

Investigations on structural, elastic, thermodynamic and electronic properties of TiN, Ti₂N and Ti₃N₂ under high pressure by first-principles

Ruike Yang^{a,*}, Chuanshuai Zhu^a, Qun Wei^a, Zheng Du^b

^a School of Physics and Optoelectronic Engineering, Xidian University, Xi'an, Shaanxi 710071, PR China

^b National Supercomputing Center in Shenzhen, Shenzhen 518055, PR China

ARTICLE INFO

Article history:

Received 11 January 2016

Received in revised form

21 April 2016

Accepted 25 May 2016

Available online 27 May 2016

Keywords:

Titanium nitrides

First-principles calculations

High pressure

Physical properties

ABSTRACT

The lattice parameters, cell volume, elastic constants, bulk modulus, shear modulus, Young's modulus and Poisson's ratio are calculated at zero pressure, and their values are in excellent agreement with the available data, for TiN, Ti₂N and Ti₃N₂. By using the elastic stability criteria, it is shown that the three structures are all stable. The brittle/ductile behaviors are assessed in the pressures from 0 GPa to 50 GPa. Our calculations present that the performances for TiN, Ti₂N and Ti₃N₂ become from brittle to ductile with pressure rise. The Debye temperature rises as pressure increase. With increasing N content, the enhancement of covalent interactions and decline of metallicity lead to the increase of the micro-hardness. Their constant volume heat capacities increase rapidly in the lower temperature, at a given pressure. At higher temperature, the heat capacities are close to the Dulong–Petit limit, and the heat capacities of TiN and Ti₂N are larger than that of c-BN. The thermal expansion coefficients of titanium nitrides are slightly larger than that of c-BN. The band structure and the total Density of States (DOS) are calculated at 0 GPa and 50 GPa. The results show that TiN and Ti₂N present metallic character. Ti₃N₂ present semiconducting character. The band structures have some discrepancies between 0 GPa and 50 GPa. The extent of energy dispersion increases slightly at 50 GPa, which means that the itinerant character of electrons becomes stronger at 50 GPa. The main bonding peaks of TiN, Ti₂N and Ti₃N₂ locate in the range from –10 to 10 eV, which originate from the contribution of valence electron numbers of Ti s, Ti p, Ti d, N s and N p orbitals. We can also find that the pressure makes that the total DOS decrease at the Fermi level for Ti₂N. The bonding behavior of N–Ti compounds is a combination of covalent and ionic nature. As N content increases, valence band broadens, valence electron concentration increases, and covalent interactions become stronger. This is reflected in shortening of Ti–N bonds.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

As one of transition-metal nitrides, Titanium nitride (TiN) was first separated by Story-Maskelyne from a meteorite. It crystallizes into well-known rock-salt structure. Titanium nitride and its derivatives have many remarkable properties and good potential applications, such as chemical stability, thermal stability, oxidative resistance, good adhesion to the substrate, high fracture toughness and high hardness [1–5]. TiN is one of the most important metal cutting tools and coating materials for surface protection due to its extreme hardness, high melting temperature, and excellent corrosion resistance [6]. TiN ceramics have a good resistance to corrosion by liquid steel for some steel making processes [7]. It is also

have been used for diffusion barriers, superconducting devices, and energy-saving coatings for windows due to their strong infrared reflection [8,9].

The interesting properties of the transition metal compound, TiN, have been studied with many methods in recent years [10–15]. Up to now, TiN is still controversial in high-pressure structural phase transitions [7]. Under high-pressure condition, the studies of new ultra-incompressible materials with novel mechanical and electronic properties, such as TiN and its derivatives, are significantly interesting and practical important. There are a number of experiments devoted to various aspects of TiN film growth and many theoretical calculations about material behaviors for TiN [16–20]. Under ambient conditions, TiN crystallizes in the NaCl (B1) structure. TiN might undergo an isostructural phase transition from B1 structure to CsCl (B2) structure or other phase [7]. Theoretically, as early as in 1996, Ahuja et al. [21] investigated the electronic structure, elastic constants and pressure-induced

* Corresponding author.

E-mail address: york1868@163.com (R. Yang).

structural phase transformation of TiN based on the Full Potential Linear Muffin-tin Orbital (FPLMTO) method. They predicted the structural phase transformation pressure for TiN from B1 structure to B2 structure to be 370 GPa. Li et al. [8] studied the interfacial structures of TiN/MgO interfaces with different orientation relationships and bonding configurations using first-principles with the density function theory (DFT). Yadav et al. [22] studied the generalized stacking faults energies in different slip planes of both TiN and MgO. Zhu et al. [7] investigated the phase sequence with pressures and elastic properties at high pressures of TiN using DFT method based on pseudopotential plane-wave method. Liu et al. [6] made first-principles calculations on the thermodynamic properties and the phase transition of TiN from B1 to B2 structure. Yin et al. [23] conducted a systematic first-principles investigation of ideal tensile stress and fracture behaviors of the TiN/VN interface. Xuan et al. [24] studied the making of TiN substrate with a high relative density and a low surface roughness. However, most of their studies focus on the stoichiometric rock-salt TiN, and there are a few studies of non-stoichiometric titanium nitrides. Yu et al. [25] made first-principles evolutionary searches for stable Ti–N compound and found, in addition to the well-known rock-salt TiN, new ground states Ti_3N_2 , Ti_4N_3 , Ti_6N_5 at atmospheric pressure, and Ti_2N and TiN_2 at higher pressure. They also gave the mechanical properties of the Ti–N compounds at 0 GPa. Hence, in our work, under pressure condition, the material behaviors for the stable Ti–N compounds are analysed based on the calculations by first-principles.

In this paper, the structural, elastic, thermodynamic, and electronic properties of TiN, Ti_2N and Ti_3N_2 are calculated in the pressures range from 0 GPa to 50 GPa. The properties of c-BN are also calculated for the sake of comparison. The study may do something which can help people know more about those novel crystal structures. We hope this study will provide guidance for experimental groups aiming to synthesize those novel crystal structures.

2. Methods

In the calculations, the structural optimization and properties predictions of TiN and its derivatives are performed by using the DFT with the local density approximation (LDA) and the generalized gradient approximation (GGA) parameterized by Perdew, Burke and Ernzerhof (PBE) as implemented in the Cambridge Serial Total Energy Package (CASTEP) code [26]. The ultrasoft pseudo-potentials introduced by Vanderbilt [27] have been employed for all the ion-electron interactions in the calculations of electronic structure. Two parameters that affect the accuracy of calculation

are cut-off energy which determines the numbers of plane waves and the number of special k-points which used for the Brillouin zone (BZ) division [28]. The k-points automatically generated with Monkhorst–Pack scheme are used for structure optimization and static self-consistent calculations, respectively. The energy cut-off values are 550 eV for c-BN, 580 eV for TiN, Ti_2N , and Ti_3N_2 . The convergence tests for k-points mesh samplings and energy cut-off are performed before choosing their respective values. Convergence tests prove that the Brillouin zone sampling and the kinetic energy cut-off are reliable to guarantee excellent convergence [29].

The tolerances for the geometry optimization are as follows: the self-consistent field tolerance threshold is 5×10^{-7} eV/atom. The convergent value of the total energy difference is less than 5×10^{-6} eV/atom. The maximum Hellmann–Feynman force is 0.01 eV/Å. The maximum stress is less than 0.02 GPa. The maximum atom displacement is smaller than 5×10^{-3} Å. The k-points in the first irreducible Brillouin zone are $14 \times 14 \times 14$, $20 \times 20 \times 20$, $10 \times 10 \times 16$ and $12 \times 17 \times 5$ for c-BN, TiN, Ti_2N and Ti_3N_2 respectively. The elastic, thermodynamic and electronic properties are calculated based on the optimized crystal structures.

The elastic constants of solids can provide adequate information concerning the stability, stiffness and structural phase change of materials, the knowledge of elastic properties plays an important role in the solid materials fields [30]. They are calculated by using the stress-strain methods. In the strain calculation, the number of steps is 6. Maximum strain amplitude is 0.003. Thermodynamic properties of Ti–N compound are calculated by using the quasi-harmonic Debye model. In the model, phonon effect is considered and the results are achieved by GIBBS program [31]. The electronic properties of the titanium nitrides are also analyzed by means of the GGA-PBE at 0 GPa and 50 GPa.

