PHYSICAL REVIEW B VOLUME 45, NUMBER 17 1 MAY 1992-I

X-ray observation of the structural phase transition of aluminum nitride under high pressure

M. Ueno and A. Onodera
Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

O. Shimomura and K. Takemura
National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305, Japan

(Received 22 January 1992)

The III-V compound AlN has been studied under pressure to 30 GPa by x-ray diffraction in a diamond-anvil cell. At 22.9 GPa the wurtzite-to-rocksalt phase transition takes place accompanied by a volume reduction of 17.9%. The structure of the high-pressure phase and the amount of volume reduction are in agreement with a recent calculation of Gorczyca *et al.* [Solid State Commun. **79**, 1033 (1991)]. On the other hand, the bulk modulus of the wurtzite phase ($B_0=207.9\pm6.2$ GPa) agrees well with a calculation of Ching and Harman [Phys. Rev. B **34**, 5305 (1986)]. The axial ratio c/a in the wurtzite phase monotonically decreases with increasing pressure from the atmospheric value of 1.60.

Aluminum nitride is one of the important materials for electronic devices; it has a high thermal conductivity (200 W/m K) and is a semiconductor with a large band gap (6.2 eV).[1] Among the tetrahedrally coordinated III-V compounds, AlN belongs to a group which favors at ambient conditions the wurtzite-type structure ($P6_3mc$) rather than the zinc-blend-type structure. The bonding character is partially ionic and partially covalent (Phillips ionicity of 0.445).[2] It is expected that AlN would undergo a pressure-induced structural phase transition into the β-Sn or rocksalt structure in a manner similar to other III-V semiconductors.

Despite the extensive studies on III-V compounds, relatively little has been made of AlN at high pressure until a recent success in retrieving the rocksalt-type phase after quenching the sample from 16.5 GPa and 1400–1600 °C in an octahedral-anvil apparatus.[3] Very shortly thereafter, a visual observation in a diamond-anvil cell showed that AlN becomes blackened between 16 and 17 GPa.[4] The pressure was in close agreement with the calculated value (16.6 GPa) for the transition from wurtzite to the rocksalt phase. These static pressure experiments are in accord with a shock compression experiment detecting a phase transition at ~21 GPa.[5] A more recent calculation[6] has suggested the high-pressure phase of AlN to be the rocksalt type. The transition pressure as well as the structure of the high-pressure phase of these recent reports[3–6] are considerably different from the prediction of Van Vechten, 90 GPa and β-Sn type.[7] There remains a question as to whether the room-temperature transition detected visually is of the same origin as that detected by the quenching experiment. In this study we have carried out *in situ* high-pressure x-ray-diffraction experiments at room temperature.

Aluminum nitride samples (> 99% pure) were commercially obtained from Tokuyama Soda and Toshiba Ceramics. Essentially there was no difference in the x-ray powder-diffraction data between the two samples. High pressure was generated in a diamond-anvil cell.[8] The culet size of the anvils was 0.4 mm in diameter. A gasket made of Ni-based alloy, U-700, was preindented to 0.1-mm thickness and a 0.15-mm-diam hole was drilled as a sample chamber. The AlN sample was ground into particles less than 5 μm in diameter and was placed into the gasket hole. Fine powders of ruby to monitor the pressure[9] were incorporated. A mixture of methanol, ethanol, and water was used as a pressure-transmitting medium to keep the condition hydrostatic until about 14 GPa.[10]

X-ray powder-diffraction patterns were obtained using a rotating-anode x-ray generator (50 kV, 250 mA) with a Mo target in an angle-dispersive mode. X rays from the Mo anode were monochromatized by pyrolytic graphite. The beam size was reduced by a double pin-hole collimator with a diameter of 0.08 mm. Diffracted x rays were exposed on an imaging plate (IP).[11] The exposure time was about 10 h. Diffraction profiles were obtained by computing the digital data of the Debye-Scherrer patterns recorded on IPs. All experiments were undertaken at room temperature.

Figure 1 shows representative x-ray-diffraction patterns under high pressure. Before transition, all the peaks except for two peaks from the gasket can be completely assigned by the hexagonal wurtzite-lattice indices as shown in Fig. 1(a). The intensities are in good agreement with previous ambient-pressure data.[12] At pressures between 18 and 20 GPa, the sample shifted from white to black in color. This change agrees with the result of Gorczyca *et al.* who observed the blackening of AlN at 16–17 GPa.[4] The pressure for the change is slightly higher in this study.

