First-principles calculation of electronic, vibrational, and thermodynamic properties of triaminoguanidinium nitrate

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Abstract

In recent years, the important energetic material triaminoguanidinium nitrate (TAGN) has been widely used, and the process of synthesizing TAGN has become more and more perfect. However, there are relatively few theoretical studies on TAGN. This paper uses first-principles calculations to more systematically study the crystal structure, electronic, vibrational and thermodynamic properties of TAGN. The calculation results show that the calculated unit cell parameters are relatively consistent with the values obtained through X-ray diffraction experiments. This article describes in detail the state density of the valence electron of each atom. By analyzing the vibrational properties of TAGN crystal, the vibration mode corresponding to each optical wave is obtained. At the same time, the vibration mode of each peak in the Raman spectrum and the infrared spectrum is described in detail. Then the calculated value is compared with the experimental value, it can be seen that the error is relatively small. According to the vibration characteristics, a series of thermodynamic functions such as enthalpy (H), Debye temperature (Θ), free energy (F), and entropy (S) are calculated. These thermodynamic functions can provide a certain reference for future research.

1. Introduction

Nowadays, energetic materials have been widely used in military industry and national life fields. In order to meet all kinds of needs, all kinds of energetic materials are bred. Triaminoguanidinium nitrate (TAGN) is a very important energetic material. With its own superior properties, it is widely used in gas generating agents, propellants, and explosive additives [1–2]. At the same time, TAGN has good thermal stability and can be stored for a long time without deterioration [3–5]. Therefore, the synthesis of TAGN has always been the focus of research. In the 1960s, research reports on TAGN appeared for the first time [6]. According to literature reports, depending on the different reactants, there are four main methods for synthesizing TAGN: dicyandiamide method [6], calcium cyanamide method [7], cyanamide method [8] and guanidine nitrate method [9]. These four methods have high yields, but the purity of the reactants is too high and the reaction time is too long, which greatly limit the production of TAGN. In order to solve this problem, in 2006, Xu and Yang optimized and improved the nitric acid arc method and synthesized kilogram-level TAGN with a productivity of 94.8% [10]. A certain scale of mass production also creates certain conditions for the wide application of TAGN. Besides its own synthesis is the focus of research, TAGN is also an important intermediate for the synthesis of energetic materials. A series of tetrazine high-nitrogen energetic compounds were synthesized by TAGN [11–13]. Meanwhile, triaminoguanidinium nitrate is also one of the important raw materials for the synthesis of other triamino arc salts [14–15]. The wide application of TAGN means that the research on TAGN is particularly important.

At present, there are many researches on the synthesis method and application performance of TAGN, but there are few researches on the electronic and thermal properties of TAGN. At the same time, lattice vibration is regarded as the basis of the microscopic theory and macroscopic process of studying the thermodynamic properties and structural phase transition of crystals. Therefore, this work research is

based on first-principles calculations, focusing on the crystal structure, electronic, vibrational and thermodynamic properties of TAGN.

2. Computational Methods

The calculations were performed by using the CASTEP code [16]. This code was based on density functional theory (DFT) and used the norm-conserving pseudopotential method. The exchange correlation potential used the Perdew-Burke-Ernzerhof (PBE) in the generalized gradient approximation (GGA) [17]. The Grimme correction of the DFT-D method was used to deal with the van der Waals interactions [18]. At the same time, to ensure the calculation convergence, the plane wave cutoff energy was set to 830eV. The H $1s^1$, C $2s^2 2p^2$, N $2s^2 2p^3$ and O $2s^2 2p^4$ were treated as valence electrons and the k-point of Brillouin zone was set to $2 \times 1 \times 2$. The total energy, residual force, residual stress and displacement were set in this article. The total energy was less than 5.0×10^{-6} eV/atom. The force acting on each atom was not more than 0.1 eV/nm. The maximum stress was 0.02 GPa, and the maximum displacement of atoms was 5×10^{-4} Å.

