Novel high-pressure phases of AlN: a first-principles study

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ABSTRACT

Four novel AlN phases with low density and high hardness are predicted by using a evolutionary methodology on structural search. All four phases are thermodynamically more favourable than the rock salt structure of AlN at ambient pressure and will be transformed to rock salt AlN at certain pressure. All these phases are mechanically and dynamically stable by checking the independent elastic constants and phonon dispersion spectra. The calculated mechanical properties reveal that the proposed AlN phases are hard, and the Vickers hardness of the AlN phases ranges from 13.2 GPa to 15.2 GPa. The calculated band structures of the novel AlN phases reveal that these AlN phases possess semiconductive properties with wide direct band gaps at G points, and the gaps range from 3.627 eV to 3.927 eV.

1. Introduction

Aluminium nitride (AlN) has been attracted extensive attention on theoretical and experimental studies due to its importance of scientific research and industrial application. At ambient conditions, AlN exists as a closely packed hexagonal wurtzite structure (wz-AlN), which has a widely applications, including cutting and machining tools, semiconductor devices, and field-emission devices because of its excellent chemical and physical properties, such as high thermal conductivity [1, 2], high melting point [3], large bulk modulus [4-6], good hardness [7-9], and corrosion resistance [10], large band gap [11].

The materials' chemical and physical properties are related to their structures. Scientists have been searching for novel allotropes of AlN, which may have other important applications. A zinc blende structure AlN (zb-AlN) has been synthesised by a solid-state reaction [12]. Scientists have acquired a rock salt structure AlN (rs-AlN) transformed from wz-AlN by utilizing high pressure technology [13-16]. This phase transition has been reported to begin at 14–16.6 GPa [13-16]. Theoretical studies on AlN structures are underway. In 1973, van Vechten predicted a transition to a β -Sn structure (for the diatomic equivalent of the β -Sn structure of binary compound; this structure was also named d- β -Sn and its space group is $I\bar{4}m2$ [17, 18]) at 90 GPa [19], whereas no phase transitions to β -Sn were observed [15, 20]. The d- β -Sn structure has been proven to be absent in several III-V/II-VI semiconductors [21], and it is not favoured at any pressure [22]. In addition, Christensen predicted a phase transition for the $rs \rightarrow$ NiAs structure between 30 and 40 GPa [20]. However, no NiAs structure was found within at least 132 GPa

by Uehara [23]. The theoretical study by Serrano illustrated that the NiAs structure cannot correspond to a stable high-pressure phase [22]. Christensen [20] stated that anti-NiAs structure cannot be the high-pressure phase of AlN, which agrees with Serrano's research [22]. Thus, the typical phases of AlN (wz, zb and rs) were adopted for comparison with the novel proposed phases.

In the present work, we have extensively searched the potential structures of AlN. Four novel high-pressure orthorhombic AlN crystal structures have been predicted. The stabilities of these structures are determined by independent elastic constants and phonon dispersion spectra. We show the results of a total energy study of several phases of AlN. The transition behaviours of various AlN phases under hydrostatic pressure are studied. Further calculations are performed to study the mechanical, thermodynamic and electronic properties of four novel AlN phases.

2. Computational methods

The crystal structure prediction software CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization code) is widely used [24, 25] and great achievements in structure prediction have been made with this software [26-29]. The evolutionary simulation method by CALYPSO was performed with none experimental information as guideline. The calculations of geometry optimisations, enthalpies, elastic constants, phonons and band structures were implemented in the CASTEP code [30]. The exchange correlation potential was described by the generalized gradient approximation with Perdew–Burke–Ernzerhof function [31, 32].

Fig. 1. Structure graphs for the four novel phases of AlN at ambient pressure: (a) $Pmn2_1$ -AlN, (b) $Pbam$ -AlN, (c) $Pbca$ -AlN and (d) Cmc -AlN. The N (blue) and Al (green) atoms are represented by the coloured spheres. The gold sticks represent the Al-N chemical bonds.