At pressures higher than 22.9 GPa, some new peaks appear in the x-ray-diffraction patterns as shown by the arrows in Fig. 1(b). At 30.0 GPa, Fig. 1(c), all the peaks in

© 1992 The American Physical Society

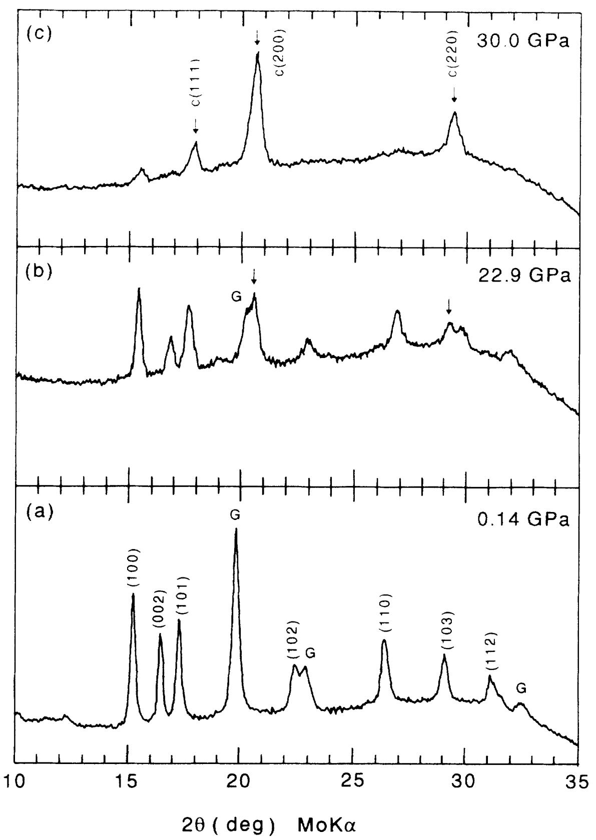

FIG. 1. Representative high-pressure x-ray-diffraction patterns taken for AlN. Each pattern was obtained by computing the digital data of the Debye-Scherrer rings recorded on imaging plates. MoKα radiation was employed as the x-ray source. The arrows and the lowercase c's denote reflections from the cubic rocksalt-type AlN.

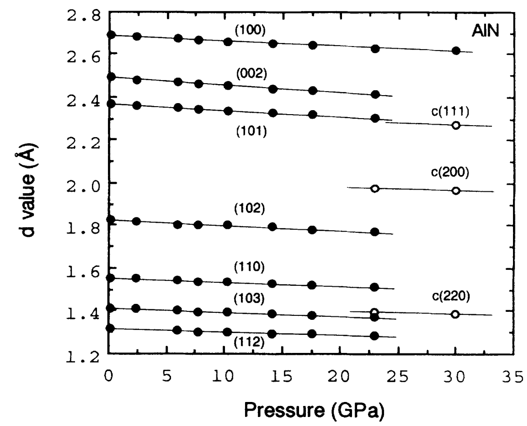

FIG. 2. Change of d values with increasing pressure for AlN. The solid line is to guide the reader's eye. The solid circles are for the wurtzite-type phase; the open circles are for the rocksalt-type phase. The lowercase c's denote the cubic rocksalt-type phase.

the wurtzite phase are very much weakened. Instead, three distinct peaks appear and can be assigned as (111), (200), and (220) reflections of the rocksalt-type lattice. Table I compares the observation with calculated d spacings and intensities for the rocksalt structure. The observed d values are in excellent agreement with the calculation. Also, the agreement in the intensities is good between the experiment and the calculation.

Figure 2 shows the change of d spacings with increasing pressure. There is a discontinuity in the d spacings between 17.6 and 22.9 GPa. The wurtzite-to-rocksalt transition should have occurred between the two pressures, approaching the pressure (18–20 GPa) of the visually observed transition. Unlike the two cubic (200) and (220) reflections, the cubic (111) reflection is not observed at 22.9 GPa. This is because the cubic (111) reflection is disturbed with the wurtzite (101) reflection having a d value very close to that of the cubic (111) reflection.

Figure 3 shows the relative volume of AlN with increasing pressure. The volume reduction at ~23 GPa is 17.9%. Table II shows the transition pressure and the amount of volume reduction.[3-6] One of the calculations[4] for the volume reduction agrees well with our data. The transition pressure at room temperature in this work should be connected to the high-temperature data[3] giving a transition pressure of 16.5 GPa or lower at 1400–1600 °C. Thus, the phase boundary between the wurtzite and rocksalt phases should have a negative slope. The negative slope for the wurtzite-rocksalt boundary has

TABLE I. Observed and calculated d spacings and integrated intensities for AlN at 30.0 ± 0.8 GPa.

