First-principle investigation on the thermodynamics of X_2N_2O (X = C, Si, Ge) compounds*

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The structures under different pressures, elastic properties, electronic structures and lattice vibrations of the X_2N_2O (X = C, Si, Ge) compounds are investigated by using the first-principle method. Based on the phonon density of state, the thermodynamic properties of the present compounds are studied under different pressures and at different temperatures. The structural parameters including the bond lengths and bond angles are in agreement with available experimental measurements and theoretical calculations. We employ the elastic theory to calculate the nine independent elastic constants (C_{ij}) and the derived elastic moduli (B, G, E, v). Results indicate that these X_2N_2O (X = C, Si, Ge) compounds are mechanically stable and show the brittle behaviors. The electronic properties of the present compounds are analyzed by using the band structure and density of states. The phonon dispersion calculations imply that the present compounds are dynamically stable. Based on the quasi-harmonic approximation, the calculations of the specific heat indicate that the temperature in a range of 0 K–1500 K and pressure in a range of 0 GPa–40 GPa have a large effect on the thermal quantities of Ge_2N_2O, compared with on those of the C_2N_2O and Si_2N_2O compounds.

Keywords: ceramics, *ab initio* calculations, crystal structure, elastic properties, thermodynamic properties

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1. Introduction

Silicon oxynitride (Si_2N_2O) and germanium oxynitride (Ge_2N_2O) are widely used as the high-temperature structural materials and viewed as the promising functional materials.[1–3] Much attention has been paid to the superior physical and chemical properties, such as good thermal shock resistance, high mechanical strength and excellent oxidation resistance.[4–7] The hypothetical carbon oxynitride C_2N_2O has the same crystal structure as the Si_2N_2O and Ge_2N_2O compounds.[8,9] It was theoretically predicted that the mechanical properties of C_2N_2O are superior to Si_2N_2O and Ge_2N_2O.[3,10]

Most of theoretical and experimental reports focus on structural and mechanical properties of X_2N_2O (X = C, Si, Ge). For example, the electronic structures and chemical bondings of these compounds were studied by the orthogonalized linear combination of atomic orbitals (OLCAO) method[11] and the full-potential linear Muffin-tin orbitals (LMTO) method.[10] The results showed that C_2N_2O has stronger covalent bonding than Si_2N_2O and Ge_2N_2O. Ding[3] and Ding *et al.*[12] studied the hardness values of the X_2N_2O (X = C, Si, Ge) and found that the C_2N_2O may be the potential superhard material, whereas the hardness of Ge_2N_2O is the smallest in these three compounds. On the experimental side, extensive studies focused on the preparation and improving mechanical properties of Si_2N_2O ceramic.[4,7,13] Wu and Li[1,14] indicated the relationship between purity and Vickers hardness of Si_2N_2O with the final sintering temperature. More recently they successfully fabricated a nano-grained Si_2N_2O ceramic without second phases. Srinivasa and Cariz,[5] and Srinivasa *et al.*[15] determined the lattice parameters, bond properties of Si_2N_2O and Ge_2N_2O at pressure P = 2.3 and 2.54 GPa by the time-of-flight neutron diffraction. Haines and Santoro[16] found the complete amorphization of Si_2N_2O occurs above P = 41 GPa by the x-ray power diffraction and the infrared absorption. Although the electronic properties and thermodynamic properties of some ceramics were reported,[17–22] as a widely used refractory, however, few experimental and theoretical data about the thermodynamic properties of X_2N_2O (X = C, Si, Ge) compounds have been reported so far.

In the present work, we systematically investigate the structures under different pressures, elastic properties, and electronic structure of X_2N_2O (X = C, Si, Ge) using the first-principle calculations. The thermodynamic properties are calculated via quasi-harmonic approximations under different pressures (0 GPa–40 GPa) and at various temperatures (0 K–1500 K). The lattice parameters, average bond lengths and bond angles are presented in detail. The results of elastic constants and lattice vibration show that these compounds are mechanically and dynamically stable and the derived mechanical moduli are further studied. The band structures of these

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compounds are calculated and the contributions of different orbitals to density of state (DOS) are discussed. The specific heat C_v values are obtained at different temperatures (0 K–1500 K) and under different pressures (0 GPa–40 GPa).

