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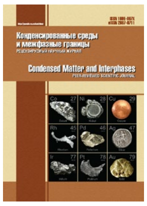

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Synthesis of chemically pure β-phase powders of gallium(III) oxide

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Abstract

The purpose of our study was to develop an optimal procedure for the synthesis of the β-phase of gallium(III) oxide with a high degree of chemical purity. Based on the analysis of the possible synthesis methods of the β-phase of gallium(III) oxide, we suggested a procedure which uses gallium(III) nitrate crystallohydrate as a precursor for obtaining the final product. The article demonstrates that during the synthesis of gallium(III) nitrate by means of direct interaction between metallic gallium and concentrated nitric acid, a hygroscopic crystallohydrate is formed with the formula $Ga(NO_3)_3 \cdot 9H_2O$.

Powders of the β-phase of Ga_2O_3 were synthesised by means of the thermal decomposition of gallium(III) nitrate in an oxygen atmosphere. Electron probe microanalysis (EPMA) and X-ray phase analysis (XRD) were used to determine the quantitative chemical composition, stoichiometry, and crystal structure of the gallium(III) oxide samples synthesised at different temperatures. The EPMA of the powders calcinated at temperatures T_{calc} = 500–950 °C demonstrated that the ratio of the elements was constant and corresponded to the stoichiometric composition of Ga_2O_3. A comparative analysis of the X-ray diffraction peaks demonstrated that with an increase in the decomposition temperature within the range T_{calc} = 500–950 °C, the symmetry of the structure of the Ga_2O_3 powders decreased from the cubic to the monoclinic. The study also determined that the samples of gallium(III) oxide synthesised at T_{calc} = 950 °C are single-phase and consist entirely of the monoclinic β-phase. The XRD data was used to calculate the crystal lattice parameters of the samples of the β-phase of Ga_2O_3 synthesised at T_{calc} = 950 °C.

Keywords: Gallium (III) oxide, Gallium (III) nitrate, Polymorphous modifications, Stoichiometry, Crystal structure, Monoclinic crystal system, Lattice parameters

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1. Introduction

The scientific progress at the turn of the 21st century and development of science-intensive technologies necessitated the creation of a new generation of microelectronic devices. Consequently, scientists began their search for semiconductor materials other than silicon and gallium arsenide [1, 2]. The range of promising materials for optical- and microelectronics has grown significantly, with experts focusing especially on studying wide-band semiconductor materials such as gallium nitride (GaN), aluminium nitride (AlN), silicon carbide (SiC), and solid solutions of gallium nitride and aluminium nitride (AlGaN).

The analysis of the literature data showed that of all the polymorphic modifications of gallium(III) oxide the β-phase of Ga_2O_3, which is thermodynamically stable in a wide range of temperatures, is the most promising material for optical- and microelectronics in the 21st century [2]. The obtained data on the physicochemical properties of single crystals and thin films of gallium(III) oxide demonstrates that this material has recently become a promising candidate for the production of certain types of devices in power electronics as well as solar energy converters and ultraviolet (UV) photodetectors [2–10]. Due to the large band gap of the β-phase of Ga_2O_3 ($\Delta E_g \sim 4.7$ eV) this material can be used to produce ionizing radiation sensors and gas sensors which provide for more opportunities than the existing technologies [11–16].

Besides the above mentioned applications, gallium(III) oxide can also be used in doping of metal oxide semiconductors with hole conductivity, for instance palladium(II) oxide [17–20]. The studies of thin and nanocrystalline palladium(II) oxide films demonstrated that the heterostructures based on them can be effectively used to create resistive gas sensors [21–23]. Doping with gallium(III) oxide can enhance the sensitivity and selectivity of gas sensors produced using nanostructures with different morphological organization based on palladium(II) oxide due to the formation of active sites, as well as devices with *p*- *n*-transitions [24–25].

Analysis of the existing literature demonstrated that electrical properties of the β-phase of Ga_2O_3 have not been thoroughly studied yet [2]. Such studies are very much hindered by the presence of the so-called unintentional impurities in gallium(III) oxide [2]. Therefore, it is important to develop a method for synthesising gallium(III) oxide of high chemical purity.

The purpose of our study was to determine the optimal method of synthesis of the β-phase of Ga_2O_3 with high chemical purity, as well as to investigate its quantitative composition and crystal structure depending on the synthesis conditions.

