7 High Pressure Science

7-1 Precise Measurement of Equation-of-State and Elastic Properties for GaN up to 16 GPa

Gallium nitride (GaN) is an important semiconductor that has the properties of a high-brightness blue/green light-emitting diode. It is well known that a GaN crystal grown on a sapphire matrix suffers a biaxial strain owing to lattice mismatch and that the strain results in introducing undesirable dislocations to the GaN crystal. Knowledge of the elastic properties of GaN may be important for the modelling of devices. Axial compressibility ($\beta = -1/l\ dl/dP$) is the most fundamental thermo-elastic property for solids along with the bulk modulus ($B_0 = -(1/V\ dV/dP)^{-1}$), where V, l, and P are volume, cell parameter, and pressure, respectively. *In situ* high-pressure experiments are suitable for the determination of these parameters. The bulk modulus of GaN has been reported by several experimental and theoretical studies. The values of B_0 reported by high-pressure experiments, however, are widely scattered from 188 to 245 GPa, in contrast to the convergence of the theoretical B_0 and the Brillouin spectroscopic B_0 to approximately 200 GPa [1,2]. This large ambiguity in the earlier high-pressure studies was probably caused by experimental deficiencies such as non-hydrostaticity. To determine the bulk modulus and axial compressibility accurately by static compression experiment, the precise measurement of the X-ray diffraction patterns of GaN at high pressures [3] is necessary. A synchrotron source is most suitable for this purpose.

The axial compressibility of GaN is also interesting from the viewpoint of its high-pressure phase transition. It has been reported that the wurtzite-type group III nitrides AlN, GaN and InN transform to NaCl-type structure under pressures of 20, 50 and 10 GPa, respectively. It should be noted that the transition pressure of GaN is considerably higher than that of other two nitrides. It has been suggested that this particularly large stability of wurtzite-type GaN under high pressure was related to lattice distortion under pressure [1].

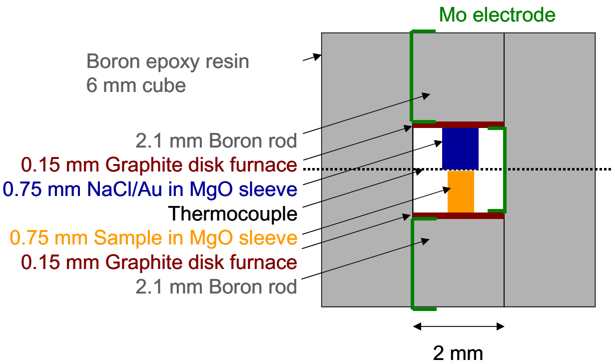

Figure 1
Schematic of the high-pressure cell assembly used in the present high-pressure experiment.

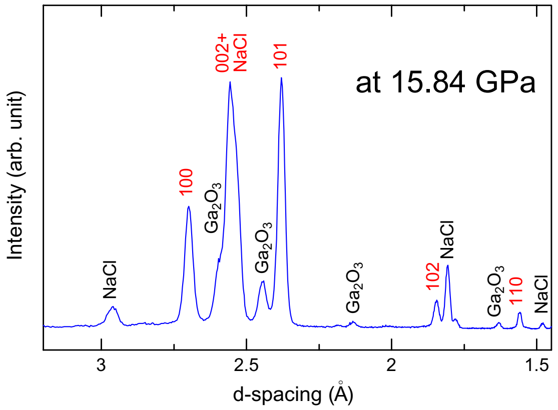

Figure 2
Energy-dispersive X-ray diffraction spectrum of GaN at 15.84 GPa. Symbols NaCl and Ga_2O_3 indicate diffractions of the pressure medium and of corundum-type Ga_2O_3, respectively

In situ X-ray observations of reagent grade polycrystalline GaN powder at high pressures were made by using a multi-anvil device, MAX80, installed at the AR-NE5C. The MAX80 was used for single-stage compression using sintered diamond anvils with anvil top size of 3 mm. The high-pressure cell assembly is shown in Fig. 1. The incident white X-rays were directed at the sample, and the diffracted beam was detected with a pure Ge solid-state detector, SSD, fixed on a vertically rotating goniometer. The temperature was monitored with a $W_{97}Re_3$-$W_{75}Re_{25}$ thermocouple. Annealing was done at 900°C with a duration of 600 s at each pressure to remove deviatric stress. The generated pressure was determined after annealing from the unit cell volume and the equation-of-state (EOS) of Au [4].