Observed		Calculated[a]		
d_{obs} (Å)	I_{obs}	d_{calc} (Å)	I_{calc}	hkl
2.273(7)	28	2.274	25.1	111
1.969(0)	100	1.969	100.0	200
1.392(0)	37	1.392	56.4	220
· · ·	· · ·	1.187	14.1	311

[a] Calculations are done for the rocksalt-type structure of a cubic lattice with a = 3.938 Å.

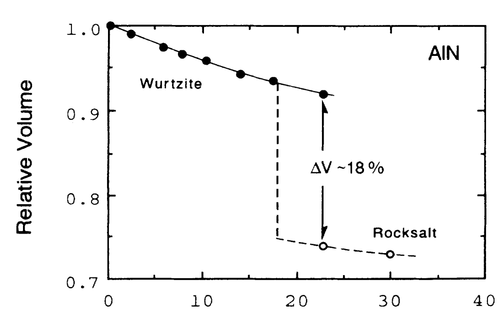

FIG. 3. Change of the relative volume of AlN with increasing pressure. The solid circles are for the wurtzite-type phase and the open circles for the rocksalt-type phase. The solid line is obtained by fitting the data with the Birch-Murnaghan equation of state. The dashed line is drawn by taking account of the visual observation of the transition at 18–20 GPa.

TABLE II. Parameters for the transition from wurtzite-to-rocksalt phase.

Method	P_t (GPa)	ΔV (%)	Reference
	Experiment		
X-ray diffraction	22.9	18	This work
Visual	18–20		This work
Quench (1400–1600 °C)	16.5	20.6	3
Visual	16–17		4
Shock Hugoniot	21	22	5
	Calculation		
LMTO	16.6	18.1	4
Pseudopotential	12.9	22.5	6

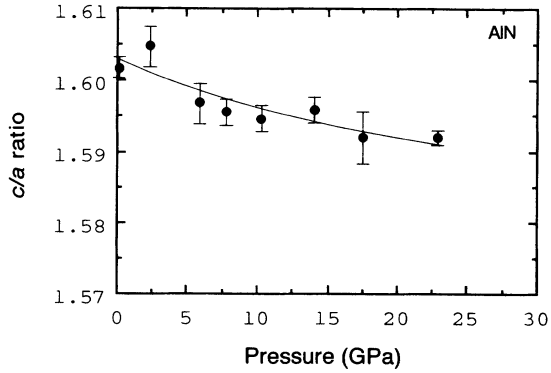

FIG. 4. Change of the axial ratio c/a of the wurtzite-type phase of AlN with increasing pressure. The vertical bar at each point represents uncertainty attached. The solid line is to guide the reader's eye.

also been observed for CdS (Refs. 13 and 14) and CdSe.[15]

The volume-pressure data for the wurtzite phase (Fig. 3) are fitted with the Birch-Murnaghan equation of state. The bulk modulus and its pressure derivative thus obtained are listed in Table III. Our B_0 is in excellent agreement with those from two of the ultrasonic measurements.[16,17] All the calculations listed in Table III are based on the local-density approximation.[4,6,19] Our data for B_0 are in excellent agreement with the LCAO calculation.[19] It is smaller than the value obtained by the LMTO method,[4] but is larger than the value obtained by the pseudopotential calculation.[6] Our B_0' is about 60% larger than the calculated values.[6,19]

A combination of Tables II and III shows that the agreement between the present experiment and the calculations is somehow complicated. The LMTO calculation[4] is closer to this study for the transition parameters whereas the LCAO calculation[19] agrees best with the elastic data. This does not necessarily mean that the pseudopotential calculation is deficient at predicting the transition pressure because the experimental transition pressures obtained in diamond-anvil cells are for the forward transition, which needs an excess pressure beyond the equilibrium pressure, while the calculation is made for thermodynamic equilibrium. After the pressure for the backward (rocksalt-to-wurtzite) transition is determined, an equilibrium pressure which is definitely lower than the pressure for the forward transition will be found.