3. Results and discussion

3.1. Structural properties

Structure of unit cell plays a very important role in understanding the nature of solid materials. Fig. 1 shows the structures of c-BN, TiN, Ti_2N and Ti_3N_2 at 0 GPa. Both of c-BN and TiN have a higher symmetrical structure. c-BN is the cubic structure with $F-43M$ space group, and TiN is the cubic structure with $Fm-3m$ space group. Ti_2N is tetragonal structure with space group of $P4_2/mnm$. Ti_3N_2 is orthorhombic structure which belongs to space group of $Immm$. By geometry optimization, the calculated lattice parameters for c-BN, TiN, Ti_2N and Ti_3N_2 at 0 GPa and 50 GPa are presented in Table 1. They are consistent with reference values

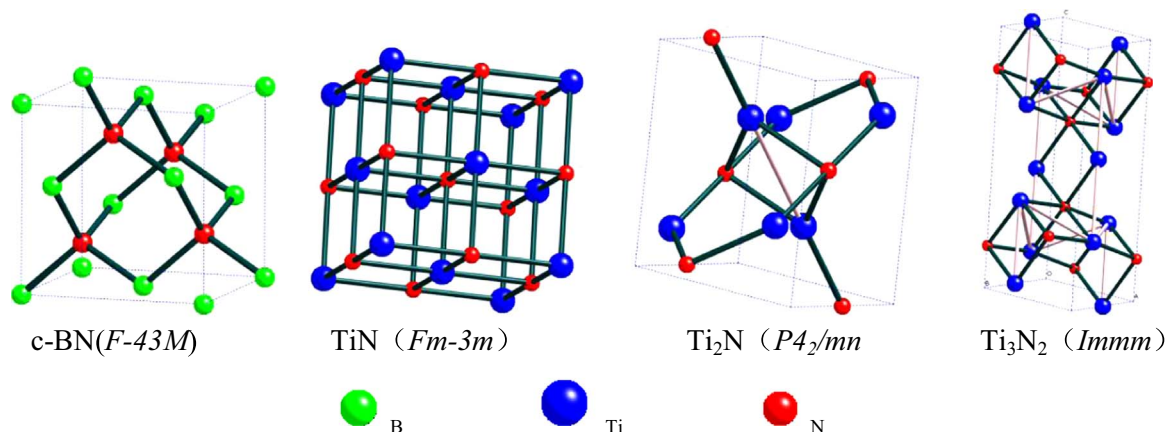


Fig. 1. Models of c-BN, TiN, Ti_2N and Ti_3N_2 at 0 GPa.

Table 1.
Lattice constants a , b , c (in Å), and cell volume per formula unit V (in Å³) at 0 and 50 GPa.

	a	b	c	V
c-BN (<i>F</i>-43M)	GGA 3.622/ 3.492			11.883/10.641
	LDA 3.576/ 3.455			11.435/10.306
TiN (<i>Fm</i>-3m)	GGA 4.246/ 4.059			19.142/16.719
	LDA 4.173/4.040			18.161/16.491
Ti₂N (<i>P</i>4₂/<i>mm</i>)	GGA 4.953/ 4.671		3.033/ 2.872	37.203/31.335
	LDA 4.864/ 4.605		2.980/ 2.855	35.245/ 30.273
Ti₃N₂ (<i>I</i>mm)	GGA 4.153/3.968	3.029/ 2.850	9.124/ 8.525	57.379/48.197
	LDA 4.086/ 3.923	2.973/2.815	8.945/ 8.406	54.334/46.418

[25,32–35], which show that the present optimization and calculations are reliable.

To compare the compressibility of TiN, Ti₂N and Ti₃N₂ under pressure, the normalized volume V/V_0 ratios (where V_0 is the equilibrium volume at zero pressure and zero temperatures) as the function of pressure are plotted in Fig. 2. The V/V_0 ratio for the well-known super-hard c-BN is also calculated for comparison, and it is a good agreement in reference [32]. We notice that TiN is more incompressible than Ti₂N and Ti₃N₂, but more compressible than c-BN. Ti₃N₂ is the most easily compressed among these four crystals. The lattice constants ratios a/a_0 , b/b_0 and c/c_0 of Ti₃N₂ (where a_0 , b_0 and c_0 are the equilibrium lattice constants at zero pressure and temperatures) as the function of applied pressure are also plotted in Fig. 2. It can be clear seen that the compression along the c -axis is the largest, and the smallest compression is exhibited along the a -axis. It indicates clearly the elastic anisotropy of Ti₃N₂.

By using first-principles and according to the Birch–Murnaghan equation of states, the unit cell volumes of c-BN, TiN, Ti₂N and Ti₃N₂ as the function of pressure are shown at Fig. 3, at zero temperature. At Fig. 3, the sign represents the results obtained by

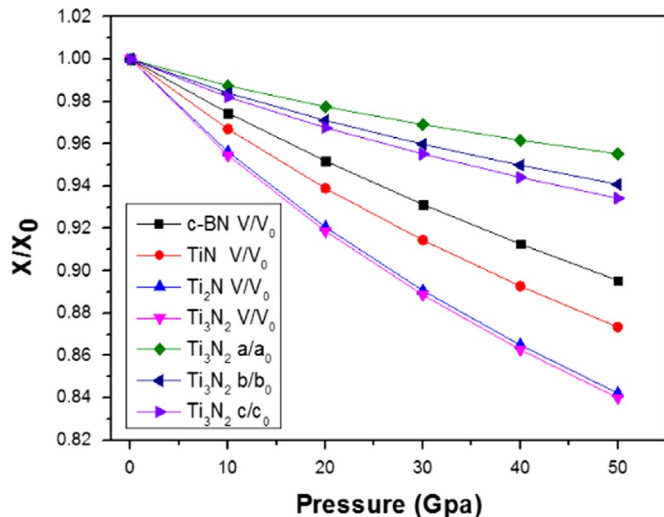


Fig. 2. The lattice constants a/a_0 , b/b_0 , c/c_0 for Ti₃N₂, and the primitive cell volume V/V_0 for c-BN, TiN, Ti₂N and Ti₃N₂ with pressure.

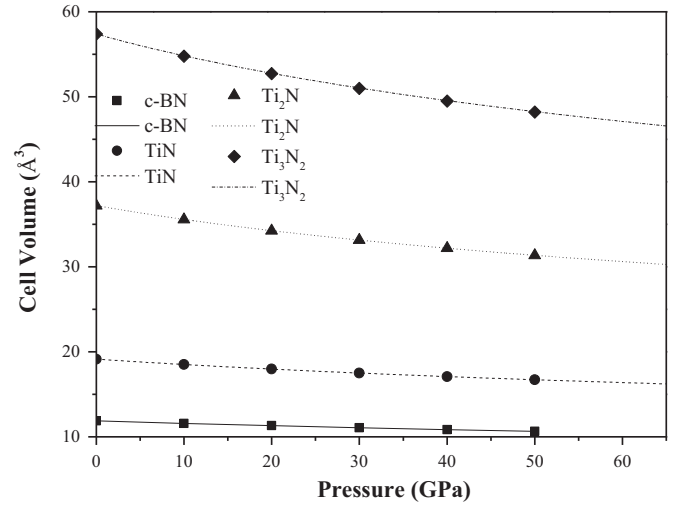


Fig. 3. Pressure dependence of the unit cell volume for c-BN, TiN, Ti₂N and Ti₃N₂ at 0 K.

first-principles and the lines are the results by Birch–Murnaghan EOS. At zero pressure, the derivatives of the bulk modulus are 3.5, 4.2, 4.2 and 4.3 for c-BN, TiN, Ti₂N and Ti₃N₂, respectively. It is shown that the results by first-principles are in accordance with the results by Birch–Murnaghan equation of states.

3.2. Elastic properties

The knowledge of elastic properties plays an important role in the solid materials fields. The elastic constants of solids can provide adequate information concerning the stability, stiffness and structural phase change of materials. For c-BN, TiN, Ti₂N and Ti₃N₂, these elastic constants are calculated with GGA and LDA. The results are shown in Table 2. The mechanical stability is examined according to the calculated elastic constants. The elastic constants for different phase structures are satisfied the correlative mechanical stability criteria. For cubic, tetragonal and orthorhombic phase structures criteria are described as follows.

