

Research Article

Electronic, Elastic, Optical, and Thermodynamic Properties Study of Ytterbium Chalcogenides Using Density Functional Theory

Lemessa Asefa Eressa 💿 and Zeleke Deressa Gerbi

Department of Physics, College of Natural and Computational Sciences, Ambo University, P.O. Box 19, Ambo, Ethiopia

Correspondence should be addressed to Lemessa Asefa Eressa; lemessaphys@gmail.com

Received 3 August 2023; Revised 17 January 2024; Accepted 12 February 2024; Published 23 February 2024

Academic Editor: Sergio Ulloa

Copyright © 2024 Lemessa Asefa Eressa and Zeleke Deressa Gerbi. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In this study, the structural, electronic, optical, elastic, and thermodynamic properties of Ytterbium chalcogenides YbX (X = S, Se and Te) were computed within the first principles using generalized gradient approximation (GGA) as implemented in the pseudopotential plane wave approach. The equilibrium total energy for YbX (X = S, Se, and Te) was calculated as a function of the energy cutoff, *k*-point grid, and lattice parameter. An optimized lattice parameter of 5.6, 5.66, and 6.136 Å were calculated for YbS, YbSe, and YbTe, respectively. The energy band gaps of YbS, YbSe, and YbTe computed are 1.14, 1.32, and 1.48 eV, respectively. In addition, the low band gap (less than 3 eV) for ytterbium chalcogenides indicated that they may have potential applications in photovoltaic cells and laser diodes. Moreover, the negative dielectric function value for a certain frequency range indicates that these compounds are suitable for specific optical and microwave circuit applications. The result of elastic and thermodynamic property computation reveals that ytterbium chalcogenides are mechanically and thermodynamically stable, which can be useful in a variety of electronic device applications.

1. Introduction

Chalcogenides, which are compounds and alloys of sulfur, selenium, and tellurium exhibit remarkable magnetic, electronic, catalytic, thermal, optical, and superconductivity properties [1]. Their excellent tuning characteristics make them suitable for use in diodes, lasers, solar cells, transistors, and sensor materials [2].

Ytterbium has been utilized in filters, glass fibers, stainless steel, and lasers [3–7]. It is a stable element that will be resistant to heat and electrical stress when used as a dopant. It also enhances the host sample's mechanical properties, strength, or efficiency. For instance, when end-pumped through both fiber ends, a ytterbium-doped large-core fiber laser produced up to 1 kW of continuous-wave output power with 80% slope efficiency and good beam quality [8, 9].

The use of ytterbium chalcogenides in nanoelectronic device applications has attracted considerable attention [10]. Ytterbium, posing a $4 f^{14} 6 s^2$ electronic structure, and the

electrons fully filled in the 4 f orbit contributes two electrons of 6 s orbit to combine with sulfur, selenide, and telluride [11]. Due to its use in the improvement of supercapacitors, ytterbium sulfide (YbS) is receiving significant attention [12]. In addition, it has applications as an electrode material [13], and ternary magnetic material [14]. Selenium nanoparticles have been shown to have anticancer, antioxidant, antibacterial, and antibioplastic properties [15]. YbSe (ytterbium selenide) nanoparticles are highly absorbable in the near-infrared range and highly photoluminescent. Ytterbium telluride (YbTe) is also a potential material for the fabrication of heterojunction diode lasers [16].

So far, neither experimentally nor theoretically have the structure, electronic, elastic, optical, or thermodynamic properties of ytterbium chalcogenides been thoroughly described. Furthermore, there was no comparative analysis of the previously mentioned characteristics of YbS, YbSe, and YbTe. This inspired the authors to conduct a thorough investigation into the structural, electronic, elastic, optical, and thermodynamic characteristics of each ytterbium chalcogenide.

2. Computational Methods

The calculations were conducted on the basis of nonspin polarized DFT (NPPD) as used in the Quantum Espresso Package to evaluate the structural, electronic, elasticity, optical, and thermodynamic properties of ytterbium chalcogenides. Quantum Espresso fosters methodological innovation in the field of electronic structure simulations and provides a wide and diverse community of end users with highly efficient, robust, and user-friendly software implementing the most recent innovations in condensed matter physics [17].

Quantum Espresso is a well-liked program for calculating materials' and molecules density functional theory (DFT). While it has some benefits and drawbacks that might make it a better fit for some applications, it is not always superior to other DFT programs. It is favored over other software because it is open source and free, allowing anyone to use, after, and contribute to its development. Additionally, it has a sizable and vibrant user and development community that offers documentation and assistance. Some DFT programs, like VASP, are proprietary and need a license to operate, which could restrict who can use them.

In this study we have used ultra soft pseudo potentials which are computationally efficient than the norm conserving pseudopotential. Moreover, we have employed the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Emzerhof (PBE) for the exchange and correlations of electrons. Because, the PBE performs well in describing a wide range of properties, including structural, electronic, and elastic properties, it has been widely used in DFT calculations for a variety of systems. It is renowned for accurately describing bond lengths, vibrational frequencies, and molecular geometries. It is also very good at simulating the behavior of solids and compounds containing transition metals [18].