3. Results And Discussion

3.1. Structure of triaminoguanidine nitrate

The crystal structure of TAGN is an orthorhombic unit cell composed with four TAGN molecules, its space group is Pbcm, and its molecular formula is $\text{CH}_9\text{N}_7\text{O}_3$. As shown in Fig. 1, the red balls represent oxygen atoms, the white balls represent hydrogen atoms, and the blue balls represent nitrogen atoms. The structure of a single TAGN molecule is shown in Fig. 2. TAGN is composed of CH_9N_6^+ cation and NO_3^- anion. From Fig. 1 we can see that for a single TAGN molecule all nitrogen atoms are on the same plane, and this plane bisects the entire molecule. There are three amino groups on the CH_9N_6^+ cation. These are the same as described in the literature [19]. As shown in Table 1, this paper calculates the bond length of C-N. We can see that the bond length of C-N is between the length of the C-N single bond and the C-N double bond. This means that C-N is a partial double bond [5, 20, 21]. There are two types of hydrogen bonds in the TAGN unit cell. $[\text{N}(2)\text{-H}(2)\cdots\text{N}(6)]$, $[\text{N}(5)\text{-H}(5)\cdots\text{N}(4)]$, $[\text{N}(3)\text{-H}(3)\cdots\text{N}(1)]$, and $[\text{N}(2)\text{-H}(2)\cdots\text{O}(1)]$ form intramolecular hydrogen bonds. At the same time, each cation will also form intermolecular hydrogen bonds with other anions. The presence of hydrogen bonds reduces the sensitivity of TAGN and makes the title compound more stable.

Table 1
The C-N bond length of TAGN.

Bond	Length(Å)
C-N2	1.34387
C-N3	1.34769
C-N5	1.34790

As shown in Table 2, the unit cell parameters calculated in this paper are in good agreement with the experimental results [19]. The maximum error will not exceed 2.40%, indicating that the calculated crystal structure of TAGN in this paper is feasible and the optimized result is reasonable.

Table 2
The experimental and calculated lattice parameters of TAGN.

Methods	a(Å)	b(Å)	c(Å)	v(Å ³)
This work	8.43017	12.7080	6.38597	684.134
Expt. [19]	8.389	12.684	6.543	696.21

3.2. Electronic properties

The band structure of TAGN along the high symmetry point of the Brillouin zone is shown in Fig. 3. It can be seen from the figure that TAGN is a direct band gap, because the lowest point of the conduction band and the highest point of the valence band are at the same symmetric point. In addition, the band gap of TAGN is calculated to be 3.039 eV. This value is very close to the calculated value 2.968eV given by Qin [22]. Unfortunately, there is no experimental value to compare with the calculated value of the paper. However, it is well known that using GGA-PBE functional calculations will underestimate the band gap of the crystal, so the actual band gap of TAGN should be greater than 3.039 eV.

In order to better understand the electronic properties of TAGN, it is necessary to consider the contribution of the density of states of each atom to the density of states of the entire TAGN molecule. For the same kind of atom, the contribution to the total density of states is also different due to the difference in its occupation and the environment. This article considers the populations of atoms, then classifies all the atoms in the TAGN molecule. As shown in Fig. 2, nitrogen atoms in TAGN molecules can be divided into 7

types, oxygen atoms are divided into 2 types, and hydrogen atoms are divided into 6 types. Figure 4 shows the total density of state and the partial density of states of various types of atoms. It can be seen from the figure that the energy band from -27.5 to -24.4eV is mainly contributed by O1-2s, O2-2s, O2-2p states and N7-2s states. From -21.4 to -17.7eV , mainly contributed by a series of state contributions such as C-2s, C-2p, O1-2s, O2-2s, N7-2p and N(1-6)-2s. From -16.4 to -12.8eV , mainly by N(1-6)-2s, C-2s, C-2p and H(1-6)-1s and other state contributions. From -10.8 to -5.4eV , the total density of states is mainly composed of N7-2s, N(1-7)-2p, C-2s, C-2p, O(1-2)-2s, O(1-2)-2p, and H(1-6)-1s. From -5.35 to -3.15eV , mainly composed of N(1-7)-2p, C-2p, and H(1-6)-1s. The valence band near the Fermi level is mainly composed of N(1-6)-2s, N(1-6)-2p, O1-2p, O2-2p, and H(1-6)-1s. The conduction band is mainly composed of N(1-7)-2s, N(1-7)-2p, C-2p, O(1-2)-2p, H(1-6)-1s and other state contributions.