2. Experimental

As follows from the literature data [26–28], there are several methods of synthesis of gallium(III) oxide. Fig. 1 presents the possible methods of synthesis of gallium(III) oxide. It might seem that the easiest way to synthesise β-phase powders of Ga_2O_3 is by the thermal decomposition of the precipitate of gallium(III) hydroxide according to the equation:

$$2Ga(OH)_3^{(S)} \rightarrow Ga_2O_3^{(S)} + 3\ H_2O^{(G)}. \quad (1)$$

Since gallium(III) hydroxide (III) is characterised by a relatively small solubility product, $Ksp(Ga(OH)_3) = 1.6 \cdot 10^{-37}$ [29], it is possible to obtain enough precipitation of the substance with a minimum loss of the initial reagents. It is known [26–28] that gallium is an amphoteric metal. Therefore, gallium(III) hydroxide can be obtained by means of two methods.

First, the precipitate of gallium(III) hydroxide can be, in theory, synthesised in a single stage by direct interaction with hot water according to the equation:

$$2Ga^{(S)} + 6H_2O^{(L)} \rightarrow 2Ga(OH)_3^{(S)} + 3H_2^{(G)}. \quad (2)$$

In fact, this reaction (2) does not take place due to the quick oxidation of the metal's surface and formation of a thick layer of gallium(III) oxide which prevents the interaction between the metal and water.

The second way, as shown in Fig. 1, is to obtain the precipitate of $Ga(OH)_3$ in two stages. During the first stage, gallium is dissolved in strong inorganic acids (HCl, H_2SO_4, and HNO_3) followed by the deposition of $Ga(OH)_3$ by means of the effect of alkali on the solution of the corresponding salt, for instance:

$$GaCl_3^{(Aq)} + 3NaOH^{(Aq)} \rightarrow Ga(OH)_3^{(S)} + 3NaCl^{(Aq)}. \quad (3)$$

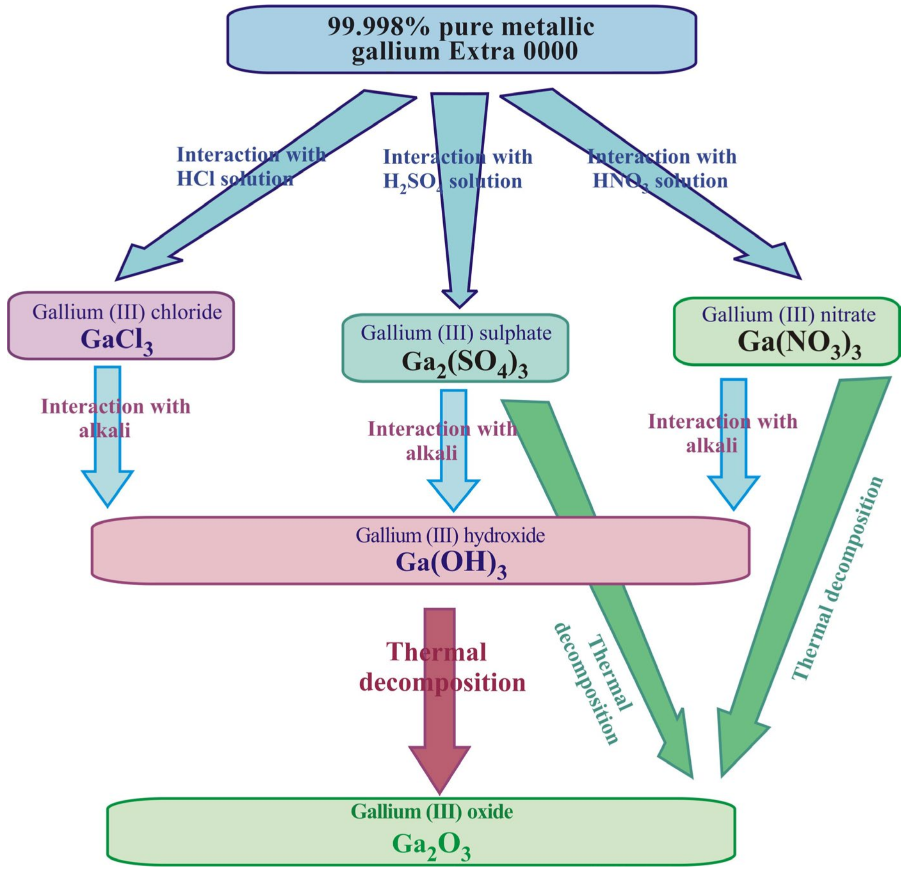


Fig. 1. Possible synthesis methods of different polymorphic modifications of gallium(III) oxide