(i) The mechanical stability criterions for cubic phase structures are [36]:

$$C_{11} > 0, C_{44} > 0; C_{11} > |C_{12}|, (C_{11} + 2C_{12}) > 0 \quad (1)$$

(ii) The mechanical stability criterions for tetragonal phase structures are [36]

$$C_{11} > 0, C_{33} > 0, C_{44} > 0, C_{66} > 0 \quad (2)$$

$$(C_{11} - C_{12}) > 0 \quad (3)$$

$$(C_{11} + C_{33} - 2C_{13}) > 0 \quad (4)$$

$$[2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0 \quad (5)$$

(iii) The mechanical stability criterions for orthorhombic phase are given by [32]:

$$C_{ij} > 0, i, j = 1-6 \quad (6)$$

$$[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0 \quad (7)$$

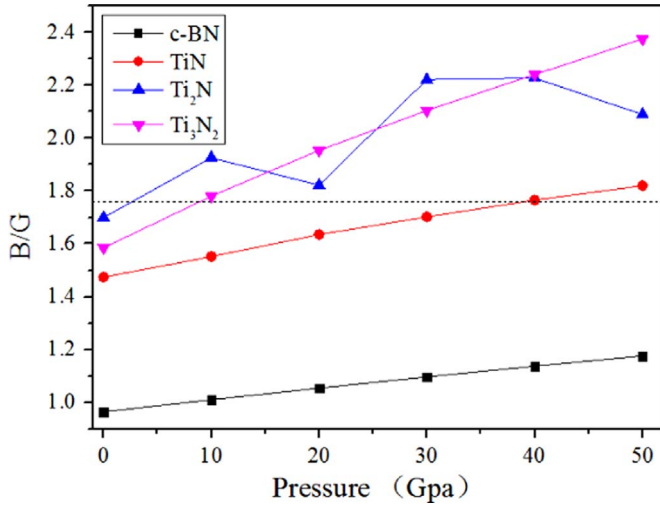
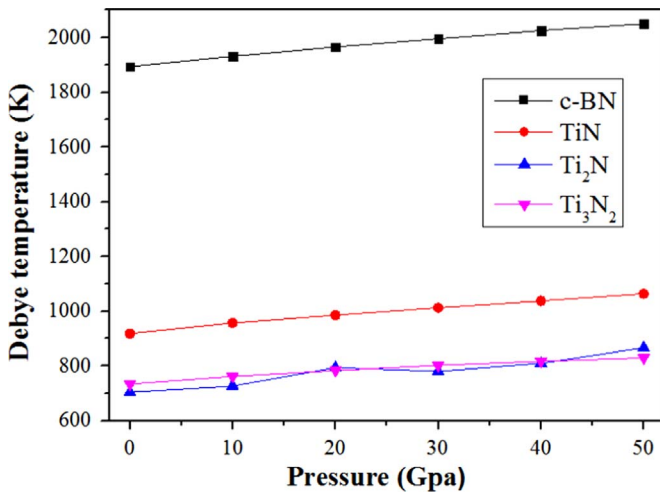
$$(C_{11} + C_{22} - 2C_{12}) > 0 \quad (8)$$

$$(C_{11} + C_{33} - 2C_{13}) > 0 \quad (9)$$

Table 2.

Calculation elastic constants C_{ij} , bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa) and Poisson's ratio ν of c-BN, TiN, Ti_2N and Ti_3N_2 at 0 GPa and 50 GPa.

		C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}	B	G	E	ν
c-BN (<i>F-43M</i>)	GGA(0)	779	165					446			370	384	856	0.114
	LDA(0)	824	186					479			399	407	911	0.119
	GGA(50)	995	317					568			543	462	1080	0.169
	LDA(50)	1038	337					596			570	483	1130	0.170
TiN (<i>Fm-3m</i>)	GGA(0)	581	126					166			277	188	460	0.223
	LDA(0)	691	135					178			320	204	505	0.237
	GGA(50)	1031	196					188			474	261	662	0.267
	LDA(50)	1144	204					198			518	282	716	0.270
Ti_2N (<i>P4₂/mmn</i>)	GGA(0)	300	190	104			428	142		149	203	119	299	0.255
	LDA(0)	352	211	123			482	154		176	233	137	344	0.254
	GGA(50)	585	342	253			687	188		266	395	189	489	0.293
	LDA(50)	611	368	273			714	202		289	418	199	515	0.295
Ti_3N_2 (<i>Immm</i>)	GGA(0)	449	87	117	391	104	337	133	93	124	198	126	312	0.238
	LDA(0)	536	104	130	449	122	380	162	99	133	229	142	353	0.243
	GGA(50)	806	214	289	641	280	556	221	110	134	394	166	437	0.315
	LDA(50)	886	223	303	678	308	588	244	113	138	422	176	464	0.317

**Fig. 4.** B/G of c-BN, TiN, Ti_2N and Ti_3N_2 at 0 K as a function of pressure.**Fig. 5.** Debye temperature of c-BN, TiN, Ti_2N and Ti_3N_2 at 0 K as a function of pressure.

$$(C_{22} + C_{33} - 2C_{23}) > 0 \quad (10)$$

The calculated elastic constants of TiN, Ti_2N and Ti_3N_2 indicate that they are mechanically stable due to the satisfaction of the mechanical stability criteria. For TiN and its derivatives, the bulk modulus B , shear modulus G , and Young's modulus E are calculated in the Voigt-Reuss-Hill approximation [37].

For a cubic crystal, there are three independent elastic stiffness constants: C_{11} , C_{12} and C_{44} . For tetragonal crystals, there are six independent elastic constants: C_{11} , C_{33} , C_{44} , C_{66} , C_{12} and C_{13} . For orthorhombic crystal, taken into account the symmetry of the crystal, there are nine independent elastic coefficients: C_{11} , C_{22} , C_{33} , C_{44} , C_{55} , C_{66} , C_{12} , C_{13} , C_{23} . Reuss and Voigt bulk modulus and shear modulus can be obtained directly by these elastic coefficients [37,38].

Hill pointed out that the Voigt and Reuss equations represent upper and lower limits of the true polycrystalline constants. The polycrystalline modulus is the arithmetic mean values of the Voigt and Reuss modulus and thus they are given by [32]:

$$B = \frac{1}{2}(B_V + B_R) \quad (11)$$

$$G = \frac{1}{2}(G_V + G_R) \quad (12)$$

By using the equations, the B and G of c-BN, TiN, Ti_2N and Ti_3N_2 are calculated.

Young's modulus E and Poisson's ratio ν are the two important physical quantities, which describe the elastic behavior of materials [16]. The Young's modulus E is calculated based on the B and G listed in Table 2, which is important for technological and engineering applications. It is defined as the ratio of the tensile stress to the corresponding tensile strain, and is used to describe the stiffness property in solid. The Young's modulus is expressed as following equations:

$$E = \frac{9BG}{3B + G} \quad (13)$$

From Table 2, the Young's modulus E of TiN, Ti_2N and Ti_3N_2 are less than that of c-BN. The E of Ti_2N is slightly smaller than that of TiN, and greater than that of Ti_3N_2 . When the value of E is large, the material is stiff. We can see that TiN possesses the largest

