

Investigation of Structural, Elastic, Electronic and Optical Properties of Ternary KLiTe: A First Principles Study

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Abstract: The structural, elastic, electronic and optical properties of KLiTe have been studied by using density functional theory (DFT). The optimized lattice parameters are in good agreement with the available experimental data. Paugh's ductility index (G/B) is calculated which show brittleness of the studied compound. The elastic constants, bulk modulus, shear modulus, Young's modulus and Poisson's ratio are calculated by using the Voigt-Reuss-Hill approximation. The values of elastic constants show that KLiTe is mechanically stable. Zener's anisotropy index shows the anisotropic characteristics of this compound. The calculated band structure exhibits the semiconducting nature of this compound. Furthermore, the densities of states (DOS) are mainly contributed by $K-3p$ at the conduction band and $Te-5s$ at the valence band. The reflectivity in the UV region is upto~98% and it could be used as coating materials to avoid solar heating.

Key Words: KLiTe, First principles, Elastic constants, Electronic properties and Optical properties.

1. INTRODUCTION

The general formula of ternary alkali metal chalcogenides is ABX, where A and B represent different alkali metals (Li, Na, K, Rb and Cs) and X is a chalcogen (O, S, Se and Te), have attracted the interest of materials researchers. The tetragonal KLiTe belongs to the same group. The position of the atoms are K: $2c (1/4, 1/4, z_K)$, Li: $2a (3/4, 1/4, 0)$ and Te: $2c (1/4, 1/4, z_{Te})$, where z_K and z_{Te} are the internal structure parameters describing the positions of the Li and Te atoms along their z-axis. The first studied inter alkali metal chalcogenides were KNaO and RbNaO. Indeed, in 1982, Sabrowsky *et al.* [1] elaborated and characterized these compounds and confirmed their tetragonal anti-PbFCl-type structure. Later on, Sabrowsky *et al.* [2-5] have explored other inter alkali metal chalcogenides such as KLiX where X = S, Se, Te. Various structural properties and experimental synthesis have been discussed by many researchers [6-10]. It was noticed that these materials adopt a tetragonal structure with space group P4/nmm (#129). The structural, electronic and elastic properties of the new ternary alkali metal chalcogenides KLiX (X = S, Se and Te) have been studied by Seddik *et al.* [11] which shows wide band gap semiconducting nature of the studied compound. The pressure dependent Optoelectronic and Charge Transport Properties of KCuX (X=Se, Te) have been studied [12]. The monolayer KCuTe exhibited a new type of 2D direct band gap semiconductor [13]. It is clear from the above discussion that there is a dearth of theoretical study on the KLiTe. Neither experimental nor theoretical details regarding the optical properties are available for a purpose of comparison.

Here in this paper our aim is to study and discuss carefully about the structural, elastic, electronic and optical properties of KLiTe crystal using first-principles methods based on DFT within the generalized gradient approximation (GGA) method as implemented in CASTEP code at 0 K temperatures. The arrangements of this paper are as follows. The computational methods are presented in second Section. The results of structural optimizations for KLiTe crystals are comparatively studied in Section 3.1. The elastic properties including independent elastic constants, Young's modulus, shear modulus, ratio of the shear and bulk modulus are systematically analyzed in Section 3.2. The electronic properties including band structures, total density of states (TDOS) and partial density of states (PDOS) are then investigated in Section 3.3. Furthermore, in Section 3.4 the optical properties such as dielectric constant, refractive index, extinction coefficient, absorption, conductivity, loss function and reflectivity are evaluated and discussed in detail. Finally, we summarize the calculated results in Section 4.

2. COMPUTATIONAL METHOD

The first-principles calculations have been performed using the CASTEP code [14] in the framework of density functional theory (DFT) with generalized gradient approximation (GGA) and the Perdew-Burke- Ernzerhof (PBE) [15]. The interactions between ion and electron are represented by ultrasoft Vanderbilt-type pseudopotentials for K, Li and Te atoms [16]. The

valence states are K-3s² 3p⁶ 4s¹, Li-1s² 2s¹, and Te-5s² 5p⁴ for KLiTe. Plane wave cut-off energy 400 eV and 16×16×19 grid of Monkhorst-Pack [17] points have been used in this study to ensure the well convergence of the computed structures and energies. For the calculation of the optical properties, which usually requires a dense mesh of uniformly distributed k-points, the Brillouin zone integration was performed. Geometrical optimization was obtained using cutoff energy change per atom less than 5×10⁻⁶eV, residual forces less than 0.01 eV/Å.

