



Insight into the Structural, Mechanical, Thermophysical and Optoelectronic Properties of K_2X_3 ($X = S, Se$) by DFT Investigation

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ABSTRACT

The structural, mechanical, thermophysical, and optoelectronic properties of K_2X_3 ($X = S, Se$) were systematically explored using the full-potential linearized augmented plane wave (FP-LAPW) method within the framework of density functional theory (DFT), as implemented in WIEN2k. The optimized structural parameters confirm the stability of both compounds. Mechanical analysis, including elastic constants, bulk modulus, shear modulus, Young's modulus, Poisson's ratio, and Pugh's ratio, reveals that K_2S_3 and K_2Se_3 are mechanically stable yet brittle, with pronounced elastic anisotropy. Phonon dispersion and density of states further validate their dynamical stability. Thermophysical evaluation shows that K_2S_3 exhibits a higher Debye temperature and lattice thermal conductivity than K_2Se_3 , reflecting stronger covalent bonding. Electronic structure calculations indicate semiconducting behavior, with band gaps reduced by ~42% upon substitution of S with Se. The density of states is dominated by S 3p orbitals in K_2S_3 and Se 4p orbitals in K_2Se_3 . Optical investigations reveal strong anisotropy, with maximum absorption and photoconductivity in the ultraviolet (UV) region. The strong UV absorption highlights its potential for applications as an efficient UV-absorbing material.

Keywords: Density Functional Theory (DFT); Mechanical stability; Lattice thermal conductivity; Debye temperature; Optoelectronic properties.

1. Introduction

Alkali metal chalcogenides and polychalcogenides occupy a distinctive position in solid-state chemistry and materials science owing to their structural diversity and versatile physical properties. Their ability to adopt varied crystal architectures, coupled with tunable electronic characteristics, has positioned them as promising candidates for next-generation functional materials. Recent advances in optoelectronic and energy-conversion technologies have

renewed interest in these compounds for applications ranging from field-effect transistors and photodetectors to photoelectrochemical cells and thermoelectric devices [1, 2]. The intrinsic interplay between structure and electronic behavior in chalcogenide systems continues to provide fertile ground for both fundamental discovery and technological innovation.

Within this family, alkali metal polychalcogenides of general formula M_2X_n (M = alkali metal; X = S, Se; n = 2–9) are particularly intriguing. These compounds feature unbranched polyanionic chains embedded in electropositive cation frameworks, producing complex bonding environments and pronounced structural sensitivity. Subtle variations in the alkali cation can significantly influence bond lengths, bond angles, and lattice stability—effects experimentally demonstrated in systems such as K_2S_3 , K_2Se_3 , Rb_2S_3 , Rb_2Se_3 , Cs_2S_3 , and Cs_2Se_3 [3]. The structural analogy between K_2S_3 , K_2Se_3 , and SrS_3 further highlights a recurring motif among trichalcogenides, suggesting transferable chemical and physical principles across this class.

Experimentally, K_2S_3 and K_2Se_3 have been synthesized and structurally characterized [4–8,10,11], most notably via high-pressure reactions in liquid ammonia, which established their orthorhombic $Cmc2_1$ crystal structure. Subsequent refinements have clarified lattice parameters, Wyckoff positions, and thermodynamic data, while resolving earlier structural ambiguities. Additional studies have examined melting behavior, phase stability, and electrochemical relevance, including recent interest in potassium–sulfur battery systems [7, 9, 11]. Despite these advances, prior research has largely emphasized synthesis, crystallography, and basic thermodynamics.

A systematic understanding of the mechanical stability, electronic structure, optical response, and thermophysical performance of K_2S_3 and K_2Se_3 remains absent. Such insights are essential for establishing robust structure–property relationships and evaluating their technological potential. In light of the growing demand for efficient, earth-abundant, and environmentally benign functional materials, this gap represents both a scientific challenge and an opportunity.

Motivated by these considerations, the present work delivers a comprehensive first-principles investigation of the structural, mechanical, thermophysical, and optoelectronic properties of K_2S_3 and K_2Se_3 . By bridging the gap between structural characterization and functional property evaluation, this study aims to deepen understanding of these trichalcogenides and lay the groundwork for their rational integration into future energy and optoelectronic technologies.

2. Computational Details

The present study investigates various physical properties of K_2X_3 (X = S, Se) using first-principles calculations. The electronic structure calculations were performed within the framework of density functional theory (DFT) [12, 13], as introduced by Hohenberg and Kohn, which is widely recognized for its accuracy in describing the electronic properties of solid-state materials. All computations were carried out using the full-potential linearized

augmented plane wave (FP-LAPW) method [14], along with the local orbital approach, as implemented in the WIEN2k package [15, 16].

The elastic properties were determined using the IRelast method [17] integrated within WIEN2k. The exchange–correlation energy was treated using the generalized gradient approximation (GGA) formulated by Perdew, Burke, and Ernzerhof (PBE) [18, 19].

For well-converged self-consistent field (SCF) calculations, the following parameters such as cutoff energy of -6.0 Ry, $R_{MT} \times K_{max} = 7$, and 10,000 k -points in the Brillouin zone were employed. The energy and charge convergence criteria were set to 0.0001 Ry and 0.001 e, respectively. The Fourier expansion of the charge density was defined by $G_{max} = 12$ (a.u.) $^{-1}$. Self-consistency was carefully checked to ensure convergence of the electronic and optical properties.

To obtain improved band-gap estimations, the modified Becke–Johnson (mBJ) potential proposed by Becke and Johnson [20] was employed for calculating the optoelectronic properties.

3. Results and Discussion

3.1 Crystal Structure and Thermodynamic Stability

WIEN2k is used to optimize the structural parameters of K_2X_3 ($X = S, Se$), which crystallize in an orthorhombic structure with space group $Cmc2_1$ (No. 36).

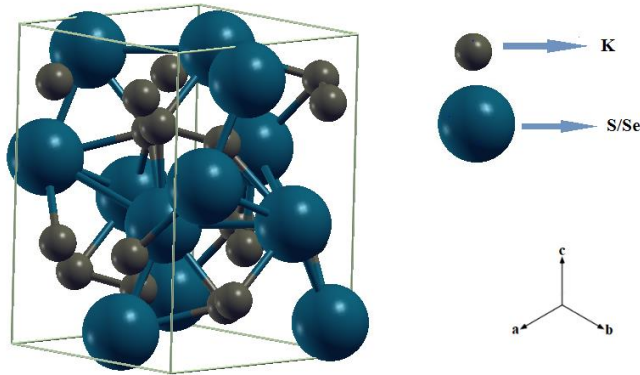


Figure 1. Three-dimensional view of the crystal structure of K_2X_3 ($X = S, Se$)

The three-dimensional unit cell is characterized by the lattice parameters a , b , and c . To determine the equilibrium structural properties, both the unit cell volume and the c/a ratio are optimized. The calculations are performed within the framework of density functional theory (DFT) using the generalized gradient approximation (GGA) at zero pressure and temperature. The total energy as a function of volume is fitted to Murnaghan equation of state to obtain the optimal energy–volume curve. From this fitting procedure, the equilibrium volume and corresponding lattice constants are extracted.

To verify the thermodynamic stability, we have calculated the cohesive energy of K_2X_3 ($X = S, Se$) using the following equation [21]:

$$E_{coh}(K_2X_3)_{fu} = \frac{E_{tot}(K_2X_3)_{fu} - 2E_s(K) - 3E_s(X)}{5} \quad (1)$$

where, $E_{tot}(K_2X_3)_{fu}$ is the total energy of K_2X_3 ($X = S, Se$) per formula unit and $E_s(K)$ and $E_s(X = S, Se)$ are the total energies of single K and S/Se atoms. Negative values of cohesive energies reveal that K_2X_3 ($X = S, Se$) are thermodynamically stable.

Table 1. Lattice parameters a , b and c (in Å), volume V (in Å³), deviation of the lattice parameters Δa , Δb and Δc (in Å) from the experimental values and cohesive energy E_{coh} (eV/atom) for K_2S_3 and K_2Se_3 .

Compounds	a	Δa	b	Δb	c	Δc	V	E_{coh}	Ref.
K_2S_3	7.333	0.024	9.947	0.033	7.424	0.049	541.51	-3.74	This
	7.309		9.914		7.473		-	-	[4] ^{Expt.}
K_2Se_3	7.714	0.022	10.440	0.032	7.672	0.045	617.93	-3.45	This
	7.692		10.408		7.717		-	-	[4] ^{Expt.}

Table 1 summarizes the optimized lattice parameters (a , b , and c), the equilibrium volume (V), their deviations from available experimental data and cohesive energy for K_2S_3 and K_2Se_3 . The close agreement between the calculated and experimental lattice parameters confirms the reliability and accuracy of the computational methodology employed in this study.

3.2 Phonon Properties and Dynamical Stability

The phonon properties of a material, including the phonon dispersion curves and the phonon density of states (DOS), provide detailed insight into its lattice vibrations. These properties are essential for understanding thermal behavior, such as heat capacity and lattice thermal conductivity, as well as dynamical stability. For K_2X_3 ($X = S, Se$), analyzing these phonon characteristics allows us to assess the material's vibrational behavior and its suitability for thermoelectric or thermal barrier applications.