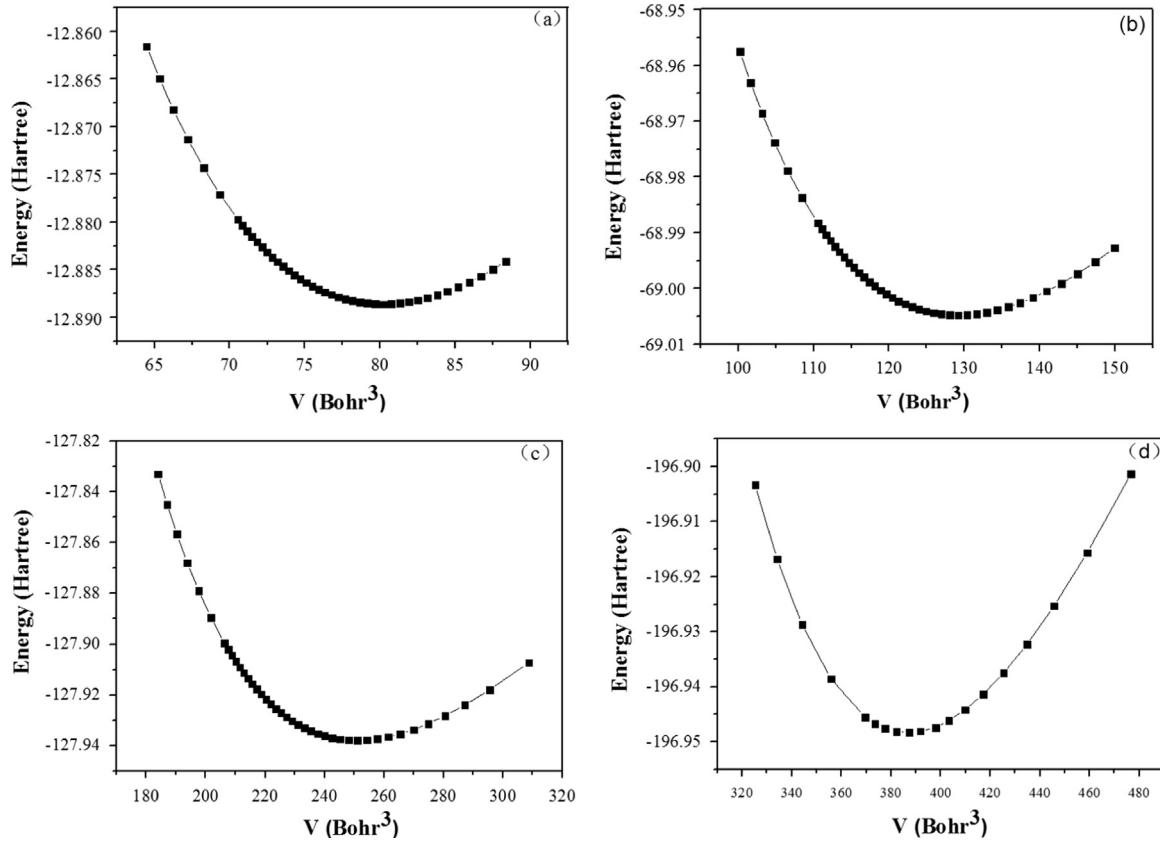


Fig. 6. Total energy (GGA) versus the primitive cell volume for c-BN (a), TiN (b), Ti₂N (c) and Ti₃N₂ (d).

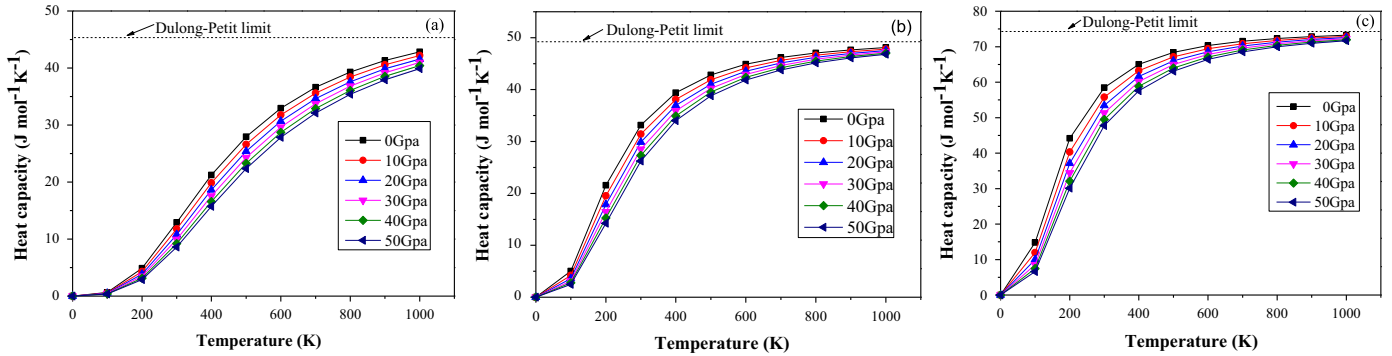


Fig. 7. Relations between the heat capacity and temperature of (a) c-BN, (b) TiN and (c) Ti₂N at various pressures.

stiffness among TiN, Ti₂N and Ti₃N₂, but less than the stiffness of c-BN.

The other important parameter in mechanical properties is the Poisson's ratio, ν . The Poisson's ratio can provide more information about the characteristics of the bonding forces than any of the other elastic constants. Poisson's ratio reflects the stability of a crystal against shear deformation. Materials with bigger Poisson's ratio show better plasticity. The Poisson's ratio is shown as following [39]:

$$\nu = \frac{3B - 2G}{2(3B + G)} \quad (14)$$

The Poisson's ratio calculations for TiN and its derivatives are larger than that for c-BN. It is shown that the TiN, Ti₂N and Ti₃N₂ have the more stable property than c-BN, and that Ti₃N₂ owns the best plasticity among c-BN, TiN, Ti₂N and Ti₃N₂ in the pressures range from 0 to 50 GPa.

From Table 2, the more information about mechanical

properties can be analysed. The bulk modulus B denotes the resistance to fracture, and the shear modulus G represents the resistance to plastic deformation. The ratio of B/G describes the ductile or brittle characters. A higher B/G ratio is associated with the more facile ductility, whereas a lower value corresponds to brittle nature. If $B/G > 1.75$, the material behaves in a ductile manner; otherwise, the material presents as a brittle manner [32]. As shown in Fig. 4, in the case of c-BN at 0 K and 0 GPa, our calculated value of B/G is 0.964 with GGA calculations, which suggests that c-BN is prone to brittle. For TiN at 0 K and 0 GPa, our calculated value of B/G is 1.474 with GGA. When the applied pressure changes from 0 GPa to 50 GPa, the ratio B/G value of TiN changes from 1.474 to 1.820, that is to say, TiN becomes from brittle behavior to ductile with increasing pressure. Ti₃N₂ has the same rule with TiN with pressure increase. The B/G of Ti₃N₂ is from 1.585 to 2.376. When the applied pressure is greater than about 3 GPa, Ti₂N behaves in a ductile manner.

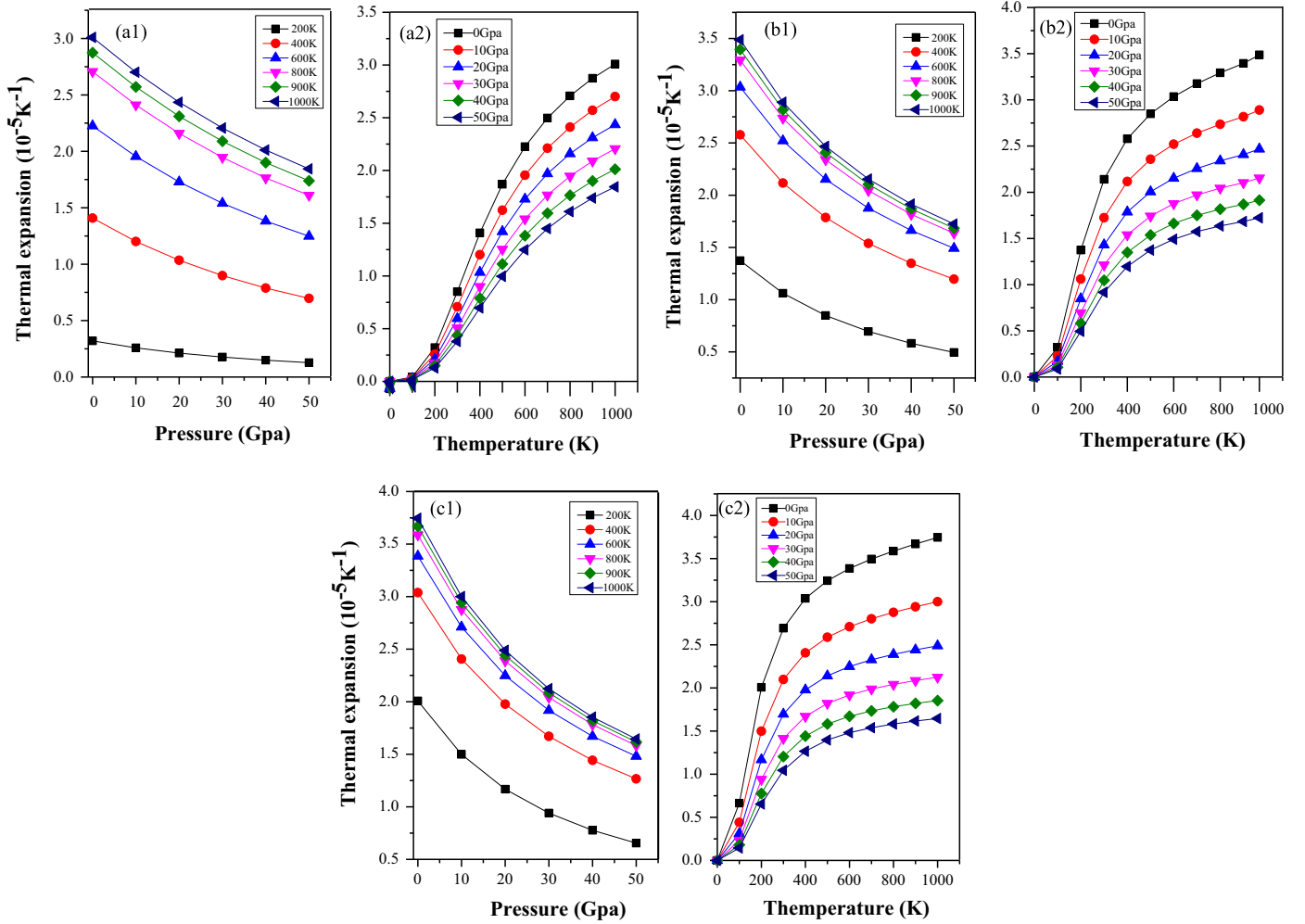


Fig. 8. The thermal expansion (10^{-5} K^{-1}) versus pressure (left) and temperature (right) of (a) c-BN, (b) TiN and (c) Ti_2N .