Figure 2 shows the energy-dispersive X-ray diffraction spectrum of GaN measured at 15.84 GPa. In addition to diffraction peaks from wurtzite-type GaN and the NaCl pressure medium, a slight trace of corundum-type Ga_2O_3, which is most probably due to the oxidation of GaN during the sample production in air, is observed. The lattice constants are calculated at 9 pressures up to 16 GPa. We found $B_0 = 202.4$ GPa and $B'_0 = 4.5$ by fitting to the third-order Birch-Murnaghan EOS function [5]. Although different from previous results using diamond-anvil cells, these values are quite consistent with the B_0 given by Brillouin spectroscopy and *ab initio* predictions.

Furthermore, we found that the axial compressibilities along the a and c directions are almost the same in GaN, being $\beta_a = 1.481 \times 10^{-3}$ and $\beta_c = 1.402 \times 10^{-3}$ (Fig. 3). This means that GaN has only a small pressure dependence on the axial ratio c/a, differing from other wurtzite-type

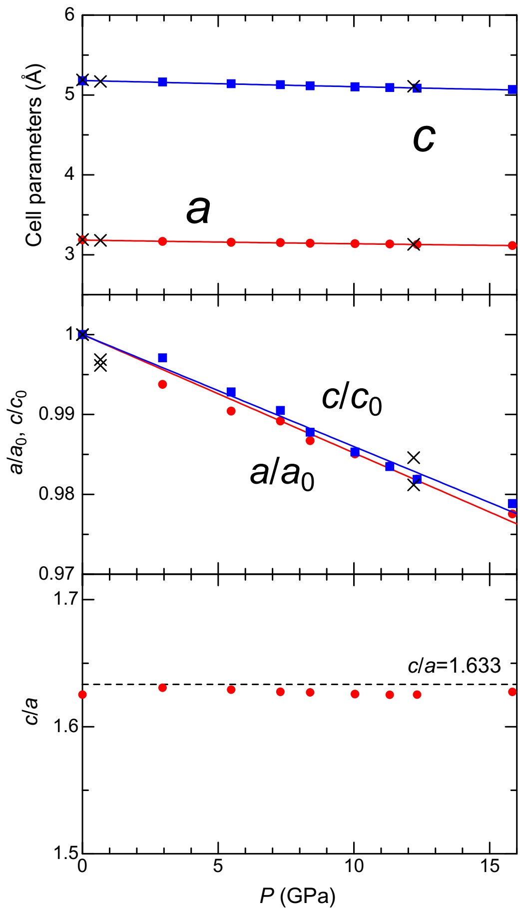

Figure 3
Pressure dependence of cell parameters (upper panel), axial compressibilities (middle panel) and axial ratio (lower panel). The present results are shown by filled points. Red and blue lines are linear fits for the *a* and *c* parameters, respectively. The cross in the upper and middle panels are the previous data from Ref. [1]. Dashed line in the lower panel indicates the ideal value of axial ratio for the hexagonal closed-pack structure (1.633).

group III nitrides. Thus, the high ideality of the hexagonal cell is conserved under high pressures (Fig. 2). This high elastic isotropy of GaN may relate to the large stability of wurtzite-type GaN. On the other hand, β_a of GaN is much larger than β_a of Al_2O_3 (1.172×10^{-3} as calculated in Ref. [6]). This means that the GaN *a* axis is easier to deform elastically than that of Al_2O_3. However, the lattice mismatch may be too large to avoid dislocation formation in the GaN crystal on the sapphire matrix.

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7-2 High-Pressure Powder X-Ray Diffraction Experiments on Zn at Low Temperature

Zinc is an anisotropic hexagonal close-packed (hcp) metal with a large *c/a* axial ratio of 1.856 at ambient pressure (Fig. 4). The deviation of the axial ratio from the value for the ideal hcp structure (1.633) has been explained by the lowering of the band structure energy through lattice distortion [1]. Pressure reduces lattice parameters and modifies band structures. The equilibrium axial ratio at each pressure is hence intimately related to the details of the band structure, specifically those near the Fermi level. In other words, Zn offers an interesting system to study the correlation between crystal structure and electronic structure. A number of energy band calculations have been carried out on Zn as a function of pressure, and these suggest anomalous changes of the axial ratio at 9-10 GPa, reflecting the topological change of the Fermi surface [2-6]. We have studied the change of the axial ratio of Zn at high pressure and low temperature in order to verify the predicted anomalies. It is important to maintain hydrostatic conditions in order to obtain reliable structural data at high pressures, since nonhydrostatic stress deforms the crystal lattice and may obscure small structural anomalies. We have used helium as a pressure-transmitting medium. Helium is soft enough to offer quasihydrostatic conditions even in the solid state at high pressure and low temperature.