The rest of the paper is organized as follows. In Section 2 we present the theoretical tool and give the important details of the numerical calculations. The results are presented and discussed in Section 3. And finally, we draw some conclusions from the present studies in Section 4.

2. Computational details

2.1. First-principle calculations

All first-principle calculations were carried out using Cambridge Series of Total Energy Package (CASTEP) code based on the density functional theory (DFT).[23] The effects of the exchange–correlation energy were described by the generalized gradient approximation (GGA) in the form of Predew–Burke–Ernzerhof (PBE) potential.[24] The optimization was performed until the forces on the atoms are less than 0.01 eV/Å and all the stress components were less than 0.05 GPa. Ultrasoft pseudo potentials were used. The electronic wave functions were expanded in a plane-wave basis set with a cutoff energy of 400 eV, and $8\times13\times13$ Monkhorst–Pack meshes were employed for the Brillouin-zone k-point samplings. The self-consistent convergence of the total energy was 5.0×10^{-6} eV/atom. The finite displacement method was employed to calculate the phonon of state and the phonon dispersion via the constructed $3\times3\times3$ supercell.

2.2. Elastic method

The stress-strain method was used to evaluate the elastic constants of the crystal structure. Owing to the crystal symmetry, the present compounds can be described by the nine independent elastic stiffness coefficients (C_{11}, C_{22}, C_{33}, C_{44},C_{55}, C_{66}, C_{12}, C_{13}, and C_{23}). For calculating the elastic constants, we used the volume-conserving strains. The maximum strain amplitude is set to be 0.003. The number of steps is 6 for each strain. The mechanical parameters such as bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (v) can be calculated via Voigt–Reuss–Hill (VRH) approximation.[25] For the orthorhombic crystal, the Voigt bound of bulk modulus ($B_{\rm V}$) and the Voigt bound of shear modulus ($G_{\rm V}$) in Voigt approximation are calculated directly from elastic constants by

$$B_{\rm V}=\frac{(C_{11}+C_{22}+C_{33})+2(C_{12}+C_{13}^{+}C_{23})}{9}, \tag{1}$$

$$G_{\rm V}=\frac{(C_{11}+C_{22}+C_{33}-C_{12}-C_{13}-C_{23})+3(C_{44}+C_{55}+C_{66})}{15}. \tag{2}$$

In Reuss approximation, the Reuss bound of bulk modulus ($B_{\rm R}$) and the Voigt bound of shear modulus ($G_{\rm R}$) are calculated by

$$B_{\rm R}=\frac{1}{(S_{11}+S_{22}+S_{33})+2(S_{12}+S_{13}+S_{23})}, \tag{3}$$

$$G_{\rm R}=\frac{1}{4(S_{11}+S_{22}+S_{33})-4(S_{12}+S_{13}+S_{23})+3(S_{44}+S_{55}+S_{66})}. \tag{4}$$

In the formulas above, the S_{ij} are elastic compliance constants, which are the inverse matrix of C_{ij}. In Voigt–Reuss–Hill method, the bulk moduli B and shear moduli $G$are calculated by arithmetic average of Voigt and Reuss bounds as follows:

$$B_{\rm H}=\frac{B_{\rm V}+B_{\rm R}}{2}, \tag{5}$$

$$G_{\rm H}=\frac{G_{\rm V}+G_{\rm R}}{2}. \tag{6}$$

Then E and v can be calculated from the following equations:

$$E=\frac{9B_{\rm H}G_{\rm H}}{3B_{\rm H}+G_{\rm H}}, \tag{7}$$

$$v=\frac{3B_{\rm H}-2G_{\rm H}}{2(3B_{\rm H}+G_{\rm H})}. \tag{8}$$

2.3. Thermodynamic calculations

As is well known, the calculations of phonon spectra can be used to compute energy (E), entropy (S), free energy (F), and lattice specific heat ($C_{\rm V}$) each as a function of temperature via the quasi-harmonic approximation.[26] The temperature dependence of the energy can be expressed as

$$E(T)=E_{\rm tot}+E_{\rm ZP}+\int\frac{\hbar\omega}{\exp(\hbar\omega/kT)-1}F(\omega)\,{\rm d}\omega, \tag{9}$$

where $E_{\rm tot}$ is the total energy and calculated at 0 K, k is the Boltzmann's constant, $\hbar$ is the Planck's constant, and $F(w)$ is the phonon density of states. The zero point vibrational energy $E_{\rm ZP}$ is evaluated as

$$E_{\rm ZP}=\frac{1}{2}\int F(\omega)\hbar\omega\,{\rm d}\omega. \tag{10}$$

The vibrational contribution to the free energy $F(T)$ is expressed as

$$F(T) = E_{\rm tot} + E_{\rm ZP} + kT \int F(\omega) \ln \left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right)\right] {\rm d}\omega. \tag{11}$$