The convergence in DFT calculations tests the total energy of an equilibrium cell to obtain energy cutoff and k-point values that achieve an error level in total energy less than 0.001 eV/atom.

In this study, the convergence test for YbX (X = S, Se, and Te) was performed by computing total energy as a function of energy cutoff, k-point, and lattice parameter consecutively. The convergence test of total energy against the energy cutoff is made with an increase in the energy cutoff by 5 Ry in the range of 30–100 Ry (in the experimental range). In the calculation, while varying the energy cutoff from 60 to 65 Ry in the input file, a change in total energy of 0.001 eV/atom was observed in all ytterbium chalcogenides. Thus, the energy cutoff 65 Ry is the value at which each ytterbium attains a stable equilibrium.

After fixing the optimal value of energy cutoff, we performed the calculation for *k*-point optimization. The total energy of YbX (X = S, Se, and Te) was calculated using various sets of *k*-points ranging from $1 \times 1 \times 1$ to $10 \times 10 \times 10$ to ensure the accuracy of the calculation. The optimized *k*-point was achieved at $5 \times 5 \times 5$ *k*-point for YbS, YbSe, and at 6×6 $\times 6 k$ -point for YbTe, respectively. Furthermore, computations of the optimized lattice parameter were employed by inserting the respective optimized energy cutoff and *k*-points in the input file. The self-consistent calculations of total energy with different values of lattice parameters were performed from 9.6 to 12.0 Bohr for YbS, from 10.0 to 12.0 Bohr for YbSe, and from 10.0 to 13.0 Bohr for YbTe, respectively. Finally, the calculated optimized energy cutoff, *k*-point and lattice parameter were used in the input file for subsequent computations of electronic, elastic, optical, and thermodynamic properties of ytterbium chalcogenides.

In this study, we have used a thermo_pw software linked with Quantum Espresso to calculate the mechanical, thermodynamic, and optical properties of ytterbium chalcogenides. Accordingly, we used what = "scf_elastic_constants", what = "scf_disp", and what = "scf_ph" in the what variable control input file of thermo_pw software for the calculation of mechanical, thermodynamic, and optical property, respectively. Finally, the respective output files output_el_cons.dat, output_therm. g1.ps and output_epsilon.ps for the mechanical, thermodynamic, and optical properties were plotted using origin software and discussed.

3. Result and Discussions

3.1. Lattice Parameter Optimization of Ytterbium Chalcogenides. YbS, YbSe, and YbTe crystallize in the cubic Fm-3 m space group of rock salt structure [16, 19, 20]. Figure 1(a)–1(c) presents the plot of total energy of ytterbium chalcogenides as a function of lattice parameter. Table 1 depicts the lattice parameter of ytterbium chalcogenides calculated using GGA-PBE approximation. The calculated lattice parameters that minimizes the DFT of total energy are 10.6 Bohr (5.6 Å) for YbS, 10.7 Bohr (5.66 Å) for YbSe, and 11.6 Bohr (6.136 Å) for YbTe, respectively. These values are consistent with literature data for YbS (5.693–5.86) Å [19, 22], YbSe 5.879 Å [20], and for YbTe 6.357 Å [16].

3.2. Electronic Properties of Ytterbium Chalcogenides

3.2.1. Density of States (DOS). The DOS is defined as the number of states per unit energy range available for the particles to be occupied. The DOS provides numerical information on the states that are available at each energy level. The value of zero DOS indicates that there are no available states for occupation in an energetic level. The results of DOS of YbX (X = S, Se, and Te) help to further elaborate the nature of the band gap as shown in Figure 2(a)–2(c).

The DOS is discontinuous for the width between the top of the valence band and the bottom of the conduction band, which is typically the ytterbium chalcogenides band gap as illustrated in Figure 2(a)-2(c). This energy band gap width is largest for YbTe than YbSe and YbS, respectively. This demonstrates once more that YbTe has a largest energy band gap than YbSe and YbS, respectively.

Figure 3(a)-3(c) depicts the partial and total DOS of ytterbium chalcogenides. The maximum total DOS about 2.5 eV is formed from the contribution of ytterbium 4 f and chalcogenides (S, Se, Te) 3 p states.



FIGURE 1: Lattice parameter of (a) YbS, (b) YbSe, and (c) YbTe.

	TABLE 1: Lattice	parameters	of	vtterbium	chal	cogenides.
--	------------------	------------	----	-----------	------	------------

Compound	Lattice	parameter
Compound	Present study	Experiment
YbS	5.6 Å	5.693 Å [19]
YbSe	5.66 Å	5.879 Å [20]
YbTe	6.136 Å	6.357 Å [16, 21]



FIGURE 2: Total density of states: (a) YbS, (b) YbSe, and (c) YbTe.

