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Structural, elastic and thermodynamic properties of the tetragonal structure of germanium carbonitride

Mengjiang Xing *, Binhua Li, Zhengtao Yu, Qi Chen

Faculty of Information Engineering & Automation, Kunming University of Science and Technology, Kunming 650051, PR China

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ABSTRACT

The structural, mechanical, electronic and thermodynamic properties of the tetragonal structure germanium carbonitride (*t*-GeCN) were first investigated using the density function theory with the ultrasoft psedopotential scheme in the frame of the generalized gradient approximation and the local density approximation. The elastic constants have confirmed that the *t*-GeCN is mechanically stable and phonon spectra have confirmed that the *t*-GeCN is dynamically stable. The anisotropy studies show that *t*-GeCN exhibits a larger anisotropy in its Poisson's ratio, Young's modulus, shear modulus, sound velocities and universal elastic anisotropy index. Electronic structure study shows that *t*-GeCN is an indirect semiconductor with band gap of 0.628 eV. The thermodynamic properties of *t*-GeCN, including Debye temperature, heat capacity, Grüneisen parameter and thermal expansion coefficient are investigated utilizing the quasi-harmonic Debye model.

1. Introduction

Many of C–N compounds have been the subject of previous extensive investigations, both experimentally and theoretically [1–7]. Carbon nitrides have attracted much attention for the belief because of its hardness may greater than diamond. Recently, carbon nitrides attracted attention due to their potential applications in photocatalysis [8], photodegradation [9] and photoelectrochemical anticorrosion [10] technology. Recently, group-14 elements carbonitride attracted much attention in materials science, especially Si–C–N. Ternary Si–C–N compounds represent a series of novel functional materials that have attracted considerable research interest because of their excellent chemical and physical properties, which include high hardness, good creep properties, thermal shock resistance, and excellent oxidation resistance over a broad temperature range. Thus, these compounds may be applied in cutting tools, high-temperature materials, and so on. The structural and mechanical properties of cubic CSi_2N_4 are studied by Zhang et al. [11] via density-functional theory. They found that the C–N bonds have stronger bonding in CSi_2N_4 and the lower ionic character induce higher hardness as well as bulk modulus in the incorporation of C. In addition, CSi_2N_4 is a potential superhard material with Vickers hardness of 52 GPa. First principles calculations are used to investigated monoclinic (C2/m phase) and orthorhombic (Cmmm phase) structures of SiC_2N_4 under pressure on the electronic, elastic and thermodynamic properties by Miao et al. [12]. C2/m phase and Cmmm phase of SiC_2N_4 are both satisfy the mechanical stability criteria within 60 GPa. The band structure show that C2/m phase is an indirect-gap semiconductor, while Cmmm phase is a direct-gap semiconductor. The degree of the anisotropy decreases fast in the C2/m phase with increasing pressure, but it remains a constant in the Cmmm phase. Du et al. [13] have investigated the phase transition and stability of the Si_2CN_4 compounds by first-principles calculations. They found that the transition pressures of α- and β- to γ-Si_2CN_4 are 29.9 GPa and 27.5 GPa predicted by thermodynamic method, respectively. Ab initio calculations for crystal structure and hardness of two ternary compounds, SiC_2N_4 and Si_2CN_4 were studied by Wang et al. [14]. Hardness calculations suggest that Cmmm phase SiC_2N_4, $P2_1/m$ and C2/m phases Si_2CN_4 possess superhardness of 58.7, 51.7 and 51.6 GPa, respectively. Otherwise, the hardness calculations by Riedel et al. [4] of Pn3m-SiC_2N_4 (16.9 GPa) and Aba2-Si_2CN_4 (28.2 GPa) indicted that the new phases of silicon carbonitride are not superhard materials. Recently, Cui et al. [15] performed an extensive structural search of Si–C–N compounds using crystal structure analysis by particle swarm optimization (CALYPSO) algorithm [16]. They reveal that the new discovered tetragonal SiCN (*t*-SiCN) was energetically stable than cubic SiCN [17], and two high-pressure phases of orthorhombic SiCN (*o*-SiCN) and hexagonal SiCN (*h*-SiCN) were also predicted. Transformations from *t*-SiCN to *o*-SiCN and *h*-SiCN occurred at 21.6 and 21.9 GPa,

* Corresponding author.
E-mail address: mjxing168668@163.com (M. Xing).

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respectively. The hardness of *t*-SiCN, *o*-SiCN and *h*-SiCN were calculated to be 41.5, 30.0, and 30.2 GPa [15], respectively. *t*-SiCN is an semiconductor with a band gap of 0.89 eV. But for *h*- and *o*-SiCN, valence band portions cross the Fermi level, which indicates that they have hole-type conductivity.

The *t*-GeCN, whose structure is based on *t*-SiCN [17], with Ge substituting Si. The structural, mechanical, and electronic properties of *t*-GeCN have not yet been studied. In this paper, a new hard tetragonal structure of germanium carbonitride (*t*-GeCN) with tetragonal $P4_2nm$ symmetry are reported.

