the condition  $h+k+l=2n+1$  or  $4n$  and for positions  $16d$  ( $1/2, 1/2, 1/2$ ) the condition  $h, k, l$  all  $2n+1$  or all  $4n$  or all  $4n+2$ .

If both positions are occupied the parity group of *forbidden* reflections may be expressed as follows:  $h+k+l=4n+2$  (negation of  $8a$ ) and *not* all indices of type  $4n+2$  (negation of  $16d$ ).

The anion occupies Wyckoff position  $32e$  ( $x,x,x$ ). No limiting condition is associated with this position. Therefore, any special limiting condition should be overruled if this position is occupied. There is, however, a very special case: If  $x=1/4$ , the atoms occupying site  $32e$  form a Cu-type *fcc* structure with  $a'_0=1/2a_0$ . Therefore, an “accidental” special condition for possible reflections is generated:  $hkl$  present only if all  $h,k,l$  are of type  $4n+2$  (corresponding to “all odd” for  $a'_0=1/2a_0$ ) or all  $h,k,l$  are of type  $4n$  (corresponding to “all even” for  $a'_0=1/2a_0$ ).

This means that reflections of the above mentioned parity group  $h+k+l=4n+2$  and *not* all indices of type  $4n+2$  are extinct as well if position  $32e$  ( $x,x,x$ ) is occupied with  $x=1/4$ . However, these reflections

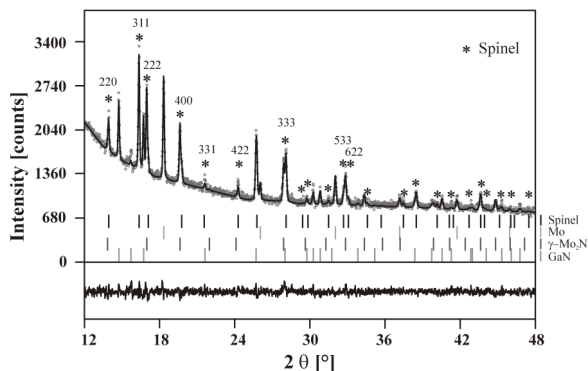


Fig. 3. Structure refinement performed on a powder X-ray diffraction pattern ( $\text{Mo-K}\alpha_1$ ) of the gallium oxonitride specimen. Next to the main spinel phase, residual particles of the Mo capsule and of the by-products  $\gamma\text{-Mo}_2\text{N}$  and hexagonal GaN contribute to the observed and calculated pattern. The Bragg positions of all four phases are displayed underneath the observed and calculated intensities, respectively, as well as the difference curve.

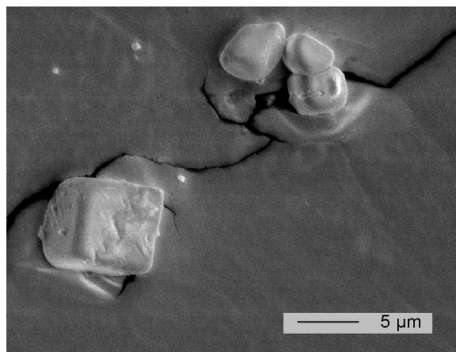


Fig. 4. The SEM picture of the gallium oxonitride sample displays the morphology of the crystals with a cubic habit though faces and edges are not developed.

gain intensity as soon as  $x$  deviates from  $1/4$ . (Note that there is no special position  $1/4, 1/4, 1/4$  in space group  $Fd\bar{3}m$ .) From the absence of those reflections in the zero order Laue zone in the diffraction pattern shown in Fig. 2 and from the degree of overexposure of the photographic negative, one can therefore conclude that  $x$  is very close to  $1/4$ . As estimated from model calculations, reflections of this parity group should be visible in Fig. 2 if  $x$  deviates by more than  $\approx 0.005$  from  $1/4$ .