3.2.2. Band Structure of Ytterbium Chalcogenides. The band structure of solid is helpful to determine different electronic properties of solid. It contains the basic ingredients to almost all the crystal properties. Since the atoms in a solid are closely packed, the interaction between them [7] perturbed the initial atomic levels when a large number of atoms are brought together. The electronic band diagram of YbX (X = S, Se, and

Te) were computed using GGA-PBE exchange-correlation functional along high-symmetry axes of the Brillion zone as shown in Figure 4(a)-4(c).

As it can be seen from Figure 4(a)-4(c), the valance bands are separated from the conduction band gap value of 1.14 and 1.32, and 1.48 eV for YbS, YbSe, and YbTe, respectively. These are consistent with the previously reported



FIGURE 3: Partial and total density of states: (a) YbS, (b) YbSe, and (c) YbTe.



FIGURE 4: Band structure of (a) YbS, (b) YbSe, and (c) YbTe.

TABLE 2:	Band	gap	energy	of	vtterbium	chal	cogenides
	2.001100	577	····	~	,		- Series

Commonia	Band gap energy				
Compound	Present study	Experimental			
YbS	1.14 eV	1.1 eV [23]			
YbSe	1.32 eV	1.35–1.45 eV [23]			
YbTe	1.48 eV	1.7–1.75 eV [23]			

values 1.1 eV for YbS, 1.35–1.45 eV for YbSe, and 1.7–1.75 eV for YbTe [23]. The energy band gap of ytterbium chalcogenides computed is below 3 eV, which classifies them as semiconductor materials. Therefore, they are promising candidate in photovoltaic, photochemical, and laser diode applications [24]. Table 2 presents the band gap energy of ytterbium chalcogenides computed using GGA-PBE approximation.

3.3. Elastic Properties of Ytterbium Chalcogenides. In order to choose a material for engineering applications, it is important to consider a material's mechanical properties, such as stability, stiffness, brittleness, and ductility [25]. Elastic constants are fundamental and essential for describing the mechanical properties of materials. The bulk modulus (B), Shear modulus (G), Young's modulus (E), and Poisson's ratio (n) of the material can all be calculated using these methods. The strain response of a body to hydrostatic stress, which involves a change in volume without a change in shape is described by the bulk modulus. The body's strain response to torsional or shear stress is related to the shear modulus. It entails a change in shape without affecting volume. The stiffness of an isotropic elastic material is measured by the Young's modulus, also referred to as the tensile modulus. In elastic regime, it is defined as the ratio of the uniaxial

				-		
Compound	C ₁₁ (GPa)		<i>C</i> ₁₂ (GPa)		C ₄₄ (GPa)	
	Present study	Experimental report	Present study	Experimental report	Present study	Experimental report
YbS	133.419	115 ± 1	10.2447	36 ± 2	31.458	26 ± 1
YbSe	113.436	116.6	6.349	12	25.793	22.8
YbTe	90.438	93.6	6.105	6.7	17.504	16.3

TABLE 3: Elastic constants of ytterbium chalcogenides.

Experimental report [27].

TABLE 4: Mechanical parameters of ytterbium chalcogenides.						
		D.f				
Mechanical property	YbS	YbSe	YbTe	Reference		
Bulk modulus (GPa)	51.30	42.04	34.21	Present study		
	74 ± 5	61 ± 5	46 ± 5	Experiment [23]		
Young's modulus (GPa)	97.66	81.61	60.44	Present study		
	97.83	92.73	113.75	Experiment [27]		
Shear modulus (GPa)	41.31	34.71	25.11	Present study		
	31	27.16	34.48	Experiment [27]		
Poisson's ratio	0.18	0.17	0.20	Present study		
	0.23	0.18	0.09	Experiment [27]		
Debye sound velocity (m/s)	2611.18	2249.85	1926.92	_		
Debye temperature (K)	270.62	226.43	181.60			

stress over the uniaxial strain. Poisson's ratio is the ratio of the longitudinal extension to the transverse compression [26]. Many fundamental solid properties, including thermal conductivity and sound velocity, are closely related to elastic properties. The elastic constants C_{ij} of ytterbium chalcogenides compounds are given in Table 3.

As it can be seen from Tables 3 and 4, the criteria of mechanical stability in the cubic crystals which is given by $(C_{12} < B < C_{11})$; $(C_{11}-C_{12}) > 0$; $(C_{11}+2C_{12}) > 0$; and $C_{44} > 0$ is fulfilled for each of ytterbium chalcogenides. The values of C_{11} , C_{12} , and C_{44} are greatest for YbS than YbSe and YbTe, respectively. These values are consistent with the previous reported literature [27].