3.3. Thermodynamic properties

Debye temperature is one of fundamental parameters for solid materials, which is correlated with many physical properties, such as thermal expansion, melting point, and Grüneisen parameter. It is used to distinguish between high and low temperature regions for a solid. At low temperatures, Debye temperature, θ , is proportional to the sound velocity and directly related to the elastic constant through bulk and shear modulus. If the temperature $T > \theta$, all modes have the energy of $\kappa_B T$, and if $T < \theta$, the high-frequency modes are frozen, i.e. the vibrational excitations arise solely from the acoustic vibrations [32]. The Debye temperature can be estimated from the averaged sound velocity, ν_m , its expression is given by the following equation [40].

$$\theta = \frac{h}{\kappa} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{1/3} \nu_m \quad (15)$$

where h is Planck's constant, κ is Boltzmann's constant, n is the number of atoms in the molecule, N_A is Avogadro's number, ρ is the density of molecule, and M is the molecular weight. The average velocity ν_m is given by

$$\nu_m = \left[\frac{1}{3} \left(\frac{2}{\nu_p^3} + \frac{1}{\nu_s^3} \right) \right]^{-1/3} \quad (16)$$

where ν_p and ν_s are the averaged aggregate velocities for longitudinal (compressional) and transverse (shear) elastic waves,

respectively. The velocities for compressional and shear waves can be described by Navier's equations as follows:

$$\nu_p = \left(\frac{B + (4G/3)}{\rho} \right)^{1/2} \quad (17)$$

$$\nu_s = \left(\frac{G}{\rho} \right)^{1/2} \quad (18)$$

For c-BN, TiN, Ti_2N and Ti_3N_2 , under pressure from 0 to 50 GPa condition, their Debye temperature are calculated by means of GGA-PBE. The results are shown in Fig. 5. It is shown that the θ rises monotonically as pressure increases from 0 to 50 GPa. For most materials, usually, the higher the Debye temperature, the larger the micro-hardness is. That is, as pressure increases, the micro-hardness becomes better and bonds become stronger. TiN has the biggest θ among TiN, Ti_2N and Ti_3N_2 , which implies that Ti-Ti metallic bonds impair the micro-hardness of Ti-N compounds. We can conclude that with increasing N content, the enhancement of directional covalent interactions and decline of metallicity lead to the increase of the micro-hardness.

The other thermodynamic properties of c-BN, TiN, Ti_2N and Ti_3N_2 under high temperature and pressure can be obtained from the quasi-harmonic Debye model, in which the phonon effect is considered. In fact, the thermodynamic properties of the crystal can be obtained by treating the lattice vibrations as quantized (phonons). This model is very computationally quick and easy,

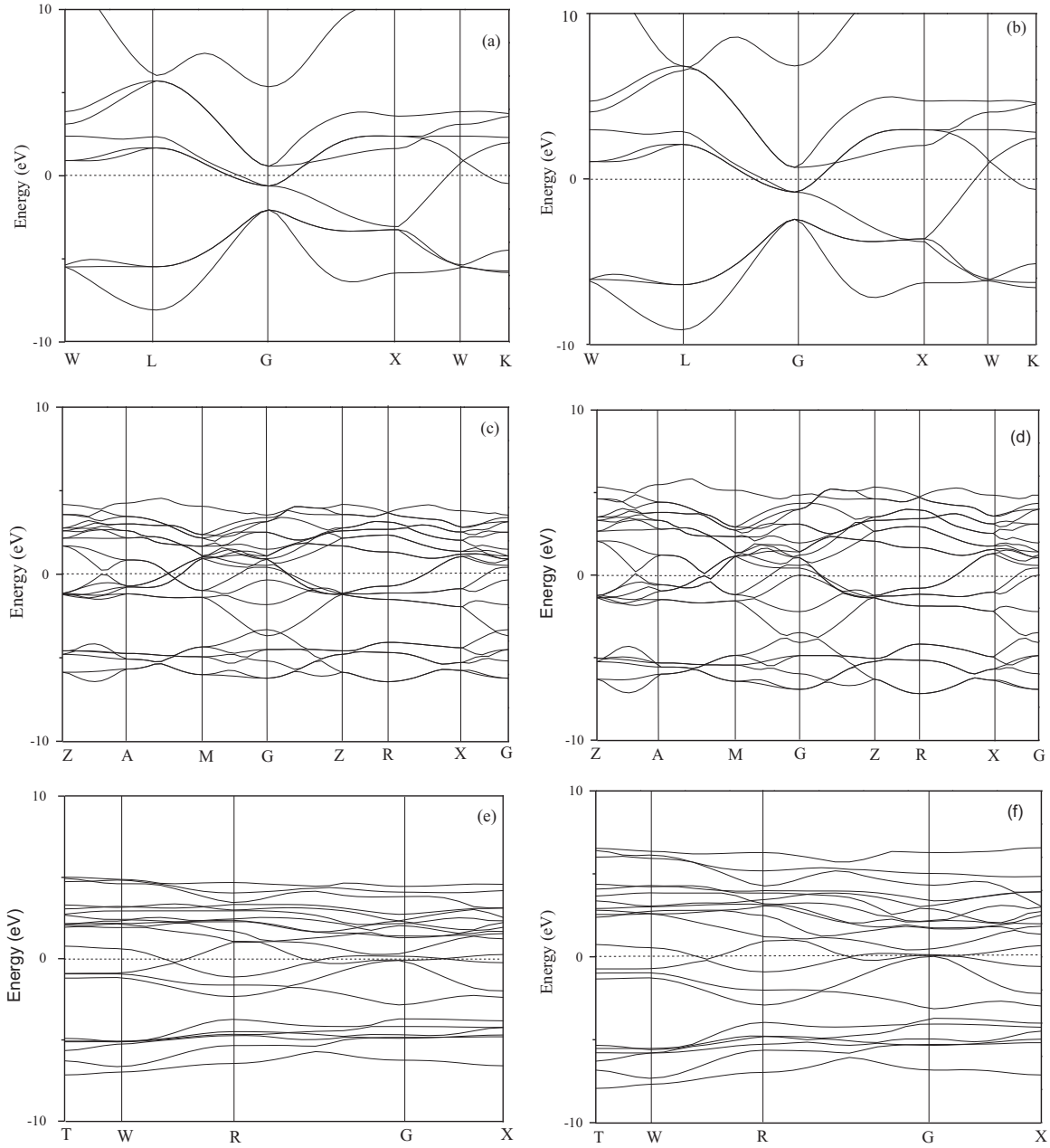


Fig. 9. Electronic band structures of TiN(*Fm-3m*), Ti₂N(*P4₂/mmn*) and Ti₃N₂(*Immm*) along the high symmetry around the Fermi level calculated with GGA: at 0 GPa (a, c, e), and at 50 GPa (b, d, f).

which has been successfully applied to predict the thermodynamic properties of some materials. In the quasi-harmonic Debye model, the non-equilibrium Gibbs function $G^*(V; P, T)$ takes the form of [41,42]

$$G^*(V; P, T) = E(V) + PV + A_{vib}(\theta(V); T) \quad (19)$$

where $E(V)$ is the total energy per unit cell, PV corresponds to the constant hydrostatic pressure condition, $\theta(V)$ is the Debye temperature, T is the absolute temperature and A_{vib} is the vibrational contribution, it can be written as

$$A_{vib}(\theta; T) = nkT \left[\frac{9}{8} \frac{\theta}{T} + 3 \ln(1 - e^{-\theta/T}) - D(\theta/T) \right] \quad (20)$$

with $D(\theta/T)$ representing the Debye integral, n is the number of atoms per formula unit.

