First-principles prediction of the structural, elastic, thermodynamic, electronic and optical properties of Li$_4$Sr$_3$Ge$_2$N$_6$ quaternary nitride

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1. Introduction

Nitride materials have attracted significant attention over the last 20 years due to their outstanding physical properties, which make them suitable for many technological applications such as: ultraviolet photodetectors, blue light emitting diodes, lasers [1,2], converting solar light into electricity, photocatalytic, hydrogen production [3], lithium ion batteries [4], magnetic and electronic devices [5,6].

Owing to their great structural variety and superior material properties like luminescence, nonlinear optical properties, or lithium-ion conductivity, the ternary and multinary nitride compounds have received an increased level of attention [7–21]. The number of discovered ternary and quaternary nitrides has greatly expanded in recent years [22]. These new multinary materials provide a wider range of electrical, optical and chemical properties responding the required properties by the technology applications. The quaternary nitride compounds provide, for example, an extra degree of freedom to control the energy band gap and lattice constants as compared with ternary and binary materials [15]. Some of the numerous recently synthesized quaternary nitrides contain lithium as a constituent [5,10,17–20,22], such as Li$_4$Sr$_3$Ge$_2$N$_6$ [10]. Unfortunately, only a few numbers of the discovered quaternary nitrides have been fully characterized due to their propensity for hydrolysis or oxidation in air [10].

Park and colleagues [10] synthesized the quaternary nitride Li$_4$Sr$_3$Ge$_2$N$_6$ as single crystals. It crystallizes in a monoclinic structure type, space group C2/m (No. 12 in the X-ray International Tables). Apart the crystalline structure, information about the physical properties of the quaternary nitride Li$_4$Sr$_3$Ge$_2$N$_6$ is scarce. In order to provide more detailed theoretical data of the fundamental physical properties, we present in this paper the results of first-principles calculations of the structural, elastic, electronic, optical and thermodynamic properties of the Li$_4$Sr$_3$Ge$_2$N$_6$ quaternary nitride. We provide a complete tensor of elastic constants of the...
considered material, electronic structure, macroscopic optical constants, thermodynamic properties and the influence of pressure on the structural parameters and the aforementioned properties. To the best of the authors’ knowledge these mentioned physical properties have neither been investigated theoretically nor experimentally.

2. Calculation method

The electronic total energy calculations were performed using the first-principles pseudopotential plane-wave method based on the density functional theory (DFT) [23] incorporated in the Cambridge total energy package (CASTEP) [24]. The Vanderbilt ultra-soft pseudo-potentials [25] with Li 1s2s2, Sr 4s4p3/2s2, Ge 4d4f7g and N 2s2p3 valence-electron configuration for Li, Sr, Ge and N atoms, respectively, were exchanged. The exchange and correlation potentials were determined in the framework of the generalized gradient approximations (GGA) with the parameterization suggested by Perdew and al. (GGA-PBEsol) [26]. The plane-wave expansion was restricted by a kinetic-energy cut-off of 350 eV. A 4 × 4 × 3 Monkhorst–Pack [27] k-points grid was chosen. This set of parameters ensures the self-consistent convergence of the total energy of 5 × 10−6 eV/atom.

The structural parameters were determined using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization technique [28], which provides a fast way to find the lowest energy structure. The crystalline structure parameters were relaxed until the forces on all atoms are below 0.01 eV/Å−1, maximum stress below 0.02 GPa, maximum displacement below 5 × 10−4 Å and self consistent convergence of the total energy below 5 × 10−6 eV/atom.

The elastic constants Cij of solids include important information on their mechanical properties. Many experimental techniques are used to measure the elastic constants, such as Brillouin scattering, ultrasonic wave propagation and neutron scattering. Generally, it is difficult to prepare single-crystals for many solids, which are necessary to measure the Cij, therefore theoretical calculation of the elastic constants become necessary. In the present work, the elastic constants Cij were estimated theoretically by using the stress–strain approach. A set of given homogeneous deformations with a finite value is imposed on the crystal structure and calculating the resulting stresses with respect to optimizing the internal atomic freedoms [29]. Four strain patterns – one with nonzero ε11 and ε22 components, the second with nonzero ε11 and ε12, the third with nonzero ε22 and the fourth with nonzero ε12, an auxilized stresses related to all 13 independent elastic constants for the monoclinic unit cell: C11, C22, C12, C66, C44, C55, C13, C14, C23, C24, C35 and C56. Three positive and three negative amplitudes were used for each strain component with a maximum strain value of 0.5%, and the elastic constants were determined from a linear fit of the calculated stress as a function of strain. For the elastic-constant calculations, the atoms were allowed to relax to their equilibrium positions when the energy change of each atom between successive steps was less than 1 × 10−11 eV/atom, the force on each atom was less than 0.002 eV/Å−1, the stress on each atom was less than 0.02 GPa, and the displacement was less than 1 × 10−1 Å.

The bulk modulus, shear modulus, elastic modulus, and Poisson ratio were thus derived from the Voigt–Reuss–Hill approximation [30–32].

