

FP-LAPW investigation of mechanical and thermodynamic properties of Na_2X ($\text{X} = \text{S}$ and Se) under pressure and temperature effects

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Structural, elastic and thermodynamic properties of sodium chalcogenides (Na_2X , $\text{X} = \text{S}$, Se) have been calculated using FP-APW+lo method. The ground state lattice parameter, bulk moduli have been obtained. The Zener anisotropy factor, Poisson's ratio, shear modulus, Young's modulus, have also been calculated. The calculated structural and elastic constants are in good agreement with the available data. We also determined the thermodynamic properties, such as heat capacities C_V and C_P , thermal expansion α , entropy S , and Debye temperature Θ_D , at various pressures and temperatures for Na_2X compounds. The elastic constants under high pressure and temperature are also calculated and elaborated.

Keywords: *sodium chalcogenides; FP-LAPW; GGA; structural properties; elastic constants; thermodynamic properties*

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1. Introduction

The alkali metal chalcogenides Na_2X ($\text{X} = \text{S}$, Se) constitute a crystalline family that has shown great technological usefulness in devices requiring high ionic conductivity [1–3] and large fundamental energy band gaps. Apart from being used in power sources, fuel cells, gas-detectors and ultra violet space technology devices [4–6], these ionic compounds also play an important role in the development of photocathodes, in supporting catalytic reactions and enhancing oxidation of semiconductor surfaces [7–14].

At room temperature these compounds crystallize into a stable anti- CaF_2 (anti-fluorite) structure type [15, 16] (space group no. 225). The CaF_2 (calcium fluoride) compound has a basic crystalline structure that consists of face-centered cubic packing of Ca cations, with F anions located in all Ca tetrahedrals. In contrast, the antimorphous to the

CaF_2 structure, in which positions of the cations and anions have been exchanged, is known as an anti-fluorite type structure. In the Na_2X ($\text{X} = \text{S}$, Se) compounds, the metal atoms (Na) are located at (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75) and the atoms (X) are located at (0, 0, 0). These compounds are subjects of many experimental and theoretical works, focusing on structural phase transformation [17–22] and electronic properties [23–27]. The electronic band structure of these materials at ambient conditions was discussed [25] using the self-consistent pseudo-potential method. Alay-e-Abbas et al. [23, 24] have studied electronic density of states of Na_2Se in the framework of density functional theory. They also predicted optical properties and discussed complex dielectric function, absorption coefficient, refractive index and reflectivity for a wide range of phonon energy.

The elastic constants determine the response of a crystal to the external forces, and obviously play an important role in determining the strength of

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materials with respect to the changes in the external macroscopic variables, such as pressure and temperature effects. Elastic properties are also linked thermodynamically with specific heat, thermal expansion, Debye temperature, and Grüneisen parameter. Most importantly, knowledge of the elastic constants is essential for many practical applications related to the mechanical properties of a solid: load deflection, thermoelastic stress, internal strain, sound velocities, and fracture toughness. For more than ten years, the elastic constants of Na₂S and Na₂Se compounds have been determined experimentally by elastic neutron scattering at low temperature [28, 29]. Lichanot *et al.* [30] and Bührer and Bill [1] have calculated the elastic constant for Na₂S compound by linear combination of atomic orbitals (LCAO) method and the shell model. Besides, Kalarasse and Bennecer [31] have used the first principle pseudo-potential method in the framework of the density functional theory [31–33] to obtain the ground state properties and applied linear response techniques [34, 35] to calculate the elastic constants, phonon spectra and related quantities. We, therefore, thought deeply to perform these calculations in the framework of the full potential augmented plane wave plus local orbitals (FP-APW+lo) method to study the structural, elastic and thermodynamic properties of Na₂S, Na₂Se in the anti-fluorite phase under high pressures and temperature, in order to provide reference data for the experimentalist and to complete the exciting theoretical work on this fascinating class of materials.

The paper is organized as follows. In the section two we give a brief description of computational methodology employed in this study. Section three deals with the results and their discussion, whereas in section four we summarize conclusions drawn from our study.

2. Computational methods

In this study, DFT calculations were completed using FP-LAPW+lo scheme of calculations [36–38] as realized in WIEN2k computational package [39]. This method has proven to be one

of the most accurate methods for the computation of the electronic structure of solids within DFT [40–45]. In this scheme of calculations APW+lo basis set is incorporated to represent the electronic band structure for all atoms as well as corresponding orbitals. Correspondingly, computational time is considerably shortened as convergence criteria are met professionally at lesser value of $R_{\text{MT}}K_{\text{max}}$. Moreover, no shape approximation is imposed for charge density as well as potential. To deal with semi-core states, local orbital extensions are mixed up. To perform calculations, a simulated crystal unit cell is partitioned into non-touching muffin tin (MT) spheres as well as interstitial space. To attain the best criterion of convergence for energy eigenvalues, in the interstitial space, wave functions are expanded into plane-waves taking a cutoff value of $R_{\text{MT}}K_{\text{max}} = 9$, whereas R_{MT} stands for muffin tin (atomic sphere) radii and K_{max} is used for the largest value of K vector used to expand the plane-waves. The values of R_{MT} , i.e. 2.1 a.u. for Na, 2.2 a.u. for S and 2.8 a.u. for Se were used. Inside the muffin tin spheres, valence wave functions were expanded equal to $l_{\text{max}} = 10$, while the value of $G_{\text{max}} = 12$ was taken into account for the Fourier expansion of the charge density. For the exchange-correlation energy functional, we employed parameterized generalized gradient approximation implemented by Wu and Cohen [46] (WC-GGA). Brillouin zone (BZ) integration was performed by employing tetrahedron technique. For a suitable set of special k -points, $9 \times 9 \times 9$ Monkhorst-Pack sampling was used to calculate the total energy. In our calculations the valence electrons were treated within the scalar relativistic limit, whereas core electrons were dealt fully relativistically.