The ultra-soft pseudopotentials were adopted to describe the electronic configurations for Al (3s2 3p1) and N (2s2 2p3)[33]. The geometry optimisation per unit cell at fixed external stress was performed with the BFGS minimisation algorithm, which provides a rapid path to find the configuration with low enthalpy [33]. The plane wave basis set for energy cutoff is 500 eV. A k-point separation ($2\pi \times 0.04 \text{ \AA}^{-1}$) was used to generate a Brillouin zone sampling grid [34]. The values of the convergence thresholds during the geometry optimization for energy (eV/atom), force (eV/Å), stress (GPa) and displacement (Å) were set as 5×10^{-6} , 0.01, 0.02 and 5×10^{-4} , respectively. To check the dynamically stability of the optimized structures, the phonon dispersion spectra are researched throughout the Brillouin zone via the linear response approach as implemented in the CASTEP code. The efficient stress-strain method is adopted to calculate the elastic constants.

3. Results and discussion

Optimisation of Crystal Structures

A large selection of candidate structures composed of AlN is studied. In addition to wz -AlN, zb -AlN, rs -AlN and the structure predecessors that have been previously studied, four novel structures of AlN have been predicted. Their space groups are $Pmn2_1$, $Pbam$, $Pbca$ and Cmc , and the phases are denoted as $Pmn2_1$ -AlN, $Pbam$ -AlN, $Pbca$ -AlN and Cmc -AlN, respectively. The four novel structures of AlN all belong to the orthorhombic crystal system. $Pmn2_1$ -AlN, $Pbam$ -AlN and $Pbca$ -AlN are all primitive-

centred (0, 0, 0) structures with 16 atoms/unit cell. Cmc -AlN is a C-centred (0, 0, 0), (0.5, 0.5, 0) structure with 24 atoms/unit cell. The schematic ambient crystal structures of $Pmn2_1$ -AlN, $Pbam$ -AlN, $Pbca$ -AlN and Cmc -AlN are shown in Fig. 1. All the atoms in the four novel structures are composed of coordinates and form $[AlN_4]/[AlN_4]$ of tetrahedrons with the four coordination atoms. No Al-Al/N-N bonds are found in the structures, thereby producing low energy.

$Pmn2_1$ -AlN (Fig. 1a): In the middle of the $Pmn2_1$ -AlN unit cell, two similar 'rectangular' structures are located; these non-standard rectangles have four different bond lengths. The two 'rectangles' are both perpendicular to the a -axis, one is located at $a = 0$ and another is at $a = 0.5$. The two terminals of the unit cell are similar to wurtzite structures. The atoms in the 'rectangular' structures and wurtzite structures are equal. Both 'rectangles' are connected by Al-N chemical bonds. In $Pmn2_1$ -AlN, the bond lengths range from 1.870 Å to 1.934 Å.

$Pbam$ -AlN (Fig. 1b): We can divide the 16 atoms into two types (A1 and A2) based on the atomic coordinates of the c axis. A1 atoms are atoms in the surface of the unit cell with $c = 0$. A2 atoms are atoms inside the unit cell with $c = 0.5$. The structure contains three kind rings: four-, six- and eight-membered rings. The planar four-membered rings and nonplanar eight-membered rings are joined together by non-planar six-membered rings. In the structure of $Pbam$ -AlN, the left part is similar to the right part. Both are two unit cells of wz -AlN and connected by the bond parallel to the a -axis. $Pbam$ -AlN can be interpreted as a result of crystal restructuring combined with several unit cells of wz -AlN.

$Pbca$ -AlN (Fig. 1c): In the $Pbca$ -AlN unit cell, four parallel atoms layers are present along the b -axis. We divide the b -axis coordinates of the bottom atom layer as u , whereas the other three b -axis coordinates are $0.5 - u$, $0.5 + u$ and $1 - u$, respectively. In this case, u takes a value of 0.133. Two kinds of rings are present in the unit cell, one is a four-membered ring and another is a six-membered ring. One atom layer ($0.5 - u$) connects to the other atom layer ($0.5 + u$) with two parallel Al-N bonds and four-membered ring forms. The four atoms in one atom layer connect with two atoms in the adjacent atom layer and form a non-planar six-membered ring. In each coordination tetrahedron, four Al-N bonds have four different lengths: 1.874, 1.879, 1.912 and 1.932 Å. All the $[AlN_4]/[AlN_4]$ tetrahedrons are not regular tetrahedrons.