Macroscopic optical constants, such as the reflectivity R(ω), absorption coefficient α(ω), refractive index n(ω), extinction coefficient k(ω) and electron energy-loss spectrum U(ω), can be computed from the complex dielectric function ε(ω)=εr(ω)+iεi(ω). The imaginary part of the optical dielectric function εi(ω) has been derived from the electronic band structure by summing all allowed direct transitions from occupied to unoccupied states. From that the real part of the dielectric function εr(ω) is calculated using the Kramer–Kronig transformation.

As rule, calculations have been done for T = 0, where there is no thermal excitation of nuclei. Attempts were made to allow for the contribution of the thermal excitation of nuclei to thermodynamic functions without using empirical parameters. There are two directions followed in those attempts. The first uses the Debye model; the second is based on the approximate construction of the phonon dispersion relations. The new feature, which allows describing the results as ab initio, is the use of values obtained in ab initio calculations instead of empirical parameters [33]. From an energy-volume (E–V) relationship in the static approximations, obtained via ab initio calculations, the Gibbs program [34], based on the quasiharmonic Debye model, allows us to evaluate the Debye temperature, to obtain the Gibbs free energy G(V, P, T) and to minimize G for deriving the thermal equation of state (EOS) V(P, T). Other macroscopic properties related to P and T can be also derived by using standard thermodynamic relations. Detailed description of the quasiharmonic Debye model can be found in [34].

3. Results and discussion

3.1. Structural properties

The Li4Sr2Ge6N6 quaternary nitride has a monoclinic structure described by the C2/m space group (No. 12) with two formula units per unit cell (Z = 2). Fig. 1 depicts one unit cell of Li4Sr2Ge6N6. In the unit cell, there are one Wyckoff atomic site for Li; L1: 8j (xL1, yL1, zL1), one Wyckoff atomic site for Ge; Ge5: 4i (xGe, 0, zGe), two different Wyckoff atomic sites for N; N2: 8j (xN2, yN2, zN2) and N6: 4i (xN6, 0, zN6), and two different Wyckoff atomic sites for Sr; Sr1: 4h (0, ySr1, 0.5) and Sr4: 2a (0, 0, 0). Therefore, the unit cell is characterized by 15 structural parameters which are not fixed by the symmetry: three lattice constants (a, b and c), angle β and 11 internal coordinates (xL1, yL1, zL1, xGe, yGe, zGe, xN2, yN2, zN2, xN6, yN6, zN6 and ySr1).

The first step in any calculation is to verify the accuracy of the chosen method to predict the physical properties of a considered material. This is accomplished by calculating the optimized geometry of the investigated material and comparing that with the corresponding available experimental results. The calculated equilibrium structural parameters of Li4Sr2Ge6N6, including the lattice parameters (a, b and c), the angle β and the 11 internal coordinates, using the calculating settings described in the previous section, are assembled in Tables 1 and 2, together with the corresponding available experimental data. Our obtained results are in very good agreement with the corresponding measured ones [10]. The relative differences between the calculated and experimental values of the lattice parameters d(%) = (Calculated value − measured value)/measured value are smaller than ±0.2%. The computed and experimental internal coordinates of all atoms (expressed in terms of the crystal lattice parameters) and the angle β are practically coinciding. This good agreement between the calculated and measured values of the lattice parameters serves as a proof of reliability and accuracy of the used theoretical method and gives confidence in the predicted results for the elastic, electronic, optical, and thermodynamic properties of the Li4Sr2Ge6N6 presented in the next sections.

The cohesive energy (Ecoh) of a material is a fundamental property measuring the strength of the forces that bind atoms together in the solid state and therefore it uses to judge the structural stability of a compound. The cohesive energy is often defined as the needed energy to decompose a compound into single atoms. In the present work, the cohesive energy (Ecoh) per atom is calculated by using the following expression [35]:

$$E_{coh} = \frac{1}{N_a + N_{Sr} + N_{Ge} + N_{N}} \left[ \frac{E_{Tot}^{Li_4Sr_2Ge_6N_6}}{N_a} \right]$$

In Eq. (1) $E_{Tot}^{Li_4Sr_2Ge_6N_6}$, $E_{Tot}^{Li_4Sr_2Ge_6N_6}$, $E_{Tot}^{Li_4Sr_2Ge_6N_6}$, $E_{Tot}^{Li_4Sr_2Ge_6N_6}$, and $E_{Tot}^{Li_4Sr_2Ge_6N_6}$ refer to the total energy of the unit cell of Li4Sr2Ge6N6 and total energies of the isolated Li, Sr, Ge and N atoms, respectively, and $N_a$, $N_{Sr}$, $N_{Ge}$, and $N_{N}$ are the numbers of Li, Sr, Ge and N atoms, respectively.

Fig. 1. A unit cell of Li4Sr2Ge6N6. The Ge atoms are at the centers of the blue octahedral, which are made of the N atoms. The numbers 1, 2, 3, 4, 5 and 6 indicated the non equivalent atomic positions, respectively. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)
in the unit cell. The calculated cohesive energy of the investigated compound, listed in Table 1, is negative, which confirms the structural stability of the Li₃Sr₃Ge₂N₆ compound.