However, this method of obtaining the precipitate of $Ga(OH)_3$ may result in smaller product yield of the reaction due to the incomplete deposition caused by the amphoterism of gallium(III) hydroxide:

$$Ga(OH)_3^{(S)} + 3NaOH^{(Aq)} \rightarrow 3Na[Ga(OH)_6]^{(Aq)}, \quad (4)$$

$$Ga(OH)_3^{(S)} + 3HCl^{(Aq)} \rightarrow GaCl_3^{(Aq)} + 3H_2O^{(L)}. \quad (5)$$

The existing literature does not provide any information about the dependence of the product yield of the deposition reaction of $Ga(OH)_3$ on the pH of the solution. There is also no data regarding the possible effect of the occurrence of sodium ions in the precipitate of $Ga(OH)_3$ obtained according to the equation (3). Nevertheless, the reviews demonstrated [2, 3] that the most common method of obtaining various polymorphic modifications of Ga_2O_3 is the thermal decomposition of $Ga(OH)_3$ hydroxide or GaOOH oxyhydroxide.

In this article, we suggest an optimal alternative method for the synthesis of gallium(III) oxide. It is based on the fact (Fig. 1) that during the synthesis of Ga_2O_3 the precursor is gallium(III) nitrate.

The suggested method has two advantages over the synthesis methods of gallium(III) oxide described above. First, this method provides for the maximum product yield of Ga_2O_3, because it prevents the loss of the initial reagents during all the stages. Second, the method allows for obtaining a product of high chemical purity.

To obtain this result, we used the following initial reagents: 99.998% pure metallic gallium Extra 000 and concentrated nitric acid (reagent grade GOST 4461-77) which was additionally purified by means of distillation. As we know [30], nitric acid can contain a certain amount of hydrochloric acid impurities. Chloride anions in the samples of Ga_2O_3 are donor centres and therefore their presence in the samples of gallium(III) oxide is highly undesirable.

The degree of purity of the nitric acid was monitored based on the qualitative reaction with silver nitrate. The nitric acid was distilled until there were no chloride anions in the distilled fraction of HNO_3. As a result, we obtained nitric acid of 1.40–1.45 g/cm^3, which corresponds to the mass fraction ω% (HNO_3) = 66 %.

As demonstrated in Fig. 1, in our study we used the process of decomposition of gallium(III) nitrate to synthesise crystalline powders of gallium(III) oxide. In this case, the synthesis of Ga_2O_3 includes two stages. During the first stage, gallium(III) nitrate was synthesised. The synthesis of $Ga(NO_3)_3$ was performed by means of direct interaction of 99.998 % pure metallic gallium Extra 000 with concentrated nitric acid at room temperature according to the equation:

$$Ga^{(S)} + 6HNO_3^{(Aq)} \rightarrow$$
$$\rightarrow Ga(NO_3)_3^{(Aq)} + 3NO_2^{(G)} + 3H_2O^{(L)} \qquad (6)$$

To initiate the formation of crystals, the solution was evaporated at the temperature of 50 °C until the first microscopic crystals appeared. The solution was then cooled to room temperature, after which it was further cooled to 0 °C in a mixture of ice and distilled water. The complete deposition of the gallium(III) nitrate crystallohydrate was obtained by keeping the solution at the temperature of 0 °C for 4 hours.

Using the calculations based on the results of the gravimetric analysis of the obtained crystals and the mass of the initial metallic gallium we determined that within the experimental error the formula of the obtained crystallohydrate is $Ga(NO_3)_3 \cdot 9H_2O$, or more precisely $[Ga(H_2O)_6](NO_3)_3 \cdot 3H_2O$.

The synthesised $Ga(NO_3)_3 \cdot 9H_2O$ crystals appeared to be highly hygroscopic and intensively absorbed moisture from air at room temperature. To prevent uncontrolled splashing of the $Ga(NO_3)_3 \cdot nH_2O$ samples, during the following calcination aimed at synthesising gallium(III) oxide, they were dehydrated by being heated to the temperature of 120 °C and exposed to isothermal endurance for 240 minutes. The temperature was monitored using chromel-alumel thermocouples and a digital voltmeter. As a result of the dehydration of $Ga(NO_3)_3 \cdot 9H_2O$ crystallohydrate under the described conditions, compact white samples were formed which practically did not absorb moisture from air. Prior to further calcination the dehydrated $Ga(NO_3)_3 \cdot nH_2O$ crystals were ground in an agate mortar for 30 minutes.