3.3. Vibrational properties

The vibrational properties of TAGN are calculated based on the density functional perturbation theory. There are four TAGN molecules in the TAGN unit cell, and each TAGN molecule has 20 atoms, so there are 80 atoms in the TAGN unit cell. This means that there are 3 acoustic vibrational modes and 237 optical vibrational modes in this TAGN molecule. According to group theory analysis [23], the irreducible expression of optical vibration is as follows: $\Gamma = 24A_u + 23B_{1u} + 36B_{2u} + 36B_{3u} + 36A_g + 36B_{1g} + 22B_{2g} + 24B_{3g}$, among which the vibrational modes of B_{1u} , B_{2u} , and B_{3u} have infrared activity. Among them, the vibrational modes of A_g , B_{1g} , B_{2g} , and B_{3g} have Raman activity. A_u does not have Raman and infrared activity. As shown in Table 3, each frequency and the corresponding vibrational mode are recorded in the table and compared with the corresponding experimental values. However, considering that the vibration at some frequencies is the coupling effect of the unit cell's overall vibration and chemical bond vibration or group vibration, the vibration form is relatively complicated and has no substantial meaning, so Table 3 does not list the corresponding frequencies at these frequencies of the form of vibration. This phenomenon is more obvious at low frequencies. At the same time, considering that this phenomenon is more obvious in the low frequency range, so the vibrational mode with a frequency lower than 200cm^{-1} does not appear in Table 3.

Table 3
The calculated and experimental vibrational modes and frequencies of TAGN

symmetry	Frequency(cm ⁻¹)	Assignments	Mode	Expt
B _{1u}	200.47	NH ₂ in-plane rocking	IR	
B _{2g}	204.03	NH ₂ in-plane rocking	Raman	
A _g	210.00	N-O rocking	Raman	
B _{1g}	210.81	N-O rocking	Raman	
B _{2u}	216.45	N-O rocking	IR	
B _{3u}	217.22	N-O rocking	IR	
B _{3g}	222.23	NH ₂ in-plane rocking	Raman	
A _u	223.15	NH ₂ in-plane rocking		
B _{2u}	238.52	NH ₂ out-plane torsion	IR	
A _g	239.45	NH ₂ out-plane torsion	Raman	
B _{1g}	246.65	NH ₂ out-plane torsion	Raman	
B _{1u}	248.78	NH ₂ out-plane torsion	IR	
B _{3u}	250.0.	NH ₂ out-plane torsion	IR	
B _{2u}	254.36	NH ₂ out-plane torsion	IR	
A _g	254.86	NH ₂ out-plane torsion	Raman	
B _{3u}	268.53	NH ₂ out-plane torsion	IR	
A _g	269.78	NH ₂ out-plane torsion	Raman	
B _{1g}	270.08	NH ₂ out-plane torsion	Raman	
B _{2g}	300.17	NH ₂ out-plane torsion	Raman	
B _{3u}	309.13	NH ₂ out-plane torsion	IR	
B _{3g}	310.05	NH ₂ out-plane torsion	Raman	
A _u	315.25	NH ₂ out-plane torsion		
B _{1u}	436.52	NH ₂ out-plane torsion + N-H rocking	IR	

