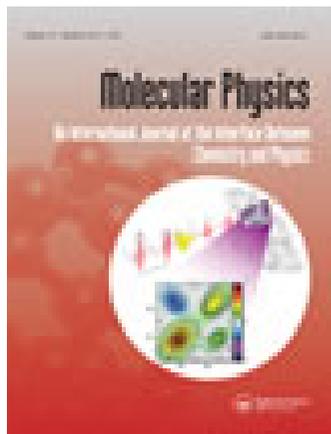


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Ying-Chun Ding^a & Min Chen^a

^a College of Optoelectronics Technology, Chengdu University of Information Technology, Chengdu 610225, People's Republic of China

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RESEARCH ARTICLE

Mechanical properties, anisotropy and hardness of group IVA ternary spinel nitrides

Ying-Chun Ding* and Min Chen

College of Optoelectronics Technology, Chengdu University of Information Technology, Chengdu 610225, People's Republic of China

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In this work, new ternary cubic spinel structures are designed by the substitutional method. The structures, elasticity properties, intrinsic hardness and Debye temperature of the cubic ternary spinel nitrides are studied by first principles based on the density-functional theory. The results show that γ -CSn₂N₄, γ -SiC₂N₄, γ -GeC₂N₄ and γ -SnC₂N₄ are not mechanically stable. The elastic constants C_{ij} of these cubic spinel structures are obtained using the stress-strain method. Derived elastic constants, such as bulk modulus, shear modulus, Young's modulus, Poisson coefficient and brittle/ductile behaviour are estimated using Voigt-Reuss-Hill theories. The B/G value, the Poisson's ratio and anisotropic factor are calculated for eight ternary stable crystals. Based on the microscopic hardness model, we further estimate the Vickers hardness of all the stable crystals. From the calculated hardness of the stable group IVA ternary spinel nitrides by Gao's and Jiang's methods, it is observed that the stable group IVA ternary spinel nitrides are not superhard materials except for γ -CSi₂N₄. Furthermore, the Debye temperature for the eight stable crystals is also estimated.

Keywords: elastic property; intrinsic hardness; Debye temperature

1. Introduction

In recent years, nitrogen has turned out to play a key role in today's most exciting technological materials. A number of works have focused on the synthesis of novel carbon nitrides and silicon nitrides. The cubic spinel structure has recently been discovered in the group IVA nitrides Si₃N₄, Ge₃N₄ and Sn₃N₄, in high-pressure and high-temperature experiments [1–13]. Silicon nitride (Si₃N₄) is one of the most important ceramic materials with numerous applications due to its unique chemical, mechanical and electronic properties. Especially, the desirable mechanical properties at high temperatures make silicon nitride an ideal material in various applications, such as engine parts, bearings and metal machining. In addition to the well-known hexagonal α and β forms are two stable phases of Si₃N₄. Both the phases are hexagonal crystal structure, in which all Si atoms are in tetrahedral bond with N atoms, with a strong covalent character [9]. The third high-density cubic spinel phase of Si₃N₄ (γ -Si₃N₄) with space group $Fd\bar{3}m$ was discovered in 1999 under high pressure of around 15 GPa and high temperature of around 2200 K [1]. The experimental and theoretical work resulted in the synthesis of spinel-type γ -Si₃N₄ and γ -Ge₃N₄ [1,12].

It is worth recalling the case for γ -Si₃N₄ that there exists a significant difference between the experimental values of the evaluated hardness and the elastic stiffness constants. Subsequently, a detailed calculation by He et al. [10] using a microscopic model obtained the hardness of 33.3 GPa,

which is in good agreement with the experimental results and demonstrated that γ -Si₃N₄ is not a superhard material. Experimental information on the cubic ternary spinel nitrides is scarce. Theoretically, these compounds have attracted the attention of some researchers [11–19]. Some systematic investigations were performed on the structure and properties of cubic spinel nitrides, including binary and ternary spinel nitrides [11–19]. Ching and Bouhemadou have studied the structural, electronic and optical properties of γ -SiGe₂N₄ by means of the first-principles orthogonalized linear combinations of atoms' orbitals (OLCAO) and methods [14–16]. Wang et al. have investigated the structure, and the electronic and optical properties of group IVA binary and ternary spinel nitrides using an ab initio full potential linearized augmented plane waves (FP-LAPW) code [17]. Neither experimental nor theoretical details of group IVA ternary spinel nitrides regarding the elastic constants, hardness and the thermodynamic properties are available. First-principles calculations offer one of the most powerful tools for carrying out theoretical studies of an important number of physical and chemical properties of the condensed matter with great accuracy. It is now possible to explain and predict properties of solids which were previously inaccessible to experiments.

The hardness of the group IVA binary spinel nitrides γ -C₃N₄, γ -Si₃N₄, γ -Ge₃N₄ and γ -Sn₃N₄ has been researched [11,20–22]. Of all the potential compounds, a hypothetical ternary nitride, cubic spinel CSi₂N₄ (γ -CSi₂N₄), was

*Corresponding author. Email: dyccqzx@yahoo.com.cn

predicted to be one of the stable phases with an indirect band gap [21]. Furthermore, γ -CSi₂N₄ shows exceptionally strong covalent bonding and a large bulk modulus, which suggests it to be a superhard material [21,23]. Based on the microscopic hardness model, γ -CSi₂N₄ is predicted to be a superhard material [21].

In the present paper, we design group IVA ternary spinel nitrides by the substitutional method. We further study the mechanical stability, the elastic moduli, the intrinsic hardness and the Debye temperature of these new ternary nitrides.

2. Calculation models and methods

Materials design technique is greatly desirable as a request to assist experiment. Two rational theoretical methods (substitutional method and global free energy minimization method) of design of superhard materials have been successfully applied [24]. ‘Substitutional method’ is an easy-to-use method, which depends on the known structural database and follows the criterion that a material with a particular chemical formula (e.g. A_mB_n) has a structural type, which is known in other chemically related materials. This method can be successful if the target crystal forms of materials are already documented in the structural database. The well-known hypothetical superhard material, hexagonal β -C₃N₄, was proposed by Cohen and Liu [25,26] through this method, with the knowledge of known β -Si₃N₄ structure by substituting C for Si. The notion that C–N bond in β -C₃N₄ is shorter than C–C bond in diamond has attracted much attention. It is then remarkably predicted that the bulk modulus of β -C₃N₄ could be higher than that of diamond [25]. Subsequent theoretical calculations further proposed other dense polymorphs of C₃N₄, e.g. hexagonal α -C₃N₄, cubic C₃N₄ (c-C₃N₄), the cubic phase with defective zinc blende structure (dzb-C₃N₄) and the pseudocubic phase (pc-C₃N₄), among which c-C₃N₄ has a zero-pressure bulk modulus exceeding that of diamond [27,28]. With the structural information of C₃N₄, several boron carbides, e.g. α -B₄C₃, β -B₄C₃ and pseudocubic B₄C₃ (pc-B₄C₃) were constructed by replacing N with B atoms [29]. The predicted hardness of these B₄C₃ phases can reach 51–63 GPa. These predictions clearly pointed out the possible existence of potential superhard candidates [29].

