Study of a new layered ternary chalcogenide CuZnTe$_2$ and its potassium intercalation effect

M K Islam$^1$, M A R Sarker$^1$, Y Inagaki$^2$ and M S Islam$^1$ ∗

$^1$ Department of Physics, Faculty of Science, Rajshahi University, Matihar, Rajshahi 6205, Bangladesh
$^2$ Department of Applied Quantum Physics, Faculty of Engineering, Kyushu University, Fukuoka 819-0395, Japan

∗ Author to whom any correspondence should be addressed.

E-mail: khadimul8906ruphy@gmail.com, razzaque_ru2000@yahoo.com, inagaki.yuji.318@m.kyushu-u.ac.jp and sislamru@gmail.com

Keywords: first-principles study, chemical intercalation, electronic band structures, optical absorption, elastic constants, specific heats

Abstract

A new layered ternary chalcogenide CuZnTe$_2$ and its effect due to potassium (K) intercalation have been investigated using ab-initio method under the framework of density functional theory (DFT). Here, we report the structural, electronic and elastic properties of both proposed parent compound CuZnTe$_2$ and intercalated KCuZnTe$_2$. The electronic band structures and the density of states (DOS) of both these chalcogenides have also been studied. The parent compound demonstrates p-type conductivity with the energy band gap of 0.7 eV but surprisingly, the increase of energy gap (1.5 eV) is found in the intercalated KCuZnTe$_2$, a direct-transition type semiconductor. The optical absorption result in KCuZnTe$_2$ also shows the identical value of gap energy calculated by Wood-Tauc theory. The density of states (DOS) in the valence band for both compounds is dominated by the partial contribution of Cu/ Zn 3d and Te 5p orbitals but the prime contribution of Cu/Zn 4s and Te 5s mainly in the conduction band DOS. The DOS value at around Fermi level in these chalcogenides is indicating the degeneracy behavior of a semiconductor. Both compounds are mechanically stable and also malleable. We also calculated the thermal properties in the intercalated KCuZnTe$_2$ using quasi-harmonic Debye model. The observed values of Debye temperature, specific heat capacities and volume expansion coefficient using this model is almost consistent with the estimated values given in theory.

1. Introduction

Over the past few decades, the layered ternary and quaternary chalcogenides, based on transition metal, have been extensively studied due to their exciting applications especially in solar photovoltaic cells, light emitting diodes, photocatalytic purpose etc. The chalcogenides are better candidates as light absorbing materials in solar cells because of large absorption coefficients with excellent coverage of the solar spectrum and high stability against solar irradiation. Again, the use of these materials in nanoscale generally improves the emission efficiency as well as photostability, which are the basic requirement for light emitting diodes [6]. Owing to their above characteristics, most of them in this family are also promising photosensitizing materials for photocatalysis [7].

First, we propose a new layered ternary chalcogenide CuZnTe$_2$, similar with CuFeTe$_2$ and CuFeS$_2$ [8], especially for device-based applications. Based on the layered structure, 50% occupancy of both Cu$^{2+}$ ions along with Zn$^{2+}$ ions are positionally indistinguishable. The type of other ternary compounds like CuInTe$_2$ [9], CuFeSe$_2$ [10], CuGaTe$_2$ [11], CuGaSe$_2$ [12] CuInS$_2$ [13], CuInSe$_2$ [14], etc have also been successively studied for
potential use in the above mentioned fields. In comparison with the existing ternary compounds, this proposed chalcogenide would be an important candidate as p-type semiconductor for collecting light in solar cells [1].

In addition, an attractive approach has been continued not only for the enrichment of this family but also for the remarkable regulation on the electrical conductivity by the chemical intercalation, defined as the reversible insertion of guest atoms or molecules into a host lattice. As a result, a quaternary chalcogenide KCuZnTe$_2$ crystallizes by intercalating potassium (K) in the parent host CuZnTe$_2$. At the end of twentieth century, Heulings et al first prepared single crystal of a quaternary telluride of KCuZnTe$_2$, isostructural with RbCuZnTe$_2$, from potassium polytelluride molten salt at 450 °C and also determined its crystal structure [15]. Later, successive works have been devoted to investigate the other mixed-transition metal quaternary compounds such as CsFe$_{0.72}$Ag$_{0.28}$Te$_2$ [16], K$_{0.33}$Ba$_{0.67}$AgTe$_2$ [17] and KFeCuTe$_2$ [18]. A recent study of layered telluride of KFeCuTe$_2$ [18] in comparison with the parent compound FeCuTe$_2$ [8, 19] shows the stoichiometry by intercalating K, resulting in the regulation on the electrical conductivity. As mentioned earlier, KCuZnTe$_2$ was only synthesized to analyze the structure in the form of single crystal but no other experimental results as well as theory available till now.

Another interesting feature of such ternary and quaternary compounds is to measure their elastic behavior because of its major significance in physical sciences, including materials science [20]. From these characteristics, one can obtain valuable information about the bonding nature between adjacent atomic planes, the crystal anisotropy and the structural stability. Other parameters such as elastic moduli and Poisson’s ratio, directly related to hardness and strength of materials [21], have been calculated for the first time. Some of the thermal parameters like Debye temperature, heat capacities and volume expansion coefficient can also be measured in intercalated KCuZnTe$_2$ using Gibbs energy program based on quasi-harmonic Debye model [22].

In this work, we focus the theoretical investigation of the structural, electronic and elastic properties of a new layered ternary telluride CuZnTe$_2$ as well as intercalated KCuZnTe$_2$. During computations, we were performed first-principles ab-initio method [23] under the framework of density functional theory (DFT) with the exchange-correlation functional of local density approximation (LDA) based on Ceperley and Alder - Perdew and Zunger (CA-PZ) local potential [24, 25].