As a reactor for the decomposition of gallium nitrate we used a resistive heating tube furnace with dry oxygen delivered to the reaction zone. The quartz boat with the ground dehydrated $Ga(NO_3)_3 \cdot nH_2O$ crystals was put into the quartz reactor so that the galluim(III) nitrate sample was in the isothermal zone of the resistive heating furnace. The furnace was first slowly heated to T = 200 °C after which oxygen was delivered to the reaction zone. Thermal decomposition of the crystals of the precursor was performed in the temperature range of 300–950 °C for 6 hours. Gallium(III) nitrate was subjected to thermal decomposition to form gallium(III) oxide according to the equation:

$$4Ga(NO_3)_3 \xrightarrow{T>400\,^\circ C} 2Ga_2O_3 + 12NO_2\uparrow + 3O_2\uparrow. \qquad (7)$$

The qualitative and quantitative elemental composition of the synthesised samples was determined by means of the electron probe microanalysis (EPMA). The analysis was performed using a JEOL-JCM 6380 LV scanning electron microscope with an Oxford Instruments INCA X-sight LN2 energy dispersive analysis system.

The crystal structure of the Ga_2O_3 samples was studied by means of X-ray phase analysis (XRD) using a DRON-4-07 diffractometer with filtered CoK_α-radiation.

3. Results and discussion

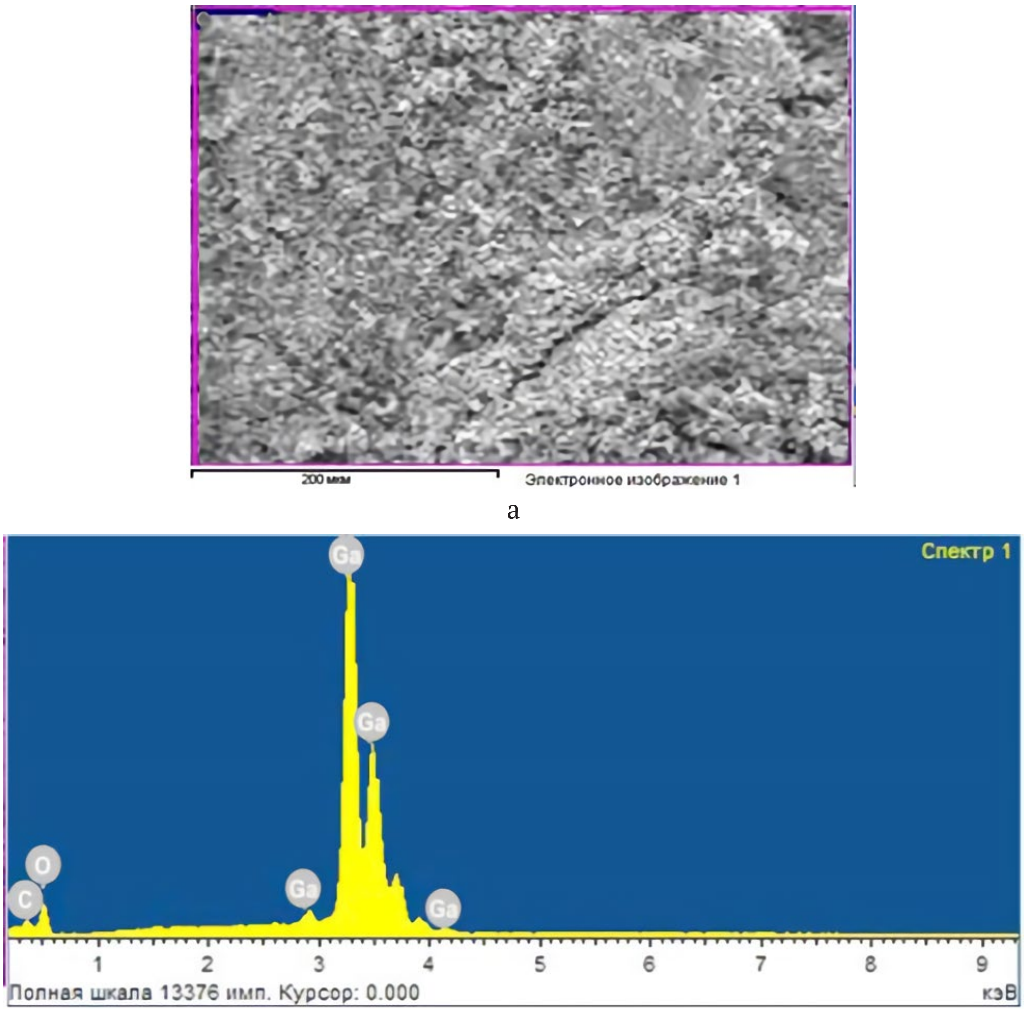
Based on the quantity of gallium nitrate and the mass of the water, we determined the formula of the precursor used in the study. The synthesised gallium nitrate can be described by a molecular formula $Ga(NO_3)_3 \cdot 9H_2O$, or more precisely $[Ga(H_2O)_6](NO_3) \cdot 3H_2O$. The X-ray analysis of the $Ga(NO_3)_3 \cdot 9H_2O$ crystallohydrate using DRON-4-07 did not present any diffraction pattern, which can be explained by the very high hygroscopy of gallium nitrate.