To investigate the thermodynamic properties of Na₂X compounds, we here applied the quasi-harmonic Debye model implemented in the Gibbs program [47]. This model allows determination of all thermodynamic quantities from the calculated energy-volume points. For the calculations, the non-equilibrium Gibbs function G^* was used:

$$G^*(V, P, T) = E(V) + PV + A_{\text{vib}}(\Theta(V), T) \quad (1)$$

here $E(V)$ is the total energy per unit cell, $P(V)$ is the constant hydrostatic pressure condition, Θ is the Debye temperature and A_{vib} is the vibrational Helmholtz free energy. According to quasiharmonic Debye model of phonon density of states, A_{vib} as in [47, 48] is described as follows:

$$A_{\text{vib}}(\Theta, T) = 7nk_B T \left[\frac{9\Theta}{8T} + 3 \ln(1 - e^{-\Theta/T}) - D(\Theta/T) \right] \quad (2)$$

where n is the number of atoms per formula unit, k_B is the Boltzmann's constant, and $D(\Theta/T)$ represents the Debye integral. For an isotropic solid, Θ is expressed as in [47, 48]:

$$\Theta = \frac{\hbar}{K} [6\pi^2 V^{1/2} n]^{1/3} f(\sigma) \sqrt{\frac{B_S}{M}} \quad (3)$$

Θ is the Debye temperature, M is the mass of per formula unit, σ is Poisson ratio and B_S is the adiabatic bulk modulus that is approximated as:

$$B_S \cong B(V) = V \frac{d^2 E(V)}{dV^2} \quad (4)$$

where $f(\nu)$ is defined as:

$$f(\nu) = \left\{ 3 \left[2 \left(\frac{2(1+\nu)}{3(1-2\nu)} \right)^{3/2} + \left(\frac{1+\nu}{3(1-\nu)} \right)^{3/2} \right]^{-1} \right\}^{1/3} \quad (5)$$

Details of the values of $f(\nu)$ and B_S are given in various references [50–53] and ν is taken as 0.25 [50]. Therefore, the non-equilibrium G^* is a function of V , P , and T . It is minimized with respect to V :

$$\left(\frac{\partial G^*(V, P, T)}{\partial V} \right)_{P, T} = 0 \quad (6)$$

By solving equation 6, we obtain the EOS $V(P, T)$. The isothermal bulk modulus B_T , the heat capacity at constant volume C_V , the heat capacity at constant pressure C_P and the thermal expansion coefficient α are given by:

$$B_T(P, T) = V \left(\frac{\partial^2 G^*(V; P, T)}{\partial V^2} \right)_{P, T} \quad (7)$$

$$C_V = 3nk_b \left[4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right] \quad (8)$$

$$C_P = C_V(1 + \alpha\gamma T) \quad (9)$$

$$\alpha = \frac{\gamma C_V}{B_T V} \quad (10)$$

$$S = nk_B [4D(\Theta/T) - 3 \ln(1 - e^{-\Theta/T})] \quad (11)$$

Here, γ is the Grüneisen parameter which is defined as follows:

$$\gamma = - \frac{d \ln \Theta(V)}{d \ln V} \quad (12)$$

3. Results and discussion

3.1. Structural properties

While calculating structural properties of Na₂S and Na₂Se crystals in anti-CaF₂ structure type, volume optimization was performed using WC-GGA exchange-correlation functional. Equilibrium lattice constants (a_0), total energies (E_0), bulk modulus (B_0) and its pressure derivatives (B'_0) were calculated by fitting Murnaghan equation of state [54] to the total energy versus volume curve. The total energy vs. volume curve for sodium chalcogenides (viz. Na₂X, X = S, Se) are shown in Fig. 1. Table 1 summarizes our calculated structural parameters (lattice constants, bulk modulus and its pressure derivative) of Na₂S and Na₂Se at ambient pressure. Our calculated lattice constant for Na₂S and Na₂Se is 6.5223 Å and 6.7756 Å, respectively. This result accords well with the experimental and theoretical ones. However, for the results of B_0 and B'_0 , we find that there is good agreement between our results and the results calculated with other theories. The temperature effect on the lattice parameters of Na₂S and Na₂Se compounds is displayed in Fig. 2. It can be seen that the lattice parameters increase linearly with increasing of temperature. The rate of increase is almost zero from $T = 0$ to 100 K and becomes very moderate for $T > 100$ K. On the other hand, as the pressure increases, the lattice parameter decreases at a given temperature. Generally speaking, the lattice constant increases as the