Table 1 Space number (S.N.), cell parameters a , b , c (Å), ρ (g/cm³) for four novel AlN phases.

Structure	S.N.	a	b	c	ρ
<i>Pmn2₁</i>	31	3.109	10.938	5.081	3.158
<i>Pbam</i>	55	10.832	5.085	3.128	3.161
<i>Pbca</i>	61	5.265	6.191	5.416	3.085
<i>Cmcm</i>	63	3.179	10.398	8.190	3.017

Cmcm-AlN (**Fig. 1d**): *Cmcm*-AlN can be viewed to consist of four six-membered rings. The six-membered rings are all perpendicular to the a -axis. The rings in the top left corner and bottom right corner share the same coordinates with $a = 0.5$. The other two rings share the coordinate $a = 0$. *Cmcm*-AlN contains four-membered rings and six-membered rings. In the top (bottom) part of the unit cell, a six-membered ring ($a = 0$) connects with another six-membered ring ($a = 0.5$) via two parallel bonds, whereas the four-membered rings form two parallel bonds and two parallel b -axis bonds. The six-membered rings are not standard circles because the bond lengths inside are not equal.

More information on the four AlN novel structures, such as space number, cell parameters a , b , c , ρ are listed in **Table 1** and atomic Wyckoff Positions listed in **Table 2**. After geometric optimisation at ambient pressure, the densities (ρ , g/cm³) of *wz*-AlN, *zb*-AlN and *rs*-AlN are 3.214, 3.205 and 4.039, respectively. *Cmcm*-AlN has the lowest ρ , which is 6.13% lower than that of *wz*-AlN. *Pbca*-AlN has a higher ρ than *Cmcm*-AlN, but its value is lower than any other phase and 4.0% lower than that of *wz*-AlN. *Pmn2₁*-AlN and *Pbam*-AlN have a similar ρ , which are 1.7% and 1.6% lower, respectively, than that of *wz*-AlN.

Table 2 Atomic Wyckoff Positions for four novel AlN phases.

Structure	Atomic Wyckoff Position
<i>Pmn2₁</i>	Al: 2a (0.5, 0.208, 0.066); (0.5, 0.041, 0.565); (0.0, 0.286, 0.565); (0.0, 0.463, 0.926) N: 2a (0.5, 0.538, 0.048); (0.5, 0.713, 0.445); (0.5, 0.208, 0.442); (0.5, 0.041, 0.943)
<i>Pbam</i>	Al: 4h (0.834, 0.180, 0.5); 4g (0.912, 0.682, 0) N: 4h (0.333, 0.696, 0.5); 4g (0.413, 0.199, 0)
<i>Pbca</i>	Al: 8c (0.177, 0.633, 0.912); N: 8c (0.690, 0.367, 0.408)
<i>Cmcm</i>	Al: 4c (0.5, 0.547, 0.75); 8f (0.0, 0.340, 0.941) N: 4c (0.0, 0.440, 0.75); 8f (0.5, 0.348, 0.436)

Table 3 C_{ij} (GPa) for four novel AlN phases.

	<i>Pmn2₁</i>	<i>Pbam</i>	<i>Pbca</i>	<i>Cmcm</i>
C_{11}	381.9	347.7	252.1	339.1
C_{22}	345.9	290.7	309.8	277.7
C_{33}	287.9	381.5	376.0	291.7
C_{44}	114.5	112.1	104.2	131.6
C_{55}	111.8	113.0	110.2	87.4
C_{66}	113.2	111.7	116.1	107.9
C_{12}	126.0	98.7	117.9	81.4
C_{13}	98.3	128.1	102.1	123.1
C_{23}	100.6	96.8	124.1	123.1

Stability Analysis

To analyse the mechanical stability and dynamical stability of the novel high-pressure phases of AlN, the elastic constants and phonon dispersion spectra are studied.

For an orthorhombic crystal system, the mechanical stability can be evaluated by [35].

$$C_{ii} > 0; (i = 1, 2, 3, 4, 5, 6); (C_{11} + C_{22} - 2C_{12}) > 0;$$

$$(C_{11} + C_{33} - 2C_{13}) > 0; (C_{22} + C_{33} - 2C_{23}) > 0;$$

$$[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0 \quad (1)$$

Fig. 2. Phonon dispersion spectra for the four novel AlN phases.

