A Systematic Investigation of the Stability Field of Spinel-type Gallium Oxonitrides

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Over the last years, the synthesis and characterization of new spinel-type gallium oxonitrides were in the focus of several working groups. Our systematic investigation of the formation of the gallium oxonitride spinel phases was done under different experimental conditions and with various educts already used in former studies. The experiments took place under high-pressure/high-temperature conditions in a multianvil apparatus, starting from the end members wurtzite-structured GaN and β-Ga_2O_3. Beside the variation of the molar ratio of the educts (w-GaN : β-Ga_2O_3 = 9 : 1 – 1 : 9), different pressures (1 – 11.5 GPa), temperatures (500 – 1350 °C), and heating protocols were studied to localize the formation area of the spinel-type gallium oxonitrides. From these results, initial conditions of 2.5 – 11.5 GPa at temperatures between 1000 – 1300 °C can be stated as leading to the formation of cubic, spinel-type gallium oxonitride phases. The temperature stability of the gallium oxonitride spinel phase as well as new results of the transformation of β-Ga_2O_3 into α-Ga_2O_3 are reported.

Key words: High-pressure Synthesis, Gallium Oxonitride, Spinel Structure, Gallium Oxide

Introduction

In recent years, research on group 13 nitrides for the industrial market and for technical applications intensified, due to their remarkable physical properties. Wurtzite-structured gallium nitride (w-GaN), belonging to the group of semiconductor materials, is well known in optical and electronic devices such as detectors, solid-state laser facilities, and laser diodes, or for its high potential for blue and white energy saving LEDs (light-emitting diodes) [1 – 4]. This system was basically modified by the addition of oxygen, leading to the substance class of gallium oxonitrides. This class of compounds may show similarities to the well explored aluminum oxonitrides, including their potential for industrial applications in analogy to the alon-system [5 – 10]. Soignard *et al.* [11] and our group [12] succeeded in the synthesis of gallium oxonitride compounds with a high degree of crystallinity, starting from different educts. The gallium oxonitride spinel compound $Ga_{2.81}O_{3.57}N_{0.43}$ was accessible *via* high-pressure/high-temperature treatment of a precursor at 7.0 GPa and 1100 °C [12]. Soignard *et al.* used a mixture of α/β-Ga_2O_3 and w-GaN in a molar ratio of 1 : 1, applying 5 GPa/1700 °C, which resulted in the compound $Ga_{2.8}N_{0.64}O_{3.24}$ [11], taking into account a charge-balanced composition.

Recently, we were able to synthesize a highly crystalline sample of a spinel-type gallium oxonitride, starting from a mixture of wurtzite-structured gallium nitride and β-Ga_2O_3 in a molar ratio of 9 : 1 at conditions of 5 GPa and 1250 °C [13]. From this experiment, single crystals of a spinel-type gallium oxonitride could be isolated for the first time. The combination of energy dispersive X-ray spectroscopy (EDS) with electron energy-loss spectroscopy (EELS) allowed the quantification of nitrogen and oxygen for the structural refinement of the single-crystal data (N/O =

0.25 ± 0.06, $a = 827.8(2)$ pm). The observation of a site occupation deficiency of the octahedral gallium site led to the composition $Ga_{2.79}\square_{0.21}(O_{3.05}N_{0.76}\square_{0.19})$ ($\square$ = vacancy) [13]. In the literature on oxonitrides, crystal defects in spinel-type materials are handled with different models, mainly by the assumption of a constant anion model [14 – 16]. The results of the single-crystal structure determination indicate that this model is doubtful, and one should take into account a model with both cation and anion vacancies. A more detailed discussion of the single-crystal refinement and the consequences for the occupation of the crystallographic sites can be found in ref. [13].

Furthermore, we performed *in situ* diamond anvil cell (DAC) investigations, using the end members w-GaN and β-Ga_2O_3 in a first route and an amorphous gallium oxonitride ceramic in a second route [17]. Both approaches led to new insights into the formation tendencies of gallium oxonitride spinel-type compounds.

Based on these results, a systematic investigation into the formation limits of gallium oxonitrides under high-pressure/high-temperature conditions, using a multianvil equipment, was started. Educts for the synthesis were wurtzite-type gallium nitride and β-gallium oxide with molar ratios of w-GaN : β-Ga_2O_3 = 9 : 1 – 1 : 9. The experiments started at low pressure of 1.0 GPa up to high pressure of 11.5 GPa. Additionally, temperatures of 500 °C up to 1350 °C with different heat treatment protocols were applied under pressure. By varying the parameters, we were able to localize the stability field of the spinel-type gallium oxonitrides.

