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► **To cite this version:**

Annaïg Denis, Graziella Goglio, Alain Largeteau, Gérard Demazeau. A New High Pressure - Low Temperature Process for the Synthesis and the Crystal Growth of Gallium Nitride. *High Pressure Research*, 2002, 22 (3-4), pp.585-588. 10.1080/08957950212409 . hal-00715266

HAL Id: hal-00715266

<https://hal.science/hal-00715266>

Submitted on 7 Jul 2023

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A NEW HIGH PRESSURE – LOW TEMPERATURE PROCESS FOR THE SYNTHESIS AND THE CRYSTAL GROWTH OF GALLIUM NITRIDE

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Gallium nitride can be synthesized by a solvothermal route using ammonia as solvent and a nitriding additive (such as hydrazine hydrochloride $\text{NH}_2\text{NH}_3\text{Cl}$ or sodium azide NaN_3) encapsulated in melt gallium as chemical reagents. The involved temperature and pressure are respectively 600 °C and 150 MPa. The synthesized products are then characterized by X-Ray Diffraction and Scanning Electron Microscopy. The synthesis parameters influence the powder morphology and purity.

Keywords: Gallium nitride; Ammonia solvent; Solvothermal synthesis; Supercritical conditions; High pressure

INTRODUCTION

Gallium nitride is a very promising wide band gap semiconductor (3.5 eV) with a very high thermal and chemical stability, which has many applications in opto- and micro-electronics. Since GaN single crystals are necessary for the elaboration of high performance devices, crystal growth of gallium nitride has become a worldwide challenge [1, 2]. Porowski *et al.* have improved the growth of very high quality crystals (1 cm × 1 cm) by the High Pressure Nitrogen Solution. The experimental conditions then imply very high pressures (1–2 GPa) and temperatures (1400–1700 °C) [3]. To reduce these parameters, we assume that the elaboration of GaN single crystals can be deduced from solvothermal crystal growth developed in the case of α -quartz replacing water by ammonia as a solvent [4]. In this way, Kollis *et al.* are working on the solubility of GaN in NH_3 with a mixture of KI and KNH_2 as mineralizers [5]. Moreover GaN must be finely divided and must exhibit a good purity in order to be used as a nutrient. We then propose a solvothermal synthesis at high pressure with a rather low temperature in order to control the size of the microcrystallites.

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SYNTHESIS

Gallium is melt (melting point = 29.8 °C) in order to be mixed with the powdered nitriding additive (additive/gallium molar ratio = 1.5). With such a method, the metal encapsulates the additives, thus the specific area of gallium is significantly increased improving its reactivity. The mixture is introduced into a high pressure vessel which is then filled with liquid ammonia and heated by a furnace. The experimental parameters are 600 °C and 150 MPa. The NH_4Cl residue, resulting from the $\text{NH}_2\text{NH}_3\text{Cl}$ decomposition, is easily sublimated by a heating at 500 °C. In order to eliminate the residues of the reaction performed with NaN_3 , the powder is washed with aqua regia and ethanol, and then dried at 110 °C. Powders are then characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

RESULTS AND DISCUSSION

XRD patterns of both samples are presented on Figure 1. The two samples are well crystallized and no impurity is detected. The indexation of all the diffraction peaks is clearly consistent with the wurtzite-type structure of the GaN samples.

On SEM images presented on Figure 2, one can see that in both cases particles have a micrometric size. With $\text{NH}_2\text{NH}_3\text{Cl}$, only small aggregated particles are present, which is consistent with a nucleation process enhanced in supercritical conditions (Fig. 2a).

With NaN_3 , the crystallites exhibit various well defined morphologies with hexagonal shapes (Fig. 2b). The average size of these hexagonal crystallites increases at higher growth