For an accurate determination of the lattice parameter  $a_0$  an XRD pattern was recorded (Fig. 3). Residuals of the molybdenum capsule caused by the sample preparation can be distinguished next to the main spinel phase in the powder XRD pattern. Additionally, the XRD diagram exhibits the diffraction patterns

| N/O                         |
|-----------------------------|
| $0.09 \pm 0.01$             |
| $0.12 \pm 0.02$             |
| $0.11 \pm 0.019$            |
| $0.15 \pm 0.015$            |
| $\bar{N}/\bar{O} = 0.12(2)$ |

Table 1. TEM analysis of the atomic ratio N/O on several different crystals and different positions of gallium oxonitride determined with EEL spectroscopy.

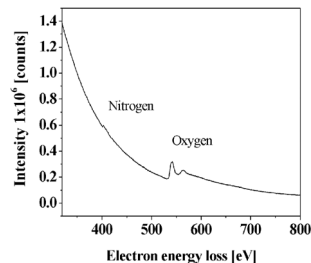


Fig. 5. Electron energy loss spectroscopy performed on a spinel gallium oxonitride crystal during TEM analysis with a beam resolution of 2 nm. The quantitative analysis of the two characteristic edges for nitrogen and oxygen results in a mean atomic ratio of  $0.12(2)$ .

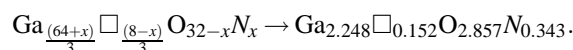
of cubic  $\gamma\text{-Mo}_2\text{N}$  and hexagonal wurtzite-GaN as by-products indicating a loss of nitrogen and formation of GaN from the gallium oxonitride ceramic during transformation to the crystalline spinel structure under high pressure. From the refined pattern the ratio of formed spinel phase to GaN was calculated to  $1 : 0.63$ . From the refined pattern the lattice parameter  $a_0$  of the spinel phase was determined to  $8.264(1) \text{ \AA}$ . This lattice parameter is slightly larger than the value of  $8.22 \text{ \AA}$  found for the metastable spinel-type structure of  $\gamma\text{-Ga}_2\text{O}_3$  first reported by Pohl [13]. In order to distinguish the new spinel phase from the known  $\gamma\text{-Ga}_2\text{O}_3$ , the nitrogen to oxygen content of the crystallites (Fig. 4) were recorded using EEL spectra in the TEM analysis (see Fig. 5). The results, which are listed in Table 1, exhibit a similar atomic N/O ratio of  $0.12(2)$  on all crystallites. Obviously, most of the nitrogen (starting ratio  $\text{N/O} = 0.86$ ) has reacted to form metal nitrides. Nevertheless, a significant part of nitrogen is retained in the spinel structure. Therefore, we propose rather a gallium oxonitride than a pure  $\gamma\text{-Ga}_2\text{O}_3$  phase. Using the assumption of a filled anion structure without any vacancies for the new gallium oxonitride spinel, the theoretical chemical formula  $\text{Ga}_{2.81}\text{O}_{3.57}\text{N}_{0.43}$  can be calculated from the N/O ratio if charge neutrality is maintained.

Considering the model developed by McCauley for the *alons* phases, the ideal spinel structure demands 32 anion sites and 24 cation sites for maintaining charge balance. This takes into account that there might be vacancies occurring in the cation sites while

Table 2. Crystallographic parameters for the Rietveld refinement and crystal data of  $\text{Ga}_{2.81}\text{O}_{3.57}\text{N}_{0.43}$ .

|                                    |  |          |       |       |
|------------------------------------|--|----------|-------|-------|
| Wavelength [Å]                     | 0.7093   |          |       |       |
| No. refined parameters             | 29   |          |       |       |
| $R_F$                              | 0.0689   |          |       |       |
| $R_{WP}$                           | 0.255  |          |       |       |
| $R_{exp}$                          | 0.225  |          |       |       |
| $\chi^2$                           | 1.283  |          |       |       |
| Empirical formula                  | Ga <sub>2.81</sub> O <sub>3.57</sub> N <sub>0.43</sub> |          |       |       |
| Space group                        | $F\bar{d}3m$ (Nr. 227)                                 |          |       |       |
| Lattice parameter $a_0$ [Å]        | 8.264 ± 0.1  |          |       |       |
| Unit cell volume [Å <sup>3</sup> ] | 564  |          |       |       |
| Z                                  | 8  |          |       |       |
| Atom                               | Wyckoff site   | $x/a$    | $y/b$ | $z/c$ |
| Ga                                 | 8a   | 1/8      | 1/8   | 1/8   |
| Ga                                 | 16d  | 1/2      | 1/2   | 1/2   |
| (O,N)                              | 32e  | 0.250(5) | $x$   | $x$   |

the occupation of the anion sites are complete [14]. This is the designated constant anion model, in which the general formula for the gallium oxonitride spinel results in:



