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# GaN SYNTHESIS BY AMMONOTHERMAL METHOD*

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It is shown that ammonothermal method can be successfully used to synthesize GaN powder of good crystallographic quality from ammonia solution at high pressure and a moderate temperature. The size of obtained GaN powder grains was of a few micrometers. The improvement of the powder crystalline quality (examined by X-ray rocking curve, scanning electron microscopy and luminescence measurements) with increasing molar proportion of mineralizer was observed. It was therefore possible to conclude that high molar proportion of mineralizer in ammonia solution plays a crucial role in the polycrystal growth process. Visible luminescence of high efficiency from the GaN powder was found.

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## 1. Introduction

GaN, the wide band gap light emitting semiconductor, is commonly regarded as a material of wide potential electronic and optoelectronic applications. At present, it is investigated mainly in the form of heteroepitaxial layers, as the effective bulk crystal growth methods are still absent or technologically difficult. Thermodynamically stable and chemically inert, GaN powder seems to be a potential raw material for production of display phosphors and special ceramics.

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Up to now there was no effective method of obtaining GaN powder of good crystallographic quality and high purity. The wide scope of methods used up to now has been reviewed in the Samsonov handbook [1]. One of the class of the methods is synthesis in flowing ammonia, in which gallium is covered by thin GaN layer. Only at the temperatures exceeding 1100°C, the volume nitridization occurs. However, at these temperatures decomposition rate of GaN is too high to obtain a nitride of good stoichiometry. These problems can be partially solved by adding a mixing agent to gallium or by GaN synthesis performed from gallium compounds. In any case, this kind of treatment leads to additional contamination and/or nonstoichiometry caused by the elevated reaction temperature.

We used a new method for growing GaN powder which allowed to obtain grains of high crystalline quality and high chemical purity.

## 2. Method

The method we applied was gallium nitridization in supercritical ammonia at high pressures and moderate temperatures. The processes were performed in special high pressure autoclave at temperatures up to 550°C and in the pressure range 1–5 kbar. The autoclave construction as well as the method itself has been described in detail in [2]. As a solvent, we used ammonia solutions of lithium and potassium amides which play the role of mineralizers. These compounds, introduced to the system usually in the metallic form, supply additional difficulties with suspending purity and demand a dry glove-box during autoclave filling manipulations.

## 3. Results

For the small molar ratio of lithium amide in ammonia solution, the drop of gallium was coated by the dark grey GaN polycrystalline layer and the further reaction was stopped. Although identified by the X-ray measurements, the morphology of GaN powder had not revealed any regular crystalline shapes (Fig. 1). In contrast to that, for higher ratio of $LiNH_2$ the whole metallic gallium passes through reaction to white GaN powder of well shaped, few micrometer long grains (Fig. 2). Also the improvement of its crystalline quality (checked by X-ray rocking curve, scanning electron microscopy and luminescence measurements) was clearly observed. It could be therefore concluded that the $LiNH_2$ : $NH_3$ molar ratio was a crucial parameter in this polycrystal growth process.

The expected higher activity of potassium amide as a mineralizer was also confirmed. The complete reaction of metallic Ga to white-yellowish GaN was observed in a much shorter time than in the case of the processes with lithium amide.

The powders obtained revealed very intensive photoluminescence and, in some cases, phosphorescence. The spectra presented in Fig. 3 show a wide photoluminescence band of powder shown in Fig. 2 in the range 1.6 to 3.0 eV with a maximum at a wavelength corresponding to bright yellow colour. In the powders obtained in ammonia–potassium system, the maximum was shifted towards lower energies.