temperature increases, and decreases as the pressure increases. The calculated equilibrium primitive cell volume V at zero pressure and room temperature is 468.10 \AA^3 and 524.79 \AA^3 for Na_2S and Na_2Se , respectively. The relationship between the bulk modulus B_0 and temperature at different pressures is shown in Fig. 3. At temperatures lower than 100 K, B_0 remains almost constant because of the small change in volume of the primitive cell. At temperatures higher than 100 K up to 1000 K, B_0 decreases with T at a given pressure which indicates that the rapid volume variation causes the bulk modulus to decrease rapidly, while it increases with P at a given temperature. It shows that the effect of increasing pressure on Na_2S and Na_2Se is the same as decreasing its temperature.

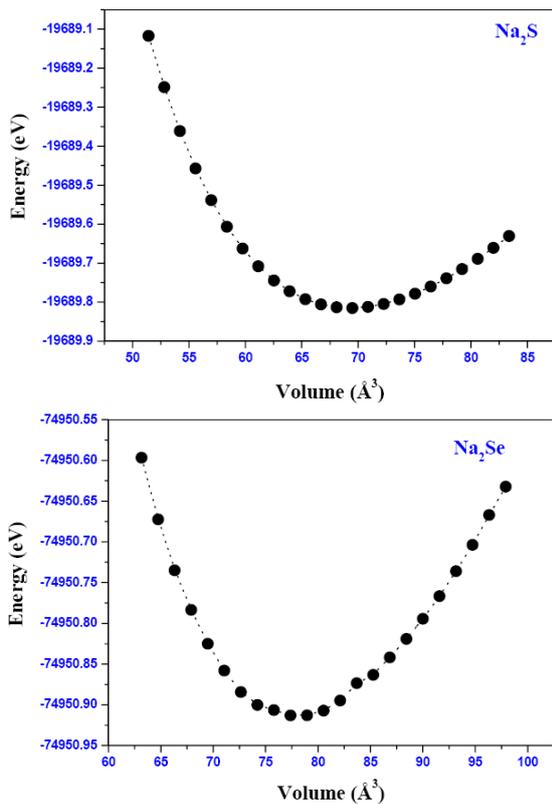


Fig. 1. Total energy as a function of volume for Na_2S and Na_2Se calculated with GGA.

3.2. Thermodynamic properties

Using the quasi-harmonic Debye model, the thermal EOS and thermodynamic properties of

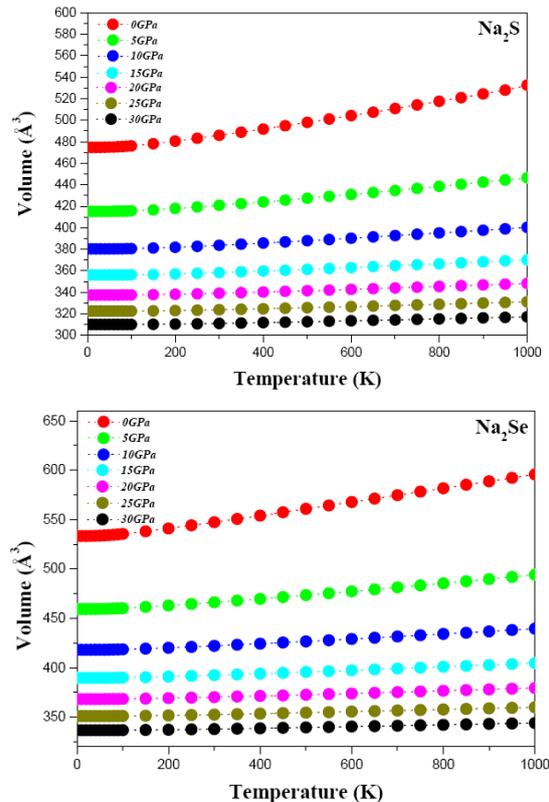


Fig. 2. The variation of the primitive cell volume as a function of temperature at different pressures of Na_2S and Na_2Se .