Phonon dispersion curve (PDC) of a material is crucial because it provides details on dynamical stability, phase transitions and vibrational contributions to characteristics including thermal expansion, Helmholtz free energy and heat capacity [22]. Here we have computed the PDC and phonon density of states (PHDOS) at the ground state to access the dynamical stability of K_2X_3 ($X = S, Se$). Phonon dispersion curves (PDCs) at ground state have been calculated using the Density Functional Perturbation Theory (DFPT) and the finite displacement method (FDM) [23, 24]. In Figs. 2(a, b), the PDC along the high symmetry directions of the Brillouin zone and the corresponding total phonon DOS of K_2X_3 ($X = S, Se$) are shown. The dynamical stability of our studied compounds is confirmed by the presence of positive phonon frequencies throughout the entire Brillouin zone.

For K_2S_3 , the unit cell contains 20 atoms. In a three-dimensional crystal, each atom contributes three vibrational degrees of freedom, resulting in a total of 60 phonon branches. These include three acoustic branches, which correspond to the collective translational motion of the lattice, and 57 optical branches, which arise from relative vibrations of atoms

within the unit cell. At the Γ point, the acoustic modes have zero phonon frequency for both compounds, which is another indication of dynamical stability of the studied compounds. The optical properties of the compounds are characterized by the optical phonon modes.

Due to the overlap between the acoustic modes and the lower optical modes, both K_2S_3 and K_2Se_3 exhibit contributions to thermal transport. In the phonon density of states (PHDOS) shown in Figs. 2(a, b), peaks are formed by the flat regions of the phonon bands, whereas the upward and downward slopes of the bands reduce the heights of these peaks. These peaks indicate regions of high phonon density.

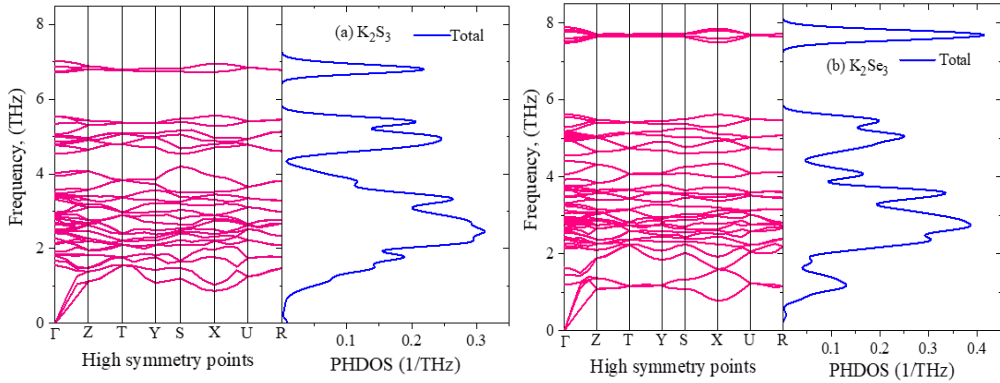


Figure 2. Calculated phonon dispersion spectra and phonon DOS of (a) K_2S_3 and (b) K_2Se_3 in the ground state

The phonon density of states (PHDOS) for K_2S_3 reveals that the most densely populated phonon bands lie within the 0.21–4.35 THz range, while medium-density regions are found at 4.35–5.80 THz and 6.42–7.21 THz, corresponding to higher optical branches. In contrast, for K_2Se_3 , high-density regions occur at 1.60–4.43 THz and 7.23–8.12 THz, with a medium-density region between 4.43–5.84 THz and a low-density region at 0.58–1.60 THz. Notably, the total density of states (TDOS) peak associated with the upper optical branches is higher in K_2Se_3 than in K_2S_3 . Regions of high phonon density critically impact thermal conductivity by increasing phonon scattering, thereby significantly influencing heat transport within the material.

3.3 Mechanical Properties

3.3.1 Elastic constants

It is necessary to compute elastic constants for assuring structural and mechanical stability. The nine elastic constants for orthorhombic symmetry are C_{11} , C_{22} , C_{33} , C_{44} , C_{55} , C_{66} , C_{12} , C_{13} and C_{23} . The necessary and sufficient Born criteria for mechanical stability for an orthorhombic system are as follows [25, 26]:

$$C_{11} > 0; C_{22} > 0; C_{33} > 0; C_{44} > 0; C_{55} > 0; C_{66} > 0; C_{11} + C_{22} - 2C_{12} > 0; C_{11} + C_{33} - 2C_{13} > 0;$$

$$C_{22} + C_{33} - 2C_{23} > 0; C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) - 2C_{12} > 0 \quad (2)$$

They meet the stability criteria. Thus, K_2S_3 and K_2Se_3 are mechanically stable. C_{11} , C_{22} and

C_{33} are the diagonal elastic constants that quantify the resistance to linear compression along the a , b and c crystallographic axes, respectively. In both compounds, C_{11} is significantly higher than C_{33} , indicating that the materials are more compressible when stress is applied along the [001] direction than along the [100] direction. Another important elastic constant, C_{44} , is commonly used to evaluate resistance to shear deformation under tangential stress applied on the (100) plane along the [010] direction of the crystal [27].

For both phases, C_{44} is considerably smaller than C_{11} and C_{33} , which suggests that the materials deform more easily under shear stress than under uniaxial compressive stress along the principal crystallographic directions. Since C_{44} reflects the electronic response to shear strain, it also represents the resistance to shape change without a corresponding change in volume [27].

Furthermore, the fact that C_{11} and C_{33} are larger than C_{12} , C_{13} , and C_{14} indicates that shear deformation is energetically more favorable than axial deformation in both compounds. Additionally, because C_{44} is lower than C_{66} , shear deformation in the (100) plane is easier than shear deformation in the (001) plane.

Table 2. The calculated elastic constants, C_{ij} (in GPa) and Kleinman parameter, ζ for K_2S_3 and K_2Se_3

Compounds	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	ζ	Ref.
K_2S_3	106.9	56.8	46.5	14.7	34.8	17.5	14.8	33.6	13.2	0.29	This
K_2Se_3	88.9	48.0	45.9	12.7	30.5	14.3	12.1	30.6	12.5	0.29	This

Additionally, the Kleinman parameter (ζ) was calculated at zero pressure. The Kleinman parameter, also known as the internal strain parameter, is an important dimensionless quantity that describes the relative contributions of bond stretching and bond bending to the elastic response of a material. It is widely used to assess a compound's stability against these two types of deformation. The Kleinman parameter can be expressed as [28]

$$\zeta = \frac{C_{11}+8C_{12}}{7C_{11}+2C_{12}} \quad (3)$$

Typically, ζ lies within the range $0 \leq \zeta \leq 1$. According to Kleinman, a value of $\zeta = 1$ corresponds to pure bond bending, whereas $\zeta = 0$ indicates pure bond stretching. Thus, higher ζ values suggest that bond bending dominates the elastic response, while lower ζ values imply that bond stretching plays a more significant role. The calculated Kleinman parameter for both K_2S_3 and K_2Se_3 is 0.29 (shown in Table 2). Since this value is closer to zero than to unity, it indicates that bond stretching contributes more significantly to the mechanical strength than bond bending in both compounds.

3.3.2 Elastic moduli

The calculated elastic constants were further employed to determine the bulk modulus (B), shear modulus (G), Young's modulus (Y), and Poisson's ratio (ν) of K_2X_3 ($X = S, Se$), as presented in Table 3 at zero pressure. These macroscopic elastic parameters provide deeper

insight into the mechanical behavior of the compounds under external stress.

To estimate the elastic properties of polycrystalline aggregates, the Voigt–Reuss–Hill (VRH) approximation is commonly adopted [29–31]. In this approach, the effective elastic moduli of a polycrystalline material are obtained by taking the arithmetic mean of the two limiting cases:

$$B_H = \frac{1}{2}(B_V + B_R) \text{ and } G_H = \frac{1}{2}(G_V + G_R) \quad (4)$$

$$B_V = (1/9)\{(C_{11} + C_{22} + C_{33}) + 2(C_{13} + C_{12} + C_{23})\} \quad (5)$$

$$G_V = (1/15)\{(C_{11} + C_{12} + C_{33}) + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})\} \quad (6)$$

$$B_R = 1/\{(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})\} \quad (7)$$

$$G_R = 15/\{4(S_{11} + S_{12} + S_{33}) + 3(S_{44} + S_{55} + S_{66}) - 4(S_{12} + S_{13} + S_{23})\} \quad (8)$$

where, S_{ij} represents the elastic compliance constants, which are obtained as the elements of the inverse matrix of the elastic stiffness matrix C_{ij} [32].

The bulk modulus (B) reflects a material's resistance to uniform compression and is often associated with resistance to fracture under hydrostatic pressure. In contrast, the shear modulus (G) characterizes resistance to plastic (shear) deformation. For K_2S_3 and K_2Se_3 , the calculated values (shown in Table 3) show that G is lower than B , indicating that shear deformation is the limiting factor governing their mechanical strength. Furthermore, the relatively low values of both B and G suggest that these compounds are mechanically soft in nature [33].

Young's modulus (Y) measures the resistance of a material to longitudinal (tensile or compressive) stress. The value of Y also influences thermal shock resistance, since the critical thermal shock parameter (R) is inversely proportional to Young's modulus [34]. Therefore, a lower Y generally corresponds to a higher R , leading to improved thermal shock resistance.

Materials intended for use as thermal barrier coatings (TBCs) are often selected based on their ability to withstand thermal shock. Notably, the Young's modulus of K_2Se_3 is significantly lower than that of K_2S_3 , suggesting that K_2Se_3 may exhibit superior thermal shock resistance and could be a more suitable candidate for TBC applications.