Pressure dependences of the normalized lattice parameters (a/a₀, b/b₀ and c/c₀), normalized unit cell volume (V/V₀), and normalize angle β (β/β₀) (where a₀, b₀, c₀, V₀ and β₀ are zero pressure equilibrium structure parameters) are illustrated in Fig. 2. It is shown that, as pressure increases, the normalized lattice parameter b/b₀ decreases more rapidly than the normalized lattice parameters a/a₀ and c/c₀, which indicates that the b-axis is more compressible than the a- and c-axes. The c-axis is more compressible than the a-axis. These results implicate that the atomic bonds along the a-direction between nearest neighbors are stronger than those along the b- and c-directions. The pressure dependence of the above mentioned normalized lattice parameters can be expressed by the following expressions:

\[
\begin{align*}
\frac{a}{a_0} & = 1 - 0.00303P + 4.80181 \times 10^{-5}P^2 - 4.66447 \times 10^{-7}P^3 \\
\frac{b}{b_0} & = 1 - 0.00429P + 7.25979 \times 10^{-5}P^2 - 7.98279 \times 10^{-7}P^3 \\
\frac{c}{c_0} & = 1 - 0.00369P + 8.07703 \times 10^{-5}P^2 - 9.47375 \times 10^{-7}P^3 \\
\frac{V}{V_0} & = 1 - 0.01095P + 2.24112 \times 10^{-4}P^2 - 2.53248 \times 10^{-6}P^3 \\
\frac{\beta}{\beta_0} & = 1 + 6.91222 \times 10^{-4}P + 1.73855 \times 10^{-5}P^2 - 2.1744 \times 10^{-7}P^3
\end{align*}
\]

(2)

To explore other bulk structural properties of Li₃Sr₃Ge₂N₆, such as the bulk modulus B and its pressure derivative B', a calculated set of total energies versus unit cell volumes (E – V) has been fitted to three different equations of states (EOS): (i) E – V Birch–Murnaghan (BM) EOS [36]; (ii) E – V Vinet EOS [37] and (iii) E – V Poirier–Tarantola (PT) EOS [38]. By fitting the calculated E – V data (Fig. 3) to these EOSs, we have obtained the B and B' values listed in Table 3. In Fig. 3, the dots represent the first-principles results for the given unit cell volume and the solid lines show the fit of these results to the Birch–Murnaghan EOS. No reported results for the bulk modulus B and its pressure derivative B' are found in the literature to be compared with our present results.

### 3.2. Elastic properties

#### 3.2.1. Elastic constants and related properties

A complete set of 13 calculated elastic constants (C₁₁, C₁₂, C₁₃, C₄₄, C₅₅, C₆₆, C₁₂, C₁₃, C₁₅, C₂₂, C₃₃, C₁₁ and C₂₃) at zero pressure for Li₃Sr₃Ge₂N₆ is given in Table 4. No reports on the elastic constants of this compound have been found in the literature, which does not allow for making comparison with either experimental or theoretical data from other sources. The elastic constants C₁₁, C₂₂ and C₃₃ represent the stiffness of the material when an axial stress is applied along the [100], [010] and [001] directions, respectively. The C₄₄ measures the shear elastic modulus along the [010] direction on the (001) plane. The C₅₅ measures the shear elastic modulus along the [010] direction on the (100) plane and the C₆₆ represents the shear along the [100] direction on the (001) plane. The obtained results show that C₃₃ > C₁₁ > C₂₂, which means that the resistance against deformation along the [001] and [100] directions are higher than along [010] direction, which is in agreement with the already obtained results about the pressure dependence of the normalized lattice constants presented in Section 3.1.

There is a considerable interest in the pressure dependence of the elastic constants. An accurate experimental determination of the elastic constants under pressure is often rather difficult, and here computer modeling can play an important role in establishing this property. In the present work, we report the obtained results
is satisfied only if a symmetric matrix $\mathbf{G}_i$ has a positive determinant [39]. The symmetric matrix $\mathbf{G}_i$ for any structure type is defined as follows:

$$
\mathbf{G}_i = \begin{bmatrix}
\hat{C}_{11} & \hat{C}_{12} & \hat{C}_{13} & 2C_{14} & 2C_{15} & 2C_{16} \\
\hat{C}_{21} & \hat{C}_{22} & \hat{C}_{23} & 2C_{24} & 2C_{25} & 2C_{26} \\
\hat{C}_{31} & \hat{C}_{32} & \hat{C}_{33} & 2C_{34} & 2C_{35} & 2C_{36} \\
2C_{41} & 2C_{42} & 2C_{43} & 4C_{44} & 4C_{45} & 4C_{46} \\
2C_{51} & 2C_{52} & 2C_{53} & 4C_{54} & 4C_{55} & 4C_{56} \\
2C_{61} & 2C_{62} & 2C_{63} & 4C_{64} & 4C_{65} & 4C_{66}
\end{bmatrix}
$$

(3)

Here, $\hat{C}_{ax} = C_{ax} - P$, where $a = 1, 2, \ldots, 6$, and $\hat{C}_{12} = C_{12} + P$. $C_{13} = C_{13} + P$, $C_{23} = C_{23} + P$. The calculated $G_i$ for Li$_4$Sr$_3$Ge$_2$N$_6$ in pressure range of 0–30 GPa obey well these conditions, which mean that this compound is mechanically stable in this investigated pressure range.