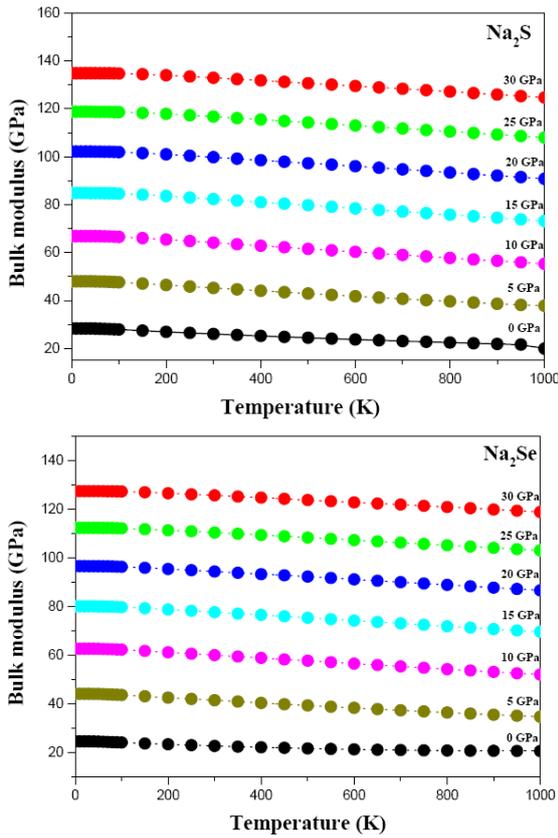
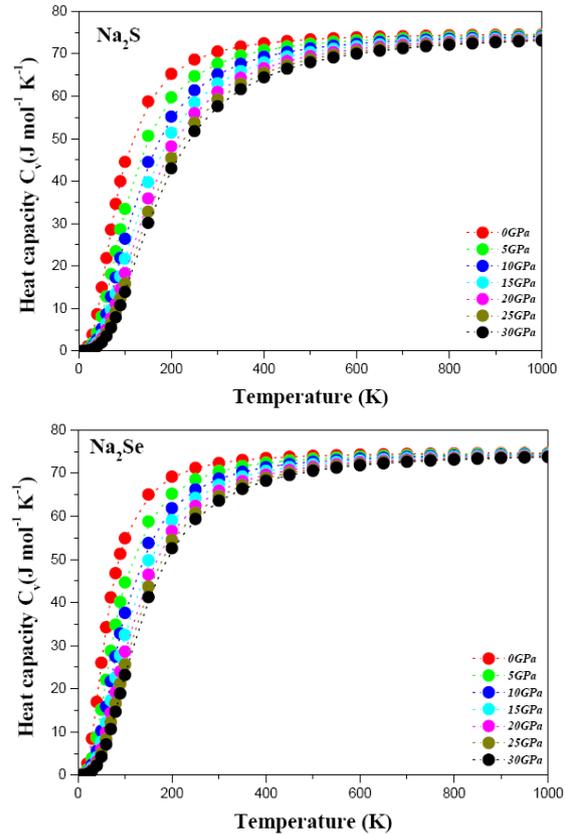
Na_2X ($X = \text{S}, \text{Se}$) with anti- CaF_2 phase compounds were investigated below the melting point (up to 1000 K), where the quasi-harmonic approximation remains fully valid. The pressure effect was studied in the range from 0 to 30 GPa.

The heat capacity is an important parameter of the condensed matter. It does not only provide a fundamental insight into the vibrational properties but is also mandatory for many applications. At intermediate temperatures, temperature dependence of the heat capacity C_V is governed by the vibrations of atoms and could be determined only experimentally for a long time past [55]. Fig. 4 and Fig. 5 show the calculated specific heats at a constant volume C_V and a constant pressure C_P of Na_2S and Na_2Se . At low temperatures, the shapes of the curves of C_V and C_P are similar. As known, the increase of heat capacity with T^3 at low temperatures is due to the harmonic approximation of the

Table 1. Calculated lattice constant a_0 (Å), bulk modulus B_0 (GPa), its first pressure derivatives B'_0 for Na₂S and Na₂Se, compared to the experimental data and previous theoretical calculations.

Parameters	Present work	Other calculations									Experimental	
Na ₂ S	a_0	6.5223	6.634 ^c	6.644 ^d	6.264 ^d	6.299 ^d	6.375 ^d	6.428 ^e	6.388 ^f	6.581 ^f	6.526 ^a	
	B_0	28.3643	28.20 ^c	39.00 ^d	38.80 ^d	34.84 ^d	29.94 ^d	32.95 ^e	33.98 ^f	28.67 ^f		49.00 ^b
	B'_0	4.0502	3.82 ^f	3.66 ^f	3.21 ^m	5.52 ^m	4.30 ^o					
Na ₂ Se	a_0	6.7756	6.796 ^l	6.856 ^l	6.651 ^l	6.763 ^o						6.81 ^{a,p}
	B_0	25.2718	24.8830 ^l	24.88 ^l	29.03 ^l	39 ^k	22.6 ^h	30.7 ⁱ	30.63 ^o			6.823 ⁿ
	B'_0	4.2571	4.15 ^o									

^a[15], ^b[29], ^c[26], ^d[20], ^e[62], ^f[63], ^g[64], ^h[65], ⁱ[66], ^k[67], ^l[23], ^m[68], ⁿ[69], ^o[31], ^p[70].

Fig. 3. Temperature dependence of bulk modulus B of Na₂S and Na₂Se at different pressures.Fig. 4. Calculated temperature dependence of heat capacity of Na₂S and Na₂Se at a constant volume (C_V).

Debye model. However, at high temperatures, when $T > 600$ K, C_V converges to a near-constant value, which is in agreement with Dulong-Petit law. However, C_p tends to be linear with

temperature. Our calculated values of C_V at zero-pressure and 300 K are 70.48 and 72.41 ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) for Na₂S and Na₂Se, respectively.

