

Lattice Parameters of Aluminium Nitride in the Range 10–291 K

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Lattice parameters for aluminium nitride were determined using X-ray powder diffraction at a synchrotron radiation source (beamline B2, HASYLAB/DESY, Hamburg) in the temperature range from 10 K to 291 K. The measurements were carried out using the Debye–Scherrer geometry. The relative change of both, a and c , on rising the temperature in the studied range (10–291 K) is about 0.03%. The results are compared with earlier laboratory data and theoretical predictions.

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1. Introduction

Aluminium nitride, AlN (wurtzite structure type) has specific physical properties like high thermal conductivity, high melting point, and large energy gap. Its applications as a component of refractory ceramics or buffer layers for GaN epilayers grown on sapphire are widely known. Elastic properties of each component of such layered structures and devices are an important factor influencing the properties of the product. Therefore, detailed studies of lattice parameter as a function of temperature may be helpful in design and improving the technologies involving aluminium nitride.

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Early work on (mainly high-temperature) thermal expansion of AlN has been briefly summarized in [1, 2]. Recent studies include experimental works on low-temperature [3] and high-temperature [4] expansivity, and calculations based on semi-empirical models [5]. As many other materials built from covalently bonded light atoms, AlN is characterized by low thermal expansivity. The experiments [3] and calculations in [5] indicate an existence of a domain of slightly negative expansion below about 100 K for both lattice parameters, the highest absolute value being of the order of 10^{-7} K^{-1} . According to Refs. [3, 5], the variation of lattice parameters below 200 K is as low as about 0.0002 Å. In the present paper, the results of experimental investigation of the unit-cell dimensions for AlN in the temperature range 10–291 K are presented.

2. Experimental

Fine AlN powder was synthesized at Warsaw University of Technology from aluminium and urea in the reaction in ammonia atmosphere using the method described in [6, 7]. Fine aluminium powder (grain size 0.5 μm) and urea were milled in the mortar under nitrogen atmosphere. The obtained mixture was heated in the tube furnace in the stream of ammonia in three steps: 0.5 h at 185°C, 0.5 h at 250°C and 3 h at 1400°C. The prepared powder was stored in a closed container in order to protect it against interaction with air. The final AlN product contains less than 0.08% carbon. The size of the grains is $\approx 2 \mu\text{m}$ [6].

The measurements were carried out at a high-resolution powder diffractometer at the B2 beamline using Debye–Scherrer geometry. The experiment consisted in data collection using temperature steps starting from the lowest available temperature, 10 K. An NaI:Tl scintillation counter was applied for the data collection. The wavelength was determined to be $\lambda = 1.20720(5) \text{ \AA}$ by least squares refinement of five reflections of silicon powder (NIST 640b diffraction standard, $a = 5.43094 \text{ \AA}$). The AlN powder was mounted within a thin-wall capillary of 25 mm length, 1 mm diameter and 0.01 mm wall thickness. The diffraction experiments were carried out with the use of a He-closed-cycle cryostat (CTI model 21 SC Cryophysics) at a low helium pressure ensuring absence of thermal gradients and allowing capillary rotation (described in Ref. [8]). The temperature was kept constant within 1 K using a PID controller and a silicon diode temperature sensor.

Powder diffraction patterns were measured with a powder diffractometer installed at the B2 beamline at HASYLAB/DESY, Hamburg, using a parallel beam monochromatized with a Ge(111) double crystal monochromator. Improved resolution of the diffractometer is ensured by a set of parallel horizontal foils at the diffracted beam of angular aperture 0.23°. The wavelength was determined to be 1.20720 Å by a least squares procedure for a silicon NBS 640b standard (with the lattice parameter $a_{\text{Si}} = 5.43094 \text{ \AA}$). The data were collected at selected angular intervals ranging up to 98° (2θ). A Rietveld refinement program, DBWS v. 94.11 [9] was used for evaluation of the lattice parameters.