The macroscopically measurable quantities characterizing the mechanical properties of a material for engineering applications are the bulk modulus $B$, which is a measure of resistance to volume change under applied pressure, shear modulus $G$, a measure of resistance to reversible deformation upon shear stress, Young’s modulus $E$, which measures the stress–strain ratio in the case of tensile forces and the Poisson’s ratio, which is defined as the negative value of lateral (or transverse) strain to the longitudinal strain under uniaxial stress and no volume change. These macroscopic parameters are related to the microscopic elastic constants via the Voigt–Reuss–Hill approach [30–32,40]. The obtained values of the above-mentioned macroscopic elastic parameters are listed in Table 5. One can note that the c value of the bulk modulus derived from the elastic constants at zero pressure is in excellent agreement with those obtained from the EOS fittings. This coincidence of the bulk modulus values as computed using two different methods gives further confidence in the reliability and accuracy of the present computed elastic constants of Li$_4$Sr$_3$Ge$_2$N$_6$.

Pugh [41] proposed the ratio of bulk modulus to shear modulus, $B/G$, as a criterion to distinguish between ductile and brittle characters of a solid. As the bulk modulus $B$ represents the resistance to fracture and the shear modulus $G$ characterizes the resistance to plastic deformation a high (low) $B/G$ value corresponds to ductility (brittle nature). According to Pugh criterion, the critical value that separates ductile and brittle materials is about 1.75. The obtained value of the $B/G$ ratio in the present work is equal to 1.52, which predicts Li$_4$Sr$_3$Ge$_2$N$_6$ to be a brittle material.

The isotropically averaged aggregate velocities for compressional sound wave $V_p$ and shear sound wave $V_s$ and their average sound wave $V_m$ can be obtained by using the following equations [42,43]:

$$
V_p = \left( \frac{3B + 4G}{3\rho} \right)^{1/2}, \quad V_s = \left( \frac{G}{\rho} \right)^{1/2}, \quad V_m = \left[ \frac{1}{3} \left( 2V_p^3 + V_s^3 \right) \right]^{-1/3}
$$

(4)

Here, $\rho$ is the density of mass. The calculated sound velocities are tabulated in Table 5. At low temperature (harmonic approximation), Debye temperature $\Theta_D$ gives a link between thermal and elastic properties. This property can be evaluated from the average sound velocity $V_m$ according to the following relation [42]:

$$
\Theta_D = \frac{h}{k_b} \left[ \frac{3\pi^2 N \rho}{4\pi} \right]^{1/3} V_m
$$

(5)

Here, $h$ is the Plank’s constant, $k_b$ is the Boltzmann’s constant, $n$ is the number of atoms per molecule, $N_A$ is the Avogadro’s number.
quaternary nitride possesses obvious elastic anisotropy. The obtained value of $b_{x}$ at 0 GPa is about 0.2, indicating the presence of some anisotropic character in the considered compound. The third approach is to plot the direction-dependent linear compressibility $\beta(l_2, l_3)$ and Young’s modulus $E(l_2, l_3, l_4)$, where $l_1$, $l_2$, and $l_3$ are the directional cosines with respect to the $x$, $y$, and $z$-axes, respectively. The above-mentioned properties are given by the following expressions [46]:

$$1/E(l) = S_{11}l_1^2 + 2S_{12}l_1l_2 + 2S_{13}l_1l_3 + 2S_{14}l_1 + S_{22}l_2^2 + 2S_{23}l_2l_3 + 2S_{24}l_2 + 2S_{33}l_3^2 + 2S_{34}l_3 + 2S_{44}l_3$$

$$\beta(l) = (S_{11} + S_{12} + S_{13})l_1^2 + (S_{12} + S_{22} + S_{23})l_2^2 + (S_{13} + S_{23} + S_{33})l_3^2$$

Here, $S_j$ stand to the elastic compliance constants that can be obtained through an inversion of the elastic constant tensor. In 3D representation of Young’s modulus $E(l_2, l_3, l_4)$ or the inverse of linear compressibility $\beta^{-1}(l_2, l_3, l_4)$ (linear bulk modulus), an isotropic system would exhibit a spherical shape, and a deviation from spherical shape indicates the degree of anisotropy. Fig. 5 clearly exhibits obvious deviations of the Young's modulus and linear bulk modulus surfaces from spherical shape, so one can conclude that the Li$_4$Sr$_3$Ge$_2$N$_6$ quaternary nitride possesses obvious elastic anisotropy. For more comprehensive visualization of the elastic anisotropy, we have also plotted in Fig. 5 the cross-section of the linear bulk modulus, the weak elastic anisotropy is observed for the $x$-plane. The other planes show a weak elastic anisotropy, we have also plotted in Fig. 5 the cross-section of the linear bulk modulus, the weak elastic anisotropy is observed for the $x$-plane. The other planes show a weak elastic anisotropy.

