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# Pressure-induced phase transition in GaN nanocrystals

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## Abstract

High-pressure *in situ* energy-dispersive x-ray diffraction experiments on GaN nanocrystals with 50 nm diameter have been carried out using a synchrotron x-ray source and a diamond-anvil cell up to about 79 GPa at room temperature. A pressure-induced first-order structural phase transition from the wurtzite-type structure to the rock-salt-type structure starts at about 48.8 GPa. The rock-salt-type phase persists to the highest pressure in our experimental range.

## 1. Introduction

Gallium nitride (GaN) is the most promising semiconductor for short-wavelength optoelectronics and high-temperature, high-power electronics to date due to its wide, direct band gap, high energy of dislocation formation, high thermal conductivity as well as large saturated electron drift velocity [1–7].

At ambient conditions, GaN tends to crystallize into the wurtzite-type structure and it has a very high ionicity, e.g. 0.5 [8] or 0.43 [9] on the Phillips scale, which is the highest among III–V compounds. Therefore, it can be expected that GaN will undergo a pressure-induced first-order phase transition into the rock-salt structure [10]. This expectation was confirmed by recent theoretical and experimental reports. But there are large discrepancies in transition pressures among different reports, i.e. 37–53 GPa for the experimental results [11–14] and 55–65 GPa for the theoretical ones [15–17]. However, structural transitions of GaN nanocrystals under high pressure have not been reported until today. Table 1 lists the transition pressures and methods used in the main works.

Nanocrystals tend to exhibit significantly different behaviours from the corresponding bulk crystals; e.g. nanocrystals of anatase (TiO<sub>2</sub>) undergo a phase transition at 16 GPa, which is remarkably higher than the transition pressure, 7.1 GPa, for bulk TiO<sub>2</sub> [18]. More detailed experimental results are needed to deduce the general trend. In this paper, we present our high-pressure *in situ* energy-dispersive x-ray diffraction (EDXRD) studies on GaN nanocrystals.

**Table 1.** Transition pressures and methods used for GaN.

	$P_t$ (GPa)	Method	Reference
GaN nanocrystals	48.8	EDXRD <sup>a</sup>	This work
	47	Raman scattering and XAFS <sup>b</sup>	[11]
	30–37	EDXRD	[12]
	52.2	XRD using Mo $K\alpha$ radiation	[13]
Bulk GaN	53.6	ADXRD <sup>c</sup> using synchrotron radiation	[14]
	55	Density functional theory	[15]
	65	LMTO <sup>d</sup>	[16]
	55.1	First-principles nonlocal pseudopotential	[17]

<sup>a</sup> Energy-dispersive x-ray diffraction.

<sup>b</sup> X-ray absorption fine structure spectra.

<sup>c</sup> Angle-dispersive x-ray diffraction.

<sup>d</sup> Linear muffin-tin orbital with atomic spheres approximation.

We expect these to be helpful for understanding the properties of the phase transition in GaN and the nature of nanocrystals.

## 2. Experimental details

The samples studied were ultrafine nanocrystal powders of gallium nitride synthesized by the direct-current plasma method through the reaction of metal gallium (Ga) with a mixture of nitrogen ( $N_2$ ) and ammonia ( $NH_3$ ) [19]. The nanocrystal powders were characterized as wurtzite structure polycrystals with average size about 50 nm diameter by small-angle x-ray diffraction (XRD) using Cu  $K\alpha$  radiation, transmission electron microscopy (TEM) and selected-area electron diffraction using a Hitachi 8100 microscope.

*In situ* high-pressure experiments were carried out on Line 3W1A of Beijing Synchrotron Radiation Facility (BSRF IHEP).

A gasketed diamond-anvil cell (DAC) driven by an accurately adjusted gear-worm system was employed for pressure generation. The gasket was made of T301 stainless steel with a hole 110  $\mu\text{m}$  in diameter drilled in the centre as the sample chamber. A mixture of methanol, ethanol and water (16:3:1 by volume) was used as a pressure-transmitting medium. Samples were placed into the gasket hole together with fine grains of platinum (Pt) for pressure calibration.