Spinel compounds belong to the space group $Fd\bar{3}m$. The spinel structure is geometrically a ternary structure with stoichiometry AB₂X₄, where A and B are, respectively, tetrahedral (8a) coordinated cations and octahedral (16d) coordinated cations, and X represents anions (32e). For γ -Si₃N₄ and γ -Ge₃N₄, all Si and Ge atoms occupy the tetrahedral and octahedral cation sites. All the N atoms are fourfold coordinated and occupy the (32e) sites [1,11–13]. In other words, γ -Si₃N₄ and γ -Ge₃N₄ comprise not only fourfold-coordinated silicon, but sixfold-coordinated

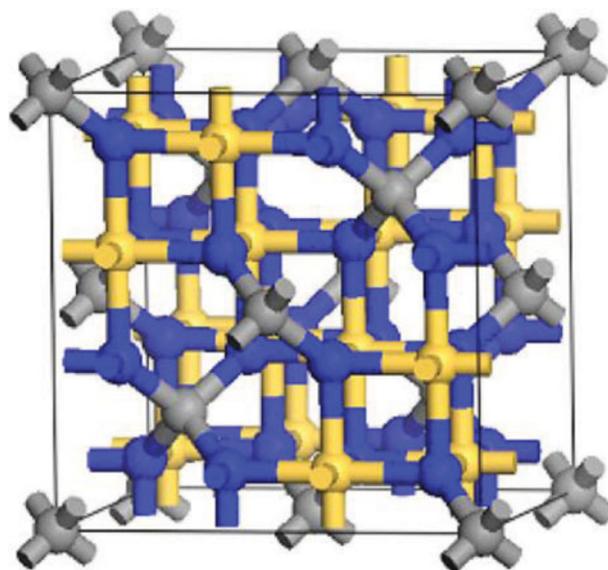


Figure 1. Crystal structure of γ -AB₂X₄. Gray spheres represent the tetrahedral (8a) coordinated cations (A sites), blue spheres are the octahedral (16d) coordinated cations (B sites) and yellow spheres are anions (32e) (X sites).

silicon as well. In this paper, we discuss about ternary spinel nitrides γ -AB₂X₄, which are the C, Si, Ge and Sn atoms that replace the tetrahedral-A and octahedral-B sites. The γ -AB₂X₄ crystal is shown in Figure 1.

Density functional theory (DFT) has played an important role. This ‘ab initio’ approach is applied at various levels and has been shown to lead to some significant results regarding the prediction of structural, elastic and thermodynamic properties [30,31]. In the present work, the first-principles calculations, based on density functional theory, were conducted in CASTEP code [32]. The plane wave basis set was used for the energy calculations. The kinetic energy cut-off value for plane wave expansions in reciprocal space was set to 400 eV. The frozen core approximation was used for the pseudoatoms. The ultra-soft pseudopotentials of Vanderbilt scheme were used to account for the electrostatic interaction between the valence electrons and the ionic core [33]. The energy integrations were performed on a discretised \mathbf{k} grid in the first irreducible Brillouin zone, and we used $10 \times 10 \times 10$ \mathbf{k} point meshes for group IVA ternary spinel nitrides. The method proposed by Monkhorst–Pack was used for generating the \mathbf{k} points in this paper [34]. The Pulay density-mixing scheme was applied to the electronic energy minimization. For the convergence, the change of total energy was set to 1×10^{-6} eV/cell; the mean Hellmann–Feynman force acting on the atom was reduced to 0.01 eV/Å. We have considered the generalized gradient approximation (GGA)–Perdew–Burke–Ernzerhof for solids (PBEsol) [35] level exchange–correlation functional.

3. Results and discussions

3.1. Elastic properties

In Table 1, the lattice parameters, elastic moduli and mechanical anisotropic factor of the group IVA ternary spinel nitrides and γ - Si_3N_4 are calculated by the GGA–PBEsol functional. For γ - Si_3N_4 , it is seen that the calculated lattice parameters in present work are in good agreement with the previous results [10,18,21,36] and available experimental data [1,3,37].

The PBEsol function was a modification of the PBE function, and the main motivation was to obtain a better description of the equilibrium lattice properties than the original PBE function. In practical calculations, the results of PBEsol are usually between local density approximation (LDA) and PBE [38]. The lattice parameter values calculated by PBEsol method fall in between the values obtained by LDA and PBE methods. The results seem to indicate that our results for lattice parameters of γ - Si_3N_4 are reliable. The calculated lattice parameters, elastic moduli and mechanical anisotropic factor for the group IVA ternary spinel nitrides are shown for PBEsol.

For γ - CSi_2N_4 , the calculated lattice constants by the GGA–PBEsol method are larger than the values predicted by the GGA–PBE method [17,21] and smaller than that predicted by the OLCAO–LDA method [18,19]. The calculated bulk modulus lies between PBE and OLCAO–LDA. For γ - CGe_2N_4 , the calculated lattice constants are larger than the predicted values by GGA–PBE and OLCAO–LDA methods [17–19]. The calculated bulk modulus (267.08 GPa) by the GGA–PBEsol method is in good agreement with the previous results (259.2 and 266.0 GPa) by GGA–PBE and OLCAO–LDA methods [17–19]. For γ - SiGe_2N_4 , the calculated bulk modulus (279 GPa) by the GGA–PBE method [15] is close to the value (277.1 GPa) obtained by OLCAO–LDA [14,18,19]. The other calculated results are also close [16,17]. The calculated bulk modulus in the present work is between these calculated results [14–19]. The C_{ij} values calculated by the PBE method of γ - SiGe_2N_4 in Refs. [15,16] are also provided and compared. There are different results of C_{ij} values. Our PBEsol results are different from the two results calculated by PBE. For γ - GeSi_2N_4 , the calculated lattice parameters in the present work are in good agreement with the previous results [14,18]. The calculated bulk modulus (288.02 GPa) in the present work is in good agreement with the value 283.2 GPa obtained by the VASP–LDA method [20]. And calculated C_{12} and C_{44} are different. For γ - SnGe_2N_4 , the calculated bulk modulus (199.88 GPa) in the present work is in good agreement with the value 192.2 GPa obtained by the OLCAO–LDA method [19]. From Table 1, we can find out that the LDA method underestimates the lattice constants of the group IVA ternary spinel nitrides, except γ - CSi_2N_4 and γ - GeSi_2N_4 [18,19]. The elastic constants and other mechanical properties are calculated by the PBEsol method. Both PBE and PBEsol methods

somewhat overestimate the lattice constants; the reported mechanical properties here are possibly underestimated. On the other hand, LDA underestimates the lattice constants; mechanical properties are possibly overestimated. The full set of elastic constants of the group IVA ternary spinel nitrides and γ - Si_3N_4 are shown in Table 1. The total number of independent elastic constants for cubic crystal classes is 3. The obtained elastic constants can be used to estimate the mechanical stability of the crystal structure through Born–Huang lattice dynamical criterion. The calculated elastic constants C_{ij} are shown in Table 1. In γ - CSn_2N_4 , the calculated C_{11} and C_{12} are negative values. For γ - SiC_2N_4 , γ - GeC_2N_4 and γ - SnC_2N_4 , the calculated C_{12} values are larger than the calculated C_{11} values. These results show that γ - CSn_2N_4 , γ - SiC_2N_4 , γ - GeC_2N_4 and γ - SnC_2N_4 are not mechanically stable because they do not satisfy the well-known Born stability criterion [39] of Equation (1). The corresponding mechanical stability conditions for cubic crystals are