3.2.2. Elastic anisotropy

In physics, an anisotropic physical property means that this property depends on the crystallographic directions. It is well known that microcracks are easily induced in the materials due to the significant elastic anisotropy [44], therefore, it is important to estimate the elastic anisotropy of a solid to identify methods of improving its mechanical durability. To do this, we have used three different approaches to characterize the elastic anisotropy of Li$_4$Sr$_3$Ge$_2$N$_6$. The first one is to calculate the percentage anisotropy in the bulk modulus and shear modulus [45], defined as following: $A_B = [(B_V - B_0)/(B_V + B_0)] \times 100$ and $A_C = [(G_V - G_0)/(G_V + G_0)] \times 100$, respectively, where $B$ and $G$ are the bulk and shear moduli, and the subscripts $V$ and $R$ represent the Voigt and Reuss bounds. For an isotropic material, $A_B$ and $A_C$ are both equal to zero. The deviation of $A_B$ ($A_C$) from zero indicates the presence of an elastic anisotropy in compression (in shear). The largest possible anisotropy occurs when $A_B = A_C = 1$. The percentage of bulk and shear anisotropies in Li$_4$Sr$_3$Ge$_2$N$_6$ are found to be about 0.4% and 2.0%, respectively. According to this index, Li$_4$Sr$_3$Ge$_2$N$_6$ has more elastic anisotropy in shear than in compression. The second approach is to calculate the universal elastic anisotropy index $A_U$, proposed by Ranganathan and Ostoj-Starzewski [46] to measure the elastic anisotropy. The $A_U$ for a crystals is defined by the following expression: $A_U^V = 5G_V/G_R + B_V/B_R - 6$. For an isotropic crystal, the $A_U^V$ is equal to zero. A value of $A_U^V$ greater than zero define the extent of crystal anisotropy. The obtained value of $A_U^V$ at 0 GPa is about 0.2, indicating the presence of some anisotropic character in the considered compound. The third approach is to plot the direction-dependent linear compressibility $\beta(l_2, l_3, l_4)$ and Young’s modulus $E(l_2, l_3, l_4)$, where $l_1$, $l_2$, and $l_3$ are the directional cosines with respect to the $x$-, $y$-, and $z$-axes, respectively. The above-mentioned properties are given by the following expressions [46]:

$$1/E(l) = S_{11}l_1^2 + 2S_{12}l_1l_2 + 2S_{13}l_1l_3 + 2S_{14}l_1 + S_{22}l_2^2 + 2S_{23}l_2l_3 + 2S_{24}l_2 + 2S_{33}l_3^2 + 2S_{34}l_3 + 2S_{44}l_3$$

$$\beta(l) = (S_{11} + S_{12} + S_{13})l_1^2 + (S_{12} + S_{22} + S_{23})l_2^2 + (S_{13} + S_{23} + S_{33})l_3^2$$

Here, $S_j$ stand to the elastic compliance constants that can be obtained through an inversion of the elastic constant tensor. In 3D representation of Young’s modulus $E(l_2, l_3, l_4)$ or the inverse of linear compressibility $\beta^{-1}(l_2, l_3, l_4)$ (linear bulk modulus), an isotropic system would exhibit a spherical shape, and a deviation from spherical shape indicates the degree of anisotropy. Fig. 5 clearly exhibits obvious deviations of the Young's modulus and linear bulk modulus surfaces from spherical shape, so one can conclude that the Li$_4$Sr$_3$Ge$_2$N$_6$ quaternary nitride possesses obvious elastic anisotropy. For more comprehensive visualization of the elastic anisotropy, we have also plotted in Fig. 5 the cross-section of the above-mentioned surfaces in the $(x = yz, xy, xz$ and $yz$ planes. From the 2D plane projection, one can see that the Young’s modulus of the $yz$ plane has a weak anisotropic character compared to the other planes. For the linear bulk modulus, the weak elastic anisotropy is observed for the $yz$ plane. The other planes show a weak elastic anisotropy. We deduce that a considerable elastic anisotropy characterizes Li$_4$Sr$_3$Ge$_2$N$_6$. Finally, the values of the linear bulk modulus along $x$, $y$, and $z$ axes are: $B_x = 311$ GPa, $B_y = 225$ GPa and $B_z = 262$ GPa. These are in agreement with the corresponding values.

<table>
<thead>
<tr>
<th>$B$</th>
<th>$B_V$</th>
<th>$B_R$</th>
<th>$B_H$</th>
<th>$G$</th>
<th>$G_V$</th>
<th>$G_R$</th>
<th>$G_H$</th>
<th>$E$</th>
<th>$\sigma$</th>
<th>$V_I$</th>
<th>$V_T$</th>
<th>$V_m$</th>
<th>$T_D$</th>
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<td>87.05</td>
<td>87.69</td>
<td>58.84</td>
<td>56.47</td>
<td>57.65</td>
<td>141.9</td>
<td>0.23</td>
<td>6078</td>
<td>3597</td>
<td>3985</td>
<td>560</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5

Calculated bulk, shear and Young's moduli ($B$, $G$, and $E$, in GPa), $B/G$ ratio, Poisson's ratio $\sigma$, longitudinal, shear and average sound velocities ($V_L$, $V_T$, and $V_m$ in m/s) and Debye temperature ($T_D$, in K). The subscript V, R and H refer to the Voigt, Reuss and Hill approximations.

and $M$ is the molecular weight. No data for this property are available in the literature to be compared with the obtained result.
obtained from the pressure dependence of the normalized structural parameters are: $B_a = 330$ GPa, $B_b = 233$ GPa and $B_c = 271$ GPa.