3. RESULTS AND DISCUSSION:

3.1 Structural properties

The Tellurium based tetragonal KLiTe with space group P4/nmm (#129) is displayed in Fig-1. The equilibrium crystal structure of KLiTe is first obtained by minimizing the total energy. The relevant optimized lattice parameters are shown in Table-1 along with experimental data. It is seen that the calculated lattice parameters deviate by 2.8% from the experimental value obtained.

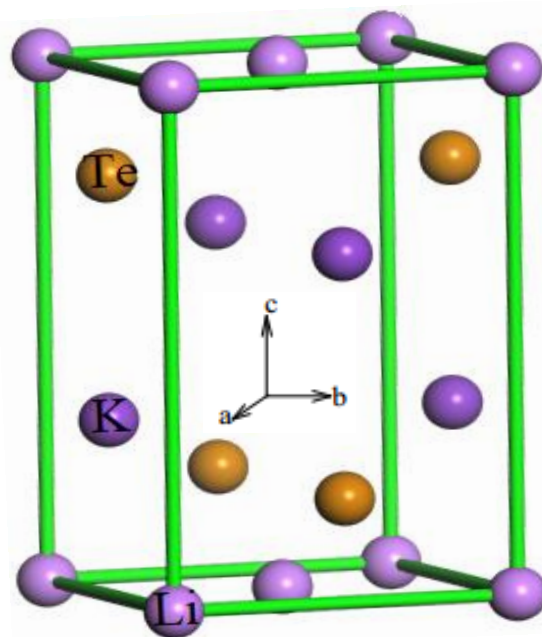


Fig-1: Crystal structure of KLiTe

Table-1: Values of calculated and experimental lattice constant a (Å), c(Å), elastic constants C_{ij} (GPa), Bulk moduli B (GPa), Shear moduli G (GPa), Young’s moduli E (GPa), G/B values, anisotropy factor A₁, Poisson’s ratio σ of KLiTe.

Structures	a=b	c	C ₁₁	C ₃₃	C ₄₄	C ₆₆	C ₁₂	C ₁₃	B	G	E _x = E _y	E _z	G/B	A ₁	σ	Ref.
KLiTe	4.86	7.85	36.05	31.0	10.884	13.96	-2.00	7.062	14.12	12.90	34.07	28.073	0.914	0.823	0.15	[This]
	4.83	7.71	-	-	-	-	-	-	-	-	-	-	-	-	-	[18]

3.2 Elastic Properties:

The elastic constants are very important for defining the mechanical properties that make a link with the forces operating in solids. The Young’s modulus (E) reflects the resistance of materials against uniaxial tensions. The bulk modulus (B) is a measure of the resistance of a material against volume change under hydrostatic pressure, while the shear modulus (G) describes the resistance to shape change caused by a shearing force. Hence we are interested to calculate elastic constants of

KLiTe at ambient pressure. For a tetragonal crystal, only six elastic constants are independent and the corresponding mechanical stability criteria are as follows [19, 20]

$$C_{tetragonal} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & & & \\ C_{12} & C_{11} & C_{13} & & & \\ C_{13} & C_{13} & C_{33} & & & \\ & & & C_{44} & & \\ & & & & C_{44} & \\ & & & & & C_{66} \end{pmatrix} \quad (1)$$

$$C_{11} > 0; C_{33} > 0; C_{44} > 0; C_{66} > 0; C_{11} > |C_{12}|; (C_{11} - C_{12}) > 0; (C_{11} + C_{33} - 2C_{13}) > 0;$$

$$[2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0; C_{11} + C_{12} - \frac{2C_{13}^2}{C_{33}} > 0 \quad (2)$$