symmetry	Frequency(cm^{-1})	Assignments	Mode	Expt
B _{2g}	446.63	NH ₂ out-plane torsion + N-H rocking	Raman	
A _u	470.28	NH ₂ out-plane torsion		
B _{3g}	471.81	NH ₂ out-plane torsion	Raman	
A _u	509.51	NH ₂ out-plane torsion		
B _{1u}	522.45	N-H rocking	IR	
B _{2g}	524.57	N-H rocking	Raman	
B _{3g}	524.96	NH ₂ out-plane torsion	Raman	
A _u	570.50	N-H rocking		
B _{3g}	570.91	N-H rocking	Raman	
B _{1u}	622.79	NH ₂ out-plane torsion	IR	
B _{3g}	651.19	N-H rocking	Raman	
A _u	653.07	N-H rocking		
A _u	659.54	N-H rocking		
B _{3g}	664.65	N-H rocking	Raman	
B _{1u}	679.07	NO ₃ ⁻ in-plane deformation +N-H rocking	IR	
B _{2g}	680.24	NO ₃ ⁻ in-plane deformation +N-H rocking	Raman	
B _{3g}	680.66	NO ₃ ⁻ in-plane deformation +N-H rocking	Raman	
A _u	681.33	NO ₃ ⁻ in-plane deformation		
B _{1u}	689.44	N-H rocking	IR	
B _{1u}	690.00	N-H rocking	IR	
B _{1g}	690.53	NO ₃ ⁻ in-plane deformation	Raman	

symmetry	Frequency(cm^{-1})	Assignments	Mode	Expt
B _{2g}	690.54	NO ₃ ⁻ in-plane deformation	Raman	
B _{2u}	690.80	NO ₃ ⁻ in-plane deformation	IR	
B _{3u}	691.13	NO ₃ ⁻ in-plane deformation	IR	
B _{1u}	702.87	N-H rocking	IR	
B _{2g}	711.08	N-H rocking	Raman	
A _u	715.16	N-H rocking		
B _{3g}	722.40	N-H rocking	Raman	
B _{1g}	781.98	NO ₃ ⁻ out-plane deformation	Raman	
A _g	782.31	NO ₃ ⁻ out-plane deformation	Raman	
B _{3u}	782.38	NO ₃ ⁻ out-plane deformation	IR	
B _{2u}	782.43	NO ₃ ⁻ out-plane deformation	IR	
B _{1g}	927.54	NH ₂ out-plane rocking	Raman	
B _{2u}	936.15	NH ₂ out-plane rocking	IR	
A _g	947.33	NH ₂ out-plane rocking	Raman	
B _{2u}	948.70	NH ₂ out-plane rocking	IR	
B _{3u}	950.18	NH ₂ out-plane rocking	IR	
B _{3u}	954.83	NH ₂ out-plane rocking	IR	
B _{1g}	961.24	NH ₂ out-plane rocking	Raman	
B _{2u}	968.17	NH ₂ out-plane rocking	IR	
A _g	976.93	NH ₂ out-plane rocking	Raman	
B _{1g}	978.09	NH ₂ out-plane rocking	Raman	
B _{3u}	985.32	NH ₂ out-plane rocking	IR	
B _{2u}	1020.73	NO ₃ ⁻ asymmetry stretch	IR	1078 [25]

symmetry	Frequency(cm^{-1})	Assignments	Mode	Expt
B _{1g}	1020.82	NO ⁻¹ ₃ symmetry stretch	Raman	
B _{3u}	1021.43	NO ⁻¹ ₃ asymmetry stretch	IR	
A _g	1021.46	NO ⁻¹ ₃ symmetry stretch	Raman	
B _{2u}	1114.28	NH ₂ out-plane rocking+ N-H rocking	IR	
B _{1g}	1115.61	NH ₂ out-plane rocking+ N-H rocking	Raman	
A _g	1119.61	NH ₂ out-plane rocking+ N-H rocking	Raman	
B _{2u}	1125.35	NH ₂ out-plane rocking+ N-H rocking	IR	
B _{3u}	1126.93	NH ₂ out-plane rocking+ N-H rocking	IR	
A _g	1133.84	NH ₂ out-plane rocking+ N-H rocking	Raman	
B _{3u}	1134.06	NH ₂ out-plane rocking+ N-H rocking	IR	
B _{1g}	1135.28	NH ₂ out-plane rocking+ N-H rocking	Raman	
B _{1g}	1176.56	NH ₂ out-plane rocking+ N-H rocking	Raman	
B _{2u}	1186.10	NH ₂ out-plane rocking+ N-H rocking	IR	
B _{3u}	1186.89	NH ₂ out-plane rocking+ N-H rocking	IR	