Poisson's ratio (ν) is an important parameter for describing the mechanical behavior of crystalline materials, as it reflects the relationship between transverse and longitudinal strain under applied stress. It is also widely used to distinguish between ductile and brittle behavior. The critical value separating ductility and brittleness is commonly taken as $\nu = 0.26$ [35, 36]. Materials with $\nu > 0.26$ are generally considered ductile, whereas those with $\nu < 0.26$ are regarded as brittle. The calculated Poisson's ratios (Table 3) for K_2S_3 and K_2Se_3 are 0.24, which is lower than the critical value. This indicates that both compounds exhibit brittle behavior.

Table 3. The bulk modulus B (in GPa), shear modulus G (in GPa), Young's modulus Y (in GPa), Poisson's ratio ν , Pugh's ratio G/B , machinability μ_M .

Compounds	B_V	B_R	B_H	G_V	G_R	G_H	Y	ν	G/B	μ_M	Ref
K_2S_3	37.03	31.64	34.34	23.31	19.84	21.57	53.50	0.24	0.63	2.33	This
K_2Se_3	32.57	29.20	30.88	20.00	17.22	18.61	46.49	0.24	0.60	2.43	This

A correlation also exists between Poisson's ratio and the nature of interatomic bonding in solids [37, 38]. When ν lies in the range 0.25–0.50, central force interactions are considered dominant in the bonding mechanism. If ν falls outside this range, non-central force interactions play a more significant role. In the present case, the value of $\nu = 0.24$ for both compounds lies slightly below this interval, suggesting the predominance of non-central force interactions. Typical Poisson's ratio values are approximately 0.10 for covalent materials, 0.25 for ionic materials, and 0.33 for metallic materials [39, 40]. Since the calculated ν values for K_2X_3 ($X = S, Se$) lie between those characteristics of purely covalent and purely ionic solids, it can be inferred that the bonding in these compounds possesses a mixed covalent–ionic character.

Brittleness and ductility can also be assessed using Pugh's ratio (G/B) [41], which relates the shear modulus (G) to the bulk modulus (B). The critical value separating ductile and brittle behavior is approximately 0.57. Materials with $G/B < 0.57$ are considered as ductile, whereas those with $G/B > 0.57$ are classified as brittle [42].

The calculated G/B values for K_2S_3 and K_2Se_3 are 0.63 and 0.60, respectively. Since both values exceed the critical limit of 0.57, the results confirm the brittle nature of both compounds, consistent with the conclusion drawn from Poisson's ratio. According to Tanaka *et al.* [43], the G/B ratio also provides insight into the directionality of bonding. In this context, the bulk modulus represents the average bond strength, while the shear modulus reflects resistance to changes in bond angles under external stress. A higher G/B value therefore suggests stronger bond directionality. Because K_2S_3 has a slightly larger G/B ratio than K_2Se_3 , it can be inferred that atomic bonding in K_2S_3 is more directional than in K_2Se_3 .

Machinability refers to the ease with which a material can be cut, shaped, or finished using machine tools, and it directly affects parameters such as cutting energy, feed rate, depth of cut, machining time, tool wear, drilling rate, and cutting force. Materials with good machinability require lower cutting forces, exhibit reduced tool wear, enable higher material removal rates, and produce better surface finishes. A key indicator of machinability is the material's ability to undergo plastic deformation, as greater plastic deformation generally corresponds to smoother machining and a higher machinability index (μ_M). Machinability index can be calculated as follows [44]:

$$\mu_M = \frac{B}{C_{44}} \quad (9)$$

High machinability is associated with a high bulk modulus, low shear resistance, and adequate thermal conductivity to efficiently dissipate heat during cutting. Materials with good machinability typically display higher plastic strain, lower feed forces, reduced friction

coefficients, and superior inherent lubricating properties. Based on the calculated μ_M values (shown in Table 3), K_2Se_3 exhibits a higher machinability index than K_2S_3 , indicating that K_2Se_3 is expected to be easier to machine under similar conditions.

3.3.3 Elastic anisotropy

Mechanical anisotropy is a fundamental characteristic of crystalline materials and plays a crucial role in engineering applications. Elastic anisotropy influences the initiation and propagation of microcracks, reflects the directional nature of chemical bonding, and affects the overall mechanical stability and durability of materials. In general, metallic bonding tends to enhance isotropy, whereas directional covalent bonding increases the degree of anisotropy within a crystal structure [27].

The elastic anisotropy of K_2X_3 ($X = S, Se$) was evaluated using several standard indices, including the Zener anisotropy factor (A), shear anisotropy factors (A_1, A_2, A_3), anisotropy in compressibility (A_B) and shear (A_G), the universal anisotropy index (A^U), the equivalent Zener anisotropy factor (A^{eq}), and the universal log-Euclidean index (A^L). The calculated values are presented in Table 4, and the widely accepted relations reported in the literature [27, 45] were employed to determine these anisotropy factors.

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (10)$$

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \quad (11)$$

$$A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}} \quad (12)$$

$$A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}} \quad (13)$$

$$A_B = \frac{B_V - B_R}{B_V + B_R} \quad (14)$$

$$A_G = \frac{G_V - G_R}{G_V + G_R} \quad (15)$$

$$A^U = \frac{B_V}{B_R} + 5 \frac{G_V}{G_R} - 6 \geq 0 \quad (16)$$

$$A^{eq} = \left(1 + \frac{5}{12}A^U\right) + \sqrt{\left(1 + \frac{5}{12}A^U\right)^2 - 1} \quad (17)$$

$$A^L = \sqrt{\left[\ln\left(\frac{B_V}{B_R}\right)\right]^2 + 5\left[\ln\left(\frac{C_{44}^V}{C_{44}^R}\right)\right]^2} \quad (18)$$

where,

$$C_{44}^R = \frac{5}{3} \frac{C_{44}(C_{11} - C_{12})}{3(C_{11} - C_{12}) + 4C_{44}}$$

is the Reuss value of C_{44} and

$$C_{44}^V = C_{44}^R + \frac{3(C_{11} - C_{12} - 2C_{44})^2}{5[3(C_{11} - C_{12}) + 4C_{44}]}$$

is the Voigt value of C_{44} .

A material is considered elastically isotropic when the calculated values of A, A_1, A_2 and A_3 are equal to unity. Any deviation from unity indicates the presence and degree of elastic

anisotropy in the crystal. Based on the computed values of A , A_1 , A_2 and A_3 , both compounds exhibit anisotropic behavior.

For an isotropic crystal, the shear anisotropy (A_G) and compressibility anisotropy (A_B) are equal to zero, and any positive deviation from zero indicates elastic anisotropy. Table 4 demonstrate that in K_2X_3 ($X = S, Se$), A_G is greater than A_B , revealing that shear anisotropy is more pronounced than compressibility anisotropy in both compounds. The universal anisotropy index (A^U), which is valid for all crystal symmetries, is zero for an elastically isotropic material; any nonzero value signifies anisotropy. As shown in Table 4, both compounds are anisotropic, with K_2S_3 exhibiting a higher degree of anisotropy than K_2Se_3 . Similarly, the equivalent Zener anisotropy factor (A^{eq}) equals 1 for isotropic crystals, whereas the calculated values of 2.45 for K_2S_3 and 2.33 for K_2Se_3 indicate strong elastic anisotropy in the studied systems.

According to Kube *et al.* [46], about 90% of crystalline compounds exhibit $A^L < 1$, with A^L ranging between 0 and 10.26, and $A^L = 0$ corresponding to a perfectly isotropic crystal. Although it is difficult to determine solely from A^L whether a crystal possesses a layered structure, nearly 78% of compounds with high A^L values display layered characteristics [47]. Based on the preceding anisotropy analyses, the studied K_2X_3 ($X = S, Se$) compounds can be predicted to exhibit significant elastic anisotropy and a likely layered nature, with K_2S_3 showing a slightly higher degree of anisotropy than K_2Se_3 .

The linear compressibility of materials in the a - and c - directions (β_a and β_c) are calculated using the following formula [29]:

$$\beta_a = \frac{C_{33} - C_{13}}{D}$$

and

$$\beta_c = \frac{C_{11} + C_{12} - 2C_{13}}{D} \quad (19)$$

with, $D = (C_{11} + C_{12})C_{33} - 2(C_{13})^2$.

Table 4. Zener anisotropy factor A , Shear anisotropy factor (A_1 , A_2 and A_3), the universal anisotropy index A^U , equivalent Zener anisotropy measure A^{eq} , anisotropy in shear A_G , anisotropy in compressibility A_B , universal log-Euclidean index A^L , linear compressibility (β_a and β_c) and their ratio β_c/β_a for K_2S_3 and K_2Se_3 in the ground state.

Compounds	A	A_1	A_2	A_3	A_B	A_G	A^U	A^{eq}	A^L	β_a	β_c	β_c/β_a	Ref.
K_2S_3	0.32	0.68	1.81	0.52	0.07	0.08	1.04	2.45	1.60	0.003	0.016	5.33	This
K_2Se_3	0.33	0.69	1.77	0.51	0.05	0.07	0.92	2.33	1.52	0.005	0.014	2.80	This

Table 4 presents the calculated values of the linear compressibility ratio (β_c / β_a), where β_c and β_a represent the linear compressibility along the c - and a -axes, respectively. For an isotropic solid, this ratio equals unity, and any deviation from unity indicates anisotropic compressibility. The estimated results reveal significant anisotropy in the linear compressibility of both compounds. Moreover, for each compound, the compressibility along the c -axis is greater than that along the a -axis, indicating a directional dependence of their mechanical response.