For the non-equilibrium Gibbs function, $G^*(V, P, T)$, can be

minimized with respect to volume V . There is

$$\left(\frac{\partial G^*(V; P, T)}{\partial V} \right)_{P,T} = 0 \quad (21)$$

By solving the Eq. (21) with respect to V , a thermal equation of state can be get. The isothermal bulk modulus, B_T , the heat capacity, C_V , and thermal expansion coefficient, α , are given as follows

$$B_T(P, T) = V \left[\frac{\partial^2 G^*(V; P, T)}{\partial V^2} \right]_{P,T} \quad (22)$$

$$C_V = 3nk \left[4D(\theta/T) - \frac{3\theta/T}{e^{\theta/T} - 1} \right] \quad (23)$$

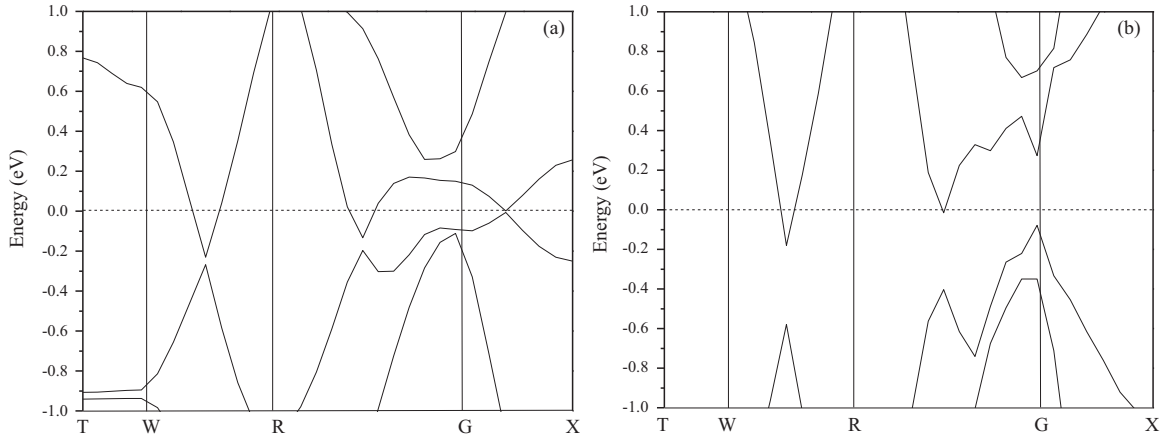


Fig. 10. Electronic band structures of $\text{Ti}_3\text{N}_2(\text{Immm})$ along the high symmetry around the Fermi level calculated with GGA (a) and with PBE0(b) at 0 GPa.

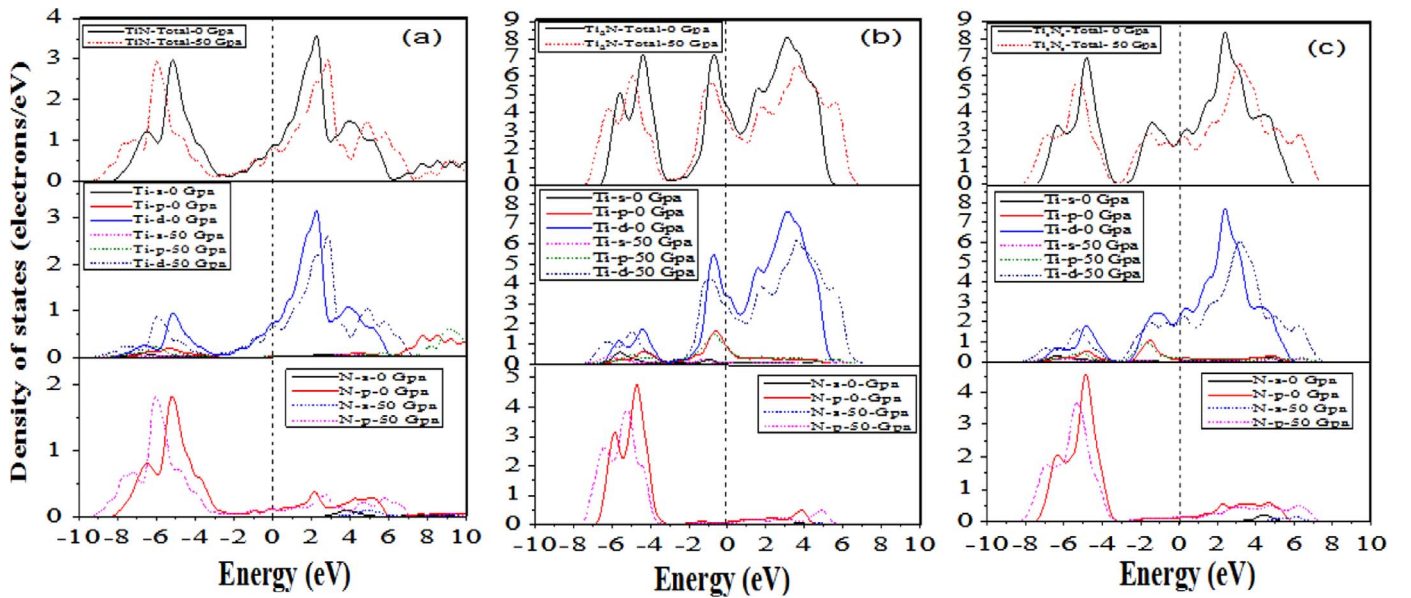


Fig. 11. The total and partial DOS (in electrons/eV) of (a) $\text{TiN}(\text{Fm-}3\text{m})$, (b) $\text{Ti}_2\text{N}(\text{P}4_2/\text{mnm})$ and (c) $\text{Ti}_3\text{N}_2(\text{Immm})$ at 0 GPa and 50 GPa with GGA. Here the Fermi level is indicated by the vertical dot-line.

$$\alpha = \frac{\gamma C_V}{B_T V} \quad (24)$$

Anharmonic effect of the vibrating lattice is usually described in terms of Grüneisen parameter, γ , which can be defined as

$$\gamma = - \frac{d \ln \theta(V)}{d \ln V} \quad (25)$$

By means of GGA method, we calculated the total energy E of these systems for various the primitive cell volume V . In Fig. 6, the relations between E and V are given for c-BN, TiN, Ti_2N , and Ti_3N_2 . The results show that there is a minimum in the relation of E with V for each formula. The minimum energy is relative to the volume at 0 GPa. Hence, their structures are most stable at 0 GPa.

In the next analysis, we only give the thermodynamic properties of c-BN, TiN and Ti_2N , due to the $\text{Immm-Ti}_3\text{N}_2$ phase loses its thermodynamic stability at 20 GPa, i.e., it becomes a metastable phase [25]. The thermodynamic properties of c-BN, TiN and Ti_2N are calculated in the temperature range from 0 K to 1000 K, where the quasi-harmonic model remains fully valid, meanwhile, the pressure effects on the thermodynamic properties are studied in the range 0–50 GPa.

The heat capacity is an important parameter in condensed

matter physics. It provides the essential information about the heat transition process and vibrational properties. The relations of the constant volume heat capacity, C_V , with temperature and pressure are presented in Fig. 7, for c-BN, TiN and Ti_2N , respectively. It can be seen that these heat capacities increase rapidly in the lower temperature, at a given pressure. At higher temperature, the anharmonic effect on C_V is suppressed, and C_V is close to the so-called Dulong–Petit limit, which is applicable to all solids at high temperature.

From the quasi-harmonic Debye model, we can determine the thermal expansion coefficients of c-BN, TiN and Ti_2N at a given pressure and temperature conditions. The results are shown in Fig. 8. It is shown that thermal expansion coefficients decrease with pressure rise at a given temperature, and they decrease gently at lower temperature. The expansion coefficients increase sharply with temperature rise at low temperatures, especially at 0 GPa, and gradually lean to a slow growth at high temperature, at a given pressure. Hence, at higher temperature and pressure, the varieties of α with temperature and pressure are correspondingly smooth, and the thermal expansion coefficients converge gradually to constant value. The influence of temperature on α is more significant than that of pressure on it.