Experimental Section

The experiments started with mixtures of fine powders of the end members wurtzite-structured gallium nitride (99.9 %, Alfa Aesar, Karlsruhe, Germany) and monoclinic β-gallium oxide (99.9 %, Sigma Aldrich, Munich, Germany) in different molar ratios from 90 mol-% w-GaN with 10 mol-% β-Ga_2O_3 up to the reversed mixture of 90 mol-% β-Ga_2O_3 and 10 mol-% w-GaN. Column 2 of Table 1 shows the name of the experiment and column 3 the molar ratio of the educts used in the corresponding experiments. The pressure conditions ranged from 1.0 GPa up to 11.5 GPa in small steps of 0.5, 1.0 or 2.5 GPa. For each experiment, the pressure is listed in column 4 of Table 1. Beside systematic pressure investigations, the influence of temperature (Table 1, column 5) on the formation of the gallium oxonitride spinel phases and their decomposition was examined. Also the heating protocols were varied to see if there were differences in the sample formation, yield, or the degree of crystallinity of the spinel phase, depending on a long or short heating protocol, a slow or fast cooling, or an annealing phase. Column 6 of Table 1 lists the heating protocols for each experiment. Distinctions between long-term heating periods, with heating segments of about 1 h (*e. g.* Table 1, column 6, Pos. 23, SH_054; Pos. 25, SH_056; Pos. 27, SH_058; Pos. 48, SH_213) and long annealing phases of 3 – 5 h were made. Also shorter heating protocols were applied, with heating up in about 10 min, holding the maximum temperature for 15 – 25 min, followed by an annealing phase of about half an hour (Table 1, column 6, *e. g.* Pos. 64, SH_06; Pos. 53, SH_020; Pos. 32, SH_031; Pos. 33, SH_034; Pos. 38, SH_045; Pos. 6, SH_077; Pos. 42, SH_123). Another special program implied two annealing phases at lower temperatures, a first one at 200 °C, holding the temperature there for 5 – 10 min, to increase it afterwards to a maximum temperature of 600 – 700 °C (Table 1, column 6, Pos. 19, SH_093; Pos. 7, SH_095; Pos. 2, SH_096; Pos. 20, SH_097; Pos. 21, SH_098). The standard heating program comprised three relatively equal heating sequences, *viz.* heating up in 5 – 10 min, holding the temperature for at least 10 – 20 min, and cooling down to a lower temperature (approximately 600 – 800 °C) in about 5 – 15 min.

All high-pressure/high-temperature experiments were performed by a modified multianvil technique [18 – 22]. Each experiment started with the preparation and assemblage of an octahedron, containing the starting mixture, which was centered in a cube that consists of eight truncated tungsten carbide cubes (TSM-10 Ceratizit, Reutte, Austria). The educts were mixed together, filled into a boron nitride crucible and closed with a BN plate (Henze BNP GmbH, HeBoSint® S10, Kempten, Germany). The crucible was positioned in two graphite furnaces (RW430, SGL Carbon, Bonn, Germany), centered by two MgO plates (Magnorite MN 399 CX, Saint-Gobain, Industrial Ceramics, Worcester) to guarantee nearly equal heating in the whole sample. After that, the sample was positioned in a zirconia sleeve (Ceramic Substrates, Newport, Isle of Wight) to insulate the graphite furnace from the outer part. Finally, the cylindrical sample was positioned into a MgO octahedron doped with Cr_2O_3 (Ceramic Substrates & Components LTD., Isle of Wight). To guarantee conductivity, a requirement to heat the sample, two molybdenum plates were positioned on top and bottom of the octahedron. The octahedron was positioned in the center of eight tungsten carbide cubes with truncated corners [23]. Pyrophyllite gaskets (Ceramic Substrates, Newport, Isle of Wight) separated the cubes. Alternatively, they were laminated with cardboards (Bristolkarton, 369 $g\,m^{-3}$) and self-adhesive Teflon foil (Fiberflon, Konstanz, Germany and Vitaflon, Bad Kreuznach, Germany), so that every foil side lay next to a side prepared with cardboard. Finally, the assembled cube was positioned into the Walker-type module. A hydraulic 1000 t press compressed the module (both devices from Voggenreiter, Mainleus, Germany).

The typical high-pressure/high-temperature protocol had three main parts: 1. increasing the pressure with a press load

Table 1. Molar ratio of the starting materials, conditions of synthesis, and products of all high-pressure/high-temperature experiments performed in this work.

			Conditions of synthesis			Identified products			
Position	Sample	w-GaN : β-Ga_2O_3	p (GPa)	T (°C)	Temperature ramp	GaON-Spinel	w-GaN	β-Ga_2O_3	α-Ga_2O_3
1	SH_152	9 : 1	1.0	1000	↑ 10 min (1000 °C) – 15 min (**1000** °C) ↓ 10 min (600 °C)		x	x	
2	SH_096	9 : 1	1.5	600	↑ 5 min (200 °C) – 10 min (200 °C) ↑ 15 min (600 °C) – 5 min (**600** °C) ↓ 1 min (25 °C)		x	x	
3	SH_154	9 : 1	2.0	1200	↑ 10 min (1200 °C) – 15 min (**1200** °C) ↓ 10 min (700 °C)		x	x	
4	SH_185	7 : 3	2.0	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 10 min (650 °C)		x	x	
5	SH_155	9 : 1	2.0	1350	↑ 10 min (1350 °C) – 15 min (**1350** °C) ↓ 10 min (800 °C)		x	x	x[a]
6	SH_077	1 : 1	2.5	1300	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 25 min (650 °C)	x	x	x	x
7	SH_095	9 : 1	2.5	500	↑ 10 min (200 °C) – 15 min (200 °C) ↑ 10 min (500 °C) – 15 min (**500** °C) ↓ 10 min (200 °C)		x		x
8	SH_130	7 : 3	2.5	1250	↑ 10 min (1250 °C) – 10 min (**1250** °C) ↓ 10 min (800 °C)	x	x	x	x
9	SH_139	7 : 3	2.5	1300	↑ 10 min (1300 °C) – 10 min (**1300** °C) ↓ 10 min (800 °C)		x		x
10	SH_131	7 : 3	3.0	1000	↑ 10 min (1000 °C) – 20 min (**1000** °C) ↓ 15 min (800 °C)		x	x	
11	SH_176	7 : 3	3.0	1250	↑ 10 min (1250 °C) – 5 min (**1250** °C) ↓ 10 min (800 °C)	x	x	x	
12	SH_180	3 : 7	3.0	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 10 min (800 °C)		x	x	
13	SH_182	4 : 6	3.0	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 10 min (800 °C)		x	x	
14	SH_184	7 : 3	3.0	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 10 min (800 °C)		x	x	
15	SH_188	3 : 7	3.0	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 10 min (800 °C)		x	x	
16	SH_068	9 : 1	3.5	1250	↑ 10 min (1250 °C) – 20 min (**1250** °C) ↓ 15 min (850 °C)	x	x		
17	SH_138	9 : 1	3.5	1350	↑ 10 min (1350 °C) – 20 min (**1350** °C) ↓ 15 min (800 °C)		x	x	[a]

Table 1 (continued).