symmetry	Frequency(cm^{-1})	Assignments	Mode	Expt
A _g	1190.94	NH ₂ out-plane rocking+ N-H rocking	Raman	
A _u	1261.25	NH ₂ out-plane torsion		
B _{3g}	1261.73	NH ₂ out-plane torsion	Raman	
B _{1u}	1265.15	NH ₂ out-plane torsion	IR	
B _{2g}	1267.46	NH ₂ out-plane torsion	Raman	
B _{2u}	1273.91	N-H rocking + N-O stretch	IR	
B _{2g}	1273.95	NH ₂ out-plane torsion	Raman	
B _{1u}	1279.13	NH ₂ out-plane torsion	IR	
B _{3g}	1281.30	NH ₂ out-plane torsion	Raman	
A _u	1282.61	NH ₂ out-plane torsion		
B _{1g}	1285.28	N-H rocking + N-O stretch	Raman	
B _{3u}	1296.37	N-H rocking + N-O stretch	IR	
A _g	1298.81	N-H rocking	Raman	
B _{1u}	1305.51	NH ₂ out-plane torsion	IR	
B _{2g}	1306.95	NH ₂ out-plane torsion	Raman	
A _u	1312.11	NH ₂ out-plane torsion		
B _{3g}	1319.03	NH ₂ out-plane torsion	Raman	
B _{1g}	1329.84	N-H rocking	Raman	
B _{2u}	1333.85	N-H rocking	IR	
B _{3u}	1337.46	N-H rocking	IR	
B _{1u}	1338.01	NH ₂ out-plane torsion	IR	
A _g	1344.32	N-H rocking	Raman	
A _g	1348.61	N-H rocking	Raman	

symmetry	Frequency(cm ⁻¹)	Assignments	Mode	Expt
B _{2u}	1349.84	N-H rocking	IR	
B _{2g}	1352.10	NH ₂ out-plane torsion	Raman	
B _{3u}	1354.59	N-H rocking	IR	
A _u	1361.70	NH ₂ out-plane torsion		
B _{1g}	1365.29	N-H rocking	Raman	
B _{3g}	1367.48	NH ₂ out-plane torsion+ N-O stretch	Raman	
B _{3u}	1439.04	N-H rocking	IR	
B _{1g}	1442.68	N-H rocking	Raman	
A _g	1447.93	N-H rocking	Raman	
B _{2u}	1450.68	N-H rocking	IR	
B _{2u}	1556.95	NH ₂ in-plane shearing	IR	
B _{1g}	1561.08	NH ₂ in-plane shearing + N-H rocking	Raman	
A _g	1579.11	NH ₂ in-plane shearing + N-H rocking	Raman	
B _{3u}	1580.92	NH ₂ in-plane shearing + N-H rocking	IR	
B _{2u}	1588.20	NH ₂ in-plane shearing + N-H rocking	IR	
B _{1g}	1596.95	NH ₂ in-plane shearing + N-H rocking	Raman	
A _g	1597.69	NH ₂ in-plane shearing + N-H rocking	Raman	
B _{3u}	1599.20	NH ₂ in-plane shearing + N-H rocking	IR	
B _{1g}	1622.46	NH ₂ in-plane shearing	Raman	
B _{2u}	1647.95	NH ₂ in-plane shearing	IR	1615 [10, 25, 26]
B _{3u}	1648.58	NH ₂ in-plane shearing	IR	
A _g	1659.28	NH ₂ in-plane shearing	Raman	