2. Calculation methods

The self-consistent calculations were performed using density function theory (DFT) [18,19] within the local density approximation (LDA) [20,21] and the generalized gradient approximation (GGA) parameterized by Perdew, Burke and Ernzerrof (PBE) [22] exchange correlation as implemented in the Cambridge Serial Total Energy Package (CASTEP) [23]. For *t*-SiCN and *t*-GeCN, a plane-wave energy cutoff energy of 400 eV and 480 eV is used, where the $2s^22p^2$, $3s^23p^3$, $4s^24p^2$ and $4s^24p^2$ are treated as valence electrons for C, N, Si and Ge atoms, respectively. The cutoff energy and the appropriate *k*-point in the Brillouin zone obtained according to the Monkhorst-Pack method [24] are enough to ensure a good precision in calculation. Integrations in the Brillouin zone are performed using special *k*-points generated with $9 \times 9 \times 6$ and $8 \times 8 \times 5$ mesh parameter grid for *t*-SiCN and *t*-GeCN, respectively. These parameters have been tested to be sufficient for the convergence. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) [25] minimization scheme was used in geometry optimization. The geometry relaxation was carried out under the condition that all forces on atoms were converged to less than 1 meV/Å.

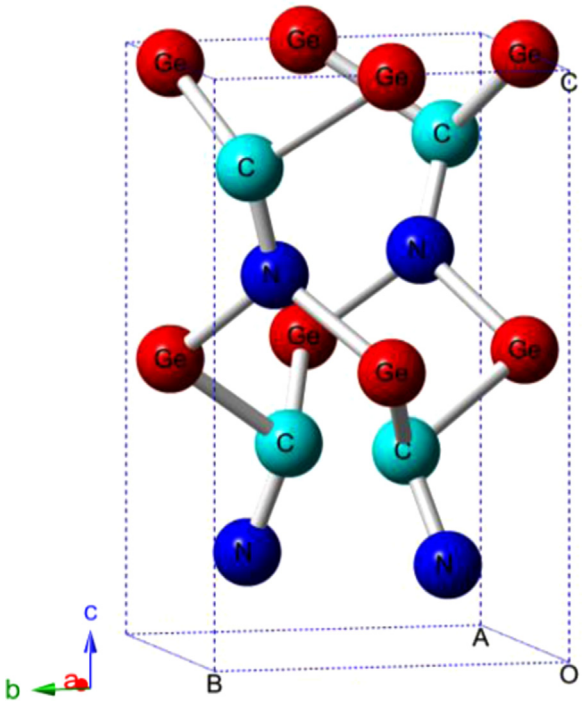

Fig. 1. The crystal structure of *t*-GeCN.

Table 1
Calculated lattice parameters (in Å) and density (in g/cm^3) of *t*-GeCN and *t*-SiCN.

		a	*c*	*V*	*ρ*
t-GeCN	GGA	4.323	7.037	131.490	4.981
	LDA	4.205	6.892	121.836	5.376
t-SiCN	GGA	4.125	6.827	116.170	3.093
	LDA	4.044	6.757	110.514	3.252
	GGA[a]	4.069	6.788	112.387	3.200
	GGA[b]	4.108	6.836	115.362	

[a] Ref [15].
[b] Ref [45].

3. Results and discussion

3.1. Structural properties

The crystal structure of *t*-GeCN is shown in Fig. 1. From Fig. 1, *t*-GeCN have 4 formula units in their conventional cell. *t*-GeCN has optimized lattice parameters of $a=b=4.323$ Å, $c=7.037$ Å, with atomic positions of Ge at (0, 0.5, −0.0037), C at (0.3676, 0.3676, 0.3401), and N at (0.2737, 0.2737, 0.1516), respectively. Table 1 shows the lattice parameters and density of *t*-GeCN and *t*-SiCN. From Table 1, we can found that the calculated lattice parameters of *t*-SiCN are in excellent agreement with previous results, indicating our calculations are valid and believable. The lattice parameters of *t*-GeCN are slightly larger than that of *t*-SiCN, because of the atomic radius of germanium is slightly larger than that of silicon.

3.2. Elastic properties

In the stress–strain method used to calculate the elastic constants, the stress is calculated as a function of the strain, with the internal coordinates optimized under each strain condition. The elastic constants of a materials describe its response to an applied stress or, conversely, the stress required to maintain a given deformation. By employing Voigt–Reuss–Hill approximation [26–28], the bulk modulus *B*, shear modulus *G*, Young's modulus *E*, and Poisson's ratio *v* were calculated. The mechanical stability criteria for tetragonal are given by [29,30]:

$$C_{ii} > 0,\ i = 1, 3, 4, 6, \tag{1}$$

$$(C_{11} - C_{12}) > 0, \tag{2}$$

$$(C_{11} + C_{33} - 2C_{13}) > 0, \tag{3}$$

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

For *t*-GeCN, according to the Voigt approximation, we obtain the isotropic bulk modulus B_V and shear modulus G_V can be

Table 2
Calculated elastic constants (in GPa) and elastic modulus (in GPa) of *t*-GeCN.

		C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}	*B*	*G*	*B*/*G*	*E*	*v*
t-GeCN	GGA	263	492	151	167	143	94	183	129	1.42	313	0.21
t-SiCN	GGA	335	629	208	227	173	107	226	175	1.29	417	0.19
	GGA[a]	341	664	206	230	184	127	241				
	GGA[b]	330	636	193	222	184	117	232	165	1.41	400	0.21

[a] Ref [15].
[b] Ref [45].