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

In the cubic crystal system, the bulk modulus is calculated by

$$B_H = B_V = B_R = (C_{11} + 2C_{12})/3 \quad (2)$$

In this work, shear modulus (G) is calculated with the following equations for the cubic crystal:

$$G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \quad (3)$$

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{3(C_{11} - C_{12}) + 4C_{44}} \quad (4)$$

$$G_H = (G_V + G_R)/2 \quad (5)$$

Then the Young's modulus (E) and Poisson's ratio (ν) are calculated by the following formulae:

$$E = 9B_H G_G / (3B_H + G_H) \quad (6)$$

$$\nu = (3B_H - 2G_H) / [2(3B_H + G_H)] \quad (7)$$

Usually, it is difficult to measure the elastic constants by experiments because a single crystal is not available and is difficult to prepare. However, the bulk modulus (B) and shear modulus (G) can be measured to indicate their elastic properties. Based on the works of Voigt [40], Reuss [41] and Hill [42], the Voigt–Reuss–Hill arithmetic average is frequently applied for estimating the mechanical moduli of the polycrystalline materials.

The calculated elastic constants, bulk modulus (B), shear modulus (G), Young's modulus (E), Poisson's ratio (ν) and B/G for stable group IVA ternary spinel nitrides,

Table 1. Calculated equilibrium lattice constant a (Å), elastic stiffness constants C_{ij} , bulk modulus (B_H), shear modulus (G_V , G_R and G_H), Young's modulus (E), Poisson's ratio (ν), B_H/G_H and elastic anisotropic factor (A) for group IVA ternary spinel nitrides. For the mechanical moduli, the units are in GPa.

	Function	a	C_{11}	C_{12}	C_{44}	Mechanical stability	B_H	G_V	G_R	G_H	E	ν	B_H/G_H	A
γ -CSi ₂ N ₄	This calc.	7.3514	711.1	147.3	355.3	Stable	335.3	325.9	321.8	323.8	660.5	0.171	1.04	1.21
	Previous calc.	7.2737	731.3	148.3	367.6		342.6			329.6	681.2	0.169	1.04	1.21
		6.9961					329.7							
		7.5209					309.5							
γ -CGe ₂ N ₄	This calc.	7.7238	538.11	222.09	145.06	Stable	267.08	211.87	211.11	211.49	502.0	0.187	1.26	0.95
	Previous calc.	7.3491					259.2							
		7.3160					266.0							
γ -CSn ₂ N ₄	This calc.	8.46176	-1933.97	-2075.15	2060.85	Unstable								
	This calc.	7.12768	227.53	427.98	417.71	Unstable								
	This calc.	8.09542	450.01	251.40	161.01	Stable	257.35	208.65	194.00	201.32	479.0	0.190	1.28	1.27
	Previous calc.	7.9285	494	172	288		279			228	537	0.1791	1.25	
		8.182	441.53	149.8	340.71		247.09			134.12	340.71	0.27		
		7.6932					241.7							
		8.0871					277.1							
γ -SiSn ₂ N ₄	This calc.	8.76415	357.34	155.34	113.10	Stable	194.51	142.05	140.09	141.07	340.8	0.208	1.38	1.07
	Previous calc.	8.6279												
		7.4007	236.00	340.11	326.74	Unstable								
γ -GeC ₂ N ₄	This calc.	7.91759	485.18	297.79	189.44	Stable	288.02	237.83	211.87	224.85	535.3	0.190	1.281	1.40
	Previous calc.	7.5213					264.8							
γ -GeSn ₂ N ₄	This calc.	8.0011					258.3							
		8.0008												
		8.95653	484.1	187.3	309.9	Stable	283.2	117.93	114.31	116.12	279.3	0.203	1.348	1.147
γ -SnC ₂ N ₄	This calc.	7.81992	158.55	213.29	281.56	Unstable								
	This calc.	8.26552	353.71	241.55	184.97	Stable	241.22	178.88	138.41	158.54	390.1	0.230	1.522	1.73
	Previous calc.	8.2479					199.88							
		8.60808	291.27	181.89	154.18	Stable	192.2	136.55	109.48	123.02	306.2	0.245	1.625	1.68
γ -Si ₃ N ₄	This calc.	7.7518	534.6	182.3	331.3	Stable	299.7	269.2	245.0	257.1	441.9	0.254	1.17	1.58
	Previous calc.	7.6482	554.3	187.9	362.5		310.0			272.9	459.1	0.253	1.14	1.65
		7.6385	558.0	191.9	362.8		313.9			272.9			1.15	1.64
		7.696					321							
Exp.	OLCAO 18	7.8367					280							
	1	7.808					290-309							
	3	7.744					317							
	37	7.734												

together with other available data previously reported, are listed in Table 1. Our calculated elastic constants of γ - CSi_2N_4 , γ - CGe_2N_4 , γ - SiGe_2N_4 , γ - GeSi_2N_4 , γ - SnGe_2N_4 and γ - Si_3N_4 agree well with other calculated results [14–21,36,37]. In these stable crystals, the calculated bulk modulus (B_H) and shear modulus (G) by the GGA–PBEsol method are in good agreement with the previous results [14–21,36,37]. The calculated Young's modulus, Poisson's ratio (ν), the ratio B/G and elastic anisotropy factor (A) of γ - CSi_2N_4 , γ - SiGe_2N_4 and γ - Si_3N_4 by the GGA–PBEsol method agree with the previous results [10,15,21].

Moreover, the ratio B/G is also a simple relationship, empirically linking the plastic properties of materials with their elastic moduli. The ratio B/G is roughly considered as a measurement to judge the brittleness [43]. A high B/G value is associated with ductility, whereas a low value corresponds to brittleness and the critical value is around 1.75, which separates ductile from brittle materials. The calculated B/G values are lesser than 1.75 by the GGA–PBEsol method for these stable crystals. The calculated B/G values for the stable group IVA ternary spinel nitrides suggest that they are brittle. The calculated B/G values, by both GGA–PBEsol and GGA–PBE methods for γ - CSi_2N_4 [21], are 1.04. For γ - Si_3N_4 , the calculated B/G values are 1.17, 1.14 and 1.15 [10,21]. It suggests that γ - CSi_2N_4 is more brittle than γ - Si_3N_4 . For other stable group IVA ternary spinel nitrides except γ - CSi_2N_4 , the calculated B/G values are larger than 1.17, but all calculated B/G results are smaller than 1.75. It suggests that other stable group IVA ternary spinel nitrides, except γ - CSi_2N_4 , are more ductile than γ - Si_3N_4 . Additionally, the brittleness and ductility can be distinguished by the Frantsevich rule [44], which suggests that the critical value of Poisson's ratio of materials is 1/3. For brittle materials such as ceramics, the Poisson's ratio is less than 1/3, whereas a higher value corresponds to ductile nature. The calculated Poisson's ratio (ν) for all stable group IVA ternary spinel nitrides is less than 1/3; hence, they can be classified as brittle materials [10,21]. Therefore, all stable group IVA ternary spinel nitrides are brittle materials. This conclusion agrees well with the result of estimation from the ratio B/G .