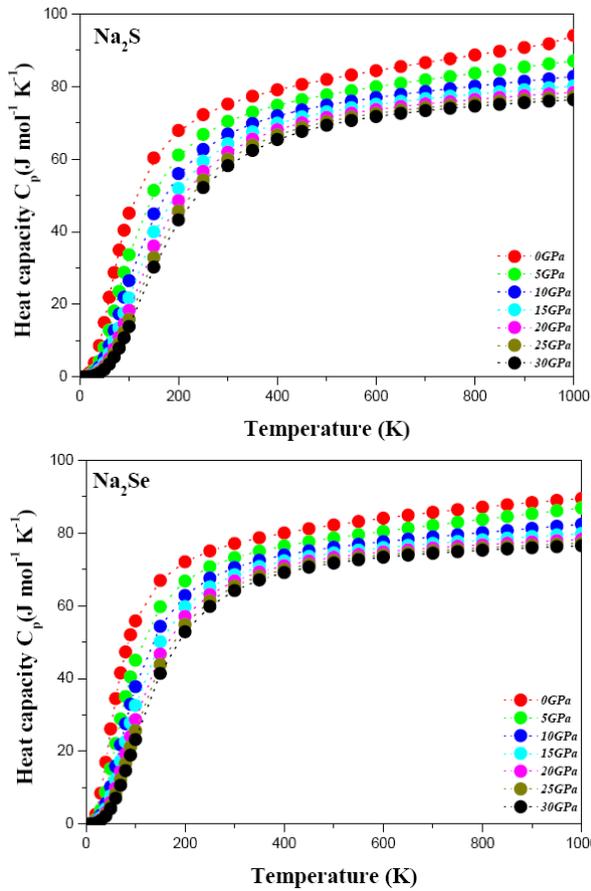


Fig. 5. Temperature dependence of heat capacity of Na₂S and Na₂Se at a constant pressure (C_p).

Variations of the thermal expansion coefficient α with temperature at 0, 10, 20, and 30 GPa are shown in Fig. 6. It is seen that for a given temperature, α decreases with an increase of pressure and becomes small at higher pressures. On the other hand, it is clear that α also increases exponentially at lower temperatures ($T < 250$ K) and starts to increase linearly at higher temperatures ($T > 300$ K). The temperature dependence of α is very small at high temperature but the variation increases linearly with temperature. At $P = 0$ GPa and $T = 300$ K, the values of α for Na₂S, Na₂Se are 12.25×10^{-5} , 12.48×10^{-5} K, respectively. The entropy S under high pressure and high temperature can be obtained according to equation 11. Fig. 7 shows the curve of entropy S at different pressures and temperatures. The curves indicate that the entropy decreases with pressure at a given

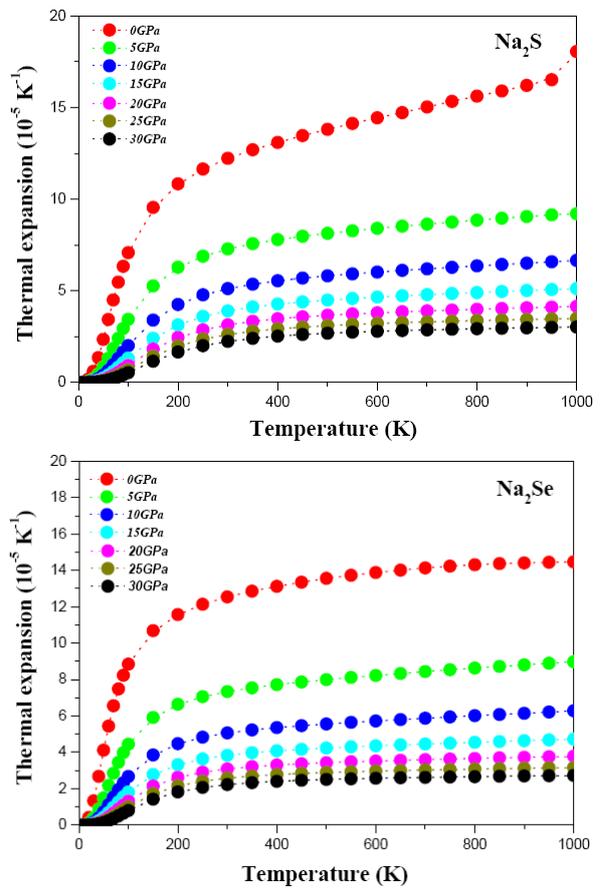


Fig. 6. Thermal expansion as a function of temperature T of Na₂S and Na₂Se at different pressures.

temperature and increases monotonously with temperature at a fixed pressure.

The Debye temperature (Θ_D) is an important parameter characteristic of the thermal properties of solids. It is the temperature above which the crystal behaves classically, because the thermal vibrations become more important than the quantum effects. The variation of the Debye temperature as a function of pressure and temperature is plotted in Fig. 8. At temperatures less than 100 K, the values of Θ_D remain constant; above 100 K, Θ_D decreases linearly with increasing of temperature. The Debye temperatures Θ_D of the Na₂X compounds at the temperature of 300 K are higher than those at 1000 K, which shows that the vibration frequency of the particles in Na chalcogens: Na₂S and Na₂Se changes with the pressure and temperature.