symmetry	Frequency(cm^{-1})	Assignments	Mode	Expt
A _g	1665.03	NH ₂ in-plane shearing	Raman	
B _{3u}	1667.16	NH ₂ in-plane shearing + N-H rocking	IR	
A _g	1667.40	NH ₂ in-plane shearing	Raman	
B _{2u}	1668.56	NH ₂ in-plane shearing	IR	
B _{2u}	1669.67	NH ₂ in-plane shearing + N-H rocking	IR	
B _{1g}	1671.38	NH ₂ in-plane shearing + N-H rocking	Raman	
B _{1g}	1685.69	NH ₂ in-plane shearing + N-H rocking	Raman	
B _{3u}	1691.42	NH ₂ in-plane shearing + N-H rocking	IR	
A _g	3194.95	N-H stretch	Raman	
B _{2u}	3196.16	N-H stretch	IR	
B _{1g}	3200.90	N-H stretch	Raman	
B _{3u}	3207.89	N-H stretch	IR	3211 [10, 26]
B _{3u}	3226.31	N-H stretch	IR	
B _{1g}	3226.59	N-H stretch	Raman	
A _g	3227.83	N-H stretch	Raman	
B _{2u}	3229.27	N-H stretch	IR	
B _{1u}	3249.04	NH ₂ asymmetry stretch	IR	
B _{1g}	3249.51	NH ₂ symmetry stretch	Raman	
A _g	3250.97	NH ₂ symmetry stretch	Raman	
B _{3u}	3259.75	NH ₂ asymmetry stretch	IR	
B _{3u}	3268.40	NH ₂ asymmetry stretch	IR	3110 [25]
A _g	3268.92	NH ₂ symmetry stretch	Raman	
B _{2u}	3273.26	NH ₂ asymmetry stretch	IR	

symmetry	Frequency(cm^{-1})	Assignments	Mode	Expt
B _{1g}	3273.83	NH ₂ symmetry stretch	Raman	
A _g	3284.69	NH ₂ symmetry stretch	Raman	
B _{1g}	3286.81	NH ₂ symmetry stretch	Raman	
B _{3u}	3287.50	NH ₂ asymmetry stretch	IR	
B _{2u}	3290.84	NH ₂ asymmetry stretch	IR	
B _{2u}	3326.47	N-H stretch	IR	
B _{1g}	3328.07	N-H stretch	Raman	
A _u	3328.74	NH ₂ symmetry stretch		
B _{3g}	3328.77	NH ₂ symmetry stretch	Raman	
B _{1u}	3328.82	NH ₂ asymmetry stretch	IR	3214 [25]
B _{3g}	3328.90	NH ₂ symmetry stretch	Raman	
A _g	3329.33	N-H stretch	Raman	
B _{3u}	3330.90	N-H stretch	IR	
B _{1u}	3351.05	NH ₂ asymmetry stretch	IR	
A _u	3351.10	NH ₂ symmetry stretch		
B _{3g}	3351.31	NH ₂ symmetry stretch	Raman	
B _{3g}	3351.37	NH ₂ symmetry stretch	Raman	
B _{2g}	3367.43	NH ₂ symmetry stretch	Raman	
B _{1u}	3367.67	NH ₂ asymmetry stretch	IR	3317 [25]
B _{3g}	3368.07	NH ₂ symmetry stretch	Raman	
A _u	3368.32	NH ₂ symmetry stretch		

Both infrared spectroscopy and Raman spectroscopy are highly characteristic and can be used to reflect the molecular structure and vibrational properties of chemical bonds [24]. Therefore, this paper also calculated the infrared spectra of TAGN, as shown in Fig. 5. The Raman spectrum is also calculated, as