3.3. Thermal properties

The evolutions of the unit cell volume $V$ and the isothermal bulk modulus $B$ with temperature $T$ up to 1000 K at $P = 0$, 10, 20 and 30 GPa for Li$_4$Sr$_3$Ge$_2$N$_6$ are shown in Fig. 6. Fig. 6 reveals that the isothermal bulk modulus $B$ is practically constant up to 100 K then it decreases linearly for $T > 100$ K, which is in accordance with the increase of the volume with the temperature. The propensity of increment of the bulk modulus $B$ with temperature does not depend on the pressure, while that of the volume slightly depends on the pressure. From Fig. 6, one can also note that the effect of pressure on the bulk modulus is more important than that of the temperature on it. At 300 K and zero pressure, the isothermal bulk modulus $B$ and the unit cell volume for MgIn$_2$S$_4$ are about 79 GPa and 198.89 Å$^3$.

The volume thermal expansion coefficient $\alpha$ measures the fractional change in the volume per degree change in temperature at a constant pressure $\alpha = \frac{1}{V} \frac{\partial V}{\partial T}$. The thermal expansion coefficient $\alpha$ is a fundamental parameter in physics which is inversely proportional to the melting temperature of solids [47], i.e. low thermal expansion coefficient corresponds to a high melting temperature. Using the quasiharmonic Debye approximation, the thermal expansion coefficient $\alpha$ of Li$_4$Sr$_3$Ge$_2$N$_6$ is calculated to reflect the temperature dependence of volume. Fig. 6-right-panel presents the evolution of the thermal expansion coefficient of Li$_4$Sr$_3$Ge$_2$N$_6$ with temperature up to 1000 K at $P = 0$, 10, 20 and 30 GPa. It found that the thermal expansion coefficient of the considered compound increases when the temperature increases. At zero pressure, the increase is the most drastic. For a given temperature, the thermal expansion coefficient $\alpha$ decreases drastically with the increase of pressure. With increasing pressure, the increase of $\alpha$ with temperature is weakened. At high temperatures and high pressures, the thermal expansion would converge to a constant value. At a given pressure, $\alpha$ increases sharply with the increasing temperature up to 300 K. For $T > 300$ K, $\alpha$ gradually approaches a linear increase with the enhanced temperature and the propensity of increment becomes moderate, which means that the temperature dependence of $\alpha$ is very small at high temperature. At 300 K and zero pressure, the thermal expansion coefficient $\alpha$ for Li$_4$Sr$_3$Ge$_2$N$_6$ is about 6.88 $\times$ 10$^{-5}$ K$^{-1}$.

Fig. 7 displays the evolution of the Debye temperature $T_D$ of Li$_4$Sr$_3$Ge$_2$N$_6$ with temperature at different fixed pressures (left-panel) and with volume at different temperatures (right-panel). It can be seen that $T_D$ is nearly constant from 0 to 100 K and decreases almost linearly but slightly with increasing temperature from $T > 200$ K. It is also shown that when the temperature is constant, the Debye temperature increases prominently almost linearly with applied pressure. Fig. 7-right-panel shows that the Debye temperature $T_D$ depends only on the volume. Our calculated $T_D$ at zero pressure and ambient temperature using the quasiharmonic model is about 480 K, which is in reasonable agreement with that calculated from the elastic constants, 460 K, which testifies the accuracy to which the quasiharmonic Debye model can describe thermal properties of the Li$_4$Sr$_3$Ge$_2$N$_6$ material.

The heat capacity of a substance not only provides essential insight into its vibrational properties, but it is mandatory for many applications. The variation of the heat capacity $C_V$ at constant volume versus temperature at 0, 10, 20 and 30 GPa pressures is shown in Fig. 8-left-panel. With increasing temperature, $C_V$ value increases rapidly at a lower temperature, then increases slowly in the high temperature and tends to the Dulong-Petit limit, which is common to all solids at high temperature. At high temperature $C_V$ approaches approximately 375 J mol$^{-1}$ K$^{-1}$. On the other side, the details of this change depend on the pressure. The initial increase in $C_V$ with $T$ under
lower pressure is more rapid than under higher pressure. It is worth to note here that at a fixed temperature the heat capacity $C_V$ decreases when the pressure increases. The obtained $C_V$ value for Li$_4$Sr$_3$Ge$_2$N$_6$ at zero pressure and 300 K is about 330 J mol$^{-1}$ K$^{-1}$.

The variation of the heat capacity $C_P$ versus temperature at fixed pressures 0, 10, 20 and 30 GPa pressures is shown in Fig. 8-right-panel. With increasing temperature, the variation feature of the $C_P$ at lower temperature is similar to that of $C_V$. However, in the high-temperature range, the change tendency of $C_P$ exhibits apparently different features under different pressures. The $C_P$ decreases with increasing pressures and do not converge to a constant value. At room temperature and zero pressure, the obtained value of $C_P$ for Li$_4$Sr$_3$Ge$_2$N$_6$ is about 343 J mol$^{-1}$ K$^{-1}$.

3.4. Electronic properties

The electronic band structure is an effective and efficient tool for describing the electronic properties of a material. The calculated electronic band structure along the high symmetric directions in the Brillouin zone for the optimized crystal structure of Li$_4$Sr$_3$Ge$_2$N$_6$ is illustrated in Fig. 9-left-panel. It is clear that no interfering between the valence bands and conductions bands around the Fermi level, which indicates the semiconducting character of the considered compound. The top of the valence band is located at the A-point of the Brillouin zone (BZ) while the bottom of the conduction band is located at the C-point in the BZ, indicating that the fundamental band gap is indirect (A–C).