It is easy to compute the bulk modulus along the crystallographic axes from the single crystal elastic constants. The uniaxial bulk modulus along a -, b - and c - axis, relaxed (isotropic) bulk modulus and anisotropies of the bulk modulus can be expressed as follows [48]:

$$B_a = a \frac{dP}{da} = \frac{\Lambda}{1+\alpha+\beta} \quad (20)$$

$$B_b = b \frac{dP}{db} = \frac{B_a}{\alpha} \quad (21)$$

$$B_c = c \frac{dP}{dc} = \frac{B_a}{\beta} \quad (22)$$

$$B_{relax} = \frac{\Lambda}{(1+\alpha+\beta)^2} \quad (23)$$

$$A_{Ba} = \frac{B_a}{B_b} = \alpha \quad (24)$$

$$A_{Bc} = \frac{B_c}{B_b} = \frac{\alpha}{\beta} \quad (25)$$

where,

$$\alpha = \frac{\Lambda = C_{11} + 2C_{12}\alpha + C_{22}\alpha^2 + 2C_{13}\beta + C_{33}\beta^2 + 2C_{23}\alpha\beta}{\{(C_{11} - C_{12})(C_{33} - C_{13})\} - \{(C_{23} - C_{13})(C_{11} - C_{13})\}}$$

$$\beta = \frac{\{(C_{22} - C_{12})(C_{11} - C_{13})\} - \{(C_{11} - C_{12})(C_{23} - C_{12})\}}{\{(C_{22} - C_{12})(C_{33} - C_{13})\} - \{(C_{12} - C_{23})(C_{13} - C_{23})\}}$$

Here, A_{Ba} and A_{Bc} represent the bulk modulus anisotropies along the a - and c -axes, respectively, relative to the b -axis. The calculated results are summarized in Table 5. For K_2X_3 ($X = S, Se$), the bulk modulus is higher along the a -axis compared to the b - and c -axes, and the uniaxial bulk modulus values are significantly greater than the corresponding isotropic bulk modulus values. A crystal is considered isotropic when $A_{Ba} = A_{Bc} = 1$; otherwise, it exhibits anisotropy. The computed A_{Ba} and A_{Bc} values for K_2X_3 ($X = S, Se$) confirm the presence of axial bulk modulus anisotropy in both compounds.

Table 5. The bulk modulus a -, b - and c - axes (B_a , B_b , and B_c), α and β , isotropic bulk modulus B_{relax} , anisotropies in bulk modulus along a - and c - axes with respect to b - axis for K_2S_3 and K_2Se_3 compounds at zero pressure.

Compounds	B_a	B_b	B_c	α	β	B_{relax}	A_{Ba}	A_{Bc}	Ref.
K_2S_3	397.78	75.47	62.74	5.27	6.34	31.54	5.27	0.83	This
K_2Se_3	250.65	62.50	67.74	4.01	3.70	28.77	4.01	1.08	This

3.3.4 Hardness

Vickers hardness (H_V) is evaluated to characterize the bonding nature and to assess both intrinsic factors (such as bond strength, cohesive energy, and crystal structure) and extrinsic factors (including defects, stress fields, and morphology) of K_2X_3 ($X = S, Se$). In this study, hardness values for K_2S_3 and K_2Se_3 are estimated using established semi-empirical correlations [27, 49-54] that relate H_V to elastic parameters such as bulk modulus (B), shear modulus (G), Young's modulus (Y), Poisson's ratio (ν), and the B/G ratio, based on

macroscopic hardness prediction models.

$$H_1 = 0.0963B \quad (26)$$

$$H_2 = 0.0607Y \quad (27)$$

$$H_3 = 0.1475G \quad (28)$$

$$H_4 = 0.0635Y \quad (29)$$

$$H_5 = -2.899 + 0.1769G \quad (30)$$

$$H_6 = \frac{(1-2\nu)B}{6(1+\nu)} \quad (31)$$

$$H_7 = \frac{(1-2\nu)Y}{6(1+\nu)} \quad (32)$$

$$H_8 = 2 \left(\frac{G^3}{B^2} \right)^{0.585} - 3 \quad (33)$$

$$H_9 = 0.92k \left(\frac{B}{G} \right)^{1.37} G^{0.708} \quad (34)$$

For semiconductors, the accuracy of hardness predictions using the aforementioned methods depends on the crystal class and the energy band gap (E_g) [55]. Using these formulas, the Vickers hardness of K_2S_3 and K_2Se_3 was calculated (shown in Table 6) to identify the most suitable model for orthorhombic crystals. Among nine approaches, the H_8 model is the most appropriate for predicting orthorhombic crystal hardness [50]. While Teter's empirical correlation [51] between hardness and shear modulus is widely used, it is not universally reliable because shear modulus reflects only elastic deformation, whereas hardness depends on both elastic and plastic responses. The results indicate that K_2X_3 ($X = S, Se$) have low hardness values, implying that both compounds are relatively soft, with K_2Se_3 expected to be softer than K_2S_3 .

Table 6. The calculated values of the hardness H (in GPa) for K_2S_3 and K_2Se_3 using different empirical formulas.

Compounds	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	Ref.
K_2S_3	3.30	3.25	3.18	3.39	0.917	2.40	3.74	3.24	4.29	This
K_2Se_3	2.97	2.82	2.74	2.95	0.393	2.16	3.24	3.08	3.62	This

3.3.5 Acoustic velocity and its anisotropy

Sound velocity in a material is a fundamental physical property that reflects how quickly mechanical (elastic) waves propagate through it. It is closely related to the material's elastic stiffness and density, and it also correlates with important properties such as thermal conductivity and, in some cases, electrical behavior.

The average sound velocity v_a in the polycrystalline material is given by the following equation [56]:

$$v_a = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (35)$$

where, v_l and v_t are longitudinal and transverse sound velocities, respectively, obtained using the shear modulus G , the bulk modulus B and density ρ from Navier's equation [56]

$$v_l = \left(\frac{3B+4G}{3\rho} \right)^{\frac{1}{2}} \quad (36)$$

and

$$v_t = \left(\frac{G}{\rho} \right)^{\frac{1}{2}} \quad (37)$$

Acoustic impedance (Z) is a fundamental property that governs the propagation of sound energy within a medium. The mismatch between the acoustic impedances of two media determines the proportion of sound energy that is reflected or transmitted when a wave encounters their interface. If the impedances of the two materials are nearly equal, most of the incident sound energy is transmitted. Conversely, a large impedance difference results in significant reflection.

Materials with high acoustic impedance generally support more efficient sound propagation within the medium. In the limiting cases, materials with $Z = 0$ and $Z \rightarrow \infty$ are regarded as ideal soft and hard boundaries, respectively. A perfect soft surface does not allow sound energy to propagate through it, while a perfectly hard surface reflects nearly all incident sound energy.

The concept of acoustic impedance mismatch is widely applied in numerous fields, including musical instrument design, transducer development, acoustic sensing, aircraft and automotive engineering, industrial manufacturing, medical ultrasound imaging, and underwater acoustics.

For a solid medium, acoustic impedance can be calculated from its density (ρ) and shear modulus (G) as [33, 57]:

$$Z = \sqrt{\rho G} \quad (38)$$

This relationship highlights the dependence of acoustic impedance on both the elastic stiffness and density of the material.

The intensity of sound radiation is a key design parameter in the construction of soundboards and other acoustic components. It characterizes how effectively a material can radiate vibrational energy as audible sound. In musical acoustics, particularly in soundboard design, materials are selected to maximize sound radiation while maintaining appropriate mechanical strength and stability. The sound radiation intensity (I) can be expressed in proportional form in terms of a material's density (ρ) and shear modulus (G) as [33, 57]:

$$I \approx \sqrt{\frac{G}{\rho^3}} \quad (39)$$

This relationship indicates that sound radiation intensity increases with higher shear modulus and decreases with increasing density. Therefore, materials that combine high stiffness with low density are especially desirable for efficient sound radiation, making them suitable for applications such as soundboards and other acoustic structures.

When selecting materials for soundboard design, careful consideration must be given to the radiation factor, defined by the expression $\sqrt{G/\rho^3}$. This parameter provides a measure of a vibrating surface's efficiency as a sound radiator. In general, a high radiation factor is desirable for soundboards because it indicates that the material can effectively convert vibrational energy into acoustic radiation. A classic example is violin construction. Spruce is the most commonly used material for the front plate due to its high radiation factor (approximately $8.6 \text{ m}^4/\text{kg}\cdot\text{s}$), which makes it highly efficient at radiating sound. In contrast, maple is typically used for the back plate. Since the back plate primarily reflects rather than radiates sound, its lower radiation factor (about $5.4 \text{ m}^4/\text{kg}\cdot\text{s}$, nearly half that of spruce) is appropriate for this function.

Table 7. Calculated density ρ (in gm/cm^3), longitudinal velocity v_l (in km/s), transverse velocity v_t (in km/s), mean velocity v_a (in km/s), acoustic impedance Z (in Rayl), Grüneisen parameter γ , and radiation factor $\sqrt{G/\rho^3}$ ($\text{m}^4/\text{kg}\cdot\text{s}$) of K_2S_3 and K_2Se_3 compounds.