The polycrystalline elastic properties such as bulk modulus B, shear modulus G, Young's modulus E, and Poisson's ratio σ are estimated from the calculated elastic constants are shown in Table-1. For a tetragonal structure, the bulk modulus can be estimated by [21]

$$B = \frac{2}{9} \left(C_{11} + C_{12} + 2C_{13} + \frac{1}{2}C_{33} \right) \quad (3)$$

The Young's modulus (E) and isotropic shear modulus (G) can be calculated by [21, 22]

$$E_x = E_y = \frac{[C_{33}(C_{11} + C_{12}) - 2C_{13}^2](C_{11} - C_{12})}{C_{11}C_{33} - C_{13}^2} \quad (4)$$

$$E_z = \frac{[C_{33}(C_{11} + C_{12}) - 2C_{13}^2]}{C_{11} - C_{12}} \quad (5)$$

$$G = \frac{1}{15} [(2C_{11} + C_{33}) - (2C_{12} + C_{13}) + 3(2C_{44} + C_{66})] \quad (6)$$

Elastic anisotropy (A_1) for {100} shear planes and Poisson's ratio [23]

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \quad (7)$$

$$\sigma = \frac{3B - 2G}{2(3B + G)} \quad (8)$$

The malleability indicators of materials are Paugh's ductility index (G/B) [24]. If the Paugh's ductility index $G/B < 0.5$ (> 0.5) the material will show ductile (brittle). According to Paugh's ductility index (G/B) the KLiTe compound show brittle behaviour.

3.3 Electronic Properties:

The energy bands at ambient conditions along with high symmetry directions in the Brillouin zones are depicted in Fig-2. No overlapping between the valence band and conduction band occurs at the Fermi level of KLiTe. Thus, indicates semiconducting behavior and the value of band gap is 2.37 eV. Energy bands indicate the direct band gap with the valence band maximum (VBM) and conduction band minimum (CBM) locating at Γ (G) point. The total density of states (TDOS) and partial density of states (PDOS) are shown in Fig-3. The upper peak in the density of states, from -2.5 to 0 eV, comes from the strong

hybridization between Te- 5p and K-3p orbitals while the peaks in 2.56 to 8.2 eV come from the strong hybridization between the K-3p and K-4s orbitals.

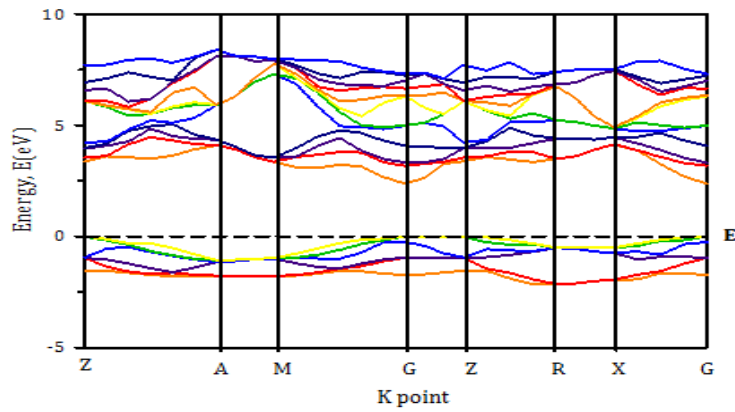


Fig-2: Band Structure of KLiTe along with high symmetry direction in the Brillouin zones.

3.4 Optical Properties:

The dielectric function, $\epsilon(\omega)$ is a crucial parameter to describe the optical properties of any homogeneous medium. This function is expressed as $\epsilon = \epsilon_1(\omega) + i\epsilon_2(\omega)$. The imaginary part $\epsilon_2(\omega)$ is obtained from the momentum matrix elements between the occupied and the unoccupied electronic states and calculated directly by using Eq.1 [25]

$$\epsilon_2(q \rightarrow O_{\hat{u}}, \hbar\omega) = \frac{2e^2\pi}{\Omega\epsilon_o} \sum_{k,v,c} \left| \langle \psi_k^c | \hat{u} \cdot \vec{r} | \psi_k^v \rangle \right|^2 \delta(E_k^c - E_k^v - E) \tag{9}$$