Using electron probe microanalysis (EPMA), we studied a number of samples obtained by means of calcination of dehydrated and ground $Ga(NO_3)_3 \cdot nH_2O$ samples in dry oxygen at the temperature range of T_{calc} = 300–950 °C.

Fig. 2 presents the typical spectrum of characteristic X-ray radiation and the scanning area of 400×400 μm of the surface of the samples obtained by means of the calcination of dehydrated ground $Ga(NO_3)_3 \cdot nH_2O$ samples in the temperature range of T_{calc} = 300–950 °C. The synthesised samples of Ga_2O_3 showed very high resistance and very low electrical conductivity. To prevent the accumulation of static electricity and ensure the stability of the electronic probe, the surfaces of the studied Ga_2O_3 samples were coated with a thin layer of amorphous carbon (Fig. 2 a). This accounts for the presence of carbon lines in the characteristic X-ray radiation spectrum (Fig. 2 b). The figure demonstrates that the spectrum contains only gallium, oxygen, and carbon lines. No other elements were observed in the spectrum. This proves that the obtained samples are characterised by a high degree of chemical purity.

The data obtained my means of EPMA (Table 1) demonstrates that complete thermal decomposition of gallium(III) nitrate followed by the formation of a single-phase Ga_2O_3 according to the equation (7) takes place at the calcination temperature T_{calc} = 500 °C. The spectra of the samples obtained at lower temperatures (T_{calc} = 300 °C) contained nitrogen lines, which indicated that the decomposition of gallium(III) nitrate was not complete.

Having determined the quantitative composition of the single-phase gallium(III) oxide powders we can conclude that the quantity of gallium and oxygen atoms in the samples obtained at $T_{calc} \geqslant 500$ °C is constant within the systematic error of the EPMA method (Table 1).



a

b

Fig. 2. a – SEM image of a section of the Ga_2O_3 sample scanned during the study of the quantitative composition by means of EPMA. b – Characteristic X-ray radiation spectrum of the Ga_2O_3 sample synthesized by calcination of $Ga(NO_3)_3 \cdot nH_2O$ in an oxygen atmosphere at T_{calc} = 750 °C

Table 1. The quantitative composition of samples obtained by calcination of dehydrated $Ga(NO_3)_3 \cdot nH_2O$ crystallohydrate in oxygen at different temperatures as determined by EPMA