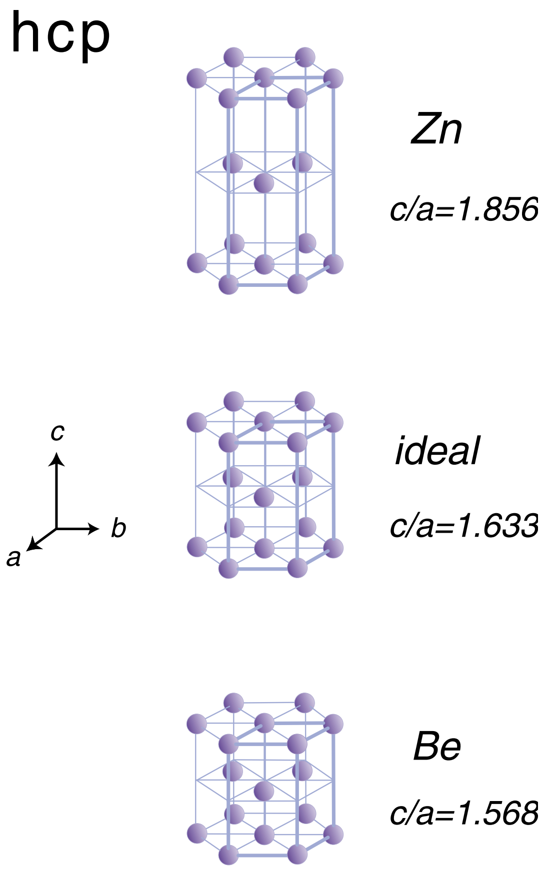

Figure 4
Hexagonal close packed (hcp) structures with various c/a axial ratios.

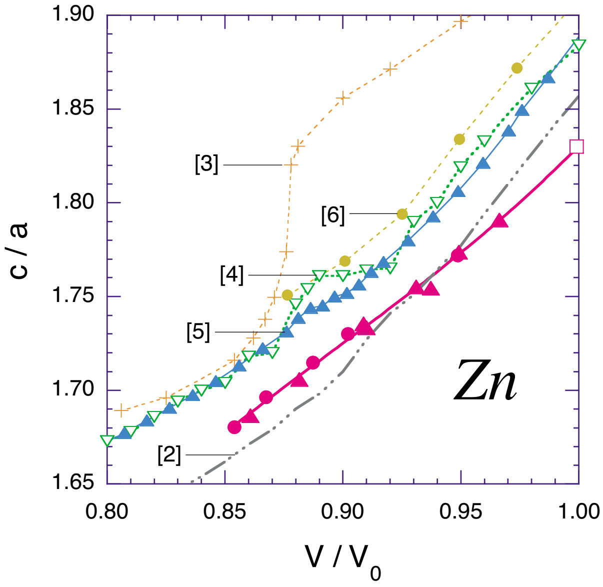

Figure 5
The axial ratio of Zn as a function of relative volume. The present experimental results are shown by red circles and red triangles, and the red open square shows the value at atmospheric pressure and at 40 K from the literature. Other curves are theoretical calculations.

High-pressure powder X-ray diffraction experiments were carried out at 40 K with a diamond-anvil cell and a closed-cycle He-cryostat at BL-18C [7,8]. The pressure was determined on the basis of the ruby pressure scale at low temperature. In order to avoid nonhydrostatic stress, the pressure was changed at high temperature (~200 K), where helium is more ductile than at lower temperatures. Figure 5 shows the change of the axial ratio of Zn at 40 K as a function of relative volume V/V_0, where V_0 refers to the volume of Zn at atmospheric pressure and 40 K. The highest pressure in the present experiments was 17.6 GPa corresponding to V/V_0 = 0.854. Two experimental runs gave reproducible results with no appreciable anomalies within the experimental uncertainty. The results of various theoretical calculations are also shown in Fig. 5. Due to the well-known difficulty in reproducing equilibrium lattice parameters, the calculated axial ratios at atmospheric pressure deviate from the experimental values, but all of the calculations indicate anomalies at V/V_0 = 0.87-0.89 (P = 9-10 GPa). The magnitude of the anomalies differs for each calculation, depending on the accuracy and the approximation made. The present experiment constrains the upper limit of the lattice anomaly to be 0.35% or 0.006 in *c/a*. Steinle-Neumann *et al.* [6] have pointed out that the number of Brillouin-zone points sampled is important in order to reach well-converged axial ratios by calculation. The most recent calculations with a large number of *k*-point sampling [5,6] show very small anomalies, in reasonable agreement with the present experiment. The correlation between lattice anomalies and electronic structure has been a theme of historical interest [9], and can be effectively studied with the use of high pressure. Further efforts continue to improve the experimental accuracy of high-pressure X-ray diffraction.

