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# Effect of Solution Composition on the Morphology of Synthesized β-$Ga_2O_3$ Particles

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**Abstract**

Micro- and nanoparticles of β-$Ga_2O_3$ are synthesized as a result of chemical reaction of an aqueous solution of gallium nitrate and various alkalis: ammonia, sodium, potassium, and lithium hydroxides. It is shown that particles morphology depends on the type and concentration of alkali. The use of microwave treatment of ammonia containing solutions made it possible to change the shape of particles from ellipsoidal to parallelepiped while maintaining their size. In contrast to the synthesis with ammonia, for other alkalis dispersed particles were obtained only at a ratio of alkali to gallium nitrate equal to 3, and these particles did not belong to the gallium oxide β-phase.

*Keywords:* Nanoparticles; Gallium oxide; Chemical synthesis; Scanning electron microscopy; X-ray diffraction

## 1. INTRODUCTION.

Gallium oxide is a promising wide-bandgap semiconductor [1]. In the last few years, interest to the study of this material has significantly grown [2]. This interest can be explained by the broad scope of application of gallium oxide in various optoelectronic devices [2–6].

The main advantages of this material are a wide band gap 4.5–5.3 eV, high dielectric permittivity and low leakage currents, which allow this material to be used for various sensors, detectors, displays, etc. In addition, the wide band gap, which is larger than the gap of many other wide-bandgap semiconductors, and high breakdown voltage make this material promising for applications in power electronics with an expected increase in their reliability and performance [2,3,7,8].

Gallium oxide can crystallize into different polymorphic forms — α-, β-, γ-, δ-, ε-, κ-phases of $Ga_2O_3$ are known [9] — which have different band gaps and crystalline structures [2,3,10–13]. The monoclinic β-$Ga_2O_3$ is of the greatest interest, as it is the most thermally and chemically stable [5,11,13–16]. Since β-$Ga_2O_3$ has good resistance to alkalis and acids, it is promising for use as the active material of gas sensors, photodetectors and photocatalysts that maintain performance under the influence of aggressive media [17,18].

In addition, it is important to mention high photocatalytic activity of β-$Ga_2O_3$ compared to other phase modifications [19]. Apart from the phase composition, the photocatalytic activity of semiconductor particles is also affected by their morphology, size and shape [20,21]. Therefore, it is very important to develop a technology that would allow obtaining dispersed particles with variable morphological characteristics.

One of the methods for obtaining dispersed particles is the chemical synthesis, the advantage of which is the possibility of producing particles of different sizes and various morphologies. In our previous work, β-$Ga_2O_3$ particles up to several micrometers in size were obtained by chemical synthesis [22]. For efficient photocatalysis that size is too big, so additional experiments were carried out with the variation of synthesis parameters to reduce particle size and obtain gallium oxide nanoparticles.

The purpose of present work is to obtain β-$Ga_2O_3$ micro- and nanoparticles with various morphology by chemical synthesis and to show the dependence of the particle shape and size on the type and concentration of the alkali in the solution.

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## 2. METHODS

Micro- and nanoparticles of β-$Ga_2O_3$ were synthesized as a result of chemical interaction of aqueous solutions of gallium nitrate hydrate [$Ga(NO_3)_3 \cdot 8H_2O$] and various alkalis: ammonia ($NH_3$), sodium hydroxide (NaOH), potassium hydroxide (KOH) and lithium hydroxide (LiOH). The synthesis was carried out at room temperature and constant stirring at a speed of 350 rpm.

Solutions with different ratios of molar concentrations of alkali to gallium nitrate (A/G) — in the range from 3 to 15 — were prepared for each of the alkalis, as well as a solution without alkali (A/G = 0).

After the adding of alkali, a white sediment was observed in each solution, which was sequentially evaporated and annealed. To do this, all the resulting solutions were heated to 105 °C and kept until the water completely evaporated. To obtain dispersed particles, sediments were annealed in air at 900 °C for one hour.

