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BY

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ON

Investigation on the solubility of GaN in supercritical ammonia containing acidic, neutral, and some basic mineralizers

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**1. Motivation**

The ammonothermal growth technique to fabricate large size ( $\geq 2$  inch) gallium nitride (GaN) crystals has recently seen increased interest due to the achievements in the technique published over the last 2-3 years. The first ever 2 inch GaN bulk crystal, to be reported in the April 2009 issue of MRS Bulletin, holds the great promise that ammonothermally produced GaN may become an important GaN substrate material due to the superior structural quality over HVPE GaN.

In order to hold up with the progress, not at least provide a scientific platform, the solubility of GaN in supercritical ammonia ( $\text{NH}_3$ ) containing mineralizers of different chemical nature was examined.

Another motivation to particularly explore the acidic mineralizers lies in the advantage that acidic mineralizers such as  $\text{NH}_4\text{Cl}$  knowingly show a higher solubility in  $\text{NH}_3$  over basic mineralizers such as  $\text{KNH}_2$  or  $\text{NaNH}_2$ : 124 g  $\text{NH}_4\text{Cl}$  (24.8 °C), 3.6 g  $\text{KNH}_2$  (25 °C) and 0.163 g  $\text{NaNH}_2$  (20 °C) per 100 g  $\text{NH}_3$  was reported.<sup>1</sup> Consequently, a higher amount of GaN would be dissolvable in ammonia containing acidic mineralizer in comparison to basic mineralizers if the solubility of GaN is a function of the amount of acidic mineralizers dissolved in ammonia.

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<sup>1</sup>*Inorganic Chemistry in Liquid Ammonia*, Monograph 17, D. Nicholls In *Topics in Inorganic and General Chemistry*, ed. R. J. H. Clark, Elsevier, Amsterdam, 1979.

# Report Documentation Page

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## 2. Experimental Conditions

The experiments were carried out at Tohoku University facilities using a high-pressure cell which simulates a typical ammonothermal autoclave. While the former model of the high-pressure cell was made of a common steel alloy, due to strong corrosion at the inner walls it was replaced by an improved model made of INCONEL alloy and partially equipped with a Pt inner container. Figure 1 shows the high-pressure cell.

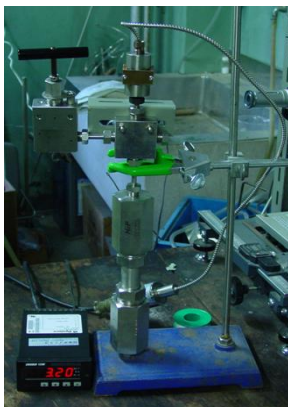
We applied the “classic” route of determining the weight difference of small GaN crystals before and after the experiment. The exact amount of  $\text{NH}_3$  and mineralizer is known. The high-pressure cell was packed in a heater system so as to provide isothermal conditions inside the cell to prevent from any parasitic nucleation which could take place on a cooler area inside the cell.

The GaN precursor material to be dissolved was HVPE-grown polycrystalline GaN as grains of 1-3 mm in diameter was. The following mineralizers could have been employed:  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ , and  $\text{NH}_4\text{I}$ , and mixtures thereof. There were in the prime focus.

A typical experimental run is composed of (i) fast heating up to target temperature of 415-540 °C within a few hours, (ii) dwell at target temperature for 120 hours, and (iii) fast cool down. Pressure up to 100 MPa built up during the dwell time. Around 6 days are to be spent for one successful experiment.

### Purity of compounds:

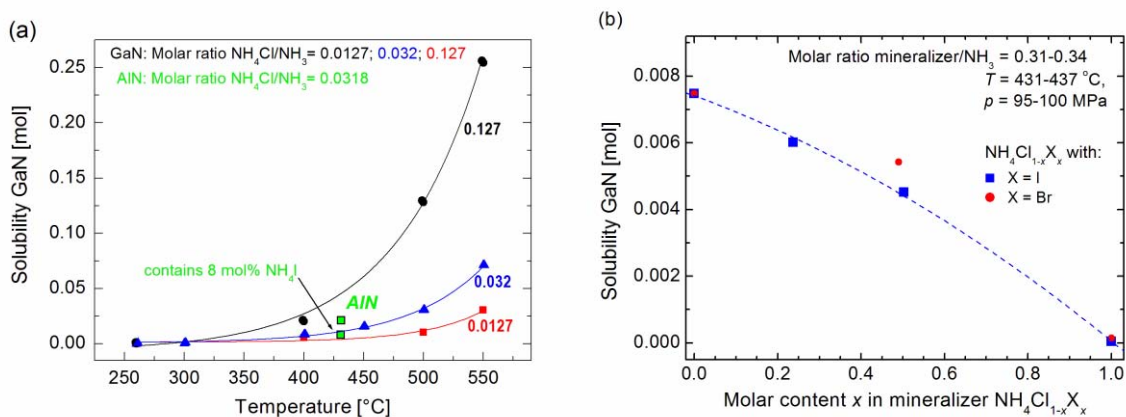
$\text{NH}_3$ :	99.999%, purchased from Japan Fine Products Co. Ltd
GaN:	$10^{17}$ - $10^{18}$ $\text{cm}^{-3}$ O and Si; provided by Mitsubishi Chemical Corp.
$\text{NH}_4\text{Cl}$ , $\text{NH}_4\text{Br}$ , $\text{NH}_4\text{I}$ :	99.995%, Alfa Aesar