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7-3 A High Pressure and High Temperature *in situ* X-Ray Diffraction Study on FeO under Lower Mantle Conditions

The properties and behavior of FeO under lower mantle conditions play a key role in understanding the nature of the Earth's core and the core-mantle boundary. Shock compression studies [1,2] have clarified the existence of a phase transformation accompanied with a large volume change at around 70 GPa, while no such transition was found at room temperature compression up to 120 GPa [3]. A diamond-anvil experiment coupled with external heating clarified the existence of a B8-structured phase at an elevated temperature of around 1000 K [4], but many conflicting results [5] have been presented recently on the stability and the structure of the B8-type phase, and the nature of this phase transition is not yet clear.

High-pressure and high-temperature *in situ* X-ray diffraction studies have been carried out at BL-13A using a diamond-anvil cell coupled with YAG-laser heating [6]. A powdered FeO sample was sandwiched with Al_2O_3 powder as a thermal insulating layer and compressed to the desired pressure at room temperature. Then a thin X-ray beam of about 30 μm in diameter irradiated the sample and diffraction patterns were collected with increasing temperature. The sample was heated using a YAG-laser beam of about 60 μm in diameter through the diamond anvil. Example diffraction patterns are shown in Fig. 6. Just after the room temperature compression up to 80 GPa (bottom pattern) all the diffraction peaks are broad due to stress inhomogeneity within the sample, but the

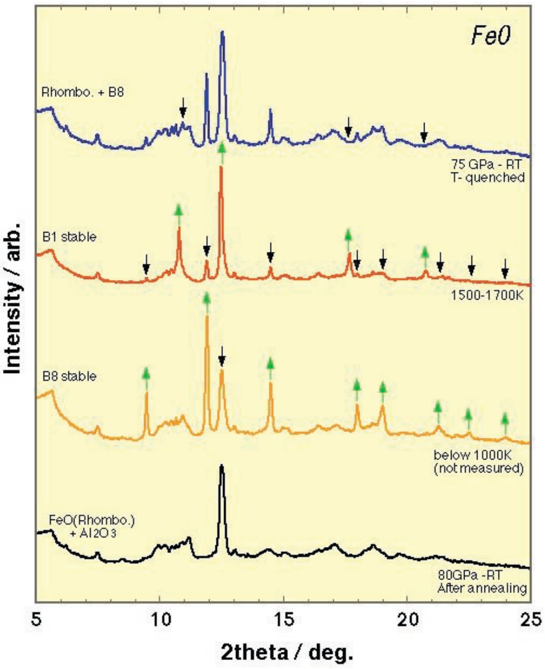

Figure 6
Examples of the high-pressure and high-temperature *in situ* X-ray diffraction patterns of FeO observed at around 80 GPa.

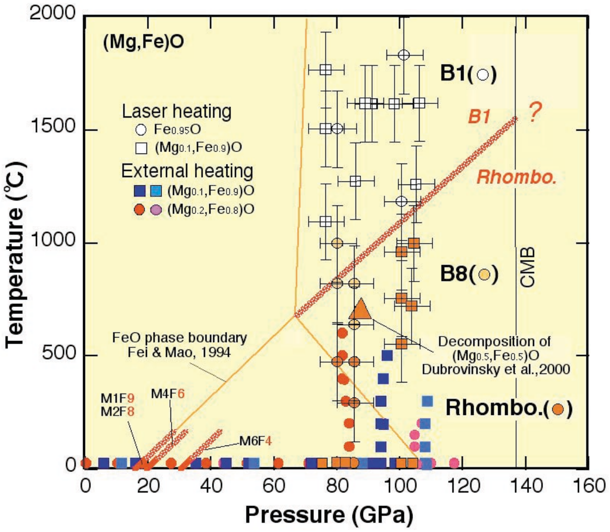

Figure 7
Phase diagram of FeO determined based on the present study. Three different phases exist under high-pressures and temperatures but the phase boundaries among these three phases have still ambiguity.

existence of rhombohedrally distorted FeO together with Al_2O_3 can be observed. With increasing temperature, the FeO transforms into the B8 phase below 1000 K, and further transformation into the B1-structured phase can be seen at around 1500-1700 K. This B1-structured phase is unquenchable upon lowering of the temperature, and only the rhombohedral and B8 phases of FeO were observed at room temperature after heating (top pattern). Such observations were repeated at various pressures up to about 120 GPa and the results are summarized in Fig. 7.

The present result [7] indicates that the stability field of the B1 phase extends to very high pressures at high temperature while that of the B8 phase is limited to relatively low temperature. Considering the temperature distribution in the Earth's deep interior, it is likely that FeO remains unchanged with a B1-structured phase in the entire region of the Earth. However, this result is not in harmony with the results obtained by shock compressions [1,2]. A possible source of the discrepancy is the non-stoichiometric nature of FeO, and further studies on $Fe_{1-x}O$ with various stoichiometries are in progress.

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