According to the abovementioned criteria, the independent elastic constants (C_{ij}) listed in **Table 3** show that $Pmn2_1$ -AlN, $Pbam$ -AlN, $Pbca$ -AlN and $Cmcm$ -AlN are all mechanically stable under ambient pressure.

The calculated phonon dispersion spectra for $Pmn2_1$ -AlN, $Pbam$ -AlN, $Pbca$ -AlN and $Cmcm$ -AlN are shown in **Fig. 2**. No imaginary frequency is observed during the whole Brillouin zone. All four structures are dynamically stable.

Phase Transformation under Pressure

As a fundamental thermodynamic variable, pressure has a significant impact on the chemical and physical properties of a material. High-pressure technology is an interesting field in materials research.

The relative enthalpies for the chosen structures are presented in **Fig. 3** and compared with those of wz -AlN as a function of pressure up to 20 GPa. wz -AlN is more favourable than any other AlN phase at ambient pressure. Zb -AlN has a constant relative enthalpy (only approximately 0.05 eV per formula unit (f.u.) higher than that of wz -AlN) within the pressure range studied. At ambient pressure, the enthalpies of $Pmn2_1$ -AlN, $Pbam$ -AlN, $Pbca$ -AlN and $Cmcm$ -AlN are more favoured than that of rs -AlN, ranging from the smallest value of 0.150 eV/f.u. ($Cmcm$ -AlN) to the largest value of 0.305 eV/f.u. ($Pmn2_1$ -AlN). When the pressure exceeds 4.34 GPa, the rs -AlN favours enthalpy more than $Cmcm$ -AlN. As the pressure increases to 9.07 GPa, rs -AlN favours enthalpy more than $Pbca$ -AlN. Finally, when the pressure reaches 11.14 GPa, all four novel phases lose their enthalpy advantage over rs -AlN.

Fig. 3. Calculated enthalpy curves (relative to wz -AlN) as a function of pressure for various AlN phases.

wz -AlN clearly transforms to rs -AlN under a hydrostatic pressure of 14 GPa, which is in good agreement with the previous experiment [13-16], and other theoretical studies [36-38]. Thus, all AlN phases undergo transformation to rs -AlN as the hydrostatic pressure reaches 14 GPa in terms of enthalpy.

The enthalpies-pressure relationship indicates that the four AlN phases are not pressure driven. Therefore, these phases might not be achieved via a high-pressure approach during loading pressure. The formation of the metastable phases is affected by the decompression rate. For example, the Si-XII (R8), Si-III (BC8) and Ge-III (ST12) phases can be acquired by releasing pressure from the β -Sn phases of Si and Ge (Si-II or Ge-II) slowly [39, 40]. However, rapid depressurisation causes the formation of the Ge-IV (BC8) phase and the tetragonal Si-VIII/IX phases [41, 42]. Similarly, the four novel AlN phases may be achieved by adjusting the pressure release rate.

Mechanical Properties

The pressure–volume relationships for four crystal structures of AlN are deduced by fitting the third-order Birch–Murnaghan equation of state (EOS) as shown in **Fig. 4** [43].

$$P(V) = \frac{3}{2} B_0 \left[\left(\frac{V}{V_0} \right)^{\frac{7}{3}} - \left(\frac{V}{V_0} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[\left(\frac{V}{V_0} \right)^{\frac{2}{3}} - 1 \right] \right\} \quad (2)$$

Fig. 4. Volume of the four AlN phases as a function of pressure. The solid geometric pattern and solid lines represent the calculated data and fitting results, respectively.

Where V_0 is the volume per f.u. at ambient pressure; V is the volume per f.u. at pressure P ; B_0 is the isothermal bulk modulus; B'_0 is the first order pressure derivative of the isothermal bulk modulus. The values of B_0 , B'_0 , and V_0 are obtained from Equation (2) and listed in **Table 4**; these values agree well with previous reports [22, 37, 44].

The volume decreases with increasing pressure for all the proposed phases. Those four phases have similar volume compressibility (~9%), thereby suggesting their good anti-compressibility. The volume compressibility is different depending on the various phases. *Pbca*-AlN has the largest volume compressibility (9.39%), whereas *Pbam*-AlN has the smallest (8.92%) among all four novel phases at the pressure range of 0–20 GPa.