Compounds	ρ	v_l	v_t	v_a	$Z (\times 10^6)$	$\sqrt{G/\rho^3}$	γ	Ref.
K_2S_3	2.14	5.43	3.17	3.52	6.79	1.48	1.45	This
	2.14	-	-	-	-	-	-	[4] ^{Exp}
K_2Se_3	3.35	4.08	2.36	2.70	7.89	0.703	1.45	This
	3.37	-	-	-	-	-	-	[5] ^{Exp}

Beyond material selection, the radiation factor also explains the coupling between structural wave propagation and the acoustic energy radiated by vibrating components. In essence, it reflects how efficiently mechanical vibrations within a structure are transformed into audible sound. As shown in Table 7, the calculated radiation factors for K_2X_3 ($X = \text{S}, \text{Se}$) indicate that both K_2S_3 and K_2Se_3 possess relatively low radiation factors, suggesting limited efficiency as sound-radiating materials compared with traditional acoustic woods such as spruce.

We have calculated the Grüneisen constant γ of K_2X_3 ($X = \text{S}, \text{Se}$) compounds which is evaluated from the Poisson's ratio by using the following expression [33, 58]:

$$\gamma = \frac{3(1 + \nu)}{2(2 - 3\nu)} \quad (40)$$

The Grüneisen parameter (γ) plays a crucial role in governing several important physical processes in solids. It influences thermal conductivity, thermal expansion, acoustic wave absorption, and the temperature dependence of elastic properties. In combination with thermal expansion, it serves as a measure of lattice anharmonicity, describing how phonon frequencies shift and how phonon damping evolves with temperature. Physically, the Grüneisen parameter quantifies the sensitivity of phonon frequencies to changes in volume. A higher γ indicates stronger anharmonic effects, meaning that lattice vibrations deviate more significantly from ideal harmonic behavior as temperature increases.

For K_2X_3 ($X = \text{S}, \text{Se}$), the estimated Grüneisen parameter is $\gamma = 1.45$ (shown in Table 7), which suggests a moderate degree of anharmonicity. This value is comparable to that of

many other compounds exhibiting intermediate lattice anharmonic behavior [33]. Such materials typically display balanced thermal properties, where phonon scattering is significant but not excessively strong.

3.4 Thermophysical Properties

3.4.1 Debye temperature

The thermal properties of solids associated with lattice vibrations are fundamentally described by the Debye model. The Debye temperature (θ_D) is a characteristic parameter that effectively represents several important thermal properties of crystalline materials, including heat capacity, melting point, thermal expansion, thermal conductivity, isothermal compressibility, and lattice enthalpy. At temperatures above θ_D , all vibrational modes are fully excited and possess an average energy of $k_B T$. In contrast, at temperatures below θ_D , the high-frequency vibrational modes become progressively frozen out [27]. In this low-temperature regime, lattice vibrations are predominantly governed by acoustic phonon modes. A low θ_D generally indicates weak interatomic bonding and, consequently, a mechanically soft material. The Debye temperature can be expressed in terms of the mean sound velocity as follows [56].

$$\theta_D = \frac{h}{k_B} \left[\frac{3n}{4\pi V_0} \right]^{1/3} v_a \quad (41)$$

where, h is Planck's constant, k_B is the Boltzmann's constant, V_0 is the volume of the unit cell and n is the number of atoms in the unit cell. The computed Debye temperatures of the compounds at 0 K are shown in Table 8.

Table 8. The Debye temperature θ_D (in K), lattice thermal conductivity κ_{ph} (in W/m-K) at 300 K, thermal expansion coefficient α (in K^{-1}), wavelength of dominant phonon mode λ_{dom} (in m) at 300 K, and heat capacity per unit volume ρC_P (in J/m^3K) of K_2S_3 and K_2Se_3 compounds.

Compounds	θ_D	$\alpha (\times 10^{-5})$	$\lambda_{dom} (\times 10^{-12})$	$\rho C_P (\times 10^6)$	κ_{ph}	Ref.
K_2S_3	349	7.42	147	1.53	3.00	This
K_2Se_3	256	8.59	113	1.34	2.27	This

The Debye temperature of K_2Se_3 is significantly lower than that of K_2S_3 . Since a lower Debye temperature generally corresponds to reduced phonon thermal conductivity, this suggests that K_2Se_3 is expected to exhibit lower lattice thermal conductivity compared to K_2S_3 . Consequently, K_2Se_3 may be a more promising candidate for thermal barrier coating applications. Furthermore, the Debye temperature also serves as an indicator of the overall bond strength within a crystal, with lower values reflecting weaker interatomic bonding.

3.4.2 Melting temperature

The melting temperature (T_m) is an essential thermophysical parameter that determines the suitability of a material for high-temperature applications. Crystals with higher melting temperatures typically exhibit greater cohesive energy, stronger bonding interactions, enhanced atomic connectivity, and lower coefficients of thermal expansion [27]. Moreover,

T_m is a fundamental parameter used to characterize both inorganic and organic materials. In the present study, the melting temperatures of K_2S_3 and K_2Se_3 were estimated from their elastic constants using the following empirical relation [59, 60]:

$$T_m = 354 + 4.5 \left(\frac{2C_{11} + C_{33}}{3} \right) \pm 300 \quad (42)$$

Table 9. Melting temperature T_m (in K) of K_2S_3 and K_2Se_3

Compound	T_m	Reference
K_2S_3	744	This
	520	[11] ^{Expt.}
	525	[11] ^{Expt.}
	565	[11] ^{Expt.}
	568	[11] ^{Expt.}
	572	[11] ^{Expt.}
	575	[11] ^{Expt.}
K_2Se_3	689	This
	649	[8] ^{Expt.}
	648	[8] ^{Expt.}

The estimated melting temperatures (T_m) of the investigated compounds are presented in Table 9. The calculated T_m values for K_2S_3 and K_2Se_3 are 744 K and 689 K, respectively. Similar to the lattice thermal conductivity (κ_{ph}), the melting temperature of a crystal is closely associated with its bonding strength. The relatively low T_m values obtained for K_2X_3 ($X = S, Se$) suggest that these compounds are comparatively soft under ambient conditions. Furthermore, the calculated melting temperatures are in good agreement with previously reported results [8, 11].

3.4.3 Lattice Thermal Conductivity

The lattice thermal conductivity (κ_{ph}) quantifies a solid's ability to transport heat through lattice vibrations (phonons). Materials with high thermal conductivity are essential for efficient heat dissipation in microelectronic and nanoelectronic devices. In contrast, materials with low thermal conductivity form the basis of advanced thermoelectric systems and thermal barrier coatings (TBCs). According to Slack's model, the lattice thermal conductivity of the compounds at 300 K can be estimated using the following relation [61-63].

$$\kappa_{ph} = A(\gamma) \frac{M_{av} \theta_D^3 \delta}{\gamma^2 n^{2/3} T} \quad (43)$$

In this formula, M_{av} refers to the average atomic mass per atom in a compound in kg/mol, θ_D is the Debye temperature in K, δ defines the cubic root of average atomic volume in m, n represents the total number of atoms in the unit cell, T is the absolute temperature in K, γ is the Grüneisen parameter and $A(\gamma)$, which is a function of γ , is evaluated from following equation (in W-mol/kg/m²/K³) [63]:

$$A = \frac{4.85625 \times 10^7}{2 \times \left(1 - \frac{0.514}{\gamma} + \frac{0.228}{\gamma^2} \right)} \quad (44)$$

The calculated room-temperature lattice thermal conductivities of the studied compounds are presented in Table 8. The low lattice thermal conductivity observed for K_2X_3 ($X = S, Se$) is consistent with their relatively low Debye temperatures, indicating a clear correlation between these two parameters. In general, higher lattice thermal conductivity is associated with stronger covalent bonding and enhanced phonon transport. The computed results suggest that the covalent bonding in K_2S_3 is considerably stronger than that in K_2Se_3 , which accounts for its comparatively higher thermal conductivity.

3.4.4 Thermal expansion coefficient and heat capacity

Thermal expansion is an intrinsic property of solids arising from anharmonic lattice vibrations. The thermal expansion coefficient (TEC) significantly influences various material properties, including thermal conductivity, specific heat, entropy, compressibility, temperature-dependent band gap variation in semiconductors, and the effective mass of charge carriers. Materials exhibiting very low thermal expansion are of considerable practical relevance and fundamental scientific interest due to their dimensional stability under thermal fluctuations. The thermal expansion coefficient of a material can be estimated from its shear modulus using the following empirical relation [28, 64]:

$$\alpha = \frac{1.6 \times 10^{-3}}{G} \quad (45)$$

where, G is the isothermal shear modulus in GPa. The thermal expansion coefficient (TEC) of a material is inversely proportional to its melting temperature and can be approximately expressed as $\alpha \approx 0.02/T_m$ [28]. The TEC of crystalline solids is temperature dependent, and the calculated values at 300 K are presented in Table 8. The results indicate that both structures exhibit extremely low thermal expansion coefficients. Materials with low thermal expansion are highly desirable for applications in electronic devices, heat-engine components, spintronic systems, and environments requiring high resistance to thermal shock (e.g., cookware designed for rapid temperature transitions from oven to freezer).