The elastic anisotropy of crystals is of great importance for both engineering science and crystal physics. Therefore, it is significant to evaluate the elastic anisotropy. The calculated anisotropic factor [21] is

$$A = \frac{(2C_{44} + C_{12})}{C_{11}} \quad (8)$$

The calculated anisotropic factor (A) for γ - CSi_2N_4 and γ - Si_3N_4 by the GGA–PBEsol method agrees with the previous results [10,21]. The results seem to indicate that our results for mechanical moduli of these crystals are reliable. For all stable group IVA ternary spinel nitrides, the calculated anisotropic factor is about 1.21 for γ - CSi_2N_4 and

1.65 for γ - Si_3N_4 . For an isotropic structure, we expect the anisotropic factor to be close to unity. The value of 1 represents a completely elastic isotropy, while values smaller or larger than 1 measure the degree of elastic anisotropy. This indicates that the isotropy increases from γ - Si_3N_4 to γ - CSi_2N_4 . This conclusion is consistent with the predicted result by Zhang et al. [21].

The calculated anisotropic factor is 0.95 for γ - CGe_2N_4 and 1.07 for γ - SiSn_2N_4 , suggesting that γ - CGe_2N_4 and γ - SiSn_2N_4 are bigger isotropic structures. The next value of anisotropic factor is 1.21 for γ - CSi_2N_4 . The values of anisotropic factor for γ - GeSi_2N_4 and γ - GeSn_2N_4 are 1.40 and 1.45, respectively, and the values of anisotropic factor for γ - SnSi_2N_4 and γ - SnGe_2N_4 are 1.73 and 1.68, respectively. These indicate that the anisotropy decreases from γ - Si_3N_4 to γ - GeSi_2N_4 and γ - GeSn_2N_4 to γ - CSi_2N_4 to γ - CGe_2N_4 γ - SiSn_2N_4 and the anisotropy increases from γ - Si_3N_4 to γ - SnSi_2N_4 and γ - SnGe_2N_4 .

The simplest way to illustrate the anisotropy of mechanical moduli is to plot them the three-dimensional space as a function of direction. Here, we plot the bulk modulus or Young's modulus at different directions using spherical coordinates. The directional dependence of bulk or Young's modulus can be evaluated using the following relationships. For orthorhombic crystal class, they are given as [45,46]

$$\frac{1}{B} = (S_{11} + S_{12} + S_{13})l_1^2 + (S_{12} + S_{22} + S_{23})l_2^2 + (S_{13} + S_{23} + S_{33})l_3^2 \quad (9)$$

$$\frac{1}{E} = S_{11}l_1^4 + 2S_{12}l_1^2l_2^2 + S_{22}l_2^4 + 2S_{23}l_2^2l_3^2 + S_{33}l_3^4 + 2S_{13}l_1^2l_3^2 + S_{44}l_2^2l_3^2 + S_{55}l_1^2l_3^2 + S_{66}l_1^2l_2^2 \quad (10)$$

For cubic crystal class, one can derive the corresponding relationships from Equations (9) and (10) for orthorhombic crystal class. In this work, they are written as

$$\frac{1}{B} = (S_{11} + 2S_{12})(\sin^2 \theta + \cos^2 \varphi) \quad (11)$$

$$\frac{1}{E} = S_{11}[\sin^4 \theta (\cos^4 \varphi + \sin^4 \varphi) + \cos^4 \theta] + (2S_{12} + S_{44}) \times (\sin^4 \theta \cos^2 \varphi \sin^2 \varphi + \sin^2 \theta \cos^2 \theta) \quad (12)$$

In the above equations, S_{ij} represents the compliance matrix, l_1 , l_2 and l_3 are the direction cosines, which are given as $l_1 = \sin \theta \cos \varphi$, $l_2 = \sin \theta \sin \varphi$ and $l_3 = \cos \theta$ under spherical coordinates. For cubic crystal structure, the mechanical anisotropy of them is approximated using Equations (11) and (12).

In Figure 2, we show the plotted graphs for the mechanical stable structures of group IVA ternary spinel nitrides. The surface in each graph represents the magnitude of bulk or Young's modulus along different orientations. From the graphs, we can clearly see that the bulk modulus