		Conditions of synthesis				Identified products			
Position	Sample	w-GaN : β-Ga$_2$O$_3$	p (GPa)	T (°C)	Temperature ramp	GaON-Spinel	w-GaN	β-Ga$_2$O$_3$	α-Ga$_2$O$_3$
18	SH_159	6 : 4	4.0	800	↑ 15 min (800 °C) – 15 min (**800** °C) ↓ 10 min (400 °C)		x	x	
19	SH_093	9 : 1	4.5	500	↑ 10 min (200 °C) – 15 min (200 °C) ↑ 10 min (500 °C) – 15 min (**500** °C) ↓ 10 min (200 °C)		x		x
20	SH_097	7 : 3	4.5	600	↑ 10 min (200 °C) – 5 min (200 °C) ↑ 10 min (600 °C) – 15 min (**600** °C) ↓ 5 min (200 °C)		x		x
21	SH_098	9 : 1	4.5	700	↑ 10 min (200 °C) – 15 min (200 °C) ↑ 10 min (700 °C) – 15 min (**700** °C) ↓ 10 min (200 °C)		x	x	x
22	SH_051	1 : 1	4.5	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 25 min (800 °C)	x	x		x
23	SH_054	1 : 1	4.5	1250	↑ 15 min (1250°C) – 60 min (**1250** °C) ↓ 300 min (500 °C)	x	x		x
24	SH_055	9 : 1	4.5	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 25 min (800 °C)	x	x		
25	SH_056	9 : 1	4.5	1250	↑ 15 min (1250 °C) – 60 min (**1250** °C) ↓ 300 min (800 °C)	x	x		
26	SH_057	2 : 8	4.5	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 25 min (800 °C)	x	x		
27	SH_058	9 : 1	4.5	1250	↑ 15 min (1250 °C) – 60 min (**1250** °C) ↓ 200 min (700 °C)	x	x		
28	SH_025	7 : 3	5.0	1200	↑ 10 min (1200 °C) – 15 min (**1200** °C) ↓ 5 min (800 °C)	x	x		
29	SH_026	1 : 1	5.0	1200	↑ 10 min (1200 °C) – 15 min (**1200** °C) ↓ 5 min (800 °C)	x	x	x	
30	SH_028	7 : 3	5.0	1200	↑ 10 min (1200 °C) – 15 min (**1200** °C) ↓ 30 min (800 °C)	x	x		
31	SH_030	9 : 1	5.0	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 25 min (800 °C)	x	x		
32	SH_031	3 : 7	5.0	1300	↑ 10 min (1300 °C) – 15 min (**1300** °C) ↓ 30 min (800 °C)	x	x	x	x
33	SH_034	4 : 6	5.0	1300	↑ 10 min (1300 °C) – 15 min (**1300** °C) ↓ 30 min (800 °C)	x	x		x
34	SH_035	5 : 5	5.0	1300	↑ 10 min (1300 °C) – 15 min (**1300** °C) ↓ 25 min (800 °C)	x	x		x

Table 1 (continued).

		Conditions of synthesis				Identified products			
Position	Sample	w-GaN : β-Ga$_2$O$_3$	p (GPa)	T (°C)	Temperature ramp	GaON-Spinel	w-GaN	β-Ga$_2$O$_3$	α-Ga$_2$O$_3$
35	SH_039	8 : 2	5.0	1200	↑ 10 min (1200 °C) – 15 min (**1200** °C) ↓ 30 min (800 °C)	x	x		x
36	SH_041	6 : 4	5.0	1200	↑ 10 min (1200 °C) – 15 min (**1200** °C) ↓ 25 min (800 °C)	x	x	x	
37	SH_042	2 : 8	5.0	1200	↑ 10 min (1200 °C) – 15 min (**1200** °C) ↓ 25 min (800 °C)	x	x		x
38	SH_045	7 : 3	5.0	1200	↑ 10 min (1200 °C) – 15 min (**1200** °C) ↓ 60 min (800 °C)	x	x	x	
39	SH_046	1 : 9	5.0	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 25 min (800 °C)	x			x
40	SH_047	2 : 8	5.0	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 30 min (800 °C)	x			x
41	SH_063	9 : 1	5.0	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 10 min (800 °C)	x	x		
42	SH_123	9 : 1	5.0	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 25 min (800 °C)	x	x		x
43	SH_133	6 : 4	5.0	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 25 min (800 °C)	x	x		x
44	SH_134	9 : 1	5.0	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 25 min (800 °C)	x	x		
45	SH_208	6 : 4	5.0	1250	↑ 15 min (1250 °C) – 10 min (**1250** °C) ↓ 10 min (800 °C)		x		x
46	SH_211	6 : 4	5.0	1100	↑ 15 min (1100 °C) – 10 min (**1100** °C) ↓ 10 min (800 °C)				x
47	SH_212	6 : 4	5.0	1200	↑ 15 min (1200 °C) – 10 min (**1200** °C) ↓ 10 min (800 °C)	x			x
48	SH_213	5 : 5	5.0	1250	↑ 10 min (1250 °C) – 15 min (**1250** °C) ↓ 300 min (1100 °C)	x	x		
49	SH_230	1 : 1	6.0	700	↑ 10 min (700 °C) – 15 min (**700** °C) ↓ 10 min (650 °C)		x		x
50	SH_227	9 : 1	6.0	800	↑ 10 min (800 °C) – 15 min (**800** °C) ↓ 10 min (650 °C)		x		x
51	SH_228	1 : 1	6.0	900	↑ 10 min (900 °C) – 15 min (**900** °C) ↓ 10 min (700 °C)				x
52	SH_229	1 : 1	6.0	1000	↑ 10 min (1000 °C) – 15 min (**1000** °C) ↓ 10 min (850 °C)	x	x		x
53	SH_020	7 : 3	6.0	1200	↑ 10 min (1200 °C) – 15 min (**1200** °C) ↓ 5 min (800 °C)	x	x		

Table 1 (continued).