The value of the fundamental energy band gap ($E_g$) is found to be equal to 2.14 eV and the smallest direct energy band gap is A–A and is equal to 2.29 eV.

The hydrostatic pressure affects significantly the electronic band structure as illustrated by Fig. 9, which shows the band structure of Li$_4$Sr$_3$Ge$_2$N$_6$ at zero pressure (left-panel) and at 5 GPa pressure (right-panel). The variations of the indirect band gap A–C and the direct one A–A are depicted in Fig. 10. Both gaps increase with increasing pressure but the increasing rate of the indirect band gap A–C is lower than that of the direct band gap A–A, therefore, a crossing of levels in the conduction band between C and A occurs at approximately 4.10 GPa pressure and consequently the material becomes direct band gap.
semiconductor for pressures higher than 4.10 GPa. The calculated band gap energies $A-I$ and $A-A$ at discrete pressures are fitted to the following polynomials:

$$E_{A-I}/C_0 = 2.13675 + 0.05306 P + 0.00168 P^2 + 1.89111 \times 10^{-5} P^3$$

$$E_{A-A}/C_0 = 2.2927 + 0.00866 P - 6.33333 \times 10^{-8} P^2$$

Knowledge on the distribution of all valence electron states can be obtained from the density of states (DOS). Fig. 11 illustrates the total density of states (TDOS, in unit states/eV/unit cell) and the orbital resolved partial density of states (PDOS, in unit states/eV/atom) projected onto Li, Sr, Ge and N contributions. The valence bands (VBs) consists of six major structures, V1, V2, V3, V4, V5 and V6, separated by gaps. The structures V6 and V5, not shown in Fig. 11 for more clarity of the figure, are centered at about $-43.6$ and $-34$ eV, respectively. The V6 consists of the Li-s states, while the V5 is formed from the Sr-s states. The V4, located in the energy region between $-17.5$ eV and $-14$ eV, is mainly due to the Sr-p, Ge-s states and N-s states. The V3 structure, located in the energy region between $-13.6$ and $-11.5$ eV, is principally originated from the N-s and Ge-s+p states. The V2 structure, located between $-7$ and $-5.3$ eV, originates mainly from the Ge-s with a small contribution from the N-p states. The V1 structure, extended in the energy region from $-4.8$ eV to the Fermi level, is due principally to the N- and Ge-p states with small contributions from Sr-s+d and Li-s states. The conduction band (CB) up to 10 eV is mainly originated from the Sr-d, Ge-s+p and N-p states. From the PDOS diagrams, one can note here the existence of slight differences between the states distributions of the same electronic orbitals of the atoms of same chemical element but with not equivalent crystallographic sites.

To have an idea about the bonding character in Li$_4$Sr$_3$Ge$_2$N$_6$, we evaluate the charge transfers between the neighboring atoms. In order to do that, the Mulliken’s [48] and Hirschfeld’s [49] charge analyses have been used. It is found that electron transfers occur from Li, Ge and Sr atoms to N atoms. The nominal oxidation states of the constituent atoms of Li$_4$Sr$_3$Ge$_2$N$_6$ are Li$^{+1}$, Sr$^{+2}$, Ge$^{4+}$ and N$^{-3}$. The calculated oxidation are Li$^{+0.8}$ ($Li^{+0.11}$), Sr$^{+0.63}$ ($Sr^{+0.34}$), and
Sr4+0.69 (Sr4+0.42), Ge+1.06 (Ge+0.34), N2/C0=1.27 (N2/C0=0.41) and N6/C0=1.09 (N6/C0=0.29) using Mulliken’s (Hirschfeld’s) charge analyses. Here, we exploit the ratio between the net charges of the atom in the material to its nominal oxidation state to evaluate the ionic bonding character percentage. From these results, we estimate the ionic bonding character to be about 47% (13%) ionic character according to the Mulliken’s (Hirschfeld’s) charge analyse. Therefore, according to this result one can conclude that the bonds in Li4Sr3Ge2N6 have a mixing of ionic and covalent characters.

3.5. Optical properties

The calculated imaginary and real parts of the complex dielectric function (ε2(ω) and ε1(ω), respectively) for Li4Sr3Ge2N6 are presented in Fig. 12. In order to describe the optical anisotropy, the ε1(ω) and ε2(ω) are calculated for incident radiations with the electric field vector E polarized along the crystallographic a-, b- and c-axes, i.e. \( \vec{E} || [100] \), \( \vec{E} || [010] \) and \( \vec{E} || [001] \). From Fig. 12, we can see that the optical spectra for incident radiations polarized along the [100] and [010] directions are coinciding, which indicates that the optical properties are isotropic for incident radiations polarized along selected directions in the ab-plane. The optical spectra for incident radiations polarized along the [001] direction is clearly different from that polarized in the ab-plane, indicating the presence of a significant optical anisotropy. The absorption edge for incident radiations polarized along the [001] direction shifts toward the higher energy compared to that one for incident radiations polarized along the [100] direction. Since the imaginary part \( \varepsilon_2(\omega) \) of the dielectric function is proportional to the crystal absorption spectrum, it is possible to explain the origin of the structures in \( \varepsilon_2(\omega) \) with the help of the DOS diagram. With the help of the DOS diagram presented in Fig. 11, it is possible to assign the strongest absorption peaks centered at energies lower than 7.0 eV to the transitions from the states of the valence band group V1 (see Fig. 11) to the bottom of the conduction band (CB), and the peaks centered at energies higher than 8.0 eV to the transitions from the valence band group V2 to the bottom of CB. The static dielectric function values are equal to the zero frequency limits of \( \varepsilon_2(\omega) \), which found to be 6.58 and 5.87 for incident radiations polarized along the [100] (or [010]) and [001] directions, respectively.