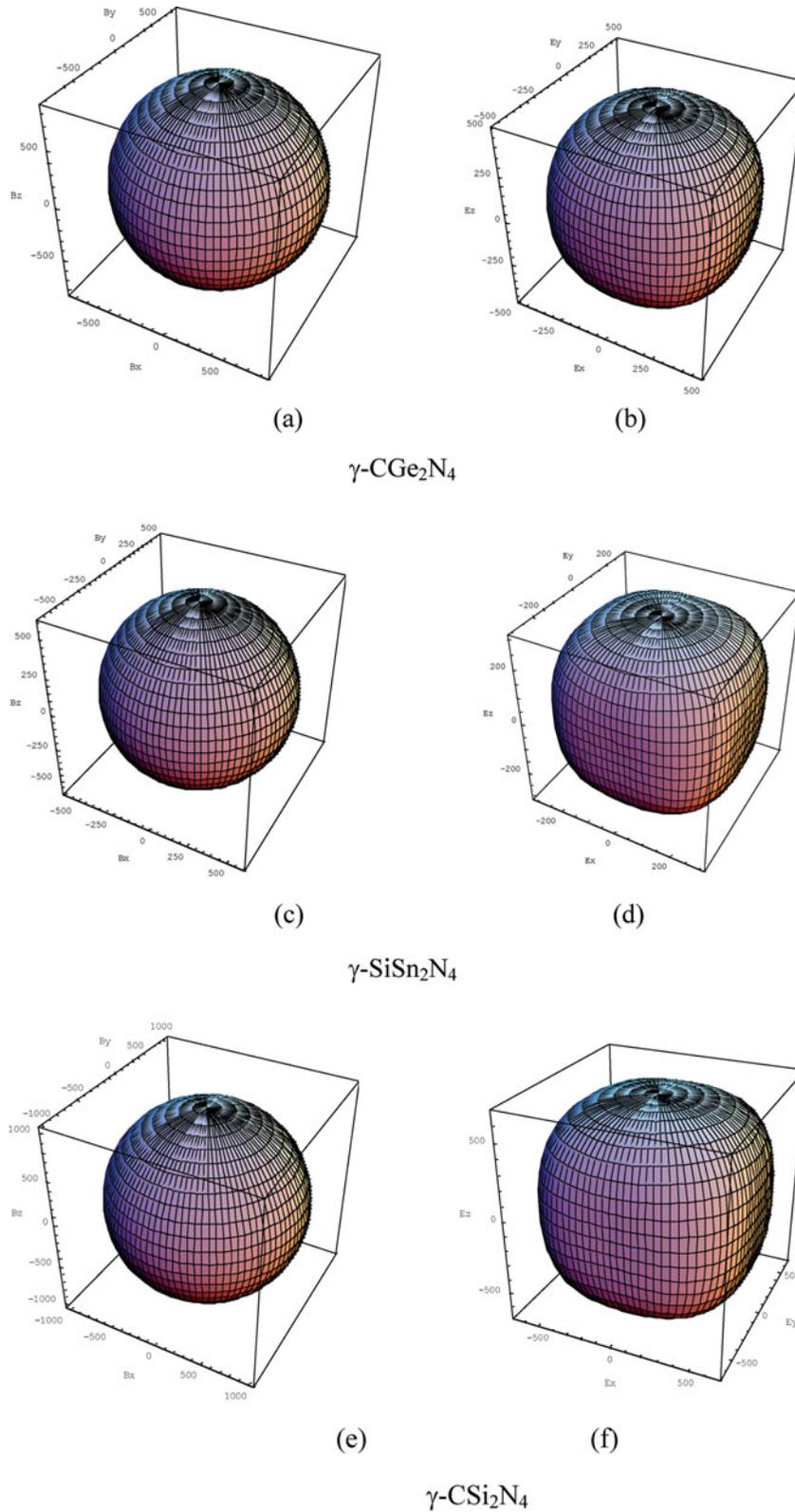
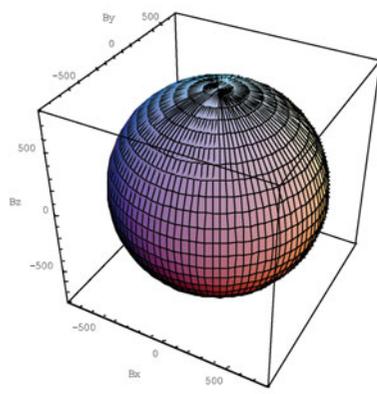
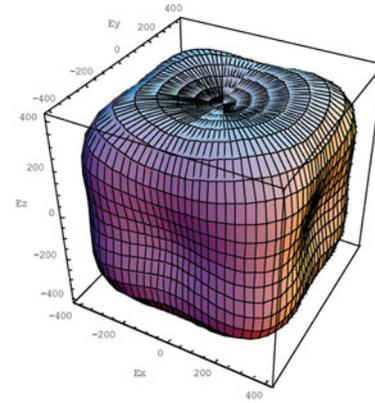


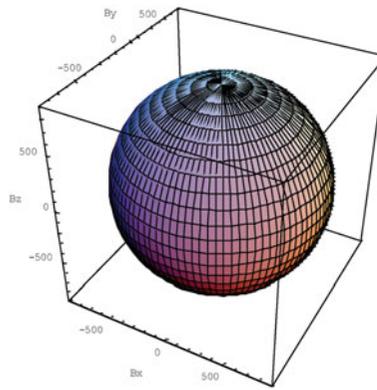
Figure 2. The surface constructions of bulk modulus (B) and Young's modulus (E) for $\gamma\text{-CGe}_2\text{N}_4$ [(a) and (b)]; $\gamma\text{-SiSn}_2\text{N}_4$ [(c) and (d)]; $\gamma\text{-CSi}_2\text{N}_4$ [(e) and (f)]; $\gamma\text{-SiGe}_2\text{N}_4$ [(g) and (h)]; $\gamma\text{-GeSi}_2\text{N}_4$ [(i) and (j)]; $\gamma\text{-GeSn}_2\text{N}_4$ [(k) and (l)]; $\gamma\text{-Si}_3\text{N}_4$ [(m) and (n)]; $\gamma\text{-SnGe}_2\text{N}_4$ [(o) and (p)]; and $\gamma\text{-SnSi}_2\text{N}_4$ [(q) and (r)]. The magnitude of bulk or Young's modulus in different directions is represented by the contour. For all graphs, the units are in gigapascal. All graphs are plotted using MATHEMATICAL 5.0 software in spherical coordinates, and one may obtain different views of these graphs by setting different box ratios and view points.



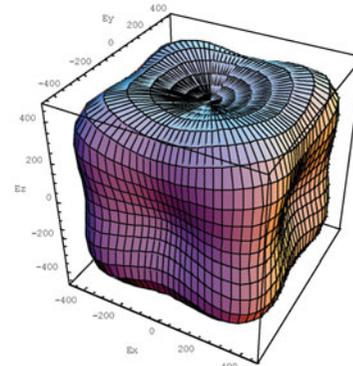
(g)



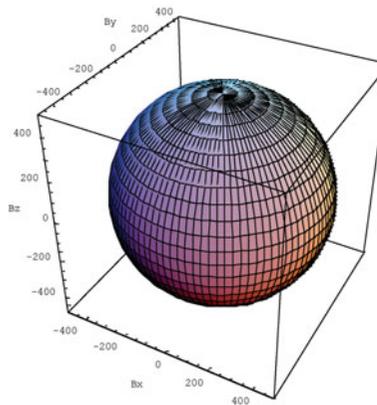
(h)

 $\gamma\text{-SiGe}_2\text{N}_4$ 

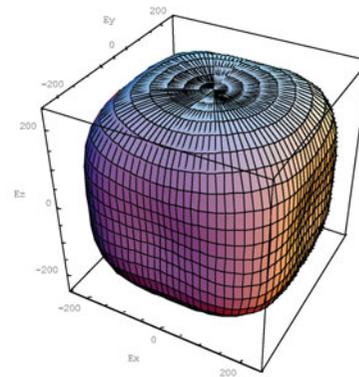
(i)



(j)

 $\gamma\text{-GeSi}_2\text{N}_4$ 

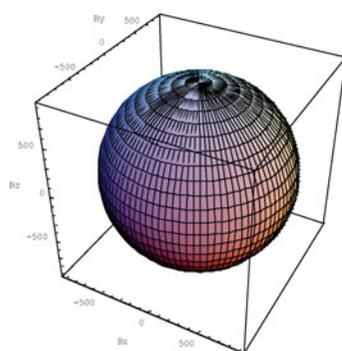
(k)



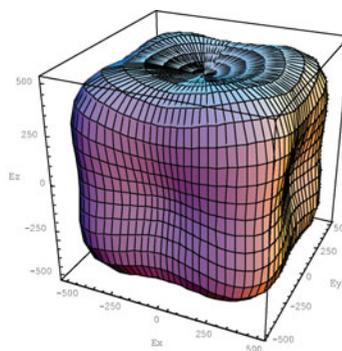
(l)

 $\gamma\text{-GeSn}_2\text{N}_4$

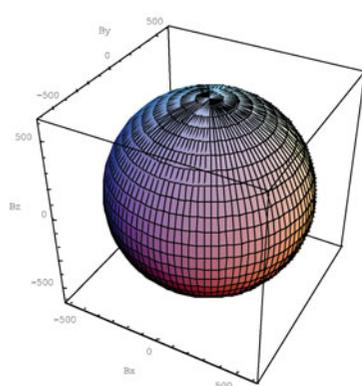
Figure 2. Continued.