The lattice contribution to the specific heat C_v is written as

$$C_v(T) = k \int \frac{(\hbar\omega/kT)^2 \exp(\hbar\omega/kT)}{[\exp(\hbar\omega/kT) - 1]^2} F(\omega) {\rm d}\omega. \tag{12}$$

3. Results and discussion

3.1. Structural properties

The X_2N_2O (X = C, Si, Ge) compounds are of the orthorhombic structure (shown in Fig. 1) with the space group symmetry $Cmc2_1$. The calculated structural parameters of X_2N_2O (X = C, Si, Ge) are listed in Table 1, along with the available data from experiments and other theoretical results. Although the structures of Ge_2N_2O and C_2N_2O are the same as that of Si_2N_2O, while Si atoms are replaced with Ge or C atoms,[5,10] their lattice parameters are very different. Owing to the larger covalent atomic radius of Ge, the lattice parameters of Ge_2N_2O are largest among three compounds (0.77 Å for C, 1.17 Å for Si, and 1.22 Å for Ge).

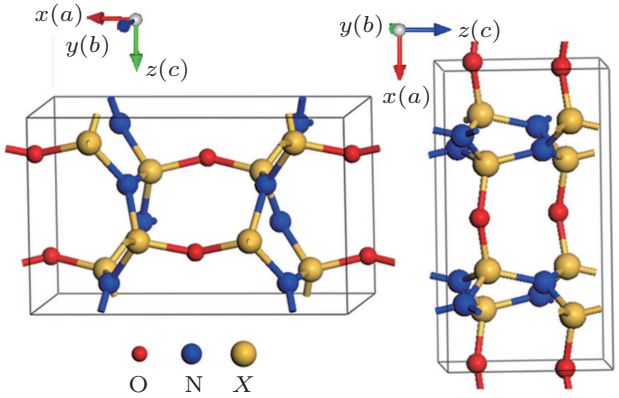


Fig. 1. (color online) Crystal structures of the orthorhombic- X_2N_2O (X = C, Si, Ge) compounds.

Table 1. Comparisons among the calculated values of equilibrium lattice parameters (a, b, c) (Å), average bond length L (Å), and bond angle (°), the experimental data and other theoretical results. For each compound, the data in the first line are from the present calculations, the data in the second line are the results cited from the references, and the data in the third line refer to the experimental results.

		Lattice constants/Å	L_{X-N}/Å	L_{X-O}/Å	∠(X—O—X)/(°)	∠(X—N—X)/(°)	∠(O—X—N)/(°)	∠(N—X—N)/(°)
C_2N_2O		$a = 7.431$, $b = 4.520$, $c = 4.037$	1.45	1.44	127.75	117.94	109.17	109.74
	Cal.[a]	$a = 7.432$, $b = 4.519$, $c = 4.036$						
Si_2N_2O		$a = 8.929$, $b = 5.535$, $c = 4.880$	1.73	1.63	147.77	119.71	109.68	109.26
	Cal. [b,c]	$a = 8.837$, $b = 5.431$, $c = 4.840$	1.72	1.62	147.40	120.00		
	Expt.[d,e]	$a = 8.866$, $b = 5.486$, $c = 4.854$	1.72	1.62	147.70		109.77	108.83
Ge_2N_2O		$a = 9.455$, $b = 5.834$, $c = 5.166$	1.85	1.77	136.27	118.00	109.26	109.64
	Cal. [b,c]	$a = 9.308$, $b = 5.748$, $c = 5.101$	1.83	1.85	122.30	118.50		
	Expt.[f,g]	$a = 9.315$, $b = 5.757$, $c = 5.105$	1.83	1.77	130.50		109.03	109.77

[a]Ref. [8], [b] Ref. [27], [c]Ref. [11], [d]Ref. [15], [e]Ref. [28], [f]Ref. [5], [g]Ref. [9].