shown in Fig. 6. In the infrared spectrum, in the high frequency range of 3000 to 3400cm^{-1} , the vibration of TAGN is mainly composed of N-H stretch and NH_2 asymmetry stretch. Among the absorption peaks of the infrared spectrum, the vibrations at frequencies of 3268.40cm^{-1} , 3328.82cm^{-1} and 3367.67cm^{-1} are NH_2 asymmetry stretch. This is very close to the experimental values [25] of NH_2 asymmetry stretch 3110cm^{-1} , 3214cm^{-1} , 3317cm^{-1} , and the maximum error does not exceed 5.1%. The frequency is N-H stretch at 3207.89cm^{-1} , which is very small different from the experimental value [10, 26] of 3211cm^{-1} , which is only 0.01%. The vibration of TAGN is mainly composed of NO_3^- asymmetry stretch, NH_2 out-plane rocking, N-H rocking, N-O stretch, NH_2 in-plane shearing, NO_3^- in-plane rotation and NH_2 , Out-plane torsion and other series of vibration composition in the intermediate frequency range of 1000 to 2000cm^{-1} . Among the absorption peaks of the infrared spectrum, the weak absorption peak at 1647.95cm^{-1} is NH_2 in-plane shearing, which is only 2.0% away from the experimental value of 1615cm^{-1} . The absorption peaks at frequencies of 1667.16cm^{-1} , 1669.67cm^{-1} and 1694.42cm^{-1} are the coupling effect of NH_2 in-plane shearing and N-H rocking. The weak infrared absorption peak in the frequency range from 1020.43 to 1021.46cm^{-1} is NO_3^- asymmetric stretch, which is only 5.4% errors from the experimental value of 1078cm^{-1} . The frequency range of 1114.28 to 1134.28cm^{-1} is the coupling effect of NH_2 out-plane rocking and N-H rocking, and the infrared absorption peaks are at the frequencies of 1134.06cm^{-1} and 1114.28cm^{-1} . The frequencies from 1261.25 to 1282.61cm^{-1} , from 1305.51 to 1319.03cm^{-1} and 1338.01cm^{-1} are NH_2 out-plane torsion, of which 1265.15cm^{-1} , 1279.13cm^{-1} and 1338.01cm^{-1} are infrared absorption peaks. The infrared absorption peak at the frequency of 1296.37cm^{-1} is N-H rocking and N-O stretch. The weak absorption peak with frequency at 1349.84cm^{-1} is N-H rocking. The frequency is in the low-frequency range of 200 to 1000cm^{-1} . The vibration of TAGN is mainly composed of NH_2 out-plane rocking, NO_3^- out-plane deformation, N-H rocking, NO_3^- in-plane deformation, NH_2 out-plane torsion, NO_3^- in-plane rotation and other vibration forms. The infrared absorption peaks at frequencies of 936.15cm^{-1} , 948.70cm^{-1} , and 954.83cm^{-1} are NH_2 out-plane rocking. The weak infrared absorption peak at 782.43cm^{-1} is NH_2 out-plane torsion. The strong infrared absorption peak of N-H rocking is at 522.45cm^{-1} . The infrared peaks at frequencies 248.78cm^{-1} and 309.13cm^{-1} are NH_2 out-plane torsion. The infrared absorption peaks at frequencies 522.45cm^{-1} and 216.45cm^{-1} are N-O rocking.

It can be clearly seen that the calculated value obtained by using density functional theory is in good agreement with the experimental value, and the maximum error does not exceed 5.4%. But in the calculations in this paper, the infrared absorption peak of C-N stretch is not observed like the experiment. This article believes that C-N stretch exists, but C-N is relatively stable, with a low vibration frequency, so the infrared absorption peak is covered by other infrared absorption peaks with large vibrational frequencies. At the same time, this paper also determined the infrared absorption peaks of N-O stretch, which can be used as the infrared characteristic peaks of TAGN and also will play an important role in the future research of TAGN.