		Conditions of synthesis				Identified products			
Position	Sample	w-GaN : β-Ga_2O_3	p (GPa)	T (°C)	Temperature ramp	GaON-Spinel	w-GaN	β-Ga_2O_3	α-Ga_2O_3
54	SH_135	1 : 9	6.0	1250	↑ 15 min (1250 °C) – 10 min (**1250** °C) ↓ 10 min (800 °C)	x	x		x
55	SH_022	7 : 3	7.0	1200	↑ 10 min (1200 °C) – 15 min (**1200** °C) ↓ 5 min (800 °C)	x	x		x
56	SH_05	7 : 3	8.0	1200	↑ 10 min (1200 °C) – 10 min (**1200** °C) ↓ 5 min (800 °C)	x	x		x
57	SH_08	1 : 1	8.0	1200	↑ 10 min (1200 °C) – 10 min (**1200** °C) ↓ 5 min (800 °C)		x		x
58	SH_010	9 : 1	8.0	1200	↑ 10 min (1200 °C) – 10 min (**1200** °C) ↓ 5 min (800 °C)		x		x
59	SH_012	7 : 3	8.0	1200	↑ 10 min (1200 °C) – 10 min (**1200** °C) ↓ 5 min (800 °C)		x		x
60	SH_014	3 : 7	8.0	1100	↑ 10 min (1100 °C) – 10 min (**1100** °C) ↓ 5 min (800 °C)		x		x
61	SH_015	3 : 7	8.0	1150	↑ 10 min (1150 °C) – 15 min (**1150** °C) ↓ 5 min (800 °C)		x		x
62	SH_016	9 : 1	8.0	1100	↑ 10 min (1100 °C) – 10 min (**1100** °C) ↓ 5 min (800 °C)		x		x
63	SH_017	7 : 3	8.0	1150	↑ 10 min (1150 °C) – 15 min (**1150** °C) ↓ 5 min (800 °C)		x		x
64	SH_06[b]	7 : 3	9.2	1300	↑ 15 min (1300 °C) – 5 min (**1300** °C) ↓ 20 min (700 °C)		x		x
65	SH_021	7 : 3	11.5	1200	↑ 10 min (1200 °C) – 15 min (**1200** °C) ↓ 5 min (800 °C)	x	x		x

[a] Additional by-product: metallic Ga; [b] crucible material Mo.

of 100 t per hour; 2. the heating period, in which the pressure was kept constant; 3. the decompression of the assembly within the threefold of the compression time. Exact information about the pressure/temperature protocols is listed in the columns 4 – 6 of Table 1. After decompression, each sample was isolated from the surrounding assembly materials and prepared for further analysis. Regularly, the samples were investigated with X-ray powder diffractometry and EDX.

A small part of the sample was ground and prepared for X-ray powder diffractometry, using Stoe Stadi P diffractometers (Stoe & Cie, Darmstadt, Germany) with monochromatized Cu$K_{\alpha1}$ (λ = 154.051 pm) or Mo$K_{\alpha1}$ (λ = 71.073 pm) radiation. Additionally, the thermal stability of the spinel phase was examined by a Stoe Stadi P powder diffractometer (Mo$K_{\alpha1}$; λ = 71.073 pm) with a computer-controlled Stoe furnace. The sample was filled into a quartz-glass capillary (Hilgenberg, $\varnothing_{ext.}$ 0.1 mm) and fixed with respect to the scattering plane of a graphite tube, which was heated electrically. The unobstructed pathways for the primary beam of the molybdenum radiation source and for the scattered radiation were granted through wells in the graphite tube. The temperature was measured by an integrated thermocouple in the graphite tube and varied within 0.2 °C.

All X-ray powder diffractograms were handled with the Stoe program package WinXpow [24]. The programs Treor [25 – 27], Ito [28], Dicvol [29], and Theo [30] allowed the indexing and handling of the diffractograms. Furthermore, Gsas [31] and Expgui [32] were used for the Rietveld refinements. The JCPDS/ICDD database [33] served for the phase analysis. To mark the starting materials, products, by-products, or impurities from assembly materials, the references of the ICDD database with the corresponding PDF numbers are shown in Table 2. The cubic gallium oxonitride spinel phase was compared to the powder

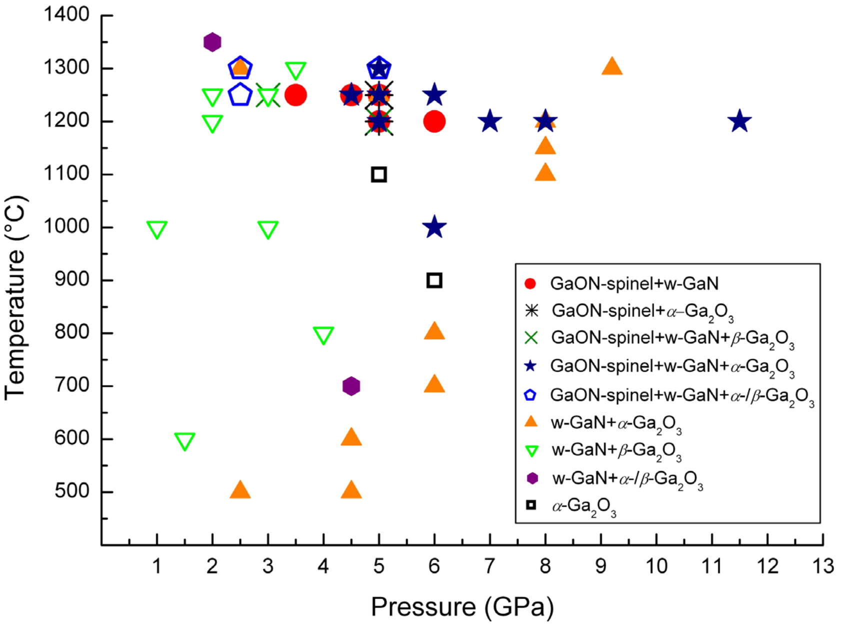

Fig. 1. (Color online) Survey of the products, obtained under specified pressure and temperature conditions with varying starting mixtures.