For X_2N_2O (X = C, Si, Ge), one oxygen atom and three nitrogen atoms form a tetrahedron structure, and the X element is located in the center of the tetrahedron structure. With the increase of atomic radius of X atom (X = C, Si, Ge), the average X–N and X–O bond lengths increase, while the X–O average bond length is shorter than the X–N ones. Whereas the average bond angles of O–X–N and N–X–N are still 109°. As is well known, the sp^3 hybrid in the carbon group results in the tetrahedron structure with a bond angle of 109°. The bond angle of X–O–X in Si_2N_2O is large, compared those of the C_2N_2O and Ge_2N_2O compounds. The N–X–N bond angle is about 120°for the three present compounds.

Considering the fact that the lattice parameters (a, b, c) of each compound are not equal to each other, we show in Fig. 2 the lattice parameter ratios each as a function of pressure P in a range of 0 GPa–40 GPa. For C_2N_2O, the b/a ratio linearly decreases (c/a linearly increases) with increasing pressure. The c/a ratio almost has no change, and b/a linearly decreases from $P = 0$ GPa to $P = 30$ GPa, then tends toward a constant between 30 GPa and 40 GPa for Si_2N_2O. With the increase of the pressure, the b/a ratio quickly decreases, whereas c/a slightly increases for P in a range of 0 GPa–10 GPa, then linearly decreases for Ge_2N_2O with the largest lattice parameters in the present compounds. The anisotropy mainly derives from the covalent bondings between X (C, Si or Ge), N and O atoms in the X_2N_2O compounds.

Comparative investigations of these structures are helpful to understand the effects of C and Ge on the elastic and thermodynamic properties in these compounds. The equilibrium structures under zero pressure are used for discussing the elastic properties, band structures, phonon information, and thermodynamic properties.

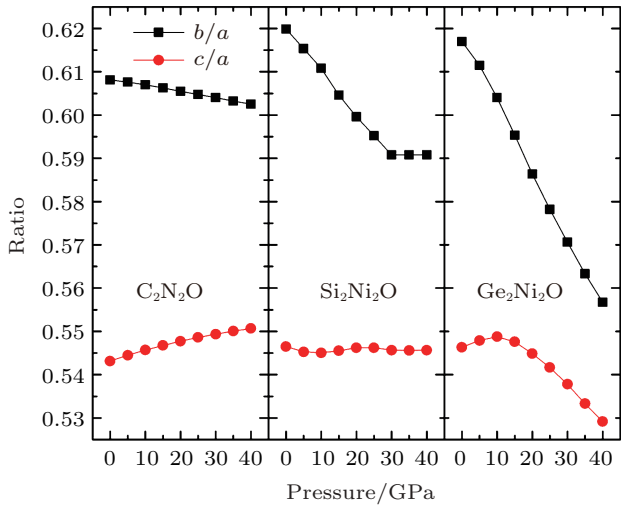


Fig. 2. (color online) Variations of lattice parameter ratio (b/a and c/a) of crystal structure with pressure for the orthorhombic- X_2N_2O (X = C, Si, Ge) compounds.

3.2. Elastic properties

Elastic constants (C_{ij}) are significant parameters of solid materials, which provide important information about the mechanical stability, anisotropic feature, bonding characteristics, ductility, etc.[31] Listed in Table 2 are the nine independent elastic constants and bulk mechanical properties derived from them for the orthorhombic-X_2N_2O (X = C, Si, Ge) compounds. All elastic constants are larger than zero ($C_{ij} > 0$), and they satisfy the known stability condition for orthorhombic crystal,[32] i.e., $C_{11}+C_{22}-2C_{12} > 0$, $C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23}) > 0$, $C_{11}+C_{33}-2C_{23} > 0$, and $C_{22}+C_{33}-2C_{23} > 0$. According to these criteria, results indicate that the orthorhombic structures of X_2N_2O (X = C, Si, Ge) are mechanically stable. Our calculations are well consistent with the theoretical results from different exchange-correlation approximations or interatomic potentials.[3,27,29,30] Compared with Si_2N_2O and Ge_2N_2O, C_2N_2O has the mechanical strength predicted by the large elastic constants and bulk modulus B, which may derive from the strong sp^3 hybridization of C_2N_2O. It is notable that the present elastic constants are calculated under $P = 0$ and at $T = 0$ K.