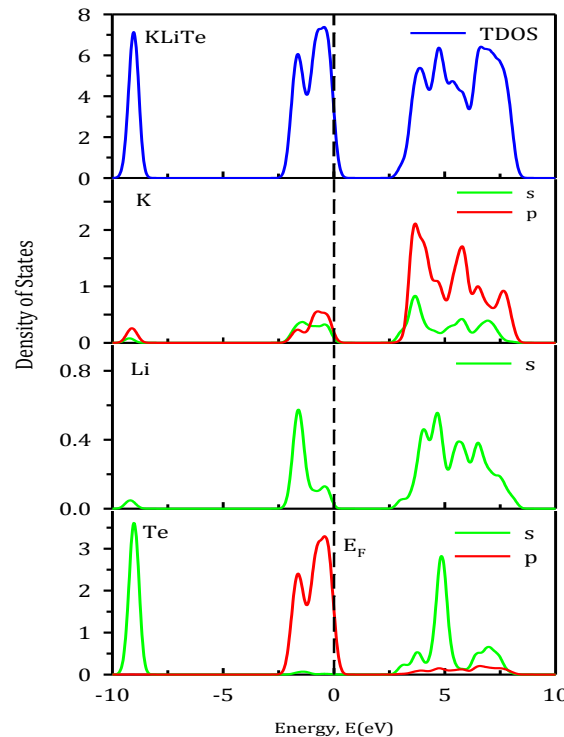


Fig-3: Total and partial density of states (DOS) of KLiTe.

where, u is the vector indicating the polarization of the incident electric field, ω is the frequency of light, e is the electronic charge; ψ_k^c and ψ_k^v are the conduction and valence band wave functions at k , respectively. The knowledge of both $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ allows the calculation of important optical constants. Other optical constants, such as refractive index, loss-function, absorption spectrum, reflectivity and conductivity can be calculated by using Eq. 49 to 54 in ref. [25]. There are two contributions of $\epsilon(\omega)$: interband and intraband transition. The real part of dielectric function $\epsilon_1(\omega)$ can be derived from the imaginary part using the Kramers-Kronig relation. The optical functions of KLiTe as a function of photon energies up to 20 eV for polarization vectors [100] are displayed in Fig-4. We have used a 0.5 eV Gaussian smearing for all calculations, which smears out the Fermi level in such a way that k -points will be more effective on the Fermi surface. Before discussing our results it is noted that there are no experimental or theoretical studies on optical properties of our studied compound.

