

Ab initio investigations of structural, electronic and mechanical properties of aluminum nitride at standard and elevated pressures



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ABSTRACT

Ab initio calculations using hybrid B3LYP functional were performed in order to investigate structural, electronic and mechanical properties of aluminum nitride as function of pressure. Electronic properties of the experimentally observed aluminum nitride modifications at standard and high pressures have been investigated. Furthermore, mechanical properties for each of the predicted and experimentally observed AlN modifications have been investigated in order to get insight into the phase stability. In addition, ductility/brittleness relationship, character of the bonding, and the relationship between calculated hardness H_v , Young's modulus E , bulk modulus B , and shear modulus K have been investigated. In this way, we address new possibilities for improving the mechanical and elastic properties of AlN based ceramic materials, as well as possible band gap tuning, which might have applications in optoelectronic devices.

1. Introduction

In the past years, aluminum nitride (AlN) is attracting great interest of the industry and scientific community due to its dielectric properties, high melting point, thermal conductivity, electrical resistivity, mechanical strength, and corrosion resistance [1,2]. In addition, AlN is a wide band gap semiconductor, piezoelectric and ceramic material with a wide range of technological applications, e.g. optoelectronic devices, mobile phones, laser diodes, and optical detectors, as well as for HT-, HP-, HF- devices, steel, metal, and semiconductor manufacturing industry, military applications, etc. [3–7]. Most of these industrial and technological applications are closely related to the structure-property relationships.

At normal conditions aluminum nitride crystallize in the wurtzite structure ($P6_3mc$, no. 186 (Fig. 1a)) and is a covalent bonded material [8]. AlN also appears in the cubic form with zinc blende (sphalerite) structure type, showing $F-43m$ (no. 216) space group (Fig. 1b) in a very thin films. The zinc blende modification converts to the wurtzite structure as the thickness of the film increases [9,10]. With the increase of pressure up to 22 GPa, a rock-salt (NaCl) type of structure ($Fm-3m$, no. 225) has been observed (Fig. 1c), both in theory and in the experiment [11–15]. Christensen et al. [16] has suggested that with further increase of pressure to above 30 GPa, the rock-salt phase would become unstable and transform to the NiAs structure type. In addition, there are several other studies dealing with various AlN modifications

at high pressures which include orthorhombic, tetragonal and hexagonal phases [12,17,18]. In principle, the existence of additional stable and metastable modifications of aluminum nitride and their related properties is still an open question.

Several experimental and theoretical methods have been applied to investigate the phase transition, high pressure structural, electronic and elastic properties of the aluminum nitride [1,19–26]. However, most of these studies investigate most common wurtzite modification, and in some instances cubic zinc blende and rock-salt phase. In our previous study, we have identified several new modifications of aluminum nitride at different pressures and temperatures which were never observed in the experiment or calculations [26]. In this work, we show, for the first time, the complete study of the electronic, elastic and mechanical properties of experimentally observed AlN modifications, as well as unknown predicted AlN phases, which show great possibilities for future industrial and technological applications.

2. Computational details

The *ab initio* calculations were performed using well established CRYSTAL14 program package [27] based on a linear combination of atomic orbitals (LCAO) as the basis set. Structure candidates have been generated using data mining combined with quantum mechanical methods [28,29]. The result of such previous searches in binary or ternary systems combining data mining and *ab initio* optimization can be

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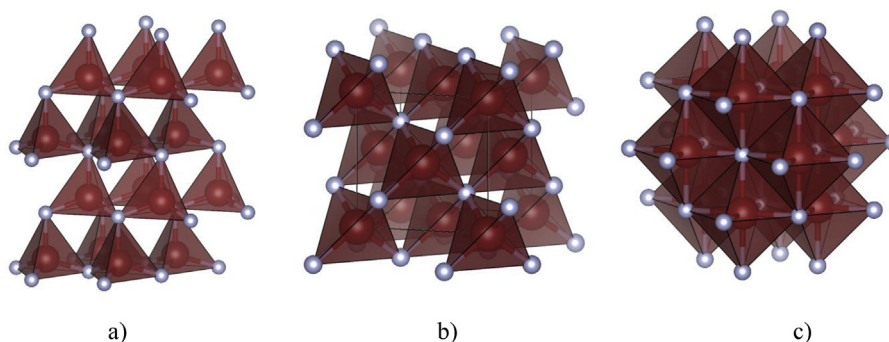


Fig. 1. Experimentally observed structures of aluminum nitride: a) the wurtzite type; b) the zinc blende type; c) the rock-salt type.

found in Refs. [30–32], while previous study of the corresponding AlN system is presented in Ref. [26]. The tolerances for the convergence on energy are set to 1.0×10^{-7} eV per atom in all electronic, elastic and mechanical properties calculations. Fock/Kohn-Sham matrix mixing of 50% has been used in order to stabilize the total energy value of the several high pressure AlN modifications [27]. A k -point meshes of $8 \times 8 \times 8$ Monkhorst-Pack scheme have been used.