Table 4. depicts the value of bulk modulus, shear modulus, Young's modulus, Poisson's ratio, Debye sound velocity, and Debye Temperature of YbX (X = S, Se, and Te) obtained with PBE calculation in the Voigt-Reus-Hill average approximations model. Moreover, the bulk modulus of YbS, YbSe, and YbTe found with PBE computations are 51.30, 42.04, and 34.21 GPa, respectively, and are consistent with the literature values [23]. The values of bulk modulus of ytterbium chalcogenides decreases along the group from sulfur to telluride. This indicates that YbTe is least affected by hydrostatic stress than YbSe and YbS, respectively. Moreover, the value of Young's modulus of YbS, YbSe, and YbTe calculated with PBE are 97.66, 81.61, and 60.44 GPa, respectively. The value of shear modulus of YbS, YbSe, and YbTe found using PBE approximation is 41.31, 34.71, and 25.11 GPa, respectively.

A material is characterized as ductile when the Poisson's ratio value is $(n \simeq \frac{1}{3})$ and as brittle materials when $(n \le \frac{1}{3})$

[28]. Table 4 illustrates that the computed Poisson's ratio for YbS, YbSe, and YbTe fails within the range of 0.17–0.2, indicating that ytterbium chalcogenides are brittle materials. This value is inline with the previously reported Poisson's ratio value of of ytterbium based compounds which is 0.09–0.27 [26, 27]. Because of this cracking susceptibility, ytterbium chalcogenides may not be used in applications where mechanical stress is a concern. Consequently, the best approach to mitigate this disadvantage is to co-dope with suitable elements that have superior elasticity qualities.

Mechanical properties and the lattice parameter are closely related because the configuration of atoms in the crystal lattice influences the material's response to outside forces. A higher lattice value may result in a more ductile material, whereas a lower lattice parameter may result in a material that is more resistant to deformation [29].

Correlating Tables 1 and 4, YbTe's ductile property is greater than YbSe's and YbS's ductile properties, respectively, since its lattice parameter (6.136 Å) is greater than those of YbSe (5.66 Å) and YbS (5.6 Å). This is almost supported by the greatest Posson's ratio values of YbTe (0.2) than that of YbSe (0.17) and YbS (0.18).

The Debye sound velocity of YbS, YbSe, and YbTe calculated with PBE approximations are 2611.18, 2249.85, and 1926.92 m/s, respectively. Moreover, the Debye temperature value of YbS, YbSe, and YbTe calculated by PBE are 270.62, 226.43, and 181.60 K, respectively. The result of elastic property investigation confirms that ytterbium chalcogenides are mechanically stable and are useful in different electronic device applications. 3.4. Optical Properties of Ytterbium Chalcogenides. The dielectric function describes the optical properties and provides the linear response of the electronic system to the applied external electric field. The dielectric function can be written with Equation (1) as [30]:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega), \tag{1}$$

where the real part $\varepsilon_1(\omega)$ and the imaginary $\varepsilon_2(\omega)$ dielectric functions, respectively, the dispersion and the absorption of the electromagnetic radiation by the medium which it crosses. $\varepsilon_2(\omega)$ spectrum is calculated by summing the electric dipole operator matrix elements between the occupied and unoccupied wave functions over the Brillouin zone while respecting the selection rules.

The real part of the dielectric ε_1 is associated with the polarization of the dielectric material in response to the incoming electric feld. It is associated with the polarization using Kramers–Kronig relations by $P = [E_o(\omega)(\varepsilon_1 - 1)]E(\omega)$ [31].

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega') d\omega'}{\omega'^2 - \omega^2}, \qquad (2)$$

$$\varepsilon_2(\omega) = \left(\frac{4\pi^2 e^2}{m^2 \omega^2}\right) \sum_{ij} \int |M| j^2 f_i (1 - f_i) \delta(E_f - E_i - \omega) d^3k,$$
(3)

where *P* is the value of the integral; *M* is a dipole matrix; *i* and *j* are the initial and final states, respectively; f_i is the Fermi distribution function for the initial state; E_i is the energy of an electron in the initial state; and ω is the frequency of the photon.

The refractive index (*n*), extinction coefficient (κ), reflectivity (*R*), and absorption (α) are calculated using the following equations [32]:

$$n(\omega) = \frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega)^{\frac{1}{2}}}{\sqrt{2}}, \qquad (4)$$

$$\kappa(\omega) = \frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)^{\frac{1}{2}}}{\sqrt{2}},$$
(5)

$$R(\omega) = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2},$$
(6)

$$\alpha(\omega) = \sqrt{2}(\omega) \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{\frac{1}{2}}.$$
 (7)

Figure 5 shows the real part $\varepsilon_1(\omega)$ of the dielectric function for ytterbium chalcogenides computed by PBE which is equivalent to Kramers–Kronig transformation.

The maximum peak of $\varepsilon_1(\omega)$ is observed at about 4.46, 4.00, and 3.33 eV for YbS, YbSe, and YbTe, respectively. Up to the photon energy of 5.33 eV, the real dielectric function of YbTe dominates that of YbSe and YbS, respectively.