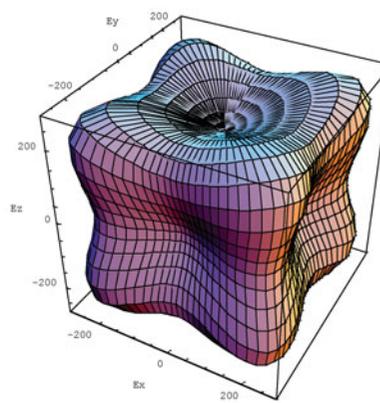
(m)



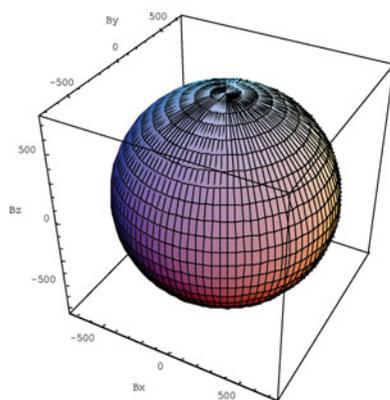
(n)

 $\gamma\text{-Si}_3\text{N}_4$ 

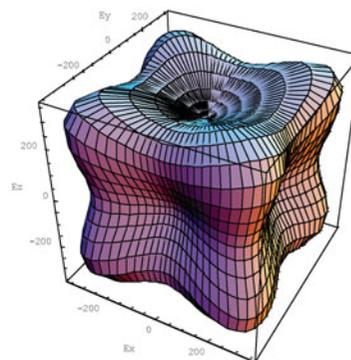
(o)



(p)

 $\gamma\text{-SnGe}_2\text{N}_4$ 

(q)



(r)

 $\gamma\text{-SnSi}_2\text{N}_4$

Figure 2. Continued.

shows strong isotropy and the Young's modulus shows some anisotropy at different orientations. We can clearly see that the Young's modulus of each of γ -CSi₂N₄, γ -SiSn₂N₄, γ -CSi₂N₄ and γ -GeSn₂N₄ shows slight anisotropy and the Young's modulus of γ -SiGe₂N₄ shows some anisotropy for different orientations. The Young's moduli of γ -GeSi₂N₄, γ -Si₃N₄, γ -SnGe₂N₄ and γ -SnSi₂N₄ show significant anisotropy for different orientations. The calculated elastic anisotropic factor (A) is in agreement with the Young's modulus graphs of γ -CGe₂N₄ [Figure 2(b)], γ -SiSn₂N₄ [Figure 2(d)], γ -CSi₂N₄ [Figure 2(f)], γ -SiGe₂N₄ [Figure 2(h)], γ -GeSi₂N₄ [Figure 2(j)], γ -GeSn₂N₄ [Figure 2(l)], γ -Si₃N₄ [Figure 2(n)], γ -SnGe₂N₄ [Figure 2(p)] and γ -SnSi₂N₄ [Figure 2(r)] for these stable group IVA ternary spinel nitrides and γ -Si₃N₄.

3.2. Intrinsic hardness

Considering that the dependence of hardness on bulk or shear modulus is not monotonic, a quantitative estimate is essential. The hardness of γ -Si₃N₄ and γ -CSi₂N₄ is evaluated using the microscopic hardness model [21,47], and the detailed strategy for computation can be referred to in the previous works [10,21,47–52], in which the theoretical hardness of typical covalent and polar covalent crystals was calculated with high accuracy. γ -CSi₂N₄ should be a potentially superhard material [21]. Therefore, we calculated the hardness of stable group IVA ternary spinel nitrides using this method. In stable group IVA ternary spinel nitrides (γ -AB₂N₄), there are two types of chemical bonds, i.e. A–N and B–N. Therefore, these stable group IVA ternary spinel nitrides are complex crystals according to the microscopic model of hardness. The hardness calculation equation can be written as follows:

$$H_V = \left[(H_V^{A-N})^{n_1} (H_V^{B-N})^{n_2} \right]^{\frac{1}{n_1+n_2}} \quad (13)$$

where H_V^{A-N} and H_V^{B-N} are the hardness of the hypothetical binary compounds made of pure X–N and Y–N bonds, respectively. They can be calculated as

$$H_V^{A(B)-N} = 350(N_e^{A(B)-N})^{2/3} e^{-1.191 f_i^{A(B)-N}} / (d^{A(B)-N})^{2.5} \quad (14)$$

where $N_e^{A(B)-N}$ is the valence electron density of the hypothetical compounds composed of A–N and B–N bonds. $f_i^{A(B)-N}$ is the Phillips ionicity of A–N and B–N bonds. $d^{A(B)-N}$ is the length of the A–N and B–N bonds. $N_e^{A(B)-N}$ can be calculated by

$$N_e^{A(B)-N} = (n_e^{A(B)-N}) / v_b^{A(B)-N} \quad (15)$$

In the above equation, $n_e^{A(B)-N}$ is the total number of valence electrons per A (B)–N bond, and $v_b^{A(B)-N}$ denotes the

bond volume. The two parameters $n_e^{A(B)-N}$ and $v_b^{A(B)-N}$ are calculated by

$$n_e^{A(B)-N} = [(Z_A^{A-N}) / N_{CA} + (Z_B^{B-N}) / N_{CB}] \quad (16)$$

$$v_b^{A(B)-N} = (d^{A(B)-N})^3 / \sum_{A(B)-N} [(d^{A(B)-N})^3 N_b^{A(B)-N}] \quad (17)$$

N_{CA} and $Z_A^{A(B)-N}$ are the coordinate number and the number of valence electrons of atoms A and B, respectively.

The $f_i^{A(B)-N}$ can be calculated as

$$f_i^{A(B)-N} = (f_h^{A(B)-N})^{0.735} \\ = [1 - \exp(-|P_c - P^{A(B)-N}| / P^{A(B)-N})]^{0.735} \quad (18)$$

where $f_i^{A(B)-N}$ is the generalized ionicity scale of the A–N and B–N bonds. $P^{A(B)-N}$ is the Mulliken overlap population of the A–N and B–N bonds that can be derived from first-principles calculations. P_c is the overlap population of a pure covalent bond in a pure covalent crystal, containing the same type of chemical bond. In the cubic spinel structures of A(t)B(o)₂N₄, P_c is 0.91 for the A(t)–N bond and 0.57 for the B(o)–N bond [19,52,53].

The calculated bond parameters and Vickers hardness are listed in Table 2. For γ -Si₃N₄, the calculated Vickers hardness is 32.45 GPa by the GGA–PBESol method. This value of γ -Si₃N₄ is in good agreement with its experimental values (30 and 35 GPa) [53,54] and other estimated values (35.6, 33.3 and 30.9 GPa) [10,22,47].