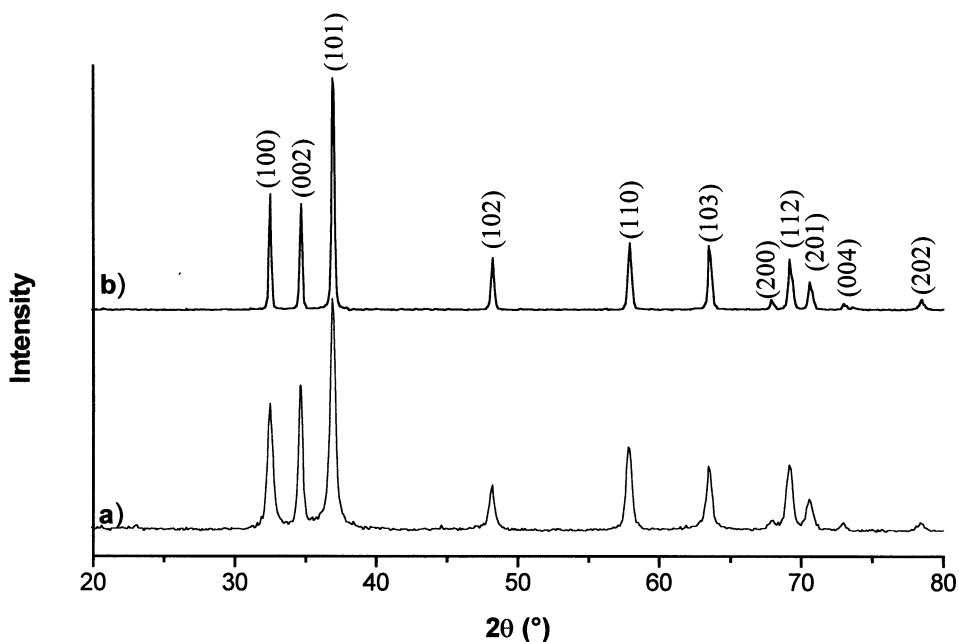


FIGURE 1 X-Ray diffraction patterns of the synthesized gallium nitride for (a) $\text{NH}_2\text{NH}_3\text{Cl}$ additive and (b) NaN_3 additive.

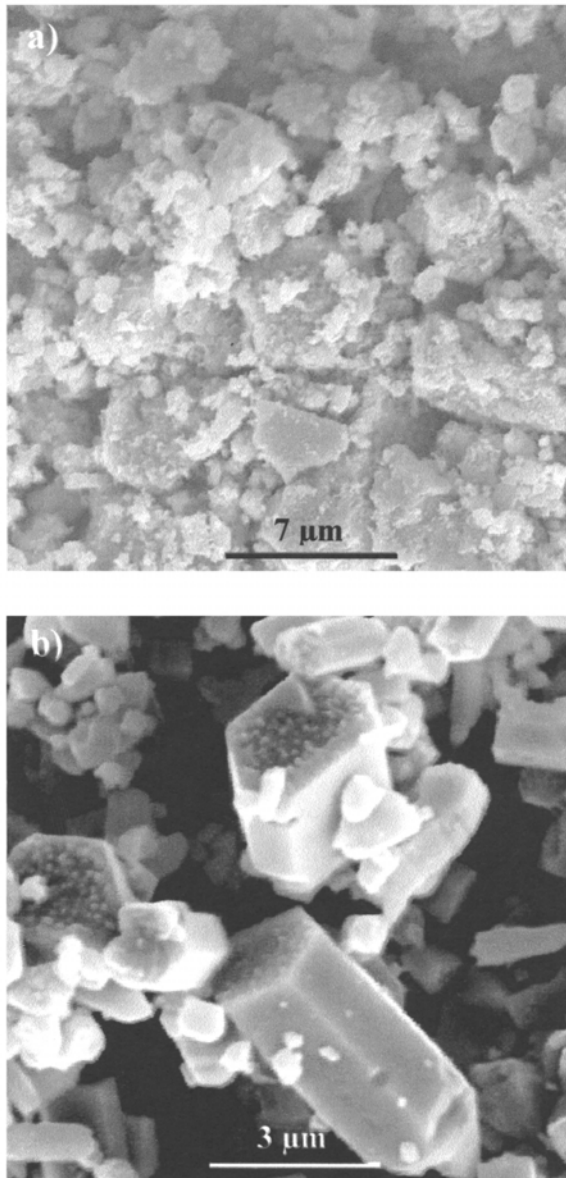


FIGURE 2 SEM images of GaN samples for (a) $\text{NH}_2\text{NH}_3\text{Cl}$ additive and (b) NaN_3 additive.

temperature, which underlines the beginning of a crystal growth process. This observation is consistent with works reported by Yamane *et al.* who used liquid Na as a flux [6].

CONCLUSION

Finely divided gallium nitride has been synthesized by ammonothermal process using gallium and nitriding additives. While nucleation processes seem to be favored with $\text{NH}_2\text{NH}_3\text{Cl}$, a beginning of crystal growth can be observed by using NaN_3 as an additive.

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