<table>
<tr><td colspan="4">Calcination temperature T_{calc} = 300 °C</td></tr>
<tr><td>Element</td><td>Spectral line</td><td>Mass fraction ω, %</td><td>Mole fraction <i>x</i>, %</td></tr>
<tr><td>Gallium</td><td><i>L</i>-line</td><td>63.26</td><td>18.985</td></tr>
<tr><td>Oxygen</td><td><i>K</i>-line</td><td>30.42</td><td>65.895</td></tr>
<tr><td>Nitrogen</td><td><i>K</i>-line</td><td>6.42</td><td>15.12</td></tr>
<tr><td>Total:</td><td></td><td>100%</td><td>100%</td></tr>
<tr><td colspan="4">Phase composition of $Ga(NO_3)_3$ + Ga_2O_3</td></tr>
<tr><td colspan="4">Calcination temperature T_{calc} = 600 °C</td></tr>
<tr><td>Element</td><td>Spectral line</td><td>Mass fraction ω, %</td><td>Mole fraction <i>x</i>, %</td></tr>
<tr><td>Gallium</td><td><i>L</i>-line</td><td>74.005</td><td>39.515</td></tr>
<tr><td>Oxygen</td><td><i>K</i>-line</td><td>25.995</td><td>60.485</td></tr>
<tr><td>Nitrogen</td><td><i>K</i>-line</td><td>…</td><td>…</td></tr>
<tr><td>Total:</td><td></td><td>100 %</td><td>100 %</td></tr>
<tr><td colspan="4">Quantitative composition of Ga_2O_3</td></tr>
<tr><td colspan="4">Calcination temperature T_{calc} = 850 °C</td></tr>
<tr><td>Element</td><td>Spectral line</td><td>Mass fraction ω, %</td><td>Mole fraction <i>x</i>, %</td></tr>
<tr><td>Gallium</td><td><i>L</i>-line</td><td>74.061</td><td>39.585</td></tr>
<tr><td>Oxygen</td><td><i>K</i>-line</td><td>25.939</td><td>60.415</td></tr>
<tr><td>Nitrogen</td><td><i>K</i>-line</td><td>…</td><td>…</td></tr>
<tr><td>Total:</td><td></td><td>100 %</td><td>100 %</td></tr>
<tr><td colspan="4">Qualitative composition of Ga_2O_3</td></tr>
</table>

Within the temperature range T_{calc} 500–950 °C, the ratio between the mole fractions of gallium and oxygen corresponds to the stoichiometric composition of Ga_2O_3 and does not depend on the calcination temperature. This data proved the assumption that the homogeneity region of Ga_2O_3 is rather narrow [2, 3].

Analysis of the literature data [2, 3, 31, 32] demonstrated that up to now five polymorphic modifications of gallium(III) oxide have been determined (Table 2). There is also data indicating the existence of a transitional form – the κ-phase of Ga_2O_3 [2, 3]. We should point out that the data regarding the crystal structure of most Ga_2O_3 modifications is rather controversial. Even more controversial is the information about the methods of obtaining most of the polymorphic modifications of Ga_2O_3, as well as about the temperatures at which each polymorphic modification of Ga_2O_3 is stable.

In our study, we used X-ray phase analysis to determine the phase composition of the Ga_2O_3 samples synthesised by means of calcination of gallium(III) nitrate in oxygen at a temperature of T_{calc} = 500–950 °C. The evolution of the X-ray diffraction pattern of the Ga_2O_3 samples synthesised at different temperatures is given in Fig. 3. The results of the identification of polymorphic modifications of the synthesised gallium(III) oxide samples based on the information in an international crystallographic database are presented in Table 3.

Fig. 3 shows that with an increase in the temperature of calcination of gallium(III) nitrate in an oxygen atmosphere the crystal structure of the Ga_2O_3 samples changes dramatically. According to the data presented in Fig. 3 and Table 3, the Ga_2O_3 samples synthesised at T_{calc} = 500 °C are single-phase and have the cubic crystal structure of a spinel (γ-phase of Ga_2O_3). When the synthesis temperature was increased to T_{calc} = 600 °C, the Ga_2O_3 samples were a mixture of two phases: the cubic γ-phase with an insignificant fraction of the δ-phase (Table 3). Further increase in the synthesis temperature of gallium(III) oxide samples in an oxygen atmosphere to T_{calc} = 750 °C resulted in the growth of the fraction of the δ-phase of Ga_2O_3

Table 2. Literature data on gallium(III) oxide polymorphous modifications [2, 3, 31 – 34].

Polymorphic modification	Crystal system	Space group	Pearson symbol
α-Ga_2O_3	Hexagonal (rhombohedral)	$R\bar{3}c$	$hR30$
β-Ga_2O_3	Monoclinic	$C2/m$	$mS20$
γ-Ga_2O_3	Cubic, defect spinel structure	$Fd\bar{3}m$	–
δ-Ga_2O_3	Cubic, possibly the structural type of bixbyite	$Ia\bar{3}$	–
ε-Ga_2O_3	Orthorhombic	$Pna2_1$	–

Table 3. Phase composition of the Ga_2O_3 samples obtained by calcination of dehydrated $Ga(NO_3)_3 \times nH_2O$ crystallohydrate in oxygen at different temperatures

Calcination temperature T_{calc}, °C	Calcination temperature t, min.	Phase nature	Phase composition
500	360	Однофазный	γ-Ga_2O_3
600	360	Гетерофазный	γ-Ga_2O_3+ δ-Ga_2O_3
750	360	Гетерофазный	δ-Ga_2O_3 + γ-Ga_2O_3
850	360	Гетерофазный	δ-Ga_2O_3 + β-Ga_2O_3
950	360	Однофазный	β-Ga_2O_3