FIGURE 5: Real dielectric function of ytterbium chalcogenides.



FIGURE 6: Imaginary dielectric function of ytterbium chalcogenides.

However, with further increase in photon energy, the real dielectric function of YbS dominates that of YbSe and YbTe, respectively. As it can be seen from Figure 5, the real dielectric function of ytterbium chalcogenides is negative for some frequency ranges. This is attributed to the plasmonic response of delocalized electrons within the materials and can be modulated by it [33]. This demonstrates their additional potential for unique optical and microwave applications such as microwave circuits, optical switches, and modulators, antenna components, in electromagnetic intereference shielding and coil-less electric inductors [34].

Figure 6 illustrates the imaginary dielectric function of ytterbium chalcogenides computed in the energy range of 0-25 eV. The calculated ε_2 curve in Figure 6 shows first absorption peak at about 5.2, 4.66, and 3.93 eV for YbS,



FIGURE 7: Index of refraction of ytterbium chalcogenides.

YbSe, and YbTe, respectively. The second peak is situated at about 6.66, 6.13, and 5.4 eV for YbS, YbSe, and YbTe, respectively. Furthermore, the third peak is obtained at 8.06, 7.13, and 6.4 eV for YbS, YbSe, and YbTe, respectively. As can bee seen from Figure 6, the existence of peaks decreases with increase in photon energy. This demonstrates that ytterbium chalcogenides are good absorber of light in the low-energy region and poor absorber in higher energy values.

Figure 7. presents the refractive index of ytterbium chalcogenides computed with DFT in the energy range of 0-25 eV.

As it can be seen form Figure 7, the initial value of refractive index (n_o) obtained for YbS, YbSe, and YbTe are 3.48, 3.3, and 3.33, respectively. Then it decreases with increase in photon energy and attains a maxima 2.48 at 4.5 eV, 3.04 at 4.64 eV, and 3.31 at 3.43 eV for YbS, YbSe, and YbTe, respectively. With further increase in photon energy beyond 6.16 eV, the refractive index of YbS dominates that of YbSe and YbTe, respectively. No specific values for the index of refraction of YbS, YbSe, and YbTe were reported in literature.

Figure 8 depicts the extinction coefficient of YbX (X = S, Se, and Te). The maximum peak was observed at 2.53 at 8.12 eV, 2.46 at 7.65 eV, and 3.05 at 6.64 eV for YbS, YbSe, and YbTe respectively. Above, photon energy of 7.26 V, the extinction coefficient of YbTe is dominated by YbS and YbSe, respectively.

Figure 9 presents the frequency dependent reflectivity of ytterbium chalcogenides. As depicted from Figure 9, the reflectivity of all ytterbium chalcogenides does not reach unity when the photon frequency tends toward zero. This indicates that these materials are transmitting incident radiations for frequencies less than their energy band gap. And, also these compounds behave as semiconductors. Figure 9 depicts that the reflectivity of YbTe dominates that of YbSe and YbS in the photon energy range of 0.78–11.58 eV.

Figure 10 presents computational absorption spectra of ytterbium chalcogenides in the energy range of 0-25 eV. The maximum absorption peaks of YbS, YbSe, and YbTe are



FIGURE 8: Extinction coefficient k of ytterbium chalcogenides.



FIGURE 9: Reflectivity of ytterbium chalcogenides.

found at 9.58, 9.09, and 6.73 eV, respectively. As the photon frequency increases beyond 9.58 eV, the absorption coefficient of YbS dominates that of YbSe and YbTe, respectively. Figure 10 also depicts that the highest absorption coefficient peak was found for YbS than that of YbSe and YbTe, respectively. The optical data of ytterbium chalcogenides are not found in the literature, and we hope that our calculations will motivate further experimental efforts on this materials.

3.5. Thermodynamic Properties of Ytterbium Chalcogenides. The thermodynamic properties have a direct influence on their phononic characteristics due to the fact that they exhibit a quantum energy of elastic strain [35]. Basically, the thermal properties of materials are based on the way they vibrate, which is called lattice vibrations, and the way lattice mechanics works [36]. The phonon dispersion



FIGURE 10: Absorption coefficient of ytterbium chalcogenides.

relation $\omega_L(q)$ describes how the phonons of mode are energetically dispersed within the Brillouin zone with respect to the wave vector. Phonons in solid materials are directly related to their thermodynamic properties. The phonon density of states can be calculated from the phonon dispersion relation. The thermodynamic lattice function is then calculated from the phonon density of states. The phonon density of states per crystal unit cell can be calculated using Equation (8) as [37]:

$$g(\omega) = \frac{1}{3N} \sum_{q,j} \delta(\omega - \omega_L(q)), \qquad (8)$$

where N is number of atoms in the unit cell.