Figure 4 shows the change of the axial ratio c/a of the wurtzite phase with increasing pressure. As the pressure is increased, the c/a ratio slightly decreases. A similar behavior has been observed from a recent high-pressure x-ray-diffraction study of AlN with a cubic-anvil apparatus.[20] The c/a ratio of AlN at ambient conditions (about 1.60) is one of the smallest bounds among the wurtzite-type compounds.[21] Since the c/a ratio for the ideal wurtzite structure is 1.633, the tetrahedrons of AlN before compression are to some extent distorted from the ideal one. The behavior in Fig. 4 suggests a further distortion of the tetrahedrons. Lawaetz has argued a relation between the c/a ratios and the ionicity charge parameters in the wurtzite-type compounds and pointed out that the charge transfer increases with a decrease in the c/a ratio.[22] Along this line, the pressure-induced decrease in c/a implies that the ionic character of AlN increases with pressure.

In conclusion, the present x-ray-diffraction study has revealed that a structural phase transition occurs at 22.9 GPa and room temperature in the wurtzite-type AlN. The high-pressure phase is determined to be the rocksalt-type structure, in agreement with recent predictions.[4,6] This room-temperature phase transition is in harmony with a quenching experiment.[3] This study has also duplicated an earlier visual observation of the transition.[4]

TABLE III. Equation of state data for the wurtzite-type phase of AlN.

	B_0 (GPa)	B_0'	Reference
	Experiment		
X-ray diffraction	207.9 ± 6.3	6.3 ± 0.9	This work
Ultrasonic measurement	201.7		16
	205.7		17
	159.9	5.2	18
	Calculation		
LMTO	221		4
Pseudopotential	195	3.74	6
LCAO	207	3.98	19

The authors thank Dr. J. Hama and Mr. R. Kato for useful discussions.

---

[1] O. Madelung, R. Blachnik, and W. Kress, in *Semiconductors,* edited by O. Madelung, M. Schulz, and H. Weiss, Landolt-Börnstein, New Series, Group III, Vol. III, Part 17a (Springer-Verlag, Berlin, 1982), p. 158.

[2] J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).

[3] H. Vollstädt, E. Ito, M. Akaishi, S. Akimoto, and O. Fukunaga, Proc. Jpn. Acad. Ser. B **66**, 7 (1990).

[4] I. Gorczyca, N. E. Christensen, P. Perlin, I. Grzegory, J. Jun, and M. Bockowski, Solid State Commun. **79**, 1033 (1991).

[5] K. Kondo, A. Sawaoka, K. Sato, and M. Ando, in *Proceedings of the Conference on Shock Waves in Condensed Matter,* edited by W. J. Nellis, AIP Conf. Proc. No. 78 (AIP, New York, 1981), p. 325.

[6] P. E. Van Camp, V. E. Van Doren, and J. T. Devreese, Phys. Rev. B **44**, 9056 (1991).

[7] J. A. Van Vechten, Phys. Rev. B **7**, 1479 (1973).

[8] K. Takemura, O. Shimomura, K. Tsuji, and S. Minomura, High Temp. High Press. **11**, 311 (1979).

[9] H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[10] S. Block, R. A. Forman, and G. J. Piermarini, in *High Pressure Research Applications in Geophysics,* edited by M. Manghnani and S. Akimoto (Academic, New York, 1977), p. 503.

[11] O. Shimomura, K. Takemura, H. Fujihisa, Y. Fujii, Y. Ohishi, T. Kikegawa, Y. Amemiya, and T. Matsushita, Rev. Sci. Instrum. **63**, 967 (1992).

[12] Powder Diffraction File No. 25-1133 (International Centre for Diffraction Data, Swarthmore, PA).

[13] G. A. Samara and A. A. Giardini, Phys. Rev. **140**, A388 (1965).

[14] J. Osugi, K. Shimizu, T. Nakamura, and A. Onodera, Rev. Phys. Chem. Jpn. **36**, 59 (1966).

[15] A. Onodera, Rev. Phys. Chem. Jpn. **39**, 65 (1970).

[16] K. Tsubouchi, K. Sugai, and N. Mikoshiba, *1981 Ultrasonic Symposium Proceedings,* Brighton (IEEE, New York, 1981), p.375.

[17] P. Boch, J. C. Glandus, J. Jarrige, J. P. Lecompte, and J. Mexmain, Ceram. Int. **8**, 34 (1982).

[18] D. Gerlich, S. L. Dole, and G. A. Slack, J. Phys. Chem. Solids **47**, 437 (1986).

[19] W. Y. Ching and B. N. Harmon, Phys. Rev. B **34**, 5305 (1986).

[20] O. Shimomura *et al.* (unpublished).

[21] R. W. G. Wyckoff, *Crystal Structures* (Wiley, New York, 1963), Vol. 1, p. 112.

[22] P. Lawaetz, Phys. Rev. B **5**, 4039 (1972).