For the orthorhombic crystal system, the Voigt form and the Reuss form of bulk modulus (B) and shear modulus (G) can be obtained from the independent elastic constants (C_{ij}) [45].

Based on the Voigt–Reuss–Hill relationship [46], the Hill form B (G) are arithmetic mean values of the Voigt form B (G) and Reuss form B (G). Young's modulus (E) and Poisson's ratio (σ) are calculated from B and G as follows:

$$E = 9BG/(3B + G); \sigma = (3B - 2G)/(6B + 2G) \quad (3)$$

The values of B , G , E , σ and B/G are presented in **Table 4**. In generally, B represents the resistance to volume change by load pressure, G represents the resistance to reversible deformations upon shear stress [47]. The higher value of E , the stiffer the material. All the novel phases of AlN have large B , G and E , which indicate their potential applications as hard materials for cutting and machining.

Table 4 B_0 (GPa), V_0 ($\text{\AA}^3/\text{f.u.}$), B'_0 , B (GPa), G (GPa), E (GPa), σ , G/B ratio and H_v (GPa) for the four novel AlN phases at ambient pressure.

	<i>Pmn2₁</i>	<i>Pbam</i>	<i>Pbca</i>	<i>Cmcm</i>
B_0	182.7	183.2	178.8	172.7
V_0	21.5	21.5	22.1	22.6
B'_0	3.40	3.38	2.74	3.81
B	183.2	183.4	178.2	173.1
G	113.6	113.5	104.5	102.2
E	282.4	282.3	262.2	256.2
σ	0.24	0.24	0.25	0.25
G/B	0.62	0.62	0.59	0.59
H_v	15.2	15.2	13.3	13.2

The fitted B values from the third-order Birch–Murnaghan EOS are almost equal to the values calculated from the independent elastic constants, thereby confirming the reliability of our calculations.

Hardness is used as one of the fundamental mechanical properties of materials. We further analysed the Vickers hardness (H_v) of different phases by adopting Chen's formula based on empirical scheme [48]:

$$H_v = 2(\kappa^2 G)^{0.585} - 3; \kappa = G/B \quad (4)$$

The obtained values of H_v according to Equation (4) are also presented in **Table 4**. The hardness of all the proposed phases range from 13.2 GPa to 15.2 GPa, which enrich the hardness of AlN compounds and may extend the industrial application of AlN.

Electronic Properties

The calculated band structures of the four novel phases of AlN along the selected high symmetry directions of the first Brillouin zone at ambient pressure are shown in **Fig. 5**. All the AlN phases possess semiconductive properties that can be attributed to the direct band gaps at the G points. For the four novel structures of AlN, the band gaps are 3.889 (*Pmn2₁*-AlN), 3.927 (*Pbam*-AlN), 3.855 (*Pbca*-AlN) and 3.627 eV (*Cmcm*-AlN). Given the wide direct band gaps, these four novel phases AlN may be used as semiconductor devices and optoelectronic devices.

Fig. 5. Calculated band structures for the four novel AlN phases at ambient pressure. The Fermi level is represented by a horizontal red line.

4. Conclusion

In this work, four novel orthorhombic AlN phases are proposed after using an evolutionary methodology. Based on first-principles calculations, the enthalpy of all four phases (*Pmn*2₁-AlN, *Pbam*-AlN, *Pbca*-AlN and *Cmcm*-AlN) will be lower than that of *rs*-AlN at ambient pressure. The calculated elastic constants and phonon dispersion spectra certify the mechanically and dynamically stabilities of the four novel phases. The calculated *H_v* is based on an empirical relation; the resulting values suggest all the four novel AlN phases possess a high hardness range from 13.2 GPa to 15.2 GPa. The electronic band structure calculations suggest that all the AlN phases possess semiconductive properties with wide direct band gaps. The superior mechanical properties and adjustable band gaps of these phases indicate that these metastable phases of AlN may have potential industrial applications in the future.

Acknowledgements

This work was supported by the National Science Foundation of China (Grant Nos. 51421091 and 51332005) and the Postgraduate Innovation Project of Hebei Province of China (Grant No. 00302-6370007).

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