The calculated values of shear modulus G, Young's modulus E, and Poisson's ratio ν are listed in Table 2, and the experimental data and other theoretical results are also given there. For C_2N_2O, our calculated values of B, G, and E are all a little smaller than the available theoretical calculations, whereas for Ge_2N_2O our calculations are slightly larger than the previously theoretical results. In the case of Si_2N_2O, our calculated G value is 96.6 GPa and E value is 238.2 GPa, which are in excellent agreement with the recent experimental values of 93.1 GPa and 223.6 GPa respectively. The Poisson ratio ν values of three compounds are also reasonable compared with the recent theoretical values.[3,27,29] Generally speaking, the material behavior is in a ductile manner when $B/G > 1.75$, otherwise in a brittle manner.[33] The B/G ratio values of C_2N_2O, Si_2N_2O, and Ge_2N_2O are 1.028, 1.540, and 1.328, respectively. It is indicated that X_2N_2O (X = C, Si, Ge) compounds are very brittle. The Poisson's ratio $\nu$is often used to study the ductility or brittleness in metallic alloy. A material is ductile when $\nu > 0.33$.[34] The alloy with large B/G often has a large Poisson's ratio ν. In the three present compounds, C_2N_2O has a slightly smaller ν of 0.133 whereas the two others have large and comparable ν values.

Table 2. Calculated elastic constants C_{ij} (GPa) and elastic moduli (GPa) of the orthorhombic-X_2N_2O (X = C, Si, Ge) compounds.

	C_{11}/GPa	C_{22}/GPa	C_{33}/GPa	C_{44}/GPa	C_{55}/GPa	C_{66}/GPa	C_{12}/GPa	C_{13}/GPa	C_{23}/GPa	B/GPa	G/GPa	E/GPa	ν
C_2N_2O	569.2	537.4	838.3	315.7	182.6	183.9	53.5	75.3	54.2	251.8	245.0	555.1	0.133
	609.5[a]	557.3[a]	895.3[a]	338.3[a]	185.0[a]	187.4[a]	59.4[a]	77.6[a]	54.3[a]	266.1[a]	255.9[a]	581.3[a]	0.136[a]
Si_2N_2O	324.7	266.3	326.0	134.4	62.6	75.1	100.5	62.7	51.1	148.8	96.6	238.2	0.233
	323.0[b]	270.0[b]	336.0[b]	139.0[b]	57.0[b]	72.0[b]	95.0[b]	68.0[b]	55.0[b]	151.0[b]	94.3[b]	234.2[b]	0.242[b]
											93.1[c]	221.6[c]	
Ge_2N_2O	175.8	163.7	236.7	98.0	36.7	43.9	39.6	27.8	24.0.	83.7	63.7	151.2	0.199
	178.2[d]	170.8[d]	238.4[d]	87.2[d]	34.5[d]	46.8[d]	54.8[d]	40.0[d]	30.4[d]	92.9[d]	60.3[d]	148.5[d]	0.232[d]

[a]Ref. [3], [b]Ref. [29], [c]Ref. [30], [d]Ref. [27].

3.3. Electronic structure

The calculated band structures and densities of state (DOSs) of X_2N_2O (X = C, Si, Ge) are shown in Fig. 3. The obtained band gap values are 5.18 eV (C_2N_2O), 5.00 eV (Si_2N_2O), and 2.76 eV (Ge_2N_2O), respectively. In order to further investigate the electronic structures, we present total densities of state and partial electron densities of states (PDOSs) for X_2N_2O (X = C, Si, Ge) in Figs. 3(b), 3(d), and 3(f). It is clear that there are three valence regions for each of these compounds. The lowest energy band (below −18 eV) for X_2N_2O (X = C, Si, Ge) is mainly composed of O-s orbitals. The DOS in the next energy band is dominated by N-s orbitals

between −18 eV and −16 eV (−13 eV) for C_2N_2O (Si_2N_2O and Ge_2N_2O). The hybridization exits between X-p and N-s orbitals for X_2N_2O in this region. The N-p orbitals of these compounds dominate the density of state in the upper valence band region. For C_2N_2O the N-p and C-s orbitals hybridize between −15 eV and −12 eV and for Si_2N_2O (Ge_2N_2O) the N-p and Si (Ge)-s hybridize between −10 eV and −7 eV. Then the p orbitals of X, N, and O hybridize with each other near the Fermi level. C-p and Si-p dominate density of states of C_2N_2O and Si_2N_2O in the conduction band region. For Ge_2N_2O, the density of state is composed of Ge-s between 3 eV and 6 eV, and Ge-p orbitals dominate the density of state from 6 eV to 10 eV.