The calculated Vickers hardness of γ -CSi₂N₄ is 43.68 GPa by the GGA–PBESol method. Our calculated value of γ -CSi₂N₄ is remarkably smaller than the calculated value (52.07 GPa) by Zhang et al. [21]. We can find that f_i^{Si-N} of γ -CSi₂N₄ calculated by the GGA–PBESol method is larger than the Zhang's calculated value by the GGA–PBE method, indicating that ionicity of Si–N bonds for γ -CSi₂N₄ may be underestimated. For a superhard compound, the Vickers hardness is assumed to be greater than 40 GPa. According to these calculated data, γ -CSi₂N₄ is also predicted to be a superhard material.

Using the GGA–PBESol function, the hardness for stable group IVA ternary spinel nitrides is calculated. We can clearly see that the hardness of the stable group IVA ternary spinel nitrides is smaller than γ -Si₃N₄ except γ -CSi₂N₄. The hardness of γ -GeSi₂N₄ is 29.57 GPa, which is in agreement with the calculated value (28 GPa) [20]. The hardness of γ -Si₃N₄ is 32.45 GPa which is slightly smaller than the experimental values (30 and 35 GPa) [53,54]. For γ -Si₃N₄, the calculated value of hardness is 32.45 GPa, which is in agreement with the other calculated values (35.6, 33.3 and 30.9 GPa) [10,22,47]. The hardness of γ -CGe₂N₄, γ -SiGe₂N₄ and γ -SnSi₂N₄ is 25.17, 20.30 and 21.54 GPa,

Table 2. Bond parameters, bond length (Å), cell volume (Å³) and calculated Vickers hardness (GPa) of group IVA ternary spinel nitrides.

Crystal		Function	Bond	Bond length	V	N_e	P	P_c	f_i	H_v^μ	H_v	$H_v(G)$	H_{Exp}
γ -CSi ₂ N ₄	This work	GGA-PBEsol	C(t)-N	1.57058	397.29	1.070	0.74	0.91	0.312	87.68	43.68	47.76	
			Si(o)-N	1.85007	397.29	0.558	0.45	0.57	0.344	34.63			
γ -CGe ₂ N ₄	Zhang et al. 21	GGA-PBE	C(t)-N	1.564	384.82	1.190	0.78	0.91	0.252	95.17	52.07		
			Si(o)-N	1.825	384.82	0.578	0.51	0.57	0.199	42.59			
γ -SiGe ₂ N ₄	This work	GGA-PBEsol	C(t)-N	1.58593	460.78	1.071	0.76	0.91	0.283	82.59	25.17	31.19	
			Ge(o)-N	1.98203	460.78	0.468	0.30	0.57	0.681	16.94			
γ -SiGe ₂ N ₄	This work	GGA-PBEsol	Si(t)-N	1.80023	530.54	0.691	0.74	0.91	0.312	43.38	20.30	29.69	
			Ge(o)-N	1.99679	530.49	0.432	0.30	0.57	0.681	15.76			
γ -SiSn ₂ N ₄	Dong et al. 20	VASP-LDA	Si(t)-N	1.7837									
			Ge(o)-N	1.9776									
γ -SiSn ₂ N ₄	Bouhemadou et al. 15	GGA-PBE	Si(t)-N	1.772	498.39		0.79						
			Ge(o)-N	1.950	498.39		0.36						
γ -SiSn ₂ N ₄	This work	GGA-PBEsol	Si(t)-N	1.83794	673.18	0.677	0.71	0.91	0.356	38.55	16.34	20.81	
			Sn(o)-N	2.22595	673.18	0.325	0.38	0.57	0.504	12.27			
γ -GeSi ₂ N ₄	This work	GGA-PBEsol	Ge(t)-N	1.87612	496.34	0.590	0.55	0.91	0.580	25.61	29.57	33.16	
			Si(o)-N	1.89055	496.34	0.492	0.47	0.57	0.300	31.03			
γ -GeSi ₂ N ₄	Dong et al. 20	VASP-LDA	Ge(t)-N	1.8523							28		
			Si(o)-N	1.8768									
γ -GeSn ₂ N ₄	This work	GGA-PBEsol	Ge(t)-N	1.96342	718.49	0.538	0.53	0.91	0.610	20.72	14.59	17.13	
			Sn(o)-N	2.22521	718.49	0.315	0.41	0.57	0.440	12.98			
γ -SnSi ₂ N ₄	This work	GGA-PBEsol	Sn(t)-N	2.05713	564.49	0.510	0.56	0.91	0.570	18.67	21.54	23.38	
			Si(o)-N	2.05713	564.49	0.435	0.46	0.57	0.320	22.60			
γ -SnGe ₂ N ₄	This work	GGA-PBEsol	Sn(t)-N	2.09432	637.89	0.420	0.67	0.91	0.470	18.98	14.42	18.14	
			Ge(o)-N	2.027771	637.89	0.394	0.27	0.57	0.750	13.16			
γ -Si ₃ N ₄	This work	GGA-PBEsol	Si(t)-N	1.7774	465.80	0.71	0.71	0.91	0.3562	47.74	32.45	37.39	30[53], 35[54]
			Si(o)-N	1.8823	465.80	0.51	0.44	0.57	0.3671	24.61			
γ -Si ₃ N ₄	He et al. 10	GGA-PBE	Si(t)-N	1.750	445.68	0.740			0.4	43.88	33.3		
			Si(o)-N	1.856	445.68	0.529			0.4	30.34			
γ -Si ₃ N ₄	Guo et al. 47	GGA-PBE	Si(t)-N	1.75		0.74			0.341	47.1	35.6		
			Si(o)-N	1.856		0.529			0.344	32.4			
γ -Si ₃ N ₄	Gao et al. 22	GGA-PBE	Si(t)-N	1.75	447.697	0.87			0.27	57.9	30.9		
			Si(o)-N	1.86	447.697	0.49			0.52	25.1			

respectively. The hardness of γ -SiSn₂N₄ is 16.34 GPa, which is slightly more than the hardness value (14.59 GPa) of γ -GeSn₂N₄. The hardness (14.59 GPa) of γ -GeSn₂N₄ is close to the hardness (14.42 GPa) of γ -SnGe₂N₄.

In Gao's method, one can calculate the hardness for each chemical bond type. From the results listed in Table 2, we can conclude that the high hardness of γ -CSi₂N₄ is mainly attributed to C(t)-N and Si(o)-N bonds. In γ -CSi₂N₄, C(t)-N bond is stronger than Si(o)-N bond. In the stable group IVA ternary spinel nitrides (γ -AB₂N₄), if atomic number A is smaller than atomic number B, we can clearly see the A-N bond is stronger than B-N bond.