Thermodynamic quantities such as lattice vibration energy and specific heat can be determined by phonon calculations using the quasi-harmonic approximation (QHA). Thermodynamic functions such as internal energy ΔE , Helmholtz-free energy $\Delta F = \Delta E - TS$, specific heat capacity C_{ν} at constant volume, and entropy *S* at temperature *T* are given by Equations (9–12) [38]:

$$\Delta F = 3Nk_{\beta}T \int_{0}^{\infty} g(\omega) \ln\left\{2\sin h\frac{\hbar\omega}{2k_{\beta}T}\right\} d\omega, \qquad (9)$$

$$\Delta E = 3N \frac{\hbar}{2} \int_{0}^{\infty} \omega g(\omega) \cot h\left(\frac{\hbar\omega}{2k_{\beta}T}\right) d\omega, \qquad (10)$$

$$C_{V} = \frac{\partial F}{\partial T} = 3Nk_{\beta} \int_{0}^{\infty} g(\omega) \left(\frac{\hbar\omega}{2k_{\beta}T}\right)^{2} \csc h^{2} \left(\frac{\hbar\omega}{2k_{\beta}T}\right) d\omega,$$
(11)



FIGURE 11: Helmholtz free energy of ytterbium chalcogenides.

$$S = 3Nk \int_{0}^{\infty} g(\omega) \left[\frac{\hbar\omega}{2k_{\beta}T} \cot h \frac{\hbar\omega}{2k_{\beta}T} - \ln\left\{ 2\sin h \frac{\hbar\omega}{2k_{\beta}T} \right\} \right] d\omega.$$
(12)

In this part, the thermodynamic properties such as Helmholtz-free energy (*F*), entropy (*S*), and constant volumetric specific heat of YbX (X = S, Se, and Te) were calculated using PBE approximation.

Figure 11 shows the temperature dependence of the Helmholtz-free energy (F) of of YbX (X = S, Se, and Te) calculated by PBE approximation. It can be seen from Figure 11, a nonlinear decrease of a Helmholtz-free energy is observed with the rise of temperature. The zero-temperature Helmholtz-free energy obtained using PBE computation are 5.0, 4.5, and 4.0 Joules for YbS, YbSe, and YbTe, respectively.

Figure 12 shows that the temperature dependence of the entropy of YbX (X = S, Se, and Te) calculated using PBE approximation. The entropy of YbX (X = S, Se, and Te) computed by PBE goes to zero at 0 K. The thermal disturbance enhances the disorder with increasing temperature in the system results in entropy increase as shown in Figure 12. The plot shows that the entropy increases with increasing temperature, mostly for YbTe than for YbSe and YbS, respectively.

At low temperatures, the well-known Debye model provides a simple yet successful one parameter model to describe the heat capacity. For the phonon contribution, the low temperature limit of the heat capacity reduces to Equation (13) as follows:

$$C = \frac{12}{5} \pi^5 N_A k_B \left(\frac{T}{\Theta_D}\right)^3,\tag{13}$$



FIGURE 12: Entropy of ytterbium chalcogenides.



FIGURE 13: Heat capacity of ytterbium chalcogenides.

where N_A is Avogadro's number, Θ_D is the Debye temperature, k_B and T are the same as defined above, and $C = C_v \approx C_p$. Thus, at sufficiently low T, C varies as T^3 , and a plot of C/T against T^2 will be a straight line.

Heat capacity is an important parameter for studying thermodynamics in chemical engineering. It reflects the ability of a substance to absorb or release heat without changing phase.

Figure 13 illustrates constant volume specific heat C_{ν} of YbX (X = S, Se, and Te) as a function of temperature. It is a common pattern that at very low temperatures, the C_{ν} of all ytterbium chalcogenides is strongly dependent on temperature and follows the Debye model, which is proportional to T^3 . When the temperature is higher, the classic Dulong–Petit law is followed and C_{ν} does not depend as much on the temperature [25].

As shown in the inset of Figure 13, there is no indication of magnetic or electronic contributions to the heat capacity in this study. Using the simple Debye model, the Debye temperature (Θ_D) was calculated to be 270.62, 226.43, and 181 K for YbS, YbSe, and YbTe, respectively. At respective Debye temperature(Θ_D), the calculated C_v values for YbS, YbSe, and YbTe are 45.0, 49.5, and 50.0 Jmol⁻¹K⁻¹, respectively. The Debye temperature of YbS is in better agreement with the previously reported experimental value 277 K [11]. The constant volume specific heat capacity of YbTe mostly increases with temperature as compared to YbSe and YbS. This is a result of the difference in phonon vibration with temperature in these chalcogenides. The result of thermodynamic properties were not compared due to the unavailability of the experimental results.

4. Conclusion

First-principle density functional theory was employed to study the structural stability, electronic properties, and optical and thermodynamic stability of ytterbium chalcogenides. The investigation of electronic property shows, ytterbium chalcogenides have a low band gap and are potential candidate for photovoltaic and laser diode applications. Moreover, from the optical property result, the negative value of real dielectric function of ytterbium chalcogenides for some frequency ranges confirmed that they have additional extra applications in microwave circuits, optical switches, and modulators. Furthermore, the thermodynamic properties, such as the free energy, entropy, and specific heat capacity result confirm ytterbium chalcogenides are thermodynamically stable and can be useful in different electronic applications. The thermodynamic properties of ytterbium chalcogenides were not compared due to the unavailability of the experimental values.