Figures 3(b), 3(d), and 3(f) separately show the typical sp hybridizations of X. The strong covalent bonding may result in the inherent brittle behaviors of the present compounds. The different values of band gap for X_2N_2O (X = C, Si, Ge) are mainly attributed to the X-s and p orbitals.

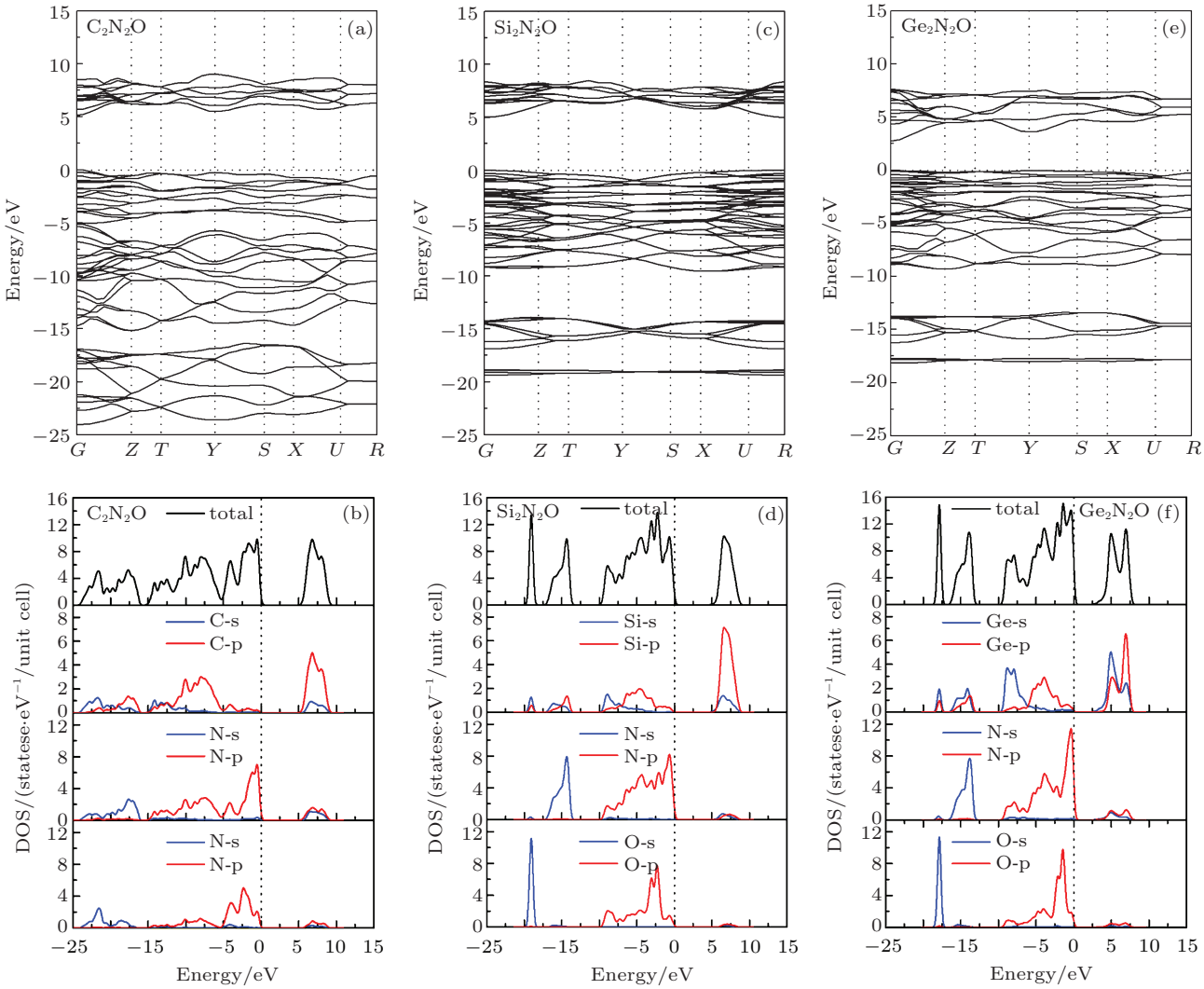


Fig. 3. (color online) Band structures and DOSs for X_2N_2O (X = C, Si, Ge).