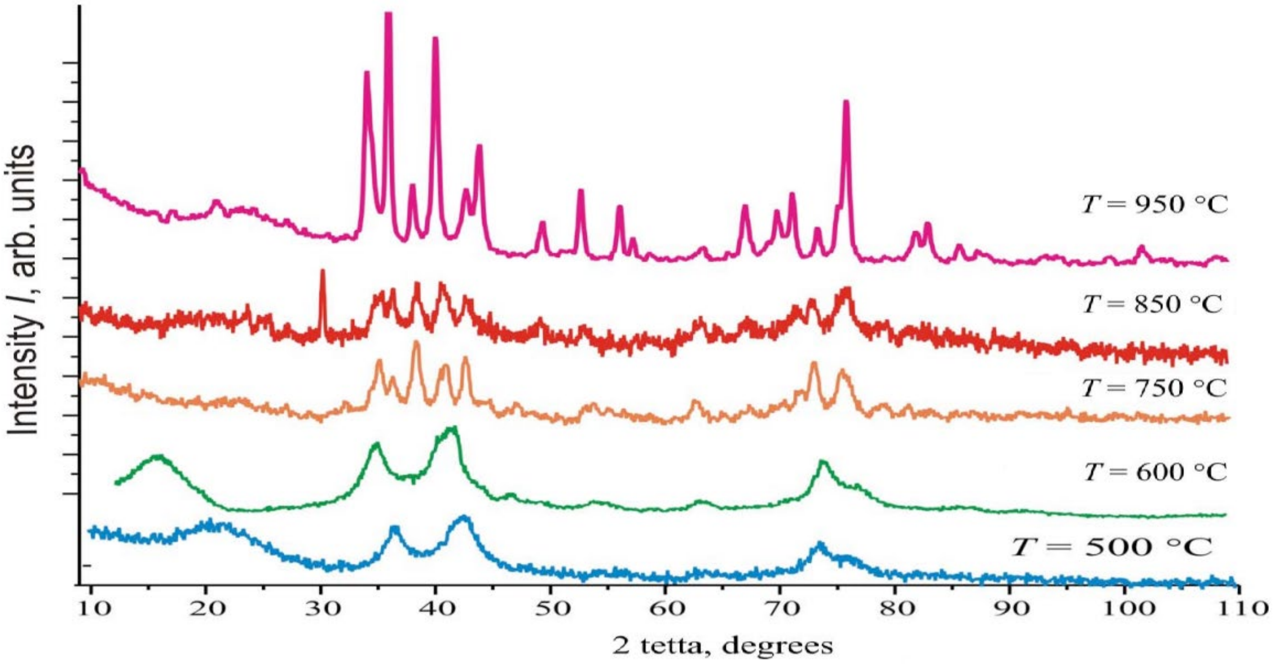


Fig. 3. X-ray diffraction patterns of gallium(III) oxide samples synthesized by calcination of dehydrated and ground $Ga(NO_3)_3 \cdot nH_2O$ samples in an oxygen atmosphere at the temperature T_{calc} = 500–950 °C (Co$K\alpha$-radiation)

with the presence of an insignificant fraction of the γ-phase of Ga_2O_3.

When the temperature was further increased to T_{calc} = 850 °C, the crystal structure of gallium(III) oxide powders also changed. The diffraction pattern did not show any peaks of the γ-phase, with the prevailing peaks of the cubic δ-phase of Ga_2O_3 being accompanied by a certain number of reflections characteristic of the monoclinic β-phase (Fig. 3 and Table 3). When the synthesis temperature was T_{calc} = 950 °C, the diffraction patterns of gallium(III) oxide samples showed only peaks of the monoclinic β-phase of Ga_2O_3 (Fig. 3 and 4). The absence of the reflections characteristic of other polymorphic modifications of gallium(III) oxide led us to the conclusion that in our study, at the temperature T_{calc} = 950 °C we synthesised chemically pure single-phase powders of the monoclinic β-phase of Ga_2O_3 (Fig. 4).

According to the obtained XRD data (Fig. 3 and Table 3), thermal decomposition of gallium(III) nitrate did not allow for obtaining of two of the polymorphic modifications of gallium(III) oxide, namely the hexagonal (rhombohedral) α-phase and the orthorhombic ε-phase (Table 2).