3. Results and discussion

Phase analysis revealed the presence of a small amount of aluminium oxide impurity (lines 012, 104, 113, 116 identified on the basis of Ref. [10], all of relative peak-height intensity as low as about 0.5%). The lattice-parameter dependence on temperature is shown in Fig. 1. Polynomial fitting yields the following relations:

$$a = 3.11054 + 6.19 \times 10^{-9}T^2 + 5.82 \times 10^{-12}T^3, \quad (1)$$

$$c = 4.98006 + 2.82 \times 10^{-8}T^2 + 1.35 \times 10^{-10}T^3. \quad (2)$$

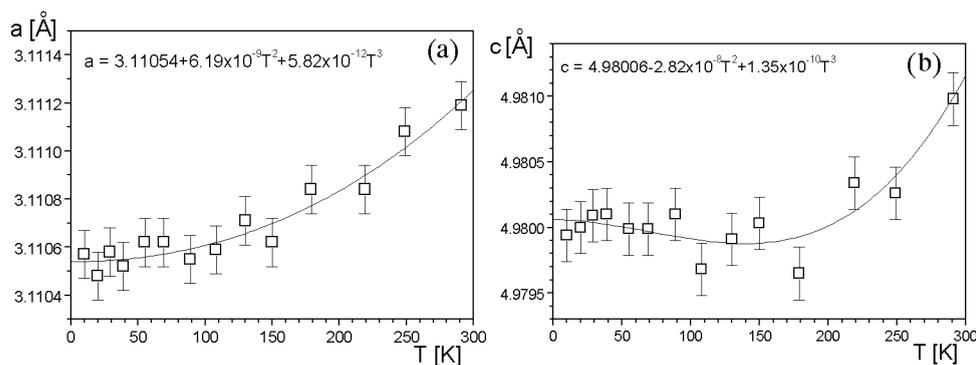


Fig. 1. Dependence of lattice parameters, a and c , on temperature for aluminium nitride (empty squares). The solid lines represent polynomial fits of the experimental data.

Measured room-temperature (291 K) values are $a_{\text{RT}} = 3.1112(1) \text{ \AA}$, $c_{\text{RT}} = 4.9810(2) \text{ \AA}$. Rietveld refinement of a full pattern collected at a Bragg–Brentano diffractometer yielded similar values, $a_{\text{RT}} = 3.1115(1) \text{ \AA}$, $c_{\text{RT}} = 4.9810(2) \text{ \AA}$ [11]. The relative increase in both parameters, a and c , on rising the temperature in the studied range (10–291 K) is about 0.03%. The axial ratio at $T = 10 \text{ K}$ is 1.6010 and its relative changes with increasing temperature are small. A scatter of a_{RT} and c_{RT} values quoted in literature for single and polycrystals synthesized by various methods is of the order of 0.1% (see Table) and in this sense the present results are consistent with other data. The dependence of both lattice parameters on temperature is shown in Fig. 1. Below about 150 K they are almost constant (their changes are comparable with the experimental errors of about 0.0001 Å for a and 0.0002 Å for c). Although the runs do not indicate any minimum for a and a possible shallow minimum for c , the magnitude of experimental errors does not allow for confirming the existence/absence of negative thermal expansion (predicted in [5] for both, a and c , variables) without additional experimental effort.

TABLE

Reported (chronologically ordered) room-temperature (R.T.) lattice parameters and axial ratio for AlN. The following radiation was applied in the reported studies: Cr K_α [3], Cu K_α [11, 13–16], synchrotron radiation (this work).

a_{RT} [Å]	c_{RT} [Å]	c/a	T [K]	Experimental details	References
3.1129	4.9819	1.6004	298		[12]
3.1105(5)	4.9788(8)	1.6006(5)	297	oxygen impurity < 1%	[1]
3.1115	4.9798	1.6004	291		[13]
3.1114(1)	4.9792(2)	1.6003	298		[14]
3.1106	4.9795	1.6008	R.T.	single crystal, oxygen impurity 800 ppm	[15]
3.1111	4.9751	1.5991	300	sample stabilized by addition of Y_2O_3	[3]
3.1122(7)	4.978(2)	1.600(1)	R.T.		[16]
3.1111	4.9788	1.6003	R.T.		[17]
3.1115(1)	4.9810(2)	1.6008(1)	299		[11]
3.1112(1)	4.9810(2)	1.6010(1)	291		this work

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