3.4. Thermodynamic properties

Figure 4 shows the phonon DOS and the phonon dispersions along the high symmetry directions for X_2N_2O (X = C, Si, and Ge). The unit cell of X_2N_2O contains ten atoms, which gives rise to 30 phonon branches in total, of which acoustical branches are three and optical modes are 27. Owing to degeneracy the actual number is reduced along each different direction. No imaginary phonon frequency in the whole Brillouin zone suggests that the present compounds are dynamically stable in ambient condition, i.e., under no compression (shown in Fig. 4) and under compression (no shown). There is a gap in optical phonon mode between the Si_2N_2O and Ge_2N_2O compounds. The acoustic phonon modes have interactions with the partial low-lying optical phonon modes. The highest frequencies of three compounds are very close to 42 THz, 35 THz, and 30 THz, respectively, due to the influences of differences among atomic mass values.

The specific heat is a measure of how well the substance stores the heat. The calculated values of specific heat C_V as a

function of temperature for all the investigated compounds at different pressures are shown in Fig. 5. We can clearly see that at high temperatures the specific heat at constant volume obeys the Dulong Petit limit. At the intermediate temperatures, the temperature dependent specific heat is governed by the details of vibrations of the atoms. With increasing pressure, C_V as a function of temperature slightly decreases. From Fig. 5 we observe that C_2N_2O has the lowest value of specific heat in all the compounds. The C_V value of Ge_2N_2O increases more remarkably than those of Si_2N_2O and C_2N_2O with increasing temperature under a given pressure before it is close to the Dulong–Petit limit.

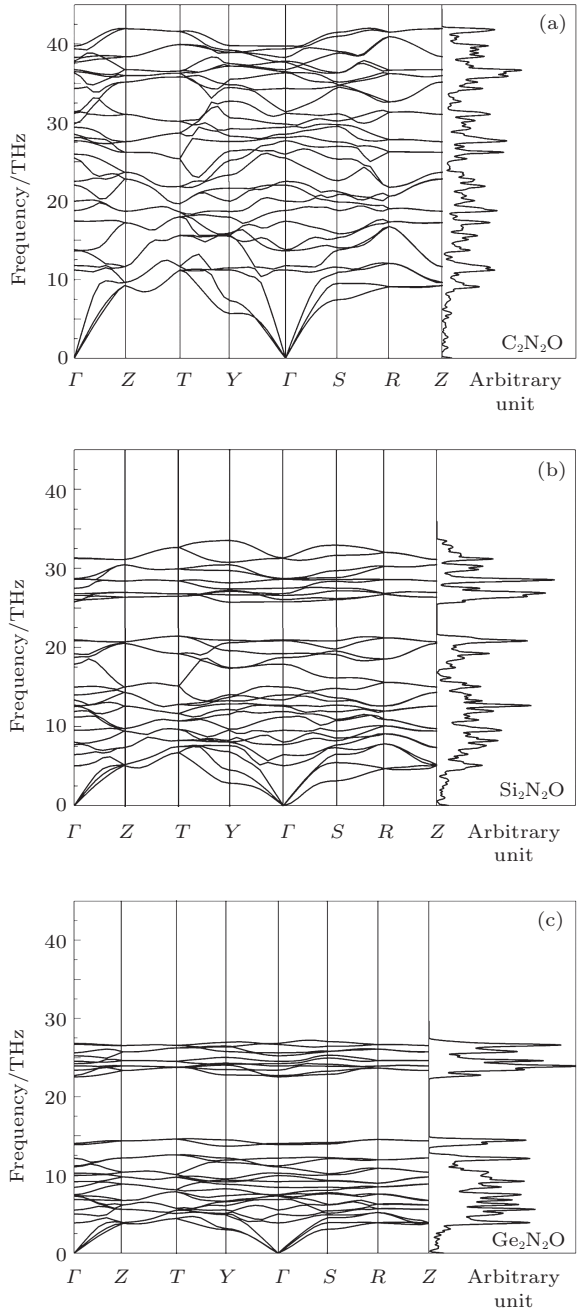


Fig. 4. Phonon dispersions and phonon DOSs for X_2N_2O [X = C, Si, Ge, corresponding to panels (a), (b), and (c)].