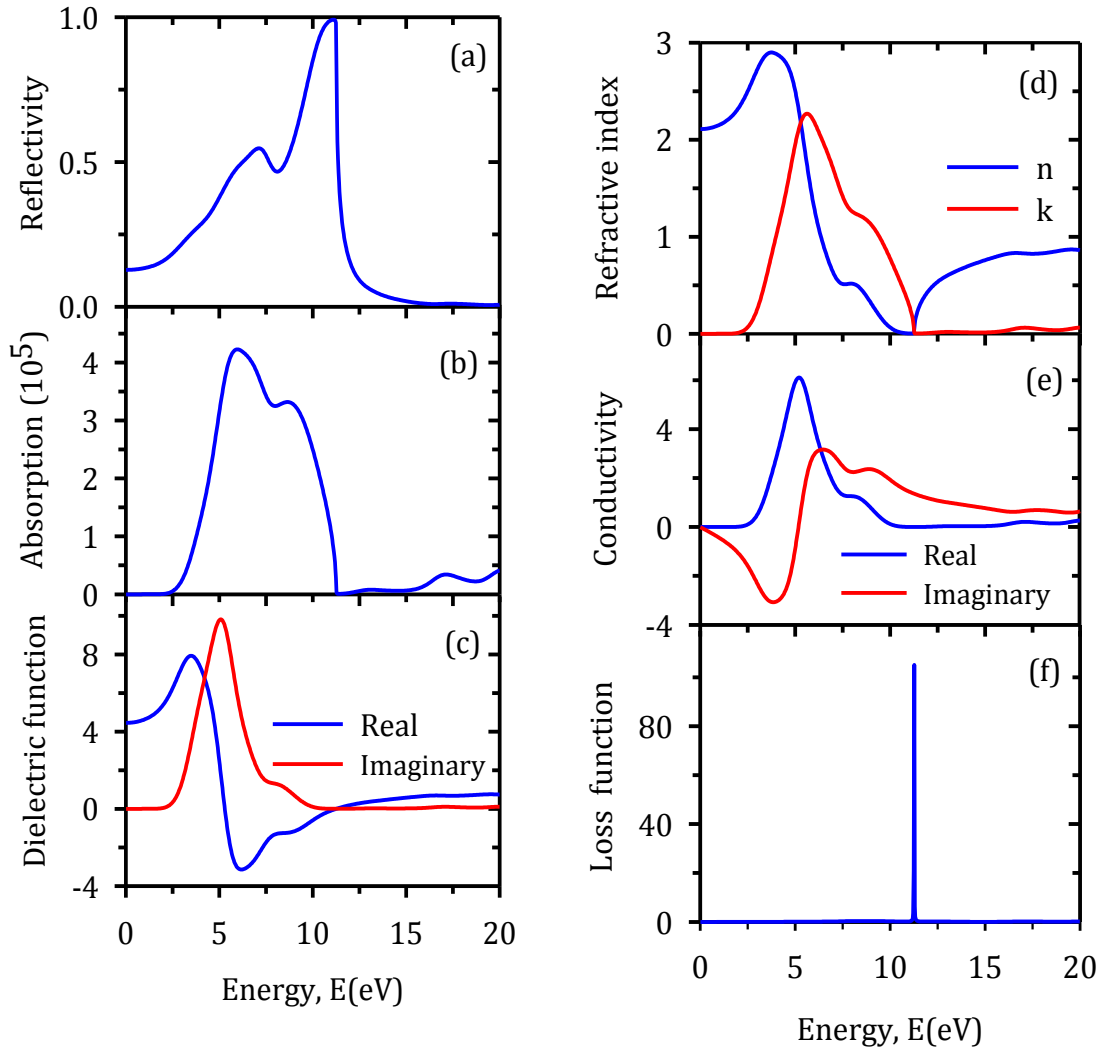


Fig-4: The energy dependent (a) reflectivity, (b) absorption, (c) dielectric function, (d) refractive index, (e) conductivity, and (f) loss function, of polarization vector [100].

The calculated optical reflectivity is displayed in Fig- 4 (a). The maximum value of reflectivity is about 98% for KLiTe in the ultraviolet region. Therefore in the ultraviolet region, this compound can be a potential candidate for coating material to avoid solar heating. From Fig-4b, it is shown that the absorption spectrum with a single peak 5.86 to eV for KLiTe which decreases slowly in the high-energy region. From Fig-4 (c) it is shown that there is a single peak of the real part of dielectric function (ϵ_1) but it starts with 4.4 at 0 eV which is known as static dielectric constant. The $\epsilon_1(\omega)$ spectra minimum is at about 5.9 eV for KLiTe. The calculated imaginary part of dielectric constant shows a single peak at 5.0 eV. It is also observed that the real part $\epsilon_1(\omega)$ goes through zero from below at about 11.2 eV and the imaginary part approaches zero from above at about 10.63 eV.

The variation of refractive index (n) and extinction coefficient (k) with photon energy is shown in Fig-4 (c) and Fig-4 (d), respectively. The calculated static refractive index $n(0)$ is found to be 2.10. It is clear from Fig-4 (e) that the optical conductivity starts at about 2.3 eV which indicates the semiconducting nature of KLiTe and consistent with the band structure presented in Fig-2. The energy loss function of a fast electron is an important factor when traversing through a material. The peak of the loss function is called the plasma frequency ω_p which is associated with the plasma resonance. The peak of $L(\omega)$ is shown at 11.27 eV from Fig-4 (f).

4. CONCLUSION

In summary, we have performed a systematic first principles study of structural, elastic, electronic and optical properties for KLiTe based on DFT calculations. The calculated lattice constants are in good agreement with the available experimental data. The Paugh's ductility index shows that KLiTe is brittle in nature. In addition, the calculated band structure shows that KLiTe is a wide and direct band gap semiconductor. The calculated reflectivity is high in the UV region and it can be used as coating materials to avoid solar heating.

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BIOGRAPHIES



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