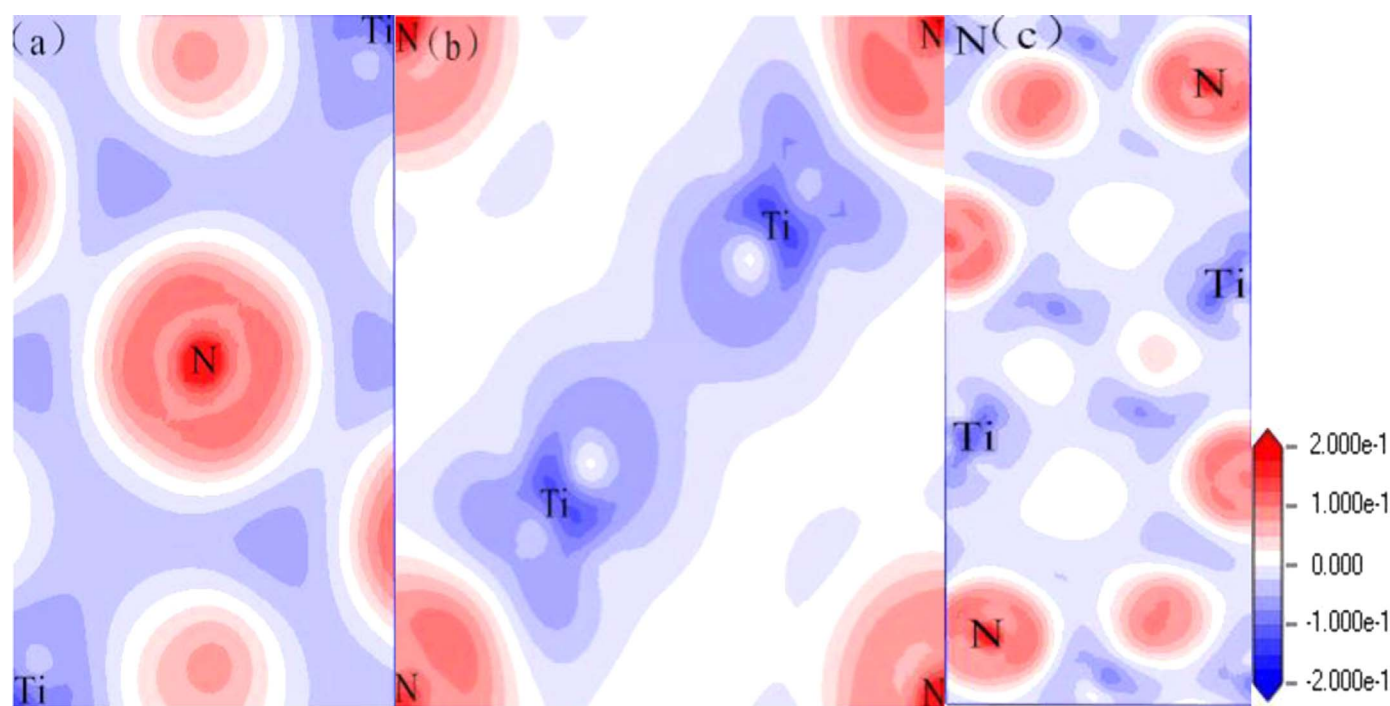


Fig. 12. Electron density difference distribution for (a) TiN, (b) Ti₂N and (c) Ti₃N₂.

Table 3.
The calculated atomic Mulliken charges (e) for TiN, Ti₂N and Ti₃N₂ crystals.

Species	s	p	d	Total	Charge/e
TiN					
N	1.68	4.06	0.00	5.74	−0.74
Ti	2.19	6.51	2.57	11.26	0.74
Ti₂N					
N	1.68	4.06	0.00	5.73	−0.73
Ti	2.19	6.79	2.65	11.63	0.37
Ti₃N₂					
N	1.68	4.05	0.00	5.73	−0.73
Ti(1)	2.17	6.63	2.63	11.43	0.57
Ti(2)	2.18	6.73	2.64	11.55	0.45

3.4. Electronic properties

3.4.1. Band structures and density of states

Here we analyze the electronic properties of the titanium nitrides structure at 0 GPa and 50 GPa. In the present work, the density of states (DOS) is calculated to have a further insight into the bonding characteristics of titanium nitrides and then to reveal the elastic properties and the fundamental structural stability mechanism. The structural stability of intermetallic compound is concerned with its bonding electron orbits. For TiN, Ti₂N and Ti₃N₂, the calculated band structures with the GGA in the Brillouin zone, at 0 GPa and 50 GPa, are obtained in the energy range of −10–10 eV as shown in Fig. 9. The total DOS (TDOS) of TiN, Ti₂N and Ti₃N₂ in the vicinity of the Fermi level under 0 GPa and 50 GPa are plotted in Fig. 11. The partial DOS (PDOS) of the constituent Ti and N are also shown in Fig. 11. The result of TiN is consistent with reference [33]. In Fig. 9, the Fermi level is set to be zero, and it is indicated by the horizontal dot-line. It is obviously shown that there is no energy gap above the Fermi level for TiN and Ti₂N, which means that TiN and Ti₂N present metallic character. However, it's hard to judge whether Ti₃N₂ present metallic character or

semiconducting character based on the calculated results by GGA. As is known all, the GGA may underestimate the energy gap of the band structure. So we recalculated the electronic band structures of Ti₃N₂ with PBE0 (which is a parameter free density functional model) at 0 GPa in Fig. 10. From Fig. 10, we can find that Ti₃N₂ present semiconducting character. When the pressure increases to 50 GPa, the band structure is similar to that under 0 GPa, but there are some discrepancies, namely, there are energy dispersion. From the DOS results at Fig. 11, the discrepancies of the energy between 0 GPa and 50 GPa are more obvious. Hence, as pressure increases, we can see that the extent of energy dispersion gets large, which means that the local character of electrons gets weaker and the itinerant character becomes stronger at 50 GPa. This is similar to other material results [42].

In Fig. 11, it can be seen that the total and partial DOS in the valence band shift slightly to low energy region, and in the conduction band it shift to high energy region under the external pressure. The offset is attributed to the change of interaction potentials, which is caused by the shortened distance between the atoms under pressure. Moreover, all peaks fall their height under pressure. This illustrates that the hybridization energy is reduced with the increasing pressure. The main bonding peaks of TiN, Ti₂N and Ti₃N₂ locate in range from −10 to 10 eV, which originate from the contribution of valance electron numbers of Ti s, Ti p, Ti d, N s and N p orbits. The total DOS of TiN, Ti₂N and Ti₃N₂ near the Fermi level originate mainly from Ti d with small contribution of Ti p and N p orbits. Below the Fermi level, the DOS in the valence band originate from Ti p, Ti d, and N p orbits with small contribution of Ti s. Above the Fermi level, the DOS in the conduction band originate from Ti d. It can be known that the valence electrons appear mainly around Ti atoms and the structural stability factors of TiN, Ti₂N and Ti₃N₂ phases due to the interaction between Ti d and N p. We can also find that the pressure makes the total DOS decrease at the Fermi level for Ti₂N, but for TiN and Ti₃N₂, that changes are very little. From Fig. 11, as N content increases, valence band broadens, valence electron concentration increases, and covalent interactions become stronger, due to the shortening of Ti–N bonds.

3.4.2. Electron density difference and Mulliken charge population

For the sake of studying the chemical bonding, we calculate the electron density difference and the results are shown in Fig. 12. The contour plots show the differences of electron densities (between -0.2 and 0.2) from the chemical bonding in TiN, Ti₂N and Ti₃N₂ lattices, which are relative to electron densities in isolated atom. The electron density difference of TiN is the discrepancy between the electron density of the total system and the unperturbed electron densities of Ti and N. For TiN, Ti₂N and Ti₃N₂, the results of the electron density differences show the electron distribution's changes due to the formation of chemical bonds. It is useful for illustrating how chemical bonds are formed. The electron density difference can help identifying the types of chemical bonds. From Fig. 12, we can see that Ti atoms lose electrons, N atoms get electrons and the electrovalent bond is formed between Ti atoms and N atoms. The combination of Ti and N atoms' is dependent on ionic effect of Coulomb attraction. In order to further understand bonding behavior of N–Ti compounds, we also obtain the Mulliken charge population for TiN, Ti₂N and Ti₃N₂. The Mulliken population results are given in Table 3. The charge transfer from Ti to N are about 0.74, 0.37, 0.57^{Ti(1)} (0.45^{Ti(2)}) electrons for TiN, Ti₂N and Ti₃N₂, respectively. Therefore, we concluded that the bonding behavior of N–Ti compounds is a combination of covalent and ionic nature.