For Raman spectroscopy, in the high frequency range, the Raman peaks at 3194.95cm^{-1} , 3227.83cm^{-1} , and 3293.33cm^{-1} are N-H stretch. The Raman peak with a frequency of 3284.69cm^{-1} is NH_2 symmetry stretch. In the intermediate frequency range, the Raman peak NO_3^{-1} symmetry stretch at the frequency of 1020.82cm^{-1} . The Raman peaks of N-H rocking are at 1298.81cm^{-1} and 1348.61cm^{-1} . The Raman peak with frequency at 1665.03cm^{-1} is NH_2 in-plane shearing. In the low frequency range, the Raman peak at 42.02cm^{-1} is NO_3^{-1} in-plane rotation. The Raman peak of N-O rocking is located at 210.81cm^{-1} . In the low frequency range, under the coupling effect of the lattice vibration and the group vibration, it is difficult to distinguish which group or chemical bond vibration the Raman peak at low frequency belongs to. At present, there are few researches on TAGN Raman spectroscopy. Although there is no comparison between the experimental value and the calculated value in this article, the calculated value in this article can provide a certain reference for future research on TAGN Raman spectrum.

3.4. Thermodynamic properties

Thermodynamic properties are one of the important parameters of materials, which play an important role in the thermal conductivity and thermal control of materials. Therefore, it is necessary to calculate the thermodynamic properties of the title compound. According to the vibration of atoms, this article calculates the Helmholtz free energy (F), enthalpy (H), entropy (S) and Debye temperature (Θ) of TAGN using statistical methods. The specific expressions are as follows [27]:

Where E_{tot} is the total energy of the TAGN crystal ground state, E_{zp} is the zero-point vibration energy, $\hbar$ is the reduced Planck constant, T is the thermodynamic temperature, k_B is the Boltzmann constant, and $N(\omega)$ is the state density of the phonon. The relationship between thermodynamic quantity and temperature in the range of 5K to 1000K is shown in Figs. 7 and 8.

Figure 7 clearly shows that enthalpy and temperature*entropy increase with the increase of temperature. The growth rate of temperature*entropy is higher than enthalpy, and the relationship between enthalpy and temperature is almost linear. Helmholtz free energy decreases with increasing temperature. The main reason is that as the temperature increases, the irregular thermal motion of the molecules becomes more intense, and the distance between the molecules becomes larger. The macro performance is the increase in system energy and entropy. Figure 8 clearly shows that the Debye temperature increases as the temperature increases. In the lower temperature range, the Debye temperature increases faster, and in the high temperature range, the Debye temperature increases slowly. The main reason is that the heat capacity of a solid is mainly contributed by two parts [28]: one is the thermal vibration of the crystal lattice; the other is the thermal movement of electrons. The contribution of the thermal motion of electrons is only obvious at low temperatures, and it can be almost ignored when the temperature is high.

4. Conclusions

In this paper, the crystal structure, electronic properties, vibrational properties and thermodynamic functions of TAGN are calculated by first-principles calculations. The following conclusions are obtained: the lattice parameters are not much different from the experimental values, which shows the rationality of the calculation results in this paper. It can be seen from the energy band diagram that TAGN is a direct band gap with a band gap of 3.039eV. Combined with the total density of states diagram and the partial density of state diagram, the electronic properties of each atom are analyzed. The infrared and Raman spectra of TAGN are calculated. The vibration frequency of each group and chemical bond consistent with the experimental value was obtained from the infrared spectrum. The thermodynamic functions are calculated. Enthalpy and temperature*entropy increase with increasing temperature, and Helmholtz free energy decreases with increasing temperature. The Debye temperature increases with the increase in temperature, but it increases faster at low temperatures and slower at high temperatures.

Declarations

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2. Conflicts of interest/Competing interests

There are no conflicts of interest to declare.

3. Availability of data and material:

The datasets used or analysed during the current study are available from the corresponding author on reasonable request.

4. Code availability:

N/A

5. Authors' contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

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Figures

Figure 1

The crystal structure of TAGN

Figure 2

A single TAGN molecule

Figure 3

The band structure of TAGN

Figure 4

The total and partial density of states of TAGN

Figure 5

The infrared spectra of TAGN

Figure 6

The Raman spectra of TAGN

Figure 7

Thermodynamic function

Figure 8

Debye temperature function