Furthermore, to change the synthesis process and the parameters of the resulting particles there also were particles synthesized in ammonia solution and under short-term microwave exposure (for about 3 seconds). Microwave exposure was used at the initial stage of synthesis immediately after stirring the components. Ordinary kitchen microwave oven (700 W) was used. The rest stages of synthesis were the same as in the procedure described above.

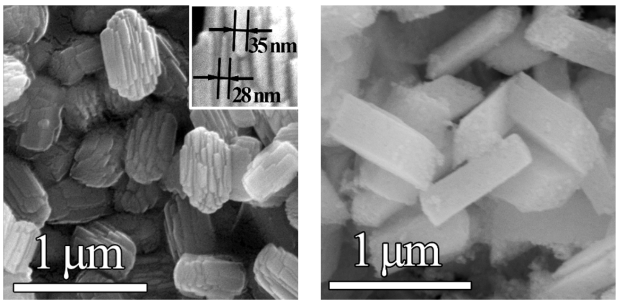
The morphology and sizes of the obtained particles were studied by scanning electron microscopy (SEM) using Mira 3 (Tescan, Czech Republic) and Digital Micrograph software (USA).

To determine the phase composition and confirm the formation of β-phase gallium oxide particles, the obtained powders were studied by X-ray diffractometry (XRD) using DRON-8 (“Burevestnik”, Russia) in a slit configuration with a copper source, providing X-rays with a wavelength of 1.540562 Å.

## 3. RESULTS AND DISCUSSION

The morphology of particles obtained from solutions in the presence of ammonia is described in detail in work [22]. From ammonia solution with ratio A/G = 3, the particles have an ellipsoidal shape with average length and diameter up to 0.6 μm and 0.25 μm, respectively (Fig. 1a). The size measurements were taken based on the SEM images. The particles have a rough and layered structure with a layer thickness about 30 nm, typical for gallium oxide [17,23].

SEM investigation showed that in the case of the synthesis of ammonia solution under the microwave influence, the particles had the parallelepiped shape and a smoother surface. It is also important to note that their size




(a) (b)

**Fig. 1.** SEM images of sediments obtained from solutions with ammonia (A/G = 3) and synthesized without (a) and under (b) microwave exposure. The insert on Fig. 1(a) shows an image of the layers in the particles and a measurement of their thickness.

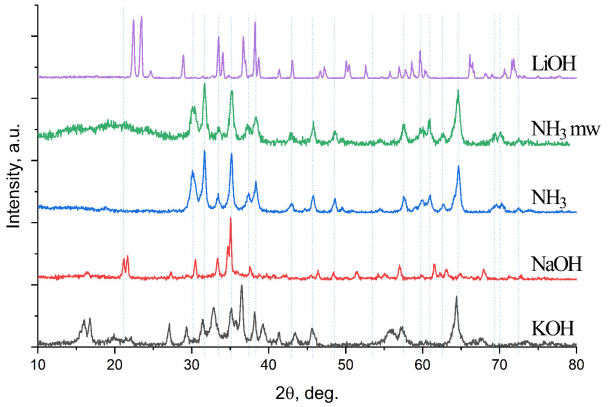
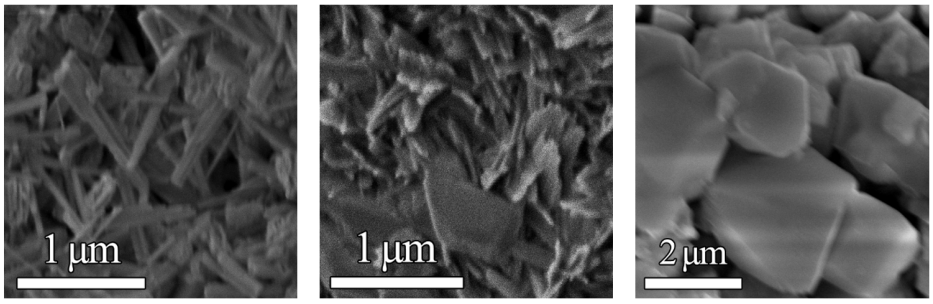



**Fig. 2.** X-Ray diffractogram of sediments obtained from solutions with A/G = 3 and with different alkalis: ammonia, synthesized without (blue line) and under (green) microwave (mw) exposure, NaOH (red), KOH (black), LiOH (violet). The dotted lines mark the reflections of β-$Ga_2O_3$.

corresponds to the size of the particles obtained without microwave exposure (Fig. 1b). XRD investigation confirmed the formation of β-$Ga_2O_3$ phases in them (Fig. 2).