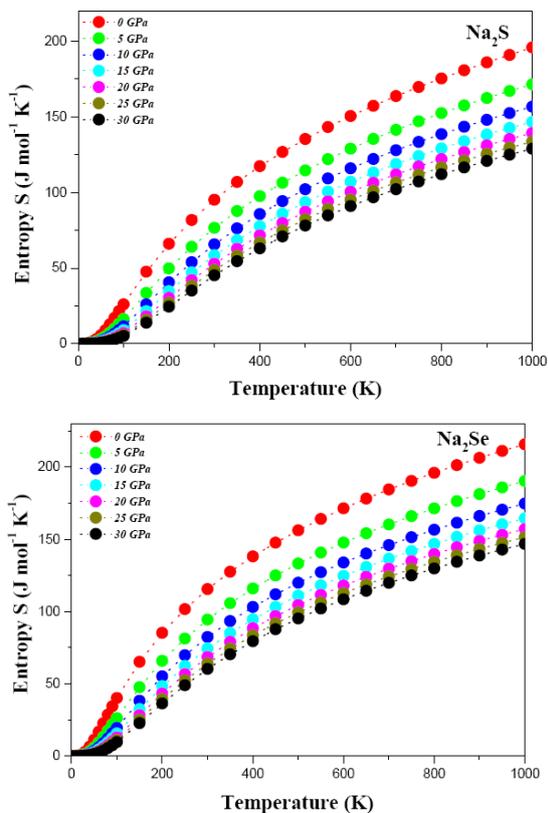


Fig. 7. The variation of entropy as a function of temperature at different pressures of Na_2S and Na_2Se .

Calculated values of Θ_D for Na_2S and Na_2Se at zero pressure and zero temperature were found to be equal to 342.62 and 258.94 K, respectively. Therefore, Θ_D decreases in the order $\text{Na}_2\text{S} < \text{Na}_2\text{Se}$. The volume dependence of the Debye temperature Θ_D is shown in Fig. 9 at some fixed temperatures and the quasi-harmonic approximation, which introduces the temperature dependence through the volume. It is noted that as the volume V increases, the value of the Debye temperature decreases. The relatively small effect of temperature on the Debye temperature can be explained by the small effect on the volume changes. It is observed that for a constant temperature, the Debye temperature of the herein studied materials increases almost linearly with a decrease of the volume.

3.3. Elastic properties

Knowledge of elastic constants of materials is essential for better understanding of their

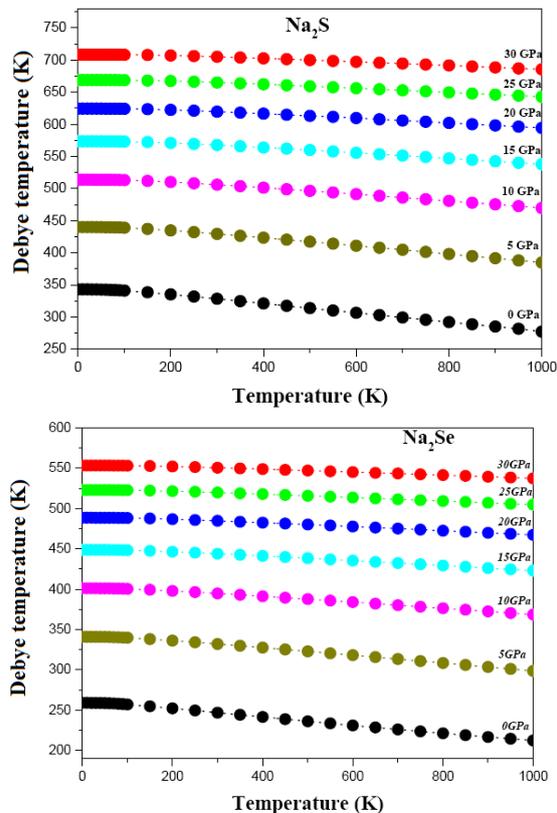


Fig. 8. The variation of the Debye temperature as a function of temperature at different pressures of Na_2S and Na_2Se .

properties. From practical viewpoint, the elastic constants describe the linear response of a material to external forces. Some basic mechanical properties can be derived from the elastic constants, such as the bulk modulus, Young's modulus, shear modulus, Poisson's ratio, which play an important role in determining the strength of the materials. From a fundamental viewpoint, the elastic constants are related to various essential solid-state properties, such as interatomic potentials, equation of state, structural stability, phonon spectra, which are linked thermodynamically to the specific heat, thermal expansion, Debye temperature, melting point, and Grüneisen parameter. In our case, these compounds have a cubic symmetry, hence, only three independent elastic constants C_{11} , C_{12} and C_{44} should be calculated. The elastic constants C_{ij} are obtained by calculating the total energy as a function of volume conserving strains using Mehl

