2. High Pressure Synthesis of Rocksalt Type of AlN

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Aluminium nitride with the wurtzite structure, w-AlN, has attracted special attention as an alternative ceramic substrate of high power applications in microcircuits.¹⁾ The conspicuous advantages are high thermal conductivity greater than 100 W/mK²⁾ and with a low coefficient of thermal expansion which, in the temperature range of interest (20–200°C), closely matches that of silicon. It also has a high electrical resistivity, a moderate dielectric loss, and good resistance to thermal shock and thermal decomposition.

On the analogy of other III–V compounds with the wurtzite structure, AlN is expected to assume the cubic structure at high pressures. Van Vechten³⁾ predicted that, at 90 GPa and room temperature, AlN would transform to a metallic phase with the β -tin structure. Kieffer *et al.*⁴⁾ reported a new phase in the system AlN–Al₂O₃, which they claimed to be cubic AlN. The new phase, however, was proved later to be AlON, occurring in hot pressing experiments in the system.⁵⁾ On the basis of the shock wave experiments on AlN, Kondo *et al.*⁶⁾ suggested a transformation to a denser phase at about 21 GPa. Despite of more general searches,^{7)–9)} no definite evidence has been obtained for the existence of the new dense phase of AlN. It is the purpose of the present paper to report the successful synthesis of the new cubic phase of AlN at high pressures and temperatures.

The fine powder of w-AlN (grain size, <1.0 μ m; purity, >99%) kindly provided by Tokuyama Soda Co. Ltd. was used as the starting material. High pressure and high temperature experiments were carried out using a uniaxial split sphere apparatus driven by 1000 ton press (USSA-1000) at the Institute for Study of the Earth's Interior. The assembly of tungsten carbide cubes with 5 mm truncation was used with semisintered magnesia octahedron of 10 mm edge length as pressure medium. The AlN starting material was charged into a cylindrical tantalum heater embedded in the octahedron. The detailed sample assembly was similar to those described elsewhere.¹⁰⁾ The sample temperature was monitored by the Pt/Pt13%Rh thermocouple. The pressure values were calibrated at room temperature by the conventional fixed points of Bi III–V (7.7 GPa), ZnS metallic transition (15.6 $\pm$ 0.6 GPa) and GaAs metallic transition (18.2 $\pm$ 0.7 GPa).

The experimental conditions were varied in the ranges of 11.5–16.5 GPa and

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Table I. High pressure and high temperature experiments on AlN

Run No.	Pressure/GPa	Temperature/°C	Time/min	Phases present*
49041	16.5	1600	30	c-AlN w-AlN
49042	16.5	1550	60	c-AlN w-AlN
89043	16.5	1400	60	w-AlN c-AlN
89044	14.0	1150	60	w-AlN
89045	11.5	1000	60	w-AlN

* c-AlN: cubic phase of AlN. w-AlN: wurtzite-structure phase of AlN.

Table II. Powder diffraction data of rocksalt type of AlN

h k l	$d_{\text{obs}}/\text{\AA}$	$d_{\text{cal}}/\text{\AA}$	I_{obs}	I_{cal}
1 1 1	2.3346	2.3354	30	29
2 0 0	2.0226	2.0225	100	100
2 2 0	1.4300	1.4301	55	70
3 1 1	1.2195	1.2196	10	15
2 2 2	1.1678	1.1677	11	19
4 0 0	1.0113	1.0113	6	9
3 3 1	0.9280	0.9280	4	8
4 2 0	0.9045	0.9046	17	35

$$a=4.0450(1)\text{\AA}, v=66.186(5)\text{\AA}^3, Z=4.$$

Fig. 1. Powder X-ray diffraction chart of rocksalt type of AlN. W denotes diffraction peaks of w-AlN.

1000–1600°C. The sample was first pressed up to the half of the desired pressure at room temperature. Then the pressure and temperature were increased simultaneously to the final values. After the sample was kept at the desired conditions for a certain duration, it was quenched by shutting off the electric power supply. The recovered samples were examined by ordinary or micro-focused X-ray diffractometer.

The experimental results are summarized in Table I. The X-ray diffraction pattern of the run products quenched at 16.5 GPa demonstrated extra peaks in addition to those of w-AlN as shown in Fig. 1. All of them can be completely indexed on the basis of a cubic lattice. The powder diffraction data of the cubic phase are shown in Table II. Taking into account the general trend of the coordination-number increase associated with high-pressure phase transformation, the cubic phase of AlN could be expected to possess the rocksalt structure. The calculated diffraction intensities are in good agreement with those observed. This may prove the high-pressure synthesis of rocksalt type of AlN. The volume contraction accompanied with the wurtzite-rocksalt transformation is about 21%.

Preliminary investigations of the electrical resistivity have been done on rocksalt type of AlN using a sample of 2.5 mm² cross section, and 0.5 mm thickness. The results show an increase in electrical resistivity by order of 4 ($\rho=5\times 10^{13} \Omega \text{ m}$). Therefore the high pressure polymorph of AlN with the rocksalt structure has still high resistivity and is different from the metallic phase predicted by Van Vechten.³⁾

Measurements of the thermal conductivity and the microhardness are in progress as well as the determination of high pressure/high temperature phase diagram.

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