A hybrid B3LYP functional (Becke's three parameter functional in combination with the correlation functional of Lee, Yang, and Parr) has been used to describe electronic exchange and correlations [33]. The calculations performed with hybrid (B3LYP) functionals showed the best agreement with previous experimental and theoretical results [1,19–22,26]. Furthermore, it is commonly observed that the semi-conducting materials investigated using Density Functional Theory (DFT) underestimates the band gap, while Hartree-Fock (HF) approach is known to overestimate the gap [34–37]. Similar effect has been observed in the AlN compound, where in the experimental conditions the band gap has been measured to ~ 6.2 eV, but various DFT functionals have underestimated the band gap to below 5 eV [21,26,38–42], while HF method has overestimated it to over 14 eV [43]. The best agreement with experiment has been found using hybrid functionals [21,22], which has been also shown in our previous theoretical study of aluminum nitride [26].

In the case of aluminum, a $[4s3p1d]$ all-electron basis set based on Gaussian-type orbitals was used. For nitrogen a $[3s2p1d]$ all-electron basis set was used [26]. (further details are presented in the supporting information). Visualization of the crystal structures was performed using the VESTA code [44] and for visualization of Young's modulus an open-source application ELATE [45] has been used. A fully automated procedure to calculate second-order elastic constants (SOEC) has been used as implemented in the CRYSTAL14 code [46]. The program replaces the existing strategy in order to calculate elastic constants using numerical first and second derivatives [47] and additional fitting and graphical programs for the manipulation of the data. The appropriate elastic constants are calculated and stored as a matrix, the eigenvalues and eigenvectors are found, and the inverse is taken, forming the compliance matrix. The bulk modulus B , is obtained from the compliance matrix elements. From computed data, other elastic properties such as shear modulus K , Young's modulus E , Poisson's ratio ν and quantities derived from the Voigt–Reuss–Hill approximation [48] can be easily obtained. The full elastic tensor has been generated for any Laue class by using keyword ELASTCON.

3. Results and discussion

3.1. Electronic properties of AlN at equilibrium and non-equilibrium conditions

In the first part of this study we have investigated the electronic properties of the aluminum nitride, in particular the influence of the pressure on the electronic properties. First, we have investigated the

electronic properties of AlN at standard conditions and at effective negative pressures. In the figures and tables presented in this part of the study, we show the results for the most relevant modifications for this pressure range (wurtzite (2H) type, zinc blende (3C) type, SiC (4H) polytype, ZnS (15 R) polytype, and β -BeO type). Note that the labels of the special points of the Brillouin zones of the wurtzite (2H) type, SiC (4H) polytype, and ZnS (15 R) polytype correspond to those of a hexagonal lattice. In the case of the zinc blende, the special points correspond to the face-centered cubic lattice, while in the case of the β -BeO structure the settings for a base-centered tetragonal lattice were applied.

In Fig. 2a and (b), results of band structure calculations and DOS of the AlN wurtzite type modification are displayed. We observe the band gap size of 6.42 eV ($0.2359 E_h$), Fermi energy is located about 4.44 eV above the valence band (Table 1), which is in very good agreement with previous experimental and theoretical findings [1,19–22]. Furthermore, we can confirm the previous experimental and theoretical investigations, where the direct band gap is observed at the Γ -point and the main contribution to the top of the valence band (TVB) comes from the $2p$ levels of N atoms, while the bottom of the conduction band (BCB) arises from the hybridization of the aluminum s and p orbitals [19–22,38–41].

Fig. 3 shows the band structure and DOS of the zinc blende modification of the aluminum nitride compound. An indirect band gap has been observed along the Γ -X direction of the Brillouin zone (Fig. 3a). Fermi level is located about 4.68 eV above the valence band (see Table 1), while computed size of the indirect band gap is 5.42 eV ($0.1992 E_h$) which is in very good agreement with previous experimental and theoretical findings [19–22,49,50]. In addition, we have calculated that the size of the direct band gap is 6.20 eV ($0.2279 E_h$) at the Γ -point using hybrid B3LYP approach, which was again in very good agreement with previous experimental and theoretical findings [38–41,49,50]. Although, we have observed that zinc blende modification of AlN causes the narrowing and displacements (change from the direct to indirect) of the band gap compared to the wurtzite structure, the main contribution to the TVB still comes from the nitrogen atoms, while the BCB continues to be dominated by aluminum (Fig. 3b).

Next, we show the band structures of the SiC-4H and ZnS-15 R polytypes in the AlN system calculated using the B3LYP functional. The SiC-4H polytype shows a direct band gap of 6.04 eV ($0.2220 E_h$) at the Γ -point (Fig. 4a) and the Fermi level is located about 4.60 eV above the valence band. On the other hand, the ZnS-15 R polytype shows an indirect band gap of 6.24 eV ($0.2293 E_h$), the TVB located at the Γ -point, while the BCB appears at the L-point of the Brillouin zone (Fig. 4b). Fermi energy is located about 4.63 eV above the valence band. We note that the rhombohedral unit cell of 15 R polytype has been converted to a hexagonal unit cell for comparison. Furthermore, slight changes in calculated DOS compared to the one of the wurtzite and zinc blende modifications have been observed (see Fig. S1 and Fig. S2 of the supporting information). Polytypic behavior is known in the literature as

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