Table 2. Identified phases of the HP/HT-experiments with ICDD reference numbers.

Category	Substance	PDF number
Product	Spinel gallium oxonitride	Kinski [12]; Huppertz [13]
Educts	w-GaN (hexagonal)	76-703
	β-Ga_2O_3 (monoclinic)	87-1901
By-products	α-Ga_2O_3 (rhombohedral)	74-1610
	Ga (orthorhombic)	5-601
Assembly materials	BN (hexagonal)	85-1068
	Graphite (rhombohedral)	75-444

pattern of the spinel phase $Ga_{2.81}O_{3.57}N_{0.43}$ found by Kinski *et al.* [12] (lattice parameter: a = 826.4(1) pm). Further analysis was done with an EDS device (*e*nergy *d*ispersive X-ray *s*pectroscopy) (JSM-6500F with field emission source, Jeol, USA), which allowed a qualitative and semi-quantitative analysis of the composition, based on the characteristic X-ray emission of the elements (EDX detector: 7418 Oxford Instruments, Abingdon, Oxfordshire, OX13 5QX, UK). This work focuses on the synthetic conditions of forming the cubic spinel-type gallium oxonitrides. The N/O ratio will be analyzed in detail elsewhere.

Results

The mixtures of the end members of the binary phase diagram wurtzite-structured gallium nitride and β-gallium oxide were systematically examined under high-pressure/high-temperature conditions, using different molar ratios (w-GaN : β-Ga_2O_3 = 9 : 1 – 1 : 9). We report here 65 experiments, performed under different high-pressure/high-temperature conditions. The starting mixtures were varied, as were the applied temperature protocols, including a variation of the heating, annealing, and cooling periods. Fig. 1 shows the identified product mixtures of the experiments, depending on the conditions of pressure and temperature. The data of reactions which also led to metallic gallium (Table 1, Pos. 5, SH_155; Pos. 17, SH_138) are not shown in Fig. 1. The comparison between the different experiments and the high-pressure/high-temperature protocols (Table 1) showed the onset of the reaction of the two end members to form the high-pressure spinel-type gallium oxonitride phase and α-Ga_2O_3 already at a pressure of 2.5 GPa and a temperature of 1250 °C (Table 1, Pos. 8, SH_0130). The lowest synthetic temperature of 1000 °C for the formation of the spinel phase could be found at a pressure of 6 GPa (Table 1, Pos. 52, SH_229) with w-GaN and α-Ga_2O_3 still not having fully reacted.

The process of the spinel formation could be traced from the experiments at a pressure condition of 6 GPa, for which Fig. 1 (Table 1) shows three experiments at 700 (△), 900 (□), and 1000 °C (⋆), which started all from mixtures of w-GaN and β-Ga_2O_3 in a molar ratio of 1 : 1. After the high-pressure/high-temperature reaction, the first experiment at 700 °C (△) revealed the starting materials w-GaN and gallium ox-

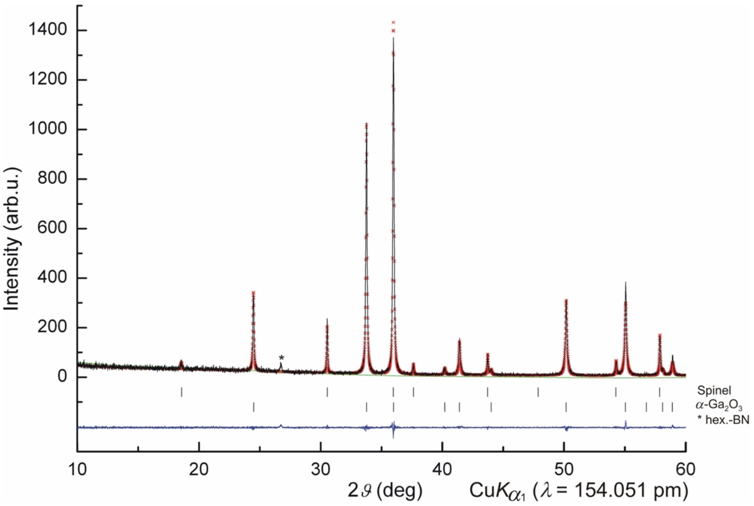

Fig. 2. (Color online) Rietveld fit of SH_046 (Pos. 39); starting mixture w-GaN : β-Ga_2O_3 = 1 : 9 (molar ratio), 5 GPa, 1250 °C, displaying spinel-type gallium oxonitride (17 %), α-Ga_2O_3 (40 %), and hex. BN (from the crucible).

ide, the latter already being transformed into the α-modification (specific conditions can be found in Table 1, Pos. 49, SH_230). Upon increasing the temperature up to 900 °C (□), the XRD pattern exhibited only α-Ga_2O_3 (Table 1, Pos. 51, SH_228). As none of the reactants could leave the crucible, a transition state of the reaction seems to appear, in which w-GaN and gallium oxide form an amorphous intermediate phase on their way to a crystalline gallium oxonitride compound. Only a part of the gallium oxide can be detected *via* the XRD pattern in the form of α-Ga_2O_3. Increasing the synthesis temperature up to 1000 °C (Table 1, Pos. 52, SH_229), the crystalline spinel-type gallium oxonitride phase can be observed (Fig. 1, ⋆) next to unreacted w-GaN and α-Ga_2O_3.