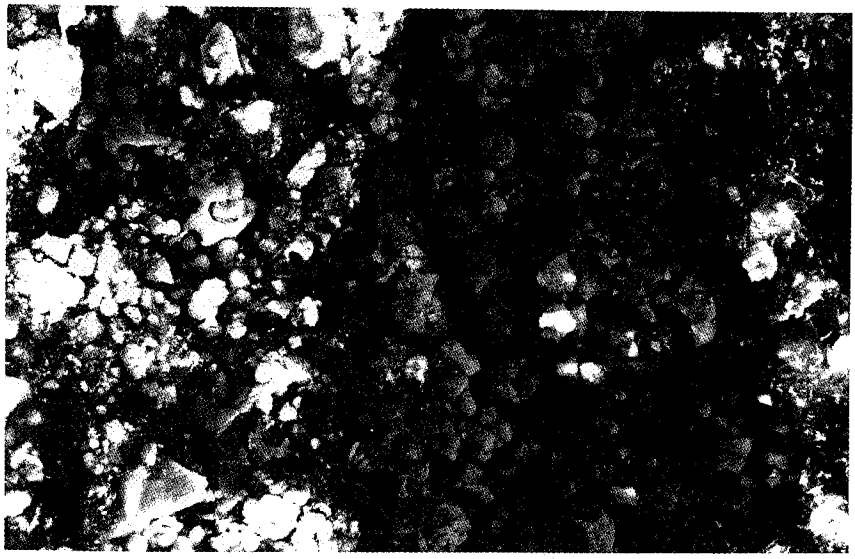

Fig.1

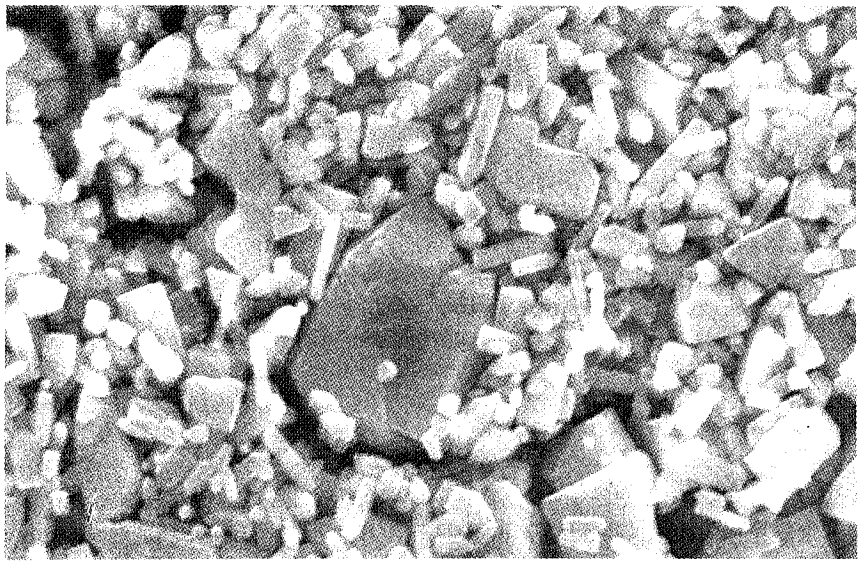

Fig.2

Fig. 1. SEM picture of GaN powder synthesized in solution containing $LiNH_2$ : $NH_3$ = 1 : 240 (small molar ratio of mineralizer). Non-regular grains of various cathodoluminescence intensity are visible.

Fig. 2 The same as in Fig. 1 except for $LiNH_2$ : $NH_3$ molar ratio which was 1 : 10 (much higher ratio of mineralizer). Regular, well shaped grains with homogeneous cathodoluminescence intensity are visible.

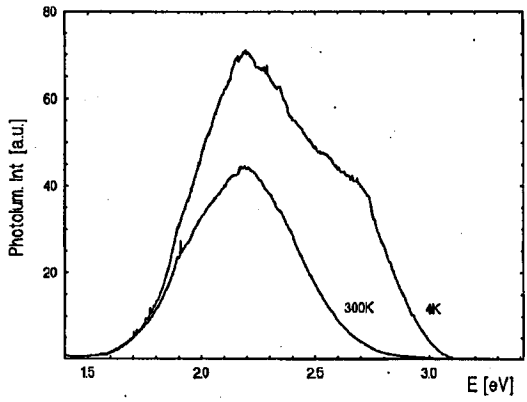


Fig. 3. Photoluminescence spectra of GaN powder shown in Fig. 2 measured at 300 K and 4 K. The spectrum obtained at helium temperature reveals higher intensity in the blue band region.

## 4. Conclusions and perspectives

Ammonothermal method was successfully used to grow GaN powder of good crystallographic quality and high luminescence efficiency in visible region. The crucial role of the mineralizers in the crystal growth process was shown: they facilitate the removal of a thin GaN layer from the gallium surface so that reaction can go to completion.

Regarding the reaction mechanisms from the chemical point of view, it can be assumed that also other nitrides of III group elements, namely AlN, InN, TaN and even BN could be synthesized by the ammonothermal method. In the case of solid solutions, like $Al_xGa_{1-x}N$ or $In_xGa_{1-x}N$, it would enable the preparation of powders with photoluminescence spectra covering the whole visible light range.

The experiments performed up to now allow to recognise the ammonothermal synthesis as a potential method for synthesis of group III nitrides in a relatively cheap and easy way.

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## References

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