Heat capacity is another fundamental thermodynamic property of a material. Compounds with higher heat capacity generally exhibit lower thermal diffusivity, as they can store a greater amount of thermal energy for a given temperature rise. In this study, the heat capacity per unit volume was calculated using the following relation [28, 64]:

$$\rho C_p = \frac{3k_B}{\Omega} \quad (46)$$

where, $N = 1/\Omega$ is the number of atoms per unit volume. Our estimated values of the heat capacity per unit volume of K_2X_3 ($X = S, Se$) are listed in Table 8.

3.4.5 Dominant phonon mode

Phonons play a crucial role in determining various physical properties of condensed matter, including heat capacity, thermal conductivity, and electrical conductivity. The sound velocity of a material can be used to estimate the wavelength of the dominant phonon mode (λ_{dom}), corresponding to the peak of the phonon distribution. For K_2X_3 ($X = S, Se$), the

wavelength of the dominant phonon mode at 300 K was calculated using the following relation [65]:

$$\lambda_{dom} = \frac{12.566 v_a}{T} \times 10^{-12} \quad (47)$$

where, v_a is the average sound velocity in ms^{-1} , T is the temperature in K. A material with a higher shear modulus, lower density, and greater average sound velocity will exhibit dominant phonons with longer wavelengths. The calculated value of λ_{dom} is also listed in Table 8.

3.5 Electronic Properties

3.5.1 Electronic band structure

The electronic band structure is a fundamental concept in solid-state physics, providing a detailed representation of the energy levels of electrons within a crystalline material. It describes how the energies of crystal orbitals vary with momentum across the Brillouin zone. Calculating the electronic band structure is essential for understanding the Fermi surface and the behavior of electrons near the Fermi level. By analyzing the characteristics and energies of the dominant bands close to the Fermi level, one can gain valuable insights into the electronic, optical, and transport properties of the material.

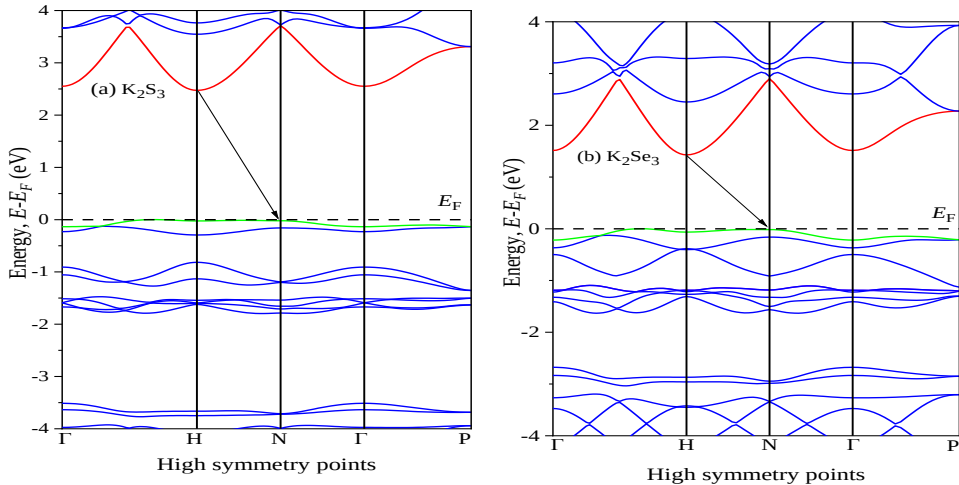


Figure 3. Calculated band structure along the high symmetry directions of the Brillouin zone for (a) K_2S_3 and (b) K_2Se_3 at $P = 0$ GPa.

Figures 3(a) and 3(b) show the electronic band structures of K_2X_3 ($\text{X} = \text{S}, \text{Se}$) at zero pressure along the high-symmetry directions (Γ -H-N- Γ -P) of the Brillouin zone, within an energy range of -4 to $+4$ eV. The horizontal dashed line at 0 eV represents the Fermi level. The valence bands (VB) and conduction bands (CB) do not overlap near the Fermi level, confirming the semiconducting nature of both compounds. The valence band maximum (VBM) and conduction band minimum (CBM) occur at different points in the first Brillouin zone at N and H, respectively, resulting in an indirect wide band gap (N-H) of 2.475 eV for K_2S_3 and 1.432 eV for K_2Se_3 .

The reduction in band gap from K_2S_3 to K_2Se_3 is primarily attributed to the increase in atomic radius of the chalcogen element ($X = S, Se$). Since sulfur has a smaller atomic radius than selenium, K_2S_3 exhibits a larger band gap compared to K_2Se_3 . As the number of available electronic states increases, the forbidden energy gap narrows due to the decreased separation between valence and conduction bands. This behavior is related to electrostatic forces, valence electrons in Se experience weaker attraction to the nucleus because they are located farther away compared to those in S. Figures 3 (a, b) also show that the dispersion of the valence band maximum is smaller than that of the conduction band minimum, indicating a higher effective mass and thus lower mobility for charge carriers in the valence band. Consequently, both compounds are expected to exhibit relatively low charge carrier transport properties.

3.5.2 Density of States

Generally, the density of states (DOS) of a system describes the number of states per interval of energy at each energy level that are available to be occupied. The density of states influences numerous bulk properties of conductive solids, including specific heat, paramagnetic susceptibility and other transport phenomena. The detailed features of band structure and the bonding nature of K_2S_3 and K_2Se_3 can be understood from the analysis of the partial and total density of states at zero pressure which are presented in Figs. 4 (a, b). The vertical line in this instance denotes the Fermi level.

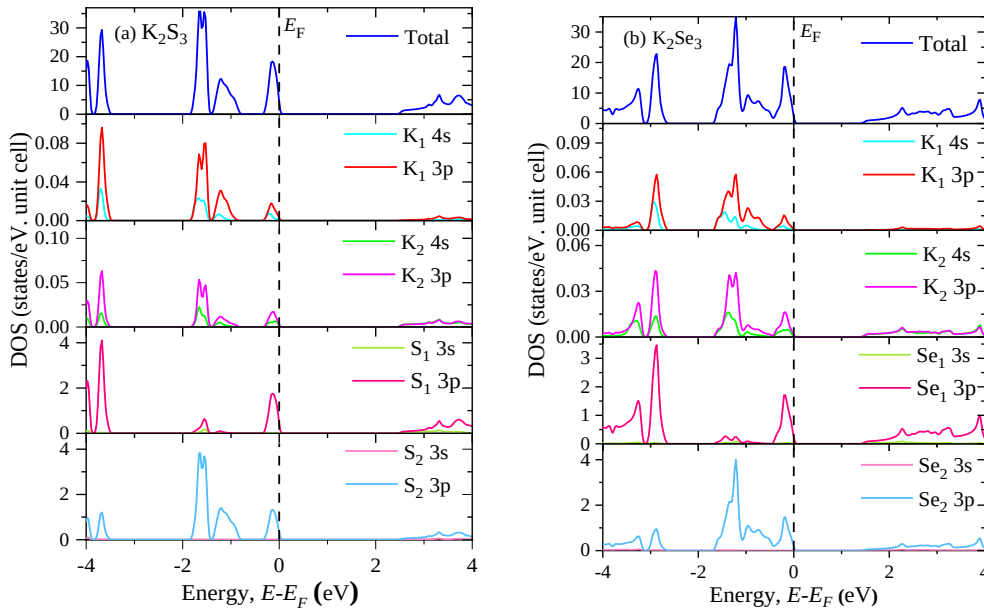


Figure 4. The total and partial density of states for (a) K_2S_3 and (b) K_2Se_3 at $P = 0$ GPa.

As observed from Fig. 4(a), the lowest-energy bands, ranging from -3.84 eV to -3.47 eV, are primarily derived from $S_1 3p$ and $S_2 3p$ states, with minor contributions from $K_1 3p$ and $K_2 3p$ states. The valence bands between -1.83 eV and -0.81 eV exhibit two prominent peaks at -1.65 eV and -1.54 eV, both corresponding to $S_2 3p$ states. The upper valence band, spanning -0.32 eV to 0 eV, is predominantly composed of $S 3p$ states. The conduction bands

are also largely contributed by S 3*p* orbitals, indicating that sulfur's *p*-states dominate both the valence and conduction regions of the electronic structure.

From Fig. 4(b), the lowest portion of the valence band, ranging from −4 eV to −2.62 eV, primarily arises from the hybridization of Se1 3*p* and Se2 3*p* states, with minor contributions from K1 3*p* and K2 3*p* states. The upper valence band, spanning −1.70 eV to 0 eV, is predominantly composed of Se2 3*p* states, with only small contributions from K1 3*p*, K2 3*p*, and Se1 3*p* states. The conduction band is mainly derived from Se 3*p* orbitals, indicating that selenium's *p*-states dominate both the valence and conduction regions of K₂Se₃.

3.6 Optical Properties

The optical properties of a material describe its interaction with incident light and are particularly important for optoelectronic device applications operating in the visible region of the electromagnetic spectrum. To understand the response of a material to incident electromagnetic radiation, several energy-dependent optical parameters are evaluated, including the dielectric function, absorption coefficient, optical conductivity, energy loss function, reflectivity, and refractive index. In this study, the optical properties of K₂S₃ and K₂Se₃ are investigated for the first time using the frequency-dependent complex dielectric function, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part of the dielectric function, $\varepsilon_2(\omega)$, is calculated using the formalism reported in Refs. [47, 48], while the real part, $\varepsilon_1(\omega)$, is obtained from $\varepsilon_2(\omega)$ through the Kramers–Kronig transformation [66, 67]. The optical functions of K₂X₃ (X = S, Se) are computed for different electric field polarization directions along [100], [010], and [001]. The polarization-dependent optical response provides valuable insight into the optical and electronic anisotropy of these compounds.