The temperature protocols had a remarkable influence on the fraction of the spinel phase. The degree of crystallinity could be improved by high heating rates and short holding times, for example upon heating up the mixture in 10 min to 1250 °C, holding the temperature for 15 min, and cooling down to 800 °C in 25 min (*e. g.* Table 1, Pos. 22, SH_051). Beside short heating segments, also long annealing phases (5 – 12 h) at temperatures of 700 – 800 °C helped to obtain highly crystalline samples with a high fraction of the spinel-type gallium oxonitride (Table 1, Pos. 25, SH_056). In the two experiments with temperatures exceeding 1300 °C, but pressures as low as 2 and 3.5 GPa, metallic gallium formed as a decomposition product, and no spinel-structured gallium oxonitride appeared (Table 1, Pos. 5, SH_155; Pos. 17, SH_138). A decrease of the initial temperature below 1000 °C at all pressures (Table 1) led to samples consisting of the educts w-GaN, β-Ga_2O_3, or the high-pressure modification α-Ga_2O_3.

Next to the issue of the necessary conditions of pressure and temperature for the formation of spinel-type structured gallium oxonitrides, the question of the starting ratio w-GaN : β-Ga_2O_3 was in our focus. Having an ideal composition of spinel-type gallium oxonitride Ga_3O_3N in mind, with the theoretically highest possible nitrogen/oxygen ratio of N/O = 0.33, the synthesis of nitrogen-rich samples had priority. Using w-GaN and β-Ga_2O_3 for the high-pressure/high-temperature experiments, the stoichiometrically required starting material to form a compound with the ideal composition Ga_3O_3N is a mixture of w-GaN : β-Ga_2O_3 in the molar ratio 1 : 1. Aiming at nitrogen-rich phases in the spinel structure, it was favorable to use starting mixtures of w-GaN and β-Ga_2O_3 in the molar ratio of 9 : 1 (high excess of w-GaN). However, the ratio of the starting mixture in the investigated system clearly was not decisive for the formation of the spinel-type structure, because both experiments, starting from the molar ratios of w-GaN : β-Ga_2O_3 = 9 : 1 and 1 : 9, resulted in the formation of the spinel-structured phases, obtained by experiments which were performed under identical conditions (Table 1, column 3, Pos. 31, SH_030 and Pos. 39, SH_046). Figs. 2 and 3 show the Rietveld refinements of the two experiments, synthesized with an identical experimental protocol (p = 5 GPa, T_{max} = 1250 °C, heating protocol: 10 min up to 1250 °C, 15 min at 1250 °C, in 25 min down to 800 °C). The comparison of both figures clearly shows that the formation of the spinel-

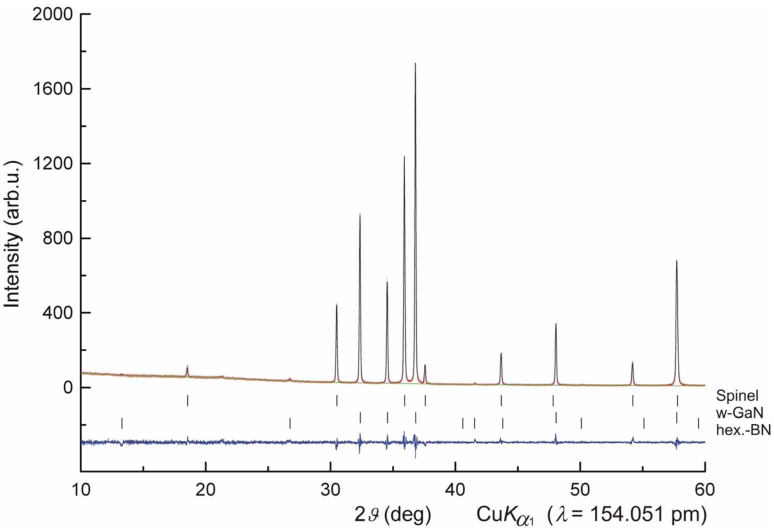

Fig. 3. Rietveld fit of SH_030 (Pos. 31); starting mixture w-GaN : β-Ga_2O_3 = 9 : 1 (molar ratio), 5 GPa, 1250 °C, displaying spinel-type gallium oxonitride (40 %), w-GaN (56 %), and hex. BN (from the crucible).

structured phase is much more favored when the starting mixture contains a higher amount of w-GaN. In detail, the Rietveld refinements of SH_030 (Table 1, Pos. 31) and SH_046 (Table 1, Pos. 39) showed a fraction of 40 and 17 % of the spinel-type gallium oxonitride phases, respectively.

Generally, we can state that the samples derived from a molar ratio of 9 : 1 of wurtzite-structured gallium nitride to β-gallium oxide so far gave the best results to produce nitrogen-rich spinel-type gallium oxonitrides. Commonly, oxide-rich starting mixtures led to products with a low fraction of the gallium oxonitride spinel phase. Nevertheless, even the lowest fraction of w-GaN in the starting mixture (10 mol-%) led to the formation of the spinel-structured material. This raised the question whether the application of identical experimental parameters could transform pure β-Ga_2O_3 into a gallium oxide crystallizing in the spinel structure (γ-Ga_2O_3 [34, 35]). Up to now, high-pressure/high-temperature experiments have only led to the high-pressure modification α-Ga_2O_3 [36–39], but not to the desired spinel-type compound γ-Ga_2O_3 [34, 35]. β-Ga_2O_3 (rel. density: δ = 5.94 g cm^{-3} [37]) has equal amounts of Ga^{3+} ions on tetrahedral and octahedral positions, while α-Ga_2O_3 (rel. density: δ = 6.48 g cm^{-3} [37]; corundum structure) exhibits Ga^{3+} exclusively in octahedral coordination. So, in principle, pressure could raise the fraction of six-fold coordinated Ga^{3+} at the expense of four-fold coordinated cations, leading to a spinel-structured γ-Ga_2O_3. But up to now, a small amount of catalytic gallium nitride is still essential for the formation of a spinel-type structured material, which corresponds to the results of McCauley, obtained and established in 2001 for the alon-system [40]. Therefore, the corresponding nitride plays a decisive role as an additive to form the respective spinel-type structured materials.