4. Conclusions

The structural, elastic, thermodynamic, and electronic properties of TiN, Ti₂N and Ti₃N₂ are analysed under high pressure. TiN is more incompressible than Ti₂N and Ti₃N₂, but more compressible than c-BN. The results by first-principles are in accordance with the results by Birch–Murnaghan equation of states. The behaviors for TiN, Ti₂N and Ti₃N₂ become from brittle to ductile with pressure rise. The Poisson's ratios of titanium nitrides are larger than that of c-BN. It is shown that the TiN, Ti₂N and Ti₃N₂ have the more stable property than c-BN, and that Ti₃N₂ owns the best plasticity among c-BN, TiN, Ti₂N and Ti₃N₂ in high pressure. The pressure dependence relations of the Debye temperature for c-BN, TiN, Ti₂N and Ti₃N₂, and the relations of the total energy of the systems versus the primitive cell volume are obtained. With increasing N content, the enhancement of covalent interactions leads to the increase of the micro-hardness. The relations of the constant volume heat capacity and the thermal expansion coefficients, with temperature and pressure are presented, for c-BN, TiN and Ti₂N, respectively. The influences of temperature on the thermal expansion coefficients are more significant than that of pressure on it.

The results of the electronic properties of TiN, Ti₂N and Ti₃N₂ show that TiN and Ti₂N present metallic character and Ti₃N₂ present semiconducting character. The extent of energy dispersion gets large when pressure increases, which means that the itinerant character of electrons becomes stronger at 50 GPa. The main bonding peaks of TiN, Ti₂N and Ti₃N₂ locate in range from -10 to 10 eV, which originate from the contribution of valence electron numbers of Ti s, Ti p, Ti d, N s and N p orbitals. The high pressure also makes that the total DOS decrease at the Fermi level of Ti₂N. We can also see that the bonding behavior of N–Ti compounds is a combination of covalent and ionic nature. As N content increases,

the valence band broadens, the valence electron concentration increases, and the covalent interactions become stronger, due to the shortening of Ti–N bonds. The analyses for Titanium nitrides compound materials properties are attractive for future experimental studies and technological applications.

References

- [1] W. Aperador, J.C. Caicedo, C. Espan, G. Cabrera, J. Phys. Chem. Solids 71 (2010) 1754–1759.
- [2] H.T. Kim, M.J. Kim, S.H. Sohn, J. Phys. Chem. Solids 73 (2012) 931–935.
- [3] S. Veprek, M.G.J. Veprek-Heijman, R.F. Zhang, J. Phys. Chem. Solids 68 (2007) 1161–1168.
- [4] C.K. Jin, K.H. Lee, C.G. Kang, Int. J. Hydrog. Energy 40 (2015) 6681–6688.
- [5] S. Veprek, S.G. Prilliman, S.M. Clark, J. Phys. Chem. Solids 71 (2010) 1175–1178.
- [6] K. L. X.L. Zhou, H.H. Chen, L.Y. Lu, J. Therm. Anal. Calorim. 110 (2011) 1–6.
- [7] B. Zhu, Y.H. Li, J. Zhu, Y.J. Hao, G. Xiang, B.R. Yu, W. Li, Comput. Mater. Sci. 86 (2014) 200–205.
- [8] T.F. Li, T.M. Liu, H.M. Wei, S. Hussain, B. Miao, W. Zeng, X.H. Peng, F.S. Pan, Comput. Mater. Sci. 105 (2015) 83–89.
- [9] D.Q. Yin, X.H. Peng, Y. Qin, Z.C. Wang, Ceram. Int. 41 (2015) 10095–10101.
- [10] Z.Y. Xiu, G.Q. Chen, M. Wang, Micron 45 (2013) 92–96.
- [11] R. Ali, M. Sebastiani, E. Bemporad, Mater. Des. 75 (2015) 47–56.
- [12] D.Q. Yin, X.G. Peng, Y. Qin, Z.C. Wang, Ceram. Int. 41 (2015) 10095–10101.
- [13] S.S. Lin, K.S. Zhou, M.J. Dai, F. Hu, Q. Shi, H.J. Hou, C.B. Wei, F.Q. Li, X. Tong, Trans. Nonferrous Met. Soc. China 25 (2015) 451–456.
- [14] D. Kiesler, T. Bastuck, R. Theissmann, F.E. Krus, J. Nanopart. Res. 17 (2015) 1–13.
- [15] C. Wang, Y.B. Dai, H.Y. Gao, X.M. Ruan, J. Wang, B.D. Sun, Solid State Commun. 150 (2010) 1370–1374.
- [16] K. Sano, M. Oose, T. Kawakubo, Jpn. J. Appl. Phys. 34 (1995) 3266–3270.
- [17] V.I. Ivashchenko, S. Veprek, P.E.A. Turchi, V.I. Shevchenko, J. Leszczynski, L. Gorb, F. Hill, Thin Solid Films 564 (2014) 284–293.
- [18] V.I. Ivashchenko, S. Veprek, A.S. Argon, P.E.A. Turchi, L. Gorb, F. Hill, J. Leszczynski, Thin Solid Films 578 (2015) 83–92.
- [19] D.Q. Yin, X.G. Peng, Y. Qin, Z.C. Wang, Phys. E 44 (2012) 1838–1845.
- [20] C. Stampfl, A.J. Freeman, Appl. Surf. Sci. 258 (2012) 5638–5645.
- [21] R. Ahuja, O. Eriksson, J.M. Wills, B. Johansson, Phys. Rev. B 53 (1996) 3072–3079.
- [22] S.K. Yadav, X.Y. Liu, J. Wang, R. Ramprasad, A. Misra, R.G. Hoagland, Philos. Mag. 94 (2013) 464–475.
- [23] D.Q. Yin, Y. Yang, X.G. Peng, Y. Qin, Z.C. Wang, Ceram. Int. 40 (2014) 14453–14462.
- [24] C.J. Xuan, H. Shibata, Z. Zhao, P.G. Jönsson, K. Nakajima, ISIJ Int. 55 (2015) 1642–1651.
- [25] S.Y. Yu, Q.F. Zeng, A.R. Oganov, G. Frapper, L.T. Zhang, Phys. Chem. Chem. Phys. 17 (2014) 11763–11769.
- [26] M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M. C. Payne, J. Phys.: Condens. Matter 14 (2002) 2717.
- [27] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892.
- [28] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.
- [29] X.D. Zhang, H.F. Shi, Lattice dynamics, thermodynamics and elastic properties of Li₂Te under high pressure: first principles study, Mater. Sci. Technol. 30 (2014) 732–738.
- [30] J.W. Yang, T. Gao, Y.R. Gong, Solid State Sci. 32 (2014) 76–82.
- [31] M.A. Blanco, E. Francisco, V. Luaña, Comput. Phys. Commun. 158 (2004) 57–72.
- [32] Q.Y. Fan, Q. Wei, H.Y. Yan, M.G. Zhang, Z.X. Zhang, J.Q. Zhang, D.G. Zhang, Comput. Mater. Sci. 85 (2014) 80–87.
- [33] M.G. Brik, C.-G. Ma, Comput. Mater. Sci. 51 (2012) 380–388.
- [34] B.D. Fulcher, X.Y. Cui, B. Delley, C. Stampfl, Phys. Rev. B. 85 (2012) 184106.
- [35] Z.T.Y. Liu, X. Zhou, S.V. Khare, D. Gall, J. Phys.: Condens. Matter 26 (2013) 025404.
- [36] S. Aydin, M. Simsek, J. Alloy. Compd. 509 (2011) 5219–5229.
- [37] B. Dong, X.L. Zhou, K. Liu, J. Chang, J. Appl. Phys. 116 (2014) 053511–053511-8.
- [38] Z.J. Wu, E.J. Zhao, H.P. Xiang, X.F. Hao, X.J. Liu, J. Meng, Phys. Rev. B 76 (2007) 054115.
- [39] X.T. Li, X.Y. Zhang, J.Q. Qin, S.H. Zhang, J.L. Ning, R. Jing, M.Z. Ma, R.P. Liu, J. Phys. Chem. Solids 75 (2014) 1234–1239.
- [40] Y. Yu, D.J. Liu, J.J. Chen, J.Y. Ji, J.P. Long, Solid State Sci. 28 (2014) 35–40.
- [41] H.Y. Yan, M.G. Zhang, D.H. Huang, Q. Wei, Solid State Sci. 18 (2013) 17–23.
- [42] J.J. Cao, X.F. Gou, X.L. Yuan, Phys. C 509 (2015) 34–41.