Inside this formula, the symbol “ $\square$ ” stands for a cation vacancy. The ideal spinel is represented by the value  $x = 8$ .

Screening the literature, Puchinger *et al.* reported on a similar gallium oxonitride with spinel-type structure proposing a composition of  $\text{Ga}_{2.8}\text{O}_{3.5}\text{N}_{0.5}$  [15]. This phase formed as an impurity in small surface areas on a thin GaN film and was determined using HRTEM-SAED coupled with EEL and Auger spectroscopy.

Interestingly, an analogous phase to the new  $\text{Ga}_{2.81}\text{O}_{3.57}\text{N}_{0.43}$  spinel phase presented here was found in the system  $\text{AlN-Al}_2\text{O}_3$ . With a given composition of  $\text{Al}_{2.81}\text{O}_{3.56}\text{N}_{0.44}$  (ICDD-JCPDS No. 80-2172, lattice parameter  $a_0 = 7.95$  Å [16]), the compound fits almost the theoretical value of the new gallium oxonitride. A comparison of the lattice parameters seems worthwhile. We consider the changes between the phase  $\gamma\text{-Al}_{2.14}\text{O}_{3.2}$  (commonly referred to

as  $\gamma\text{-Al}_2\text{O}_3$ ) and the analogous  $\gamma\text{-Ga}_2\text{O}_3$  phase, in which the substitution of  $\text{Al}^{3+}$  against  $\text{Ga}^{3+}$  leads to an increase of the lattice parameter from  $a_0 = 7.911$  Å ( $\gamma\text{-Al}_{2.14}\text{O}_{3.2}$  [17]) to  $a_0 = 8.22$  Å ( $\gamma\text{-Ga}_2\text{O}_3$  [13]) corresponding to an increase of 3.9%. Increasing the value of phase  $\text{Al}_{2.81}\text{O}_{3.56}\text{N}_{0.44}$  ( $a_0 = 7.95$  Å) by 3.9% leads to an expected lattice parameter of about 8.26 Å for the analogous Ga-compound, which fits well with the measured value of 8.264(1) Å for  $\text{Ga}_{2.81}\text{O}_{3.57}\text{N}_{0.43}$ .

## Conclusion

Though there are some reports on gallium oxonitrides in the literature, assignments of structural features of these compounds were only tentative. Previous investigations suffered from low degrees of crystallinity. With the synthesis of  $\text{Ga}_{2.81}\text{O}_{3.57}\text{N}_{0.43}$ , a highly crystalline phase of the solid solution between the binary compounds GaN and  $\text{Ga}_2\text{O}_3$  became accessible for the first time. This phase crystallizes under high-pressure / high-temperature conditions in a spinel-type structure with space group  $F\bar{d}3m$  (No. 227) exhibiting a lattice parameter of  $a_0 = 8.264(1)$  Å and an  $x$  parameter of 0.250(5) causing extinctions in the TEM diffraction pattern. The high degree of crystallinity was not only revealed by electron diffraction but also by powder X-ray diffraction.

Due to the presented results, we have strong evidence in realizing further compounds in the system GaN/ $\text{Ga}_2\text{O}_3$  using different gallium oxonitride ceramics in combination with extreme conditions of pressure and temperature. Furthermore, it is obvious that highly crystalline  $\gamma\text{-Ga}_2\text{O}_3$  can be formed under high-pressure / high-temperature conditions, and a detailed characterization will be a future goal of our investigations.

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