The colors of the products are determined by the starting materials. Compounds resulting from a mixture with an excess of nitride always revealed a dark greenish/grey color. Samples synthesized with less nitride showed a brighter color than samples derived from nitride-rich starting mixtures.

Fig. 4 gives a survey of the experiments to produce spinel-type gallium oxonitrides. The graphic illustrates the effect of the parameters pressure, temperature, and molar ratio of the starting mixture. The left side of Fig. 4 provides a view over the pressure and temperature conditions; the right side shows the same results, turned by 90°, to expose the corresponding molar ratios of the starting mixtures. Fig. 4 does not include information about heating protocols, remaining educts (w-GaN and β-Ga_2O_3), or transformed α-Ga_2O_3. Such information is available from Table 1 and Fig. 1.

All in all, a minimum pressure of 2.5 GPa and an initial temperature of 1250 °C (Table 1, Pos. 8, SH_130) are required to form the crystalline spinel-type gallium oxonitrides. Also higher pressure (> 8 GPa) produces the spinel phase, but the degree of crystallinity of the products decreases dramatically. Presumably, a shift to

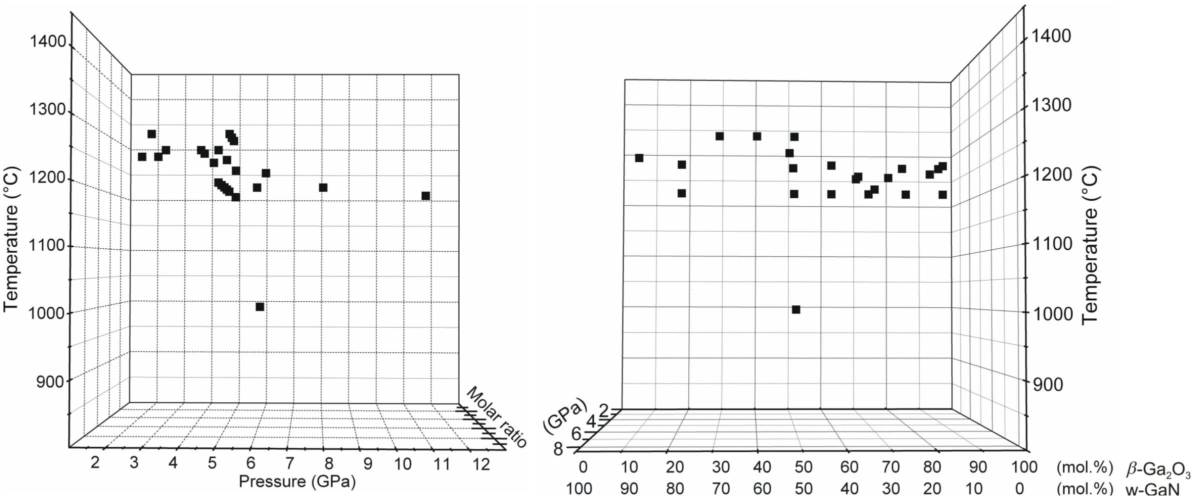

Fig. 4. Survey of the experiments leading to the cubic spinel-type gallium oxonitrides in dependence of pressure, temperature, and molar ratio w-GaN : β-Ga_2O_3 of the starting mixture.

higher temperatures (> 1350 °C) might lead to better results (faster kinetics). The observation that cubic spinel-type gallium oxonitrides can be synthesized at pressures $\geq$ 2.5 GPa is of high interest, because this pressure can be realized on a commercial scale. To date, the lowest pressure, reported by Soignard *et al.*, was 5 GPa at 1700 °C [11], starting from a mixture of α/β-Ga_2O_3 with w-GaN in the molar ratio of 1 : 1.

This result corresponds with that of recent investigations in our group, where a spinel-structured gallium oxonitride was obtained *via* diamond anvil cell synthesis at a pressure of 3 GPa and a temperature of around 1300 °C [17]. Taking an amorphous gallium oxonitride ceramic, which was derived from a precursor, the gallium oxonitride spinel phase was synthesized at an even lower pressure of 0.7 GPa [17].

The thermal behavior of the spinel-type gallium oxonitride was examined *via in situ* temperature-programmed X-ray powder diffraction. Fig. 5a shows the powder diffraction diagram of the crystalline sample, resulting from a mixture with the molar ratio w-GaN : β-Ga_2O_3 = 1 : 1 and synthesized under high-pressure/high-temperature conditions of 4.5 GPa and 1250 °C (Table 1, Pos. 23, SH_054, column 6, Fig. 5a). This product, which contained also a small amount of w-GaN (15 %), was tested by an *in situ* X-ray powder diffraction experiment. The powdered sample was heated up from r. t to 1100 °C in steps of 50 °C (Fig. 5b). Cooling down the sample to room temperature was also done in steps of 50 °C. Each temperature was kept constant for at least 10 min, before the measurements started. Fig. 5b shows that successive heating of the product led to a shift of the reflections of the gallium oxonitride phase towards larger *d* values (larger cell volume). The reflections of w-GaN disappeared at a temperature of 1000 °C. No decomposition of the spinel-type gallium oxonitride could be observed up to a temperature of 1100 °C.