The calculated spectra of the reflectivity coefficient \( R(\omega) \), absorption coefficient \( \alpha(\omega) \), refractive index \( n(\omega) \), extinction coefficient \( k(\omega) \) and electron energy-loss function \( L(\omega) \) for incident radiations polarized along the [100], [010] and [001] directions in the energy range 0–40 eV are plotted in Fig. 13. The reflectivity coefficient has a value of 19% ([100]) and 17% ([001]) for the zero frequency limits. The \( R(\omega) \) increases with the increasing photon energy to reach a maximum value of about 38% ([001]) for photon energy of 10.7 eV, then it decreases to its minimum level for photon energy of about 17.5 eV and then it increase again to reach its second maximum of about 30% ([001]) for photon energy of
quaternary nitride have been investi-
gated. The fundamental band gap increases with increasing pressure and changes into direct one at 4.10 GPa pressure. Analysis of the Mulliken’s and Hirschfeld’s charge transfers between neighboring atoms indicates the presence of mixing covalent and ionic bonding character. Finally, the dielectric function, absorption coefficient, refractive index, extinction coefficient, reflectivity and electron energy-loss function are computed for three different polarizations of the incident radiations. The obtained spectra clearly indicate the optical anisotropy in Li$_4$Sr$_3$Ge$_2$N$_6$. We hope that these reported results can help to offer a theoretical basis for experimental and application of Li$_4$Sr$_3$Ge$_2$N$_6$.

25.7 eV. The absorption coefficient $\alpha(\omega)$ increases rapidly when the photon energy is higher than the absorption edge, decreases for the photon energy range 10–17.5 eV, then it increases to reach its maximum value for photon energy equal to 24.5 eV ([001]). The calculated static refractive indices are 2.5 and 2.4 for incident radiation polarized along the [100] and [001] directions, respectively. The electron energy-loss function $\omega(\omega)$ is an important factor describing the energy-loss of a fast electron traversing in a material. For incident radiation polarized along the [100] direction, $\omega(\omega)$ has a main peak, the so called plasmon frequency ($\omega_p$), at about 27 eV ([001]) and at 28 eV ([100]), which correspond to the abrupt reductions of reflectivity.

4. Conclusion

In this study, the structural parameters, elastic constants, thermodynamic properties, electronic structures and optical properties of the monoclinic Li$_4$Sr$_3$Ge$_2$N$_6$ quaternary nitride have been investigated by using first-principles pseudopotential plane-wave method. The calculated structural parameters are in excellent agreement with the experimental findings. From the optimized crystal structures at different pressures, the bulk modulus, its pressure derivative and pressure coefficients for the pressure-induced contraction of the lattice constants were all evaluated. It is found that Li$_4$Sr$_3$Ge$_2$N$_6$ is more compressible along the [010] direction than along the [100] and [001] ones.

The 13 independent components of the elastic constants tensor are predicted for Li$_4$Sr$_3$Ge$_2$N$_6$. The reliability of these first numerical estimations of the $C_{ij}$ is confirmed by the good agreement between the bulk modulus value derived from the $C_{ij}$ and that one estimated from the EOS fits. The calculated $C_{ij}$ of Li$_4$Sr$_3$Ge$_2$N$_6$ at zero pressure and under pressures up to 30 GPa obey the mechanical stability criteria. According to three different indexes, Li$_4$Sr$_3$Ge$_2$N$_6$ is characterized by a pronounced elastic anisotropy. Li$_4$Sr$_3$Ge$_2$N$_6$ has a brittle behavior according to Pugh criterion.

The pressure and temperature dependence of the normalized volume, isothermal bulk modulus, heat capacity, volume thermal expansion coefficient and Debye temperature are predicted in a wide range of temperature and pressure through the quasiharmonic Debye model.

It is found that Li$_4$Sr$_3$Ge$_2$N$_6$ has a semiconducting character with an indirect fundamental band gap equal to 2.14 eV. The fundamental band gap increases with increasing pressure and changes into direct one at 4.10 GPa pressure. Analysis of the Mulliken’s and Hirschfeld’s charge transfers between neighboring atoms indicates the presence of mixing covalent and ionic bonding character. Finally, the dielectric function, absorption coefficient, refractive index, extinction coefficient, reflectivity and electron energy-loss function are computed for three different polarizations of the incident radiations. The obtained spectra clearly indicate the optical anisotropy in Li$_4$Sr$_3$Ge$_2$N$_6$. We hope that these reported results can help to offer a theoretical basis for experimental and application of Li$_4$Sr$_3$Ge$_2$N$_6$.

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