## 3. Results and discussion

Figure 1 shows the EDXRD patterns of GaN nanocrystals. In the pattern taken before pressurization, six diffraction peaks are observed, which can be completely assigned to the wurtzite-type structure. This phase persists to about 51.1 GPa. At 48.8 GPa, the intensities of all the peaks of the wurtzite phase decrease and a new peak appears. With pressure increasing the intensity of the new peak increases. At 58.3 GPa, all peaks of wurtzite-type structure phase totally disappear. The crystal structure of the new phase is a rock-salt-type structure according to EDXRD analysis.

In the pattern recorded at 58.3 GPa, the peaks from the wurtzite phase have completely disappeared while two new peaks appear instead. These new peaks can be indexed as (111) and (200) of the rock-salt-type phase of GaN [11–17]. Therefore, GaN nanocrystals transform to the same high-pressure phase as bulk samples.

The change of the relative volume of GaN nanocrystals as a function of pressure is shown in figure 2. The volume decreases slowly and monotonically with increasing pressure and

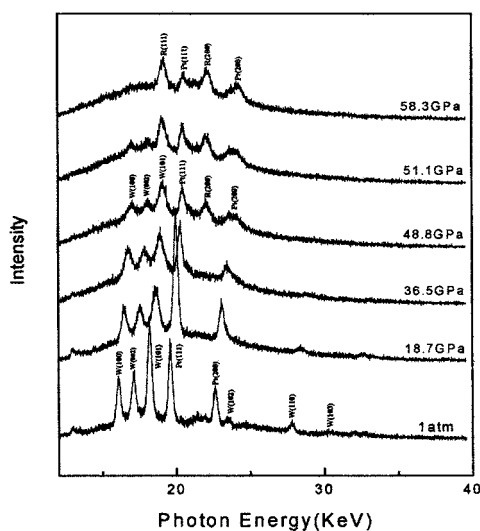


Figure 1. X-ray synchrotron radiation patterns of GaN.

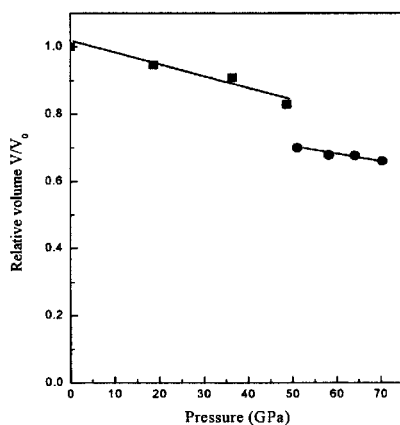


Figure 2. Change of the relative volume of GaN with increasing pressure. The squares are for the wurtzite-type phase, and the circles for the rock-salt-type phase.

drops dramatically at 48.8 GPa demonstrating the first-order characterization of the phase transition. There is a coexisting zone of wurtzite-type phase and rock-salt-type phase for GaN nanocrystals between 48.8 and 51.1 GPa at least. This phenomenon was not reported for bulk GaN.

One can see from table 1 that our result is in good agreement with some of the earlier experiments on bulk GaN [11] while it differs from other results [12–14]. Ueno *et al* [13] have pointed out that the differences in experimental transition pressure ( $P_t$ ) might arise from the differences in the transition probing techniques. Comparing our study with [12] and [14] which employed synchrotron x-ray radiation as the probing technique, we suppose that at least in the context of GaN, probing techniques may not be a dominant factor, while physical loading of samples and pressure calibration techniques may play an important role in the determination of  $P_t$ . Note that Xia *et al* [12] placed only GaN in the gasket hole and used the equation of state

of GaN as self-calibration to avoid the interference of marker material while others (see [14] and this study) placed the samples and the calibration materials (platinum or ruby) together into the sample chamber. In addition, inherent hysteresis [11, 12] further hampers the accurate determination of the transition pressure.

#### 4. Conclusions

The high-pressure behaviour of wurtzite-type nanocrystals of GaN was studied by synchrotron XRD. A first-order phase transition to the rock-salt-type structure has been observed at 48.8 GPa indicating that GaN nanocrystals have the same high-pressure phase as the bulk crystals. We cannot determine whether GaN nanocrystals transform at a higher or lower pressure than bulk samples due to the dispersion of the experimental transition pressures available.

#### Acknowledgment

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