The dielectric function describes how a material responds to incident electromagnetic radiation and is closely related to its electronic band structure. Figures 5(a–d) present the real and imaginary parts of the dielectric function for K₂S₃ and K₂Se₃. From Figures 5(a) and 5(b), the calculated static dielectric constants, $\varepsilon_1(0)$ for K₂S₃ are 3.88, 2.47, and 2.96 along the [100], [010], and [001] directions, respectively. For K₂Se₃, the corresponding values are 5.97, 2.95, and 4.51. It is evident that $\varepsilon_1(0)$ is higher for K₂Se₃ than for K₂S₃, indicating an inverse relationship between the band gap and the static dielectric constant; a larger band gap generally results in a smaller $\varepsilon_1(0)$. Beyond the zero-frequency limit, $\varepsilon_1(\omega)$ increases with photon energy and reaches maximum values at 6.95 (1.88), 7.06 (6.58), and 6.87 (1.57) eV for K₂S₃ (K₂Se₃) along the [100], [010], and [001] directions, respectively. After attaining these peak values, the spectra gradually decrease and eventually approach zero. At this point, the material loses its dielectric response and begins to exhibit metallic behavior.

The imaginary part of the dielectric function, $\varepsilon_2(\omega)$, is shown in Figs. 5(c) and 5(d). The onset (threshold) of $\varepsilon_2(\omega)$ corresponds to the fundamental absorption edge and is directly related to the band gap of the material. From the position of this threshold, it is clear that the band gap decreases when moving from K₂S₃ to K₂Se₃. Beyond the absorption edge, $\varepsilon_2(\omega)$ increases sharply due to the occurrence of major interband electronic transitions and reaches its maximum peak value. For the [100] polarization direction, the highest peak appears at 7.74 eV for K₂S₃ and 3.53 eV for K₂Se₃. Along the [010] and [001] directions, $\varepsilon_2(\omega)$ exhibits

maximum peaks at 9.83 eV and 8.24 eV for K_2S_3 , and at 8.49 eV and 7.89 eV for K_2Se_3 , respectively. These pronounced peaks originate from strong optical transitions between the occupied valence band states and unoccupied conduction band states, further reflecting the anisotropic optical response of both compounds.

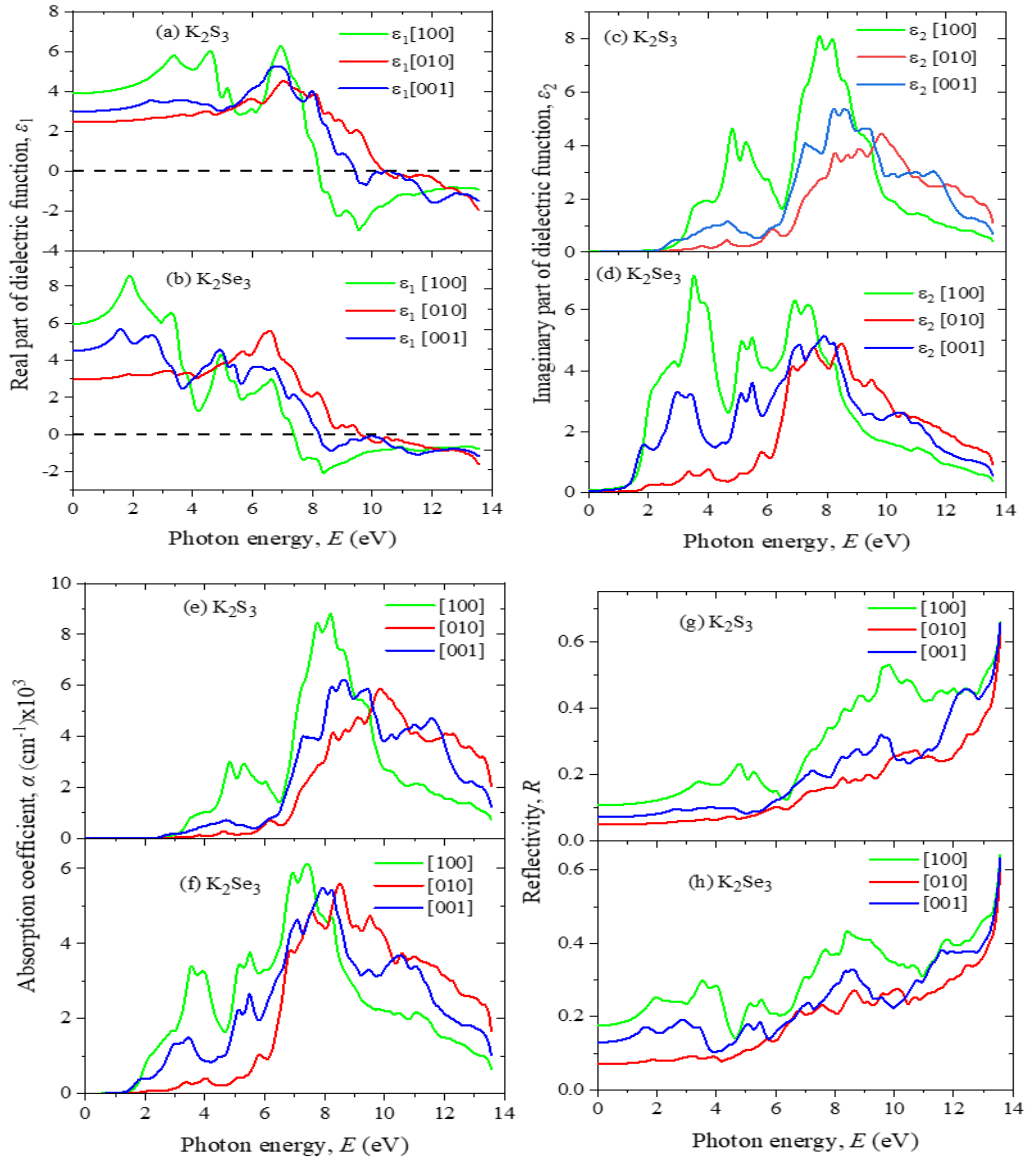


Figure 5. Real part of dielectric function, ϵ_1 , (a, b), imaginary part of dielectric function, ϵ_2 , (c, d), absorption coefficient, α , (e, f) and reflectivity, R , (g, h) as a function of photon energy, E for K_2S_3 and K_2Se_3 along [100], [010] and [001] directions, respectively.

The absorption coefficient (α) provides important information regarding the optical response of a material and its potential for solar energy conversion applications. It describes how

deeply light of a given photon energy can penetrate into a material before being absorbed. This quantity strongly depends on both the wavelength of the incident light and the intrinsic electronic structure of the material. The calculated absorption coefficients of K_2X_3 ($X = S, Se$) are presented in Figs. 5(e) and 5(f). No absorption is observed in the low-energy region, as expected, since photon energies below the optical band gap are insufficient to excite electrons across the band gap. Optical absorption begins at photon energies of 2.57 eV for K_2S_3 and 1.30 eV for K_2Se_3 , consistent with their respective band gap values. For K_2S_3 , the principal absorption peaks are located at 8.17, 9.85, and 8.66 eV along the [100], [010], and [001] directions, respectively. In the case of K_2Se_3 , the main peaks appear at 7.41, 8.53, and 7.91 eV along the same crystallographic directions. It is evident that the strongest absorption occurs in the energy range of 7–10 eV, which lies in the ultraviolet (UV) region for both compounds. These results indicate that K_2S_3 and K_2Se_3 exhibit strong absorption in the UV region, suggesting their potential suitability as effective UV radiation absorbing materials.

Reflectivity is defined as the ratio of the energy of the reflected electromagnetic wave to that of the incident wave at the material surface. The calculated reflectivity spectra $R(\omega)$ of K_2S_3 and K_2Se_3 as a function of photon energy are presented in Figs. 5(g) and 5(h) for the polarization directions [100], [010], and [001]. For both compounds, the reflectivity spectra exhibit nearly similar features along the three crystallographic directions, with only slight anisotropic variations. The static reflectivity values $R(0)$ are calculated to be 0.11, 0.05, and 0.07 along the [100], [010], and [001] directions, respectively, for K_2S_3 , while for K_2Se_3 the corresponding values are 0.18, 0.07, and 0.13. These results indicate that K_2Se_3 possesses slightly higher reflectivity than K_2S_3 across the investigated energy range. The highest peaks in the frequency-dependent reflectivity spectra of both compounds are observed within the energy range of 6.26–12.84 eV, which lies in the ultraviolet (UV) region. The pronounced peaks in this region suggest that K_2S_3 and K_2Se_3 could serve as potential materials for UV radiation shielding applications. Furthermore, a sharp increase in reflectivity is observed between 12.50 and 13.50 eV for both compounds, which may be attributed to strong interband electronic transitions occurring at higher photon energies.