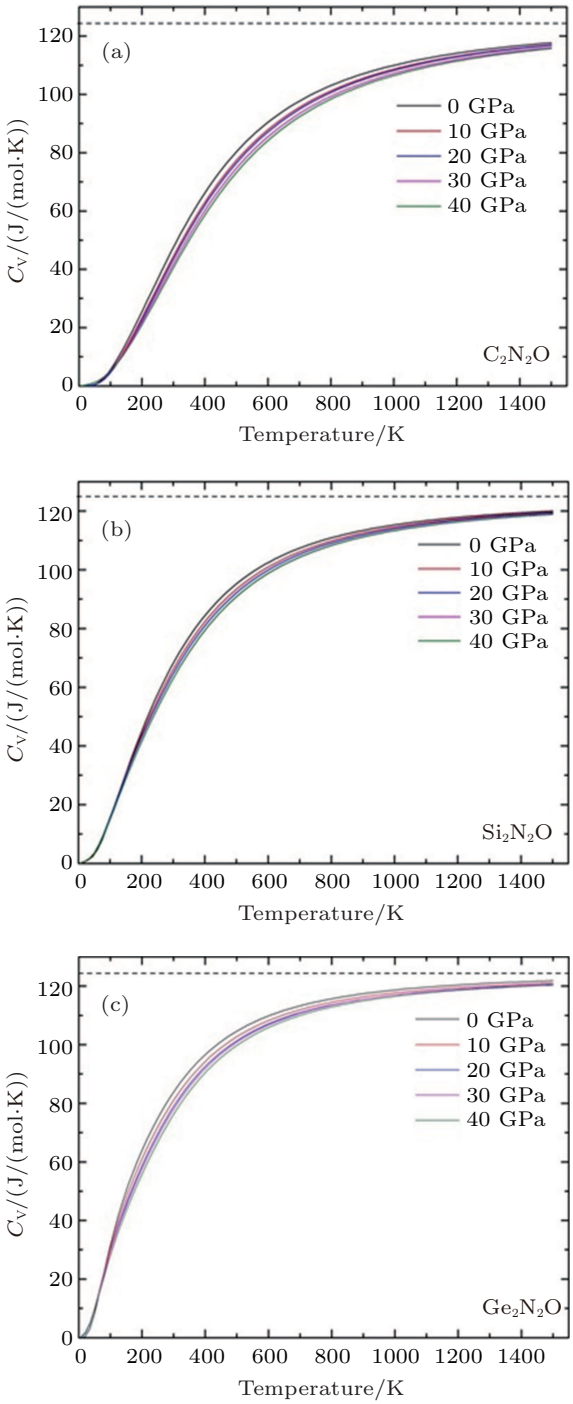


Fig. 5. (color online) Variations of C_v with temperature T at different pressures for X_2N_2O [X = C, Si, Ge, corresponding to panels (a), (b), and (c)].

4. Conclusions

In this work, the crystal structures, elastic properties, electronic structures and thermodynamic properties of X_2N_2O (X = C, Si, Ge) are investigated using the first-principle method. The orthorhombic structure is thermodynamically stable indicated by the calculations of the elastic constants and the lattice vibration. The obtained results of the structural parameters, elastic constants (C_{ij}), and aggregate elastic moduli (B, G, E) are in agreement with the corresponding experimen-

tal and theoretical results. The lattice parameters each as a function of pressure imply the strong anisotropies of X_2N_2O. The different values of band gap for X_2N_2O (X = C, Si, Ge) are mainly attributed to the X-s and p orbitals. The specific heat C_V values are calculated at different temperatures and under different pressures via the quasi-harmonic approximation. Compared with the cases of the Si_2N_2O and C_2N_2O compounds, the specific heat at constant volume of Ge_2N_2O remarkably increases with increasing temperature at given pressure before it is close to the Dulong–Petit limit.

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