Data Availability

All relevant data to this publications are included in the manuscript.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

References

- A. A. Ansary, A. Syed, A. M. Elgorban, A. H. Bahkali, R. S. Varma, and M. S. Khan, "Neodymium selenide nanoparticles: greener synthesis and structural characterization," *Biomimetics*, vol. 7, no. 4, Article ID 150, 2022.
- [2] I. L. Ikhioya, A. C. Nkele, S. N. Ezema, M. Maaza, and F. Ezema, "A study on the effects of varying concentrations on the properties of ytterbium-doped cobalt selenide thin films," *Optical Materials*, vol. 101, Article ID 109731, 2020.
- [3] D. A. Grukh, V. A. Bogatyrev, A. A. Sysolyatin, V. M. Paramonov, A. S. Kurkov, and E. M. Dianov, "Broadband radiation source based on an ytterbium-doped fibre with fibre-length-distributed pumping," *Quantum Electronics*, vol. 34, no. 3, Article ID 247, 2004.

- [5] S. Unger, A. Schwuchow, S. Jetschke, V. Reichel, A. Scheffel, and J. Kirchhof, "Optical properties of Yb-doped laser fibers in dependence on codopants and preparation conditions," in *Proceedings Volume 6890, Optical Components and Materials V*; 689016, SPIE, San Jose, California, United States, February 2008.
- [6] J. I. Larruquert, J. A. Aznárez, J. A. Méndez, and J. Calvo-Angós, "Optical properties of ytterbium films in the far and the extreme ultraviolet," *Applied Optics*, vol. 42, no. 22, pp. 4566– 4572, 2003.
- [7] X. Chen, Y. Wu, N. Wei et al., "The roles of cation additives on the color center and optical properties of Yb:YAG transparent ceramic," *Journal of the European Ceramic Society*, vol. 38, no. 4, pp. 1957–1965, 2018.
- [8] Y. Jeong, J. K. Sahu, D. N. Payne, and J. Nilsson, "Ytterbiumdoped large-core fiber laser with 1 kW continuous-wave output power," in *Advanced Solid-State Photonics, OSA Technical Digest*, Optica Publishing Group, 2004.
- [9] J. Nilsson, W. A. Clarkson, R. Selvas et al., "High-power wavelength-tunable cladding-pumped rare-earth-doped silica fiber lasers," *Optical Fiber Technology*, vol. 10, no. 1, pp. 5–30, 2004.
- [10] M. A. Kudryashov, A. A. Logunov, and L. A. Mochalov, "Direct one-stage plasma-chemical synthesis of chalcogenide films doped with ytterbium," *Journal of Physics: Conference Series*, vol. 1967, Article ID 012005, 2021.
- [11] Y. Chen, L. Li, and S. Hirai, "Fabrication, sintering, heat capacity, magnetic and magnetroresistivity properties of ytterbium sulfides," *Journal of Magnetism and Magnetic Materials*, vol. 476, pp. 289– 296, 2019.
- [12] S. B. Ubale, R. N. Bulakhe, V. J. Mane, D. B. Malavekar, I. In, and C. D. Lokhande, "Chemical synthesis of nano-grained ytterbium sulfide thin films for supercapacitor application," *Applied Nanoscience*, vol. 10, pp. 5085–5097, 2020.
- [13] E. V. Koshurnikova, L. A. Kalinina, Y. N. Ushakova, M. V. P'yankova, and I. V. Murin, "Synthesis, structure, and physico-chemical properties of sulfide ceramics CaY₂S₄–Yb₂S₃," *Russian Journal of Electrochemistry*, vol. 49, pp. 769–775, 2013.
- [14] R. Iizuka, R. Numakura, S. Michimura, S. Katano, and M. Kosaka, "Magnetic properties of rare-earth sulfide YbAgS₂," *Physica B: Condensed Matter*, vol. 536, pp. 314–316, 2018.
- [15] M. Vahdati and T. Tohidi Moghadam, "Synthesis and characterization of selenium nanoparticles-lysozyme nanohybrid system with synergistic antibacterial properties," *Scientific Reports*, vol. 10, Article ID 510, 2020.
- [16] D. L. Partin, "Growth and characterization of lead-tin-ytterbium-telluride for diode lasers," *Journal of Electronic Materials*, vol. 12, pp. 917–929, 1983.
- [17] P. Giannozzi, S. Baroni, N. Bonini et al., "QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials," *Journal of Physics: Condensed Matter*, vol. 21, Article ID 395502, 2009.
- [18] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Physical Review Letters*, vol. 77, no. 18, pp. 3865–3868, 1996.
- [19] S. S. Aplesnin, A. M. Kharkov, O. B. Romanova et al., "Spin state of cations and magnetoelastic effect in the Mn_{1-X} Yb_XS," *Journal of Magnetism and Magnetic Materials*, vol. 352, pp. 1– 5, 2014.
- [20] S. Ariponnammal, S. Radhika, and P. Sivakumar, "Study of charge transfer and structure factor calculation in ytterbium

selenide," *Modern Physics Letters B*, vol. 20, no. 12, pp. 691–696, 2006.