**Figure 1:** The high-pressure cell for solubility experiments.

## 3. Results and Discussion

The solution of supercritical ammonia and mineralizers strongly forces corrosion of most of the commonly used alloys. While our first experiments were carried out in a commercially available cell corrosion leading to increasingly distorted results were



**Figure 2:** Solubility of GaN and AlN based on data sets obtained with the old high-pressure cell (a) and the solubility of GaN in the systems  $\text{NH}_4\text{Cl}-\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{Cl}-\text{NH}_4\text{I}$  based on data sets obtained with the recent model of the high-pressure cell (b).

experienced. It has to be noted that the general tendency still is correct, however, absolute values were different. Figure 2a shows a graph based on data sets obtained with the old high-pressure cell model.  $\text{NH}_4\text{Cl}$  was employed as the mineralizer of choice due to the lowest acidity among the mineralizers of the series  $\text{NH}_4\text{X}$  with  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$ . The molar ratio  $\text{NH}_4\text{Cl}/\text{NH}_3$  was 0.0127, 0.032, and 0.127.

We show in Fig. 2a that the acidic mineralizer  $\text{NH}_4\text{X}$  provides a regular solubility, at least for the investigated temperature window  $T = 260-550^\circ\text{C}$ . What gets also clear is that increasing the amount of mineralizer leads to increase the amount of GaN dissolved by the solution. This can be fitted exponentially, giving a linear fit in the Arrhenius plot (log-log scale). This can be interpreted as having one dominating chemical reaction under given conditions. Such a result is of high importance as it clearly shows that the growth of GaN can be controlled. According to Fig. 2a, we believe that a minimum  $T = 500^\circ\text{C}$  is required and at least should the molar ratio  $\text{NH}_4\text{Cl}/\text{NH}_3$  be 0.13 in order to obtain a reasonable solubility.

Aluminum nitride (AlN) was used as precursor in a few experiments on the solubility. Figure 2a depicts that under similar conditions the solubility of AlN is higher than this of GaN. Increasing the acidity of the solution by adding  $\text{NH}_4\text{I}$  lowers the solubility of AlN.

The effect of mixed mineralizer systems in order to tune the acidity is shown in Fig. 2b. Two mixed systems have been investigated, namely  $\text{NH}_4\text{Cl}-\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{Cl}-\text{NH}_4\text{I}$ . Note that  $\text{NH}_4\text{I}$  provides the highest acidity and  $\text{NH}_4\text{Cl}$  the lowest.<sup>2</sup> The temperature was constant at  $T = 431-437^\circ\text{C}$  and  $p = 95-100\text{ MPa}$ . The result shows that the solubility is actually decreasing with increasing acidity. It is yet not clear whether the small size of the

<sup>2</sup>We had recently been treating this issue along with phase stability of GaN in our publication D. Ehrentraut et al., *J. Mater. Chem.* **17**, 886, 2007. It turned out that the yield of GaN, i.e., the amount of GaN precursor which is dissolved and afterwards deposited in the cooler growth zone of the autoclave was higher as the acidity of the mineralizer increased from  $\text{NH}_4\text{Cl}$  to  $\text{NH}_4\text{Br}$  to  $\text{NH}_4\text{I}$ . This would point to a higher reaction rate.

high-pressure cell (10 mL) is an obstacle. We have planned to investigate this effect in the future.

Other mineralizers like LiCl, NaCl, KCl or KNH<sub>2</sub> have not been investigated due to unexpected corrosion problem which made the exchange of the high-pressure cell necessary. According to literature, the neutral mineralizers did not improve the solubility of GaN in NH<sub>3</sub> and the mixture NH<sub>4</sub>Cl/LiCl caused the nucleation of the cubic GaN phase.<sup>3</sup>

#### 4. Publications, Others

Results obtained from the experiments were published in following paper and book chapter:

1. D. Ehrentraut, K. Kagamitani, C. Yokoyama, T. Fukuda, “*Physico-chemical features of the acidic ammonothermal growth of GaN*”, Journal of Crystal Growth **2008**, 310, 891-895.
2. D. Ehrentraut, Y. Kagamitani  
“*Acidic ammonothermal technology for bulk GaN*” in Technology of GaN Crystal Growth, edited by D. Ehrentraut, E. Meissner, and M. Boćkowski, (Springer-Verlag, Heidelberg, to appear **2009**), pp. ?-?

and at conferences:

3. D. Ehrentraut, T. Fukuda, “*Ammonothermal growth for mass-production of GaN*”, SPIE – Photonics West, Integrated Optoelectronic Devices (OPTO 2009), San Jose, CA, January 24–29, 2009, paper 7216-12. **Invited**
4. D. Ehrentraut, T. Fukuda, “*Ammonothermal technology for the growth of group-III nitride crystals: Special focus on GaN*”, International Solvothermal & Hydrothermal Association Conference (ISHA 2008), Nottingham, England, September 8-10, 2008.
5. D. Ehrentraut, T. Fukuda, “*Progress in the ammonothermal growth of GaN*”, XXI Congress of the International Union of Crystallography (IUCr 2008), Osaka, Japan, 2008. **Invited**
6. D. Ehrentraut, “*Bulk crystal growth of GaN by the acidic ammonothermal technology*”, 4<sup>th</sup> Asian Conference on Crystal Growth & Technology (CGCT), Sendai, Japan, 2008, paper Z-24AM1-II-3A-2K. **Invited Keynote**

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<sup>3</sup>A.P. Purdy, R.J. Jouet, C.F. George, Cryst. Growth Des. **2**, 141, 2002; A. Purdy, J. Cryst. Growth **281**, 355, 2005.