The refractive index is an important optical parameter associated with microscopic electronic polarizability and provides insight into the transparency of semiconductor materials across the solar spectrum. The refractive index, $n(\omega)$, exhibits a frequency-dependent behavior similar to that of the real part of the dielectric function, $\epsilon_1(\omega)$. The calculated frequency-dependent refractive indices of K_2S_3 and K_2Se_3 are presented in Figs. 6(a) and 6(b). The static refractive index values, $n(0)$, for K_2S_3 are 1.97, 1.56, and 1.73 along the [100], [010], and [001] directions, respectively. For K_2Se_3 , the corresponding values are 2.43, 1.71, and 2.11. The comparatively lower refractive index of K_2S_3 indicates that it is more optically transparent than K_2Se_3 . This observation is consistent with the band structure results, which show that K_2S_3 possesses a larger band gap than K_2Se_3 , since materials with wider band gaps generally exhibit lower refractive indices. For K_2S_3 , the refractive index reaches maximum values of 2.63 at 7.03 eV along [100], 2.15 at 7.07 eV along [010], and 2.36 at 7.00 eV along [001]. In contrast, K_2Se_3 exhibits principal peaks of 2.94 at 1.94 eV along [100], 2.44 at 6.64 eV along [010], and 2.41 at 1.56 eV along [001]. The variation of the refractive index with photon energy further confirms the anisotropic optical behavior of both compounds and

supports their potential applicability in optoelectronic and UV-related device applications.

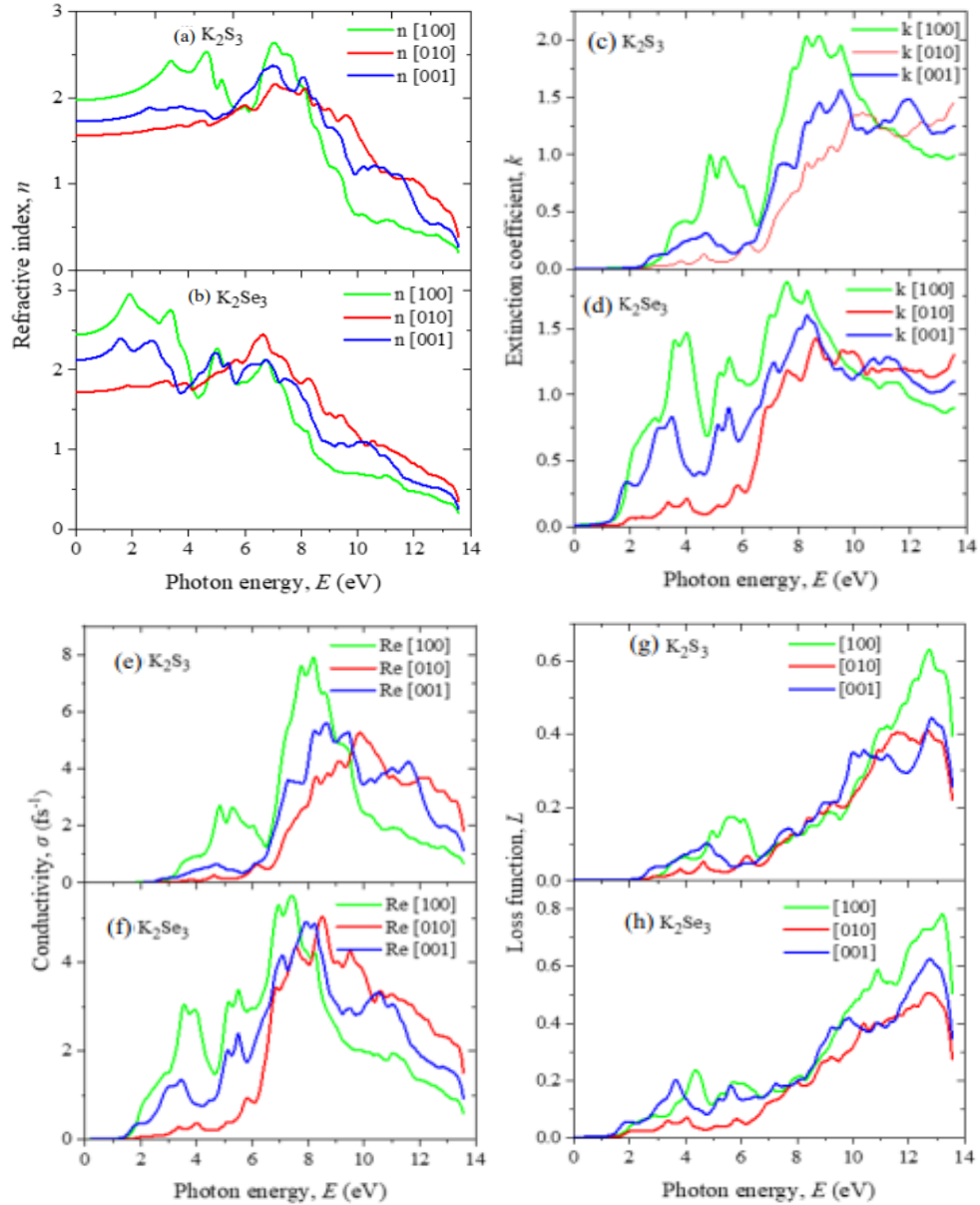


Figure 6. Refractive index, n , (a, b), extinction coefficient, k , (c, d), conductivity, σ , (e, f) and loss function, L , (g, h) as a function of photon energy, E for K_2S_3 and K_2Se_3 along [100], [010] and [001] directions, respectively

The extinction coefficient, $k(\omega)$, describes the attenuation of electromagnetic waves inside a material and is directly related to its absorption behavior [68]. The calculated $k(\omega)$ spectra of K_2X_3 ($X = S, Se$) are shown in Figs. 6(c) and 6(d). Similar to $\epsilon_2(\omega)$, the extinction

coefficient begins at threshold energies of approximately 2.25 eV for K_2S_3 and 1.0 eV for K_2Se_3 , corresponding to the onset of interband transitions. For K_2S_3 , the main peaks appear at 8.73, 10.34, and 9.52 eV along the [100], [010], and [001] directions, respectively, while K_2Se_3 exhibits peaks at 7.58, 8.65, and 8.31 eV along the same directions. Beyond the peak positions, $k(\omega)$ decreases with increasing photon energy. The directional variation confirms the anisotropic optical response of both compounds and is consistent with the dielectric and absorption results.

Photoconductivity, $\sigma(\omega)$, represents the increase in electrical conductivity of a material upon absorption of electromagnetic radiation, such as visible or ultraviolet light. The real part of the optical conductivity spectra for K_2S_3 and K_2Se_3 , shown in Figs. 6(e) and 6(f), does not start at zero photon energy, confirming the presence of finite band gaps in both compounds. For K_2S_3 , the maximum optical conductivity occurs at 8.17, 9.83 and 8.63 eV along the [100], [010] and [001], respectively. In the case of K_2Se_3 , the corresponding peak values are observed at 7.41 eV ([100]), 8.50 eV ([010]), and 7.95 eV ([001]). In both materials, the highest optical conductivity appears in the ultraviolet region. A sharp decrease in the spectra is noticeable within the energy range of 11–13.5 eV.

The electron energy loss function, $L(\omega)$, is an important optical parameter that describes the energy dissipated by fast electrons traversing a material. The calculated energy loss spectra of K_2X_3 ($X = S, Se$), shown in Figs. 6(g) and 6(h), are plotted over the energy range of 0–14 eV. The loss function begins to rise at approximately 2.20 eV for K_2S_3 and 1.26 eV for K_2Se_3 , corresponding to the onset of electronic excitations. For K_2S_3 , the prominent peaks are observed at 12.75, 12.70 and 12.82 eV along the [100], [010] and [001], respectively. In the case of K_2Se_3 , the maximum peaks occur at 13.24 eV ([100]), 12.75 eV ([010]), and 12.77 eV ([001]). Beyond these peak energies, $L(\omega)$ gradually decreases for both compounds. These pronounced peaks are associated with plasma resonances, further confirming the anisotropic optical behavior of K_2S_3 and K_2Se_3 .

4. Conclusions

This work presents a comprehensive first-principles investigation of the structural, mechanical, thermophysical, electronic, and optical properties of K_2X_3 ($X = S, Se$) within the FP-LAPW framework of density functional theory. The optimized lattice parameters and unit cell volumes exhibit excellent agreement with available experimental data, reinforcing the reliability of the computational approach. Elastic constant analysis confirms that both K_2S_3 and K_2Se_3 are mechanically stable, brittle, and elastically anisotropic, while phonon dispersion calculations validate their dynamical stability through the absence of imaginary frequencies across the Brillouin zone.

Thermophysical results reveal low Debye temperatures and correspondingly low lattice thermal conductivities at room temperature, underscoring the intimate link between lattice dynamics and heat transport. Stronger covalent bonding is shown to enhance phonon propagation and thermal conductivity, with K_2S_3 displaying more robust covalent interactions than K_2Se_3 , thereby achieving comparatively higher conductivity. These insights highlight the critical role of bonding characteristics in governing thermal transport behavior.

Electronic structure analysis confirms wide band-gap semiconducting behavior in both compounds, with band gaps significantly reduced upon substitution of sulfur by selenium. The density of states is dominated by the *p*-orbitals of the chalcogen atoms, reflecting their decisive role in electronic properties. Optical investigations reveal pronounced anisotropy across the dielectric function, refractive index, extinction coefficient, reflectivity, photoconductivity, and energy-loss spectra. Both materials exhibit strong ultraviolet absorption and high photoconductivity, making them promising candidates for ultraviolet absorption applications.

In summary, this study establishes a robust structure–property relationship for K_2S_3 and K_2Se_3 , offering valuable guidance for their potential integration into future optoelectronic and energy-related technologies.

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