Another interesting point of our experimental work was the structural behavior of β-Ga_2O_3. Several times, a phase transformation of the educt β-Ga_2O_3 into the high-pressure modification α-Ga_2O_3 was observed (*e. g.* Table 1, Pos. 5 – 9). In the literature, a recent investigation of Machon *et al.* has shown that the phase transformation could be observed in a diamond anvil cell at pressures of 20 – 22 GPa and ambient temperature [39]. The authors presume a structural disorder of the Ga^{3+} cations among the octahedral sites of the structure as the most likely explanation. Using temperature as an additional parameter, the transformation of β-Ga_2O_3 into the corundum-type structure of α-Ga_2O_3 was described at conditions of 4.4 GPa/1000 °C [36, 37]. Kroll *et al.* calculated the stability of β-Ga_2O_3 and obtained conditions of 2.6 or 6 GPa for the transformation (depending on the *d* electron handling [41]). From these results we can assert that the phase transformation of β-Ga_2O_3 into α-Ga_2O_3 in the presence of w-GaN already starts at pressures of 2 GPa (at high temperatures; 1350 °C).

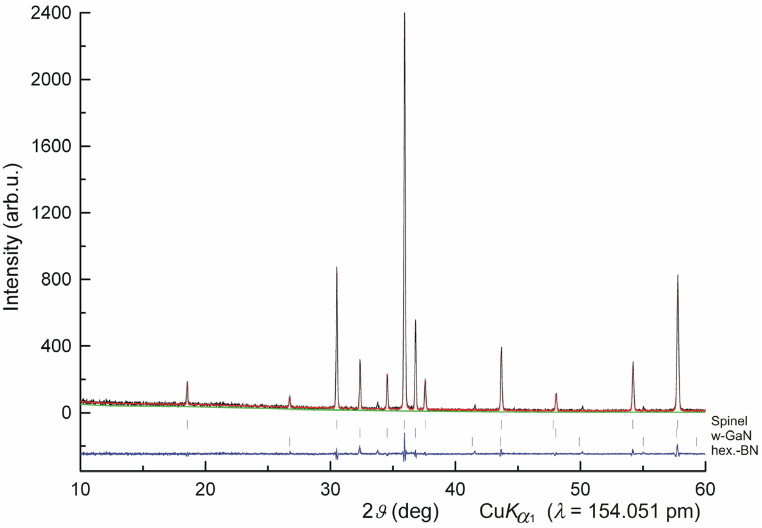

Fig. 5a. (Color online) Rietveld fit of SH_054 (Pos. 23); starting mixture w-GaN : β-Ga_2O_3 = 1 : 1 (molar ratio), 4.5 GPa, 1250 °C, displaying spinel-type gallium oxonitride (45 %), w-GaN (15 %), and hex. BN (from the crucible).

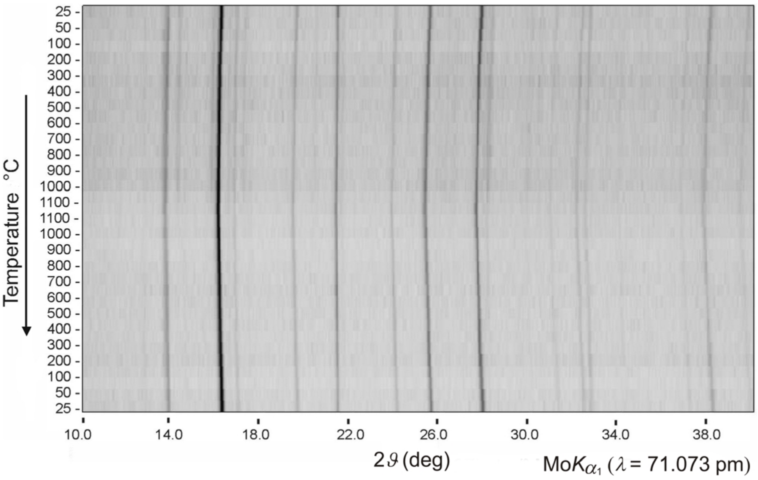

Fig. 5b. *In situ* temperature-programmed X-ray powder diffraction patterns (radiation: Mo$K_{\alpha1}$, λ = 71.073 pm), showing the thermal behavior of the spinel-type gallium oxonitride sample SH_054 (Table 1, Pos. 23).

Conclusion

This contribution describes a systematic investigation of the formation of cubic spinel-type gallium oxonitrides under high-pressure/high-temperature conditions, starting from mixtures of w-GaN and β-Ga_2O_3 in different molar ratios, using the multianvil technique. Starting at 2.5 GPa and 1250 °C (Table 1, Pos. 8, SH_130), the formation of the gallium oxonitride spinel can be observed up to pressures of 8 GPa and at a temperature of 1200 °C (Table 1, Pos. 56, SH_05). The increase of pressure up to 11.5 GPa at this temperature led to samples containing cubic spinel-type material with a low degree of crystallinity (Table 1, Pos. 65, SH_021). Depending on the mixture of the starting materials (w-GaN and β-Ga_2O_3 in the different molar ratios of 9 : 1 up to 1 : 9), the results varied, *e. g.* a high amount of nitride led to spinel-type gallium oxonitrides with a high degree of crystallinity in good yield. *In situ* X-ray powder diffraction experiments revealed that the cubic gallium oxonitride spinel phase is stable up to temperatures of 1100 °C, without decomposition or cell distortion. Furthermore, we could observe the phase transformation of β-Ga_2O_3 into α-Ga_2O_3 in the presence of w-GaN at a minimum pressure of 2 GPa.

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