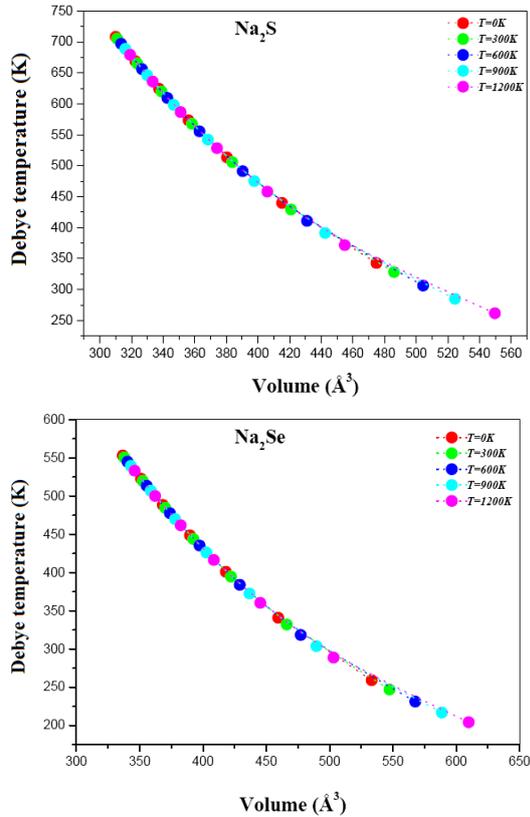


Fig. 9. The variation of the Debye temperature as a function of volume at different pressures of Na₂S and Na₂Se.

method [56]. The calculated elastic constants for Na₂X compounds are given in Table 2, together with other theoretical data. The traditional mechanical stability conditions of the elastic constants in a cubic crystal are known as $C_{11} + 2C_{12} > 0$, $C_{11} - C_{12} > 0$, $C_{44} > 0$. The calculated elastic constants in Table 2 satisfy these stability conditions in anti-CaF₂ structure, indicating that it is in mechanically stable state at ambient pressure.

The Zener anisotropy factor A, Poisson's ratio σ , shear modulus G, and Young's modulus E, which are the most interesting elastic properties for applications, are often measured for polycrystalline materials when investigating their hardness. These quantities are calculated in terms of the elastic constants C_{ij} , using the following relations [57]:

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (13)$$

$$\sigma = \frac{1}{2} \left(\frac{B - \frac{2}{3}G}{B + \frac{1}{3}G} \right) \quad (14)$$

$$E = \frac{9BG_H}{3B + G_H} \quad (15)$$

where $B = (C_{11} + 2C_{12})/3$ is the bulk modulus and $G = (G_V + G_R)/2$ is the isotropic shear modulus, G_V is the Voigt's shear modulus corresponding to the upper bound of G values and G_R is the Reuss's shear modulus corresponding to the lower bound of G values; they can be written as [58]:

$$G_V = \frac{(C_{11} - C_{12} + 3C_{44})}{5} \quad (16)$$

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \quad (17)$$

The calculated relative quantities of elastic properties are listed in Table 3. As can be seen from the Table 3, the Na₂S and Na₂Se compounds are considered as isotropic materials. Poisson's ratio provides more information about the characteristics of the bonding forces than any other elastic constants. 0.25 and 0.5 are the lower and the upper limits for central force solids. The calculated Poisson ratio of Na₂S and Na₂Se is very close to 0.22, 0.23, respectively, which means that Na₂S and Na₂Se are with predominantly central interatomic forces [59]. The bulk modulus B_0 represents the resistance to fracture, while the shear modulus G represents the resistance to plastic deformation [60]. A high Pugh's B/G ratio is associated with ductility, whereas a low value corresponds to the brittle nature. The critical value which separates ductile and brittle material is 1.75; i.e. if $B/G > 1.75$, the material behaves in a ductile manner; otherwise the material behaves in a brittle manner [61]. The calculated results for our materials Na₂S, Na₂Se are 1.46 and 1.58, respectively, so they can be classified as brittle at ambient conditions.

We further studied the high-pressure elastic behavior of Na₂S and Na₂Se by computing the second-order elastic constants and their variation

Table 2. Calculated elastic constants (in GPa) for Na₂S and Na₂Se in anti-CaF₂ structure.

Material	Parameters	Present work	Other calculations						Experimental	
Na ₂ S	C ₁₁	53.94	64.4 ^c	58.4 ^a	54.07 ^f	61.36 ^f	92.2 ^m	72.8 ^m	61.24 ^o	81.0 ^d
	C ₁₂	15.50	21.7 ^c	13.6 ^a	15.96 ^f	20.28 ^f	21.7 ^m	41.2 ^m	21.99 ^o	33.0 ^d
	C ₄₄	19.00	17.9 ^c	20.0 ^a	19.94 ^f	21.42 ^f	22.9 ^m	21.7 ^m	20.40 ^o	21.0 ^d
Na ₂ Se	C ₁₁	46.09	50.84 ^o							
	C ₁₂	14.01	19.18 ^o							
	C ₄₄	15.28	17.17 ^o 22.86 ^o							

^a[30], ^c[1], ^d[28], ^f[63], ^m[68], ^o[31].

with pressure as shown in Fig. 10. The elastic constant C₁₁ represents the elasticity in length, which changes with longitudinal strain. The elastic constants C₁₂ and C₄₄ are related to the elasticity in shape. It can be seen that C₁₁ and C₁₂ increase linearly with pressure. C₁₁ and C₁₂ are more sensitive to the change in pressure compared to C₄₄.