- [21] E. Kaldis and W. Peteler, "High temperature evaporation of YbTe: thermodynamics, mass spectrometry and surface analysis," *Journal of Crystal Growth*, vol. 52, Part 1, pp. 125–130, 1981.
- [22] G. V. Lashkarev, L. A. Ivanchenko, and Y. B. Paderno, "Optical investigation of ytterbium monochalcogenides," *Physica Status Solidi* (b), vol. 49, no. 1, pp. K61–K65, 1972.
- [23] A. Werner, H. D. Hochheimer, A. Jayaraman, and J. M. Leger, "Pressure induced valence change in ytterbium monoxide," *Solid State Communications*, vol. 38, no. 4, pp. 325–327, 1981.
- [24] L. Azzouz, M. Halit, Z. Charifi, and C. F. Matta, "Tellurium doping and the structural, electronic, and optical properties of NaYS₂ (1–x) Te_{2x} alloys," ACS Omega, vol. 4, no. 6, pp. 11320– 11331, 2019.
- [25] F. Sultana, M. M. Uddin, M. A. Ali, M. M. Hossain, S. H. Naqib, and A. K. M. A. Islam, "First principles study of M₂InC (M = Zr, Hf and Ta) MAX phases: the effect of M atomic species," *Results in Physics*, vol. 11, pp. 869–876, 2018.
- [26] W. H. Wang, "The elastic properties, elastic models and elastic perspectives of metallic glasses," *Progress in Materials Science*, vol. 57, no. 3, pp. 487–656, 2012.
- [27] R. Dubey and S. Singh, "High pressure phase transition and elastic properties of ytterbium compounds YbX (X = O, S, Se and Te)," *Journal of Optoelectronics and Advanced Materials*, vol. 16, pp. 1328–1338, 2014.
- [28] P. F. Weck, P.-A. Juan, R. Dingreville, and E. Kim, "Density functional analysis of fluorite-structured (Ce, Zr) O₂/CeO₂ interfaces," *The Journal of Physical Chemistry C*, vol. 121, no. 27, pp. 14678–14687, 2017.
- [29] X. Yang, Y. Zhang, and P. K. Liaw, "Microstructure and compressive properties of NbTiVTaAlx high entropy alloys," *Procedia Engineering*, vol. 36, pp. 292–298, 2012.
- [30] Q. Mahmood, M. Yaseen, M. Hassan, M. S. Rashid, I. Tlili, and A. Laref, "The first-principle study of mechanical, optoelectronic and thermoelectric properties of CsGeBr₃ and CsSnBr₃ perovskites," *Materials Research Express*, vol. 6, no. 4, Article ID 045901, 2019.
- [31] S. N. S. Srinivas, M. Sharma, V. Yadav, and U. Kumar, "Comprehensive study of CsGeBr₃ perovskite: optical, electronic, and thermoelectric properties," *Emergent Materials*, vol. 6, pp. 1685–1696, 2023.
- [32] M. Hassan, I. Arshad, and Q. Mahmood, "Computational study of electronic, optical and thermoelectric properties of X₃PbO (X = Ca, Sr, Ba) anti-perovskites," *Semiconductor Science and Technology*, vol. 32, no. 11, Article ID 115002, 2017.
- [33] G. Fan, K. Sun, Q. Hou, Z. Wang, Y. Liu, and R. Fan, "Epsilonnegative media from the viewpoint of materials science," *EPJ Applied Metamaterials*, vol. 8, Article ID 11, 2021.
- [34] S. K. Balu, N. P. Shanker, M. Manikandan et al., "Crossover to negative dielectric constant in perovskite PrMnO₃," *Physica Status Solidi (a)*, vol. 217, no. 17, Article ID 2000230, 2020.
- [35] I. N. Frantsevich, "Elastic constants and elastic moduli of metals and insulators," *Reference Book*, 1982.
- [36] M. Born, K. Huang, and M. Lax, "Dynamical theory of crystal lattices," *American Journal of Physics*, vol. 23, no. 7, Article ID 474, 1955.
- [37] O. Hellman, Thermal Properties of Materials from First Principles, Linköping University Electronic Press, 2012.
- [38] T. D. Morrison, E. S. Wood, P. F. Weck et al., "A comprehensive assessment of the low-temperature thermal properties and thermodynamic functions of CeO₂," *The Journal of Chemical Physics*, vol. 151, no. 4, Article ID 044202, 2019.