In several previous works, Teter [55] and Brazhkin et al. [56] have clearly noted that the bulk modulus has been suggested as a possible indicator of the hardness values. The correlation is very poor. However, the shear modulus is a much better measure to correlate with predicted hardness [55,56]. Recently, Jiang et al. [57] also proposed some empirical relationships between mechanical moduli

(bulk modulus (B), shear modulus (G) and Young's modulus (E)) and Vickers hardness. The results clearly indicate that hardness is highly correlated to shear modulus (G), but the correlation of hardness to bulk or Young's modulus is poor. The following relationship is obtained for shear modulus (G) and Vickers hardness:

$$G = 6.78H_V \quad (19)$$

The estimated microhardness H_V using Equation (19) is also listed in Table 2. We find that the calculated hardness of the stable group IVA ternary spinel nitrides using Equation (19) is larger than the calculated results by Gao's method. For γ -Si₃N₄, the calculated value is 37.39 GPa using Equation (19), which is significantly larger than the experimental values (30 and 35 GPa) [53,54]. The calculated hardness of the stable group IVA ternary spinel nitrides by Gao's and Jiang's methods indicates that the group's ternary spinel nitrides, except γ -CSi₂N₄, are not superhard materials.

Table 3. Calculated Debye temperature (Θ_D , K), the calculated theoretical density (ρ , g/cm³), and the longitudinal, shear and average sound wave velocities (v_l , v_t and v_m ; m/s).

Species	Function	ρ	v_l	v_t	v_m	Θ_D
γ -CSi ₂ N ₄	GGA-PBEsol	4.153	13590.21	8829.93	9683.89	1501.14
γ -CGe ₂ N ₄	GGA-PBEsol	6.147	9450.95	5865.54	6466.36	953.79
γ -SiGe ₂ N ₄	GGA-PBEsol	5.741	9569.64	5921.59	6530.22	919.13
	GGA-PBE 15	6.32	9604	6005	7584	1090
	GGA-PBE 16	6.347	3501	1962	2559	356
γ -SiSn ₂ N ₄	GGA-PBEsol	6.344	7765.73	4715.48	5210.29	677.48
γ -GeSi ₂ N ₄	GGA-PBEsol	4.946	10901.98	6742.63	7436.04	1070.36
γ -GeSn ₂ N ₄	GGA-PBEsol	6.767	6783.58	4142.43	4574.49	582.01
γ -SnSi ₂ N ₄	GGA-PBEsol	5.432	9128.42	5402.62	5984.44	825.08
γ -SnGe ₂ N ₄	GGA-PBEsol	6.662	7390.88	4297.23	4767.77	631.11
γ -Si ₃ N ₄	GGA-PBEsol	4.001	12672.72	8016.17	8818.85	1296.44
	Other calc. 36	4.180				1050–1100
	Expt. 37					1150

3.3. Debye temperature

Mechanical properties can be related to a thermodynamic parameter, such as Debye temperature, specific heat, thermal expansion and melting point. [58] We have calculated the Debye temperature (Θ_D) for the stable group IVA ternary spinel nitrides. By the relation between the mean sound velocity (v_m) and Debye temperature (Θ_D), we have [59,60]

$$\Theta_D = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{1/3} v_m \quad (20)$$

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_l^3} + \frac{1}{v_t^3} \right) \right]^{-1/3} \quad (21)$$

$$v_l = \sqrt{\frac{B + \left(\frac{4}{3}\right)G}{\rho}} \quad (22)$$

$$v_t = \sqrt{\frac{G}{\rho}} \quad (23)$$

where Θ_D is the Debye temperature, h is the Planck's constant, k_B is the Boltzmann constant, N_A is the Avagadro's constant, n is the number of atoms per formula, M is the molecular weight, v_l and v_t are the longitudinal and transverse velocities, respectively; ρ is the theoretical density of the compound, and B and G are bulk modulus and shear modulus, respectively.

In this paper, the Debye temperature of the stable group IVA ternary spinel nitrides is calculated by the GGA-PBEsol method, as per Equation (20) and is shown in Table 3. The Debye temperature (Θ_D) for γ -Si₃N₄ by the GGA-PBEsol method is slightly larger than the other calculated result [36] and experimental value [37]. The Debye temperature (Θ_D) of γ -SiGe₂N₄ is 919.13 K, which is slightly smaller than the value calculated by Bouhemadou

et al. (1090 K) [15]. However, we can see that the Debye temperature (Θ_D) of γ -SiGe₂N₄ is 356 K by Moakafi et al. [16]. This value is significantly smaller than the value calculated by Bouhemadou et al. [15]. As can be seen from Table 3, the computed sound velocities of γ -CSi₂N₄ and γ -CSi₂N₄ are very large, especially for longitudinal sound velocity, because γ -CSi₂N₄ has the largest mechanical moduli. Therefore, the calculated Debye temperature and the average sound velocity of γ -CSi₂N₄ are larger than the other stable structures. The Debye temperatures for most crystals are around 200–400 K. The calculated Debye temperature of γ -CSi₂N₄ is 1501.14 K, indicating that γ -CSi₂N₄ is the hardest of these stable group IVA ternary spinel nitrides. For γ -GeSi₂N₄, the calculated Debye temperature is about 1070.36 K, suggesting that γ -GeSi₂N₄ is just as hard as γ -Si₃N₄. This conclusion supports the calculated hardness of γ -GeSi₂N₄ and γ -Si₃N₄. In Table 3, the other stable structures have larger Debye temperature, suggesting that these materials have higher hardness.

4. Conclusions

In summary, we study theoretically the elastic properties, intrinsic hardness and Debye temperature of ternary cubic spinel nitrides. The new cubic spinel structures are designed by the substitutional method. The results indicate that eight ternary cubic spinel structures – γ -CSi₂N₄, γ -CGe₂N₄, γ -SiGe₂N₄, γ -SiSn₂N₄, γ -GeSi₂N₄, γ -SiSn₂N₄, γ -SnSi₂N₄ and γ -SnGe₂N₄ – are mechanically stable. γ -CSn₂N₄, γ -SiC₂N₄, γ -GeC₂N₄ and γ -SnC₂N₄ are not mechanically stable. The elastic constants of the eight stable ternary nitrides are calculated using the stress-strain method in the CASTEP code. We found that these spinel ternary nitrides have relatively larger elastic constants. Derived elastic constants, such as bulk modulus, shear modulus, Young's modulus, Poisson coefficient and brittle/ductile behaviour, are estimated with the polycrystalline approach

using Voigt–Reuss–Hill theories. The calculated B/G values and the Poisson's ratio for γ - CSi_2N_4 suggest that γ - CSi_2N_4 is the most brittle of these eight crystals. The calculated anisotropic factors for the stable ternary cubic spinel structures show that γ - CGe_2N_4 , γ - SiSn_2N_4 and γ - CSi_2N_4 have higher isotropy, and γ - SnSi_2N_4 and γ - SnGe_2N_4 have higher anisotropy than γ - Si_3N_4 . The intrinsic hardness and the Debye temperature are predicted by the semi-empirical theory. In terms of the results, γ - CSi_2N_4 should be viewed as a superhard material, with some peculiar mechanical properties. γ - CSi_2N_4 and γ - GeSi_2N_4 have large Debye temperatures. It is expected that greater attention will be paid on synthesizing these materials in the future.

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