SEM study also showed a difference between the shape and size of the particles synthesized with the usage of different alkalis. However, in contrast to the synthesis with ammonia, where the dispersed particles were obtained in the full range of A/G ratios (from 3 to 15), for solutions with other alkalis (KOH, NaOH) dispersed particles were obtained only for alkali to gallium nitrate ratio equal to 3. At other ratio values dispersed particles were not observed, as was previously seen in the solution without ammonia [22]. Therefore, for further research, the parameters of the particles obtained from solutions with various alkalis were compared at fixed ratio of A/G = 3.

In the synthesis from solutions with potassium or sodium hydroxides, particles had shape of elongated nanorods and lamellae up to 0.6 μm in size (Figs. 3a,b). When the particles were synthesized using lithium hydroxide, no dispersed nanoparticles were obtained; large objects with a smooth surface were observed in the sediment (Fig. 3c).




(a) (b) (c)

**Fig. 3.** SEM images of sediments obtained from solutions with ratio A/G = 3 with: (a) KOH, (b) NaOH, (c) LiOH.

XRD study showed that the resulting sediment with all applied hydroxides (KOH, NaOH, LiOH) did not belong to β-phases of gallium oxide (Fig. 2). X-ray diffraction patterns of these samples did not demonstrate the reflections characteristic for gallium oxide, and they also did not match to various solutions of Ga with Li, K, Na, O, N, H (taking into account possible options of chemical synthesis). Only the possibility of the presence of such phases as $Li_2O_2$, $KNO_3$ and $NaNO_3$ was found, or, probably, the sediments obtained with the LiOH, KOH, NaOH represent more complex compounds.

## 4. CONCLUSIONS

As a result, the β-$Ga_2O_3$ particles with various morphology were obtained by the method of chemical synthesis and the dependence of the shape and size of the particles on the type and the concentration of alkali was shown. In contrast to the synthesis with ammonia, for which gallium oxide microparticles were obtained in the full range of alkali to gallium nitrate ratio (from 3 to 15), for solutions with potassium and sodium hydroxides the obtained sediment did not relate to the gallium oxide phase, and dispersed particles were obtained only for alkali to gallium nitrate ratio equal to 3. For other ratio values, as well as for a solution without alkali, dispersed particles were not observed. For the solution with lithium hydroxide, large crystallites were observed that did not relate to the gallium oxide β-phase. The use of microwaves exposure on solutions with ammonia allowed changing the shape of particles from ellipsoidal to parallelepiped while maintaining their size.

The results of this work can be used to develop chemical synthesis methods for obtaining dispersed gallium oxide particles suitable for use as a photocatalysis material.

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УДК 544.77

# Влияние состава раствора на морфологию синтезируемых дисперсных частиц β-$Ga_2O_3$

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**Аннотация.** Микро- и наночастицы β-$Ga_2O_3$ синтезированы в результате химического взаимодействия водного раствора нитрата галлия и различных щелочей: водных растворов аммиака ($NH_3$), гидроксида натрия (NaOH), гидроксида калия (KOH) и гидроксида лития (LiOH). В результате исследования были получены частицы с различной морфологией и показана зависимость формы и размера частиц от типа и концентрации щелочи. Использование СВЧ-воздействия в процессе синтеза раствора позволило получить частицы другой формы, сохранив их размеры. В отличии от синтеза с аммиаком, для других щелочей дисперсные частицы были получены только при отношении щелочи к нитрату галлия, равном 3, и эти частицы не относились к β-фазе оксида галлия.

*Ключевые слова:* наночастицы; оксид галлия; химический синтез; растровая электронная микроскопия; рентгеновская дифрактометрия