We should point out that the values of interplanar distances of the samples of the β-phase of Ga_2O_3 synthesised in our study are the closest to the recently obtained literature data [33, 34]. Based on the obtained X-ray diffraction patterns and the literature data [32 – 34] we calculated the parameters of the crystal lattice of the synthesised monoclinic b-phase of Ga_2O_3 (Table 4) using the UnitCell software and regression analysis [35]. The obtained parameters of the crystal lattice of the monoclinic β-phase of Ga_2O_3 and the unit cell volume were in maximum agreement with the results obtained in [34].

Table 4. Parameters of the crystal lattice of the β-phase of Ga_2O_3 synthesized at T_{calc} = 950 °C calculated by means of the method suggested by TJB Holland & SAT Redfern (1995) using the Unitcell software [35]

Crystal lattice parameter	Data source			
	[32]	[33]	[34]	The article
a, nm	0.58	1.2227(1)	1.2214(3)	1.22061
b, nm	0.304	0.30389(2)	0.30371(9)	0.30413
c, nm	1.223	0.58079(4)	0.57981(9)	0.57768
β, degrees	103.7	103.820(6)	103.83(2)	103.3706
Unit cell volume V_{uc}, nm³	0,2095	0.20955	0.20885	0.208636

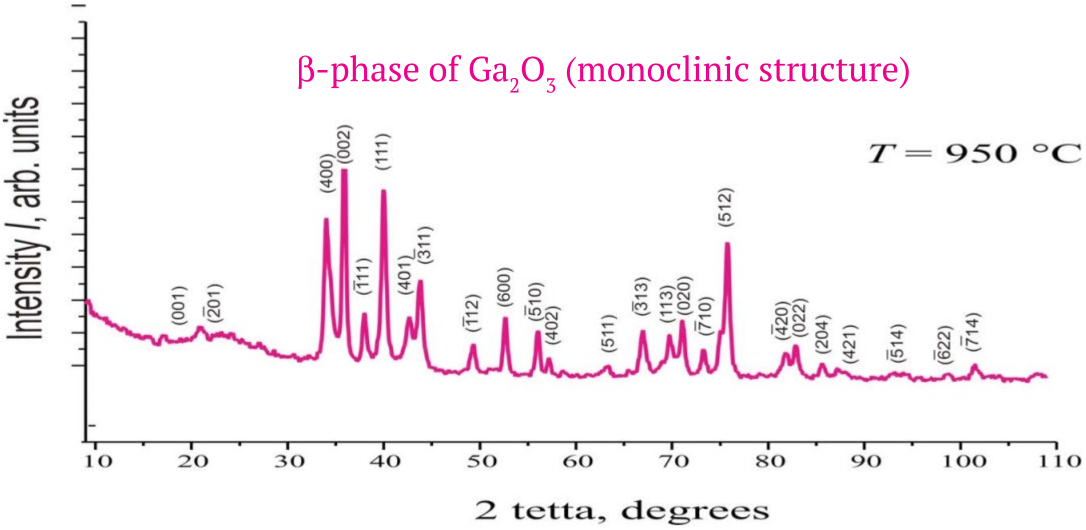


Fig. 4. X-ray diffraction patterns of the sample of the β-phase of gallium(III) oxide synthesized by calcination in oxygen at T_{calc} = 950 °C

4. Conclusions

In our study, we developed a synthesis method of gallium(III) oxide powders of high chemical purity with maximum product yield. The interaction between metallic gallium and concentrated nitric acid resulted in the formation of gallium(III) nitrate crystallohydrate with the general formula $Ga(NO_3)_3 \cdot 9H_2O$. The study determined that complete thermal decomposition of gallium(III) nitrate and formation of gallium(III) oxide occurs at the temperature $T_{calc} \geqslant 500$ °C. Based on the results of the EPMA we determined that within the range of calcination temperature $T_{calc} = 500–950$ °C, the ratio between gallium and oxygen atoms is stable within the systematic error, which corresponds to the stoichiometric composition of Ga_2O_3, and does not depend on the treatment temperature. The X-ray phase analysis proved that the crystal structure of the gallium(III) oxide powder whose synthesis temperature increased from $T_{calc} = 500$ °C to $T_{calc} = 950$ °C, changes with symmetry decreased from the cubic to the monoclinic structure. The determined parameters of the crystal lattice of the synthesised monoclinic phase are in full agreement with the reference data, which demonstrates great perfection of the structure of the synthesised samples of the β-phase of Ga_2O_3.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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