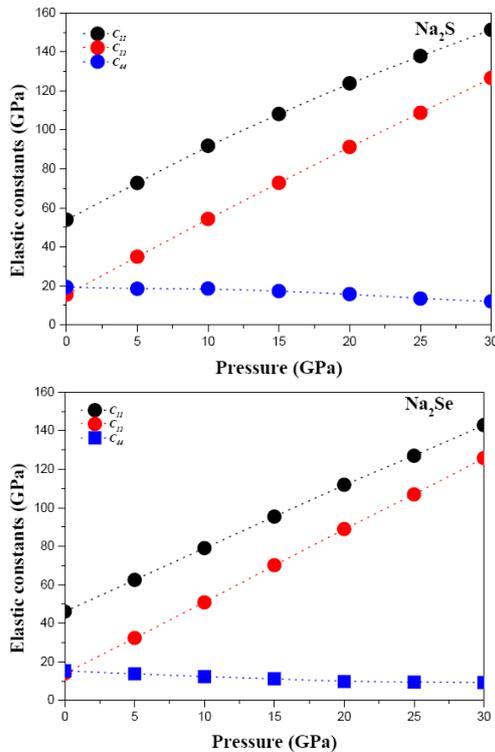


Fig. 10. Pressure dependence of the elastic constants (C₁₁, C₁₂ and C₄₄) of Na₂S and Na₂Se.

In order to study the temperature dependence of the elastic properties of these compounds, we

have focused our study on the temperature range from 0 to 1000 K. The temperature variations of the isothermal elastic constants C_{ij}^T for Na₂X compounds are presented in Fig. 11. We can observe that the elastic constants: C₁₁^T and C₁₂^T decrease slightly when the temperature is enhanced. However, we have found almost constant behavior of C₄₄^T versus temperature. The variation of C₁₁^T and C₁₂^T with temperature is found to be larger as compared with C₄₄^T which is related to the elasticity in shape (connected with shear constant). It is known that a longitudinal strain produces a change in volume without a change in shape, and from that we can conclude that the change in volume is related to the temperature and, thus, it produces some changes in C₁₁^T and C₁₂^T. On the other hand, a transverse strain or shearing causes a change in shape without a change in volume. Thus, C₄₄^T is less sensitive to temperature.

4. Conclusion

In the present work, first principles calculations have been used to study the structural, elastic and thermodynamic properties of anti-CaF₂ type compounds, Na₂X, X = S, Se. The calculations indicate that the obtained values of equilibrium lattice constant, a₀ and bulk modulus, B₀ are in good agreement with available theoretical and experimental studies. Furthermore, the elastic constants are in reasonable agreement with available data and indicate that these compounds are stable against elastic deformations and demonstrate that the Na₂S and Na₂Se in anti-CaF₂ phase keep dynamic

Table 3. Calculated Zener anisotropy factor A, Poisson's ratio ν , bulk modulus B (in GPa), shear modulus G (in GPa), Young's modulus E (in GPa).

Material	Reference	B	G	E	A	B/G	ν
Na ₂ S	GGA	28.34	19.34	47.26	1.01	1.46	0.22
	Theoretical	28.67 ^a	19.58 ^a	47.84 ^a	–	1.46	0.22 ^a
Na ₂ Se	GGA	24.71	15.58	38.62	0.95	1.58	0.23
	Theoretical						

^a[63].

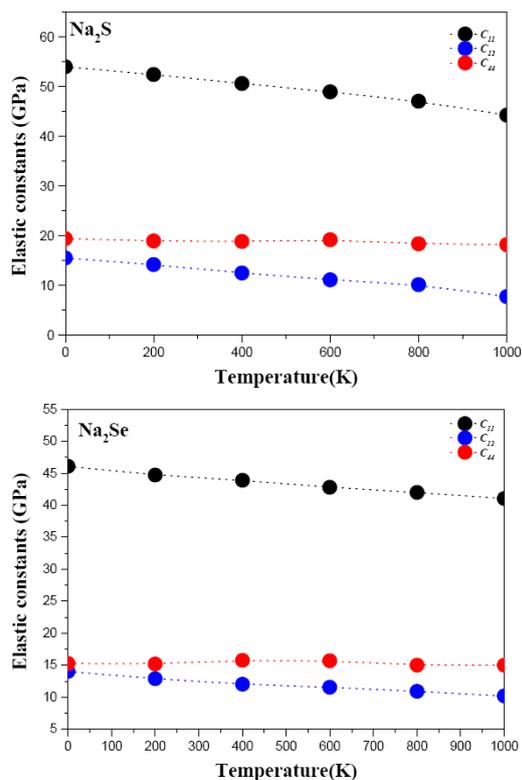


Fig. 11. Temperature dependence of the elastic constants (C_{11} , C_{12} and C_{44}) of Na₂S and Na₂Se.

stability up to 30 GPa. We have also calculated and presented the thermodynamic quantities, elastic constants C_{ij} and interrelated quantities under high pressure and temperature. The thermal contribution to the elastic constants is very significant, and in the range of 0 to 1000 K, the values of the SOEC are changing remarkably.

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