2. Theoretical details

Theoretical computations were carried out by performing the geometry optimizations through minimizing the total energy using the Cambridge Serial Total Energy Package (CASTEP) code [23] based upon density functional theory (DFT). Local density approximation (LDA) of Ceperley and Alder - Perdew and Zunger (CA-PZ) was the exchange-correlation functionals [24, 25]. The plane wave energy cut-off 550 eV was used for both of these chalcogenides. The self-consistent field tolerance was $2 \times 10^{-6}$ eV/atom for CuZnTe$_2$ and $5 \times 10^{-7}$ eV/atom for KCuZnTe$_2$. Monkhorst–Pack [26] grid parameters $7 \times 7 \times 2$ were set for the sampling of the Brillouin zone in both of these ternary and quaternary chalcogenides. Geometry optimization for the parent host is conducted using the convergence thresholds of $2 \times 10^{-5}$ eV/atom for the total energy, 0.05 eVÅ$^{-1}$ for the maximum force, 0.1 GPa for the maximum stress and 0.002 Å for the maximum displacement. In an intercalated KCuZnTe$_2$, we were used the convergence thresholds of $5 \times 10^{-6}$ eV/atom for the total energy, 0.01 eVÅ$^{-1}$ for the maximum force, 0.02 GPa for the maximum stress and 0.0005 Å for the maximum displacement to perform the geometry optimization. The set of OTFG ultrasoft pseudopotentials used in the calculations for describing the interactions between the ion and electron [27]. The elastic constants were calculated by the ‘stress–strain’ method. Finally, a quasi-harmonic Debye model [22] was used to calculate the thermal properties in KCuZnTe$_2$.

3. Results and discussion

3.1. Structural properties

The crystal structures of a new layered ternary CuZnTe$_2$ and quaternary KCuZnTe$_2$ compounds, shown in figure 1, were constructed by tetragonal symmetry with space group P4/nmm and P4/mmm, respectively. First, the geometry optimization was performed at ambient condition using CASTEP code for the minimization of the total energy for both of these chalcogenides. The number of formula units in the unit cell (Z), the optimized lattice parameters and their bonding information for CuZnTe$_2$ and KCuZnTe$_2$ have been listed in table 1, which agrees well with the other available experimental data [8, 15, 19, 28].

Figure 2 illustrates the comparison of the structural parameters between CuZnTe$_2$ and KCuZnTe$_2$. After inserting guest atom of K into host lattice CuZnTe$_2$, it is seen that the bond length of Cu/Zn-Te is slightly increased from 2.555 Å to 2.619 Å. The bond (Te-Cu/Zn-Te) angle is also elongated from 104° to 106° with the compression of Cu$_{0.35}$Zn$_{0.65}$Te tetrahedron along c axis. Similar enhancement of interatomic distance and bond angle has been observed while the potassium is intercalated in parent host of Fe$_{1+x}$CuTe$_2$ [18]. In that case, the
interstitial Fe\(^{2+}\) found in Fe\(_{1+x}\)CuTe\(_2\) was removed by the K intercalation that was confirmed by the x-ray Photoelectron Spectroscopy result. But in the present case, we only propose a layered structure of a parent chalcogenide, in which the Cu and Zn atoms occupy the identical position that exactly consistent with the structure given in [8]. We would like to mention that the K intercalation in the parent host provides the structural evolution that could be the essential key for electronic characteristics.

3.2. Electronic band structures and effective masses

The electronic band structures of a new layered ternary compound CuZnTe\(_2\) and its daughter compound KCuZnTe\(_2\) were computed by using the first-principles DFT approach with local density approximation (LDA). The potential of the constituent atoms is evaluated by assuming the neutral atomic configurations of K (19) → 4s\(^1\), Cu (29) → 3d\(^{10}\)4s\(^1\), Zn (30) → 3d\(^{10}\)4s\(^2\), and Te (52) → 5s\(^2\)5p\(^4\) with the CASTEP code [23]. The values of wave vector (k) within the particular directions/points of the Brillouin Zone (BZ) are assigned by the conventional names like Z - A - M - Γ' - Z - R - X - Γ'. The Fermi level is chosen to be the zero of the energy scale.

The energy band structure of CuZnTe\(_2\) is illustrated in the left panel of figure 3. As shown in figure 3, the Fermi level is slightly entered into the valence band, indicating the p-type conductivity. As a result, an indirect energy gap of 0.7 eV is obtained in the proposed parent compound, which is almost consistent with an indirect band gap of 0.63 eV found in CuFeS\(_2\) [29]. Although, Kradinova et al. experimentally observed an n-type conductivity to measure the temperature dependent Hall coefficient and specific conductivity in CuFeS\(_2\) and CuFeTe\(_2\) [8]. But a recent study of nanocrystal films of CuFeS\(_2\) possess p-type conductivity [30, 31]. As a majority charge carriers, holes in such a film play the vital role for the transport phenomena in opto-electronic devices. According to the band structure result in the parent host, CuZnTe\(_2\) would also be favorable to study the hole transport properties especially in the solar cells.

Figure 4 shows the band structure of KCuZnTe\(_2\) along the highly symmetric directions of the Brillouin Zone at ambient condition. When a guest element of K is intercalated in the parent compound CuZnTe\(_2\), there is a remarkable change in the energy band structure because of the intercalating K increases both of the interatomic distances and the bond angles as already discussed in the structural properties subsection (figure 2). This similar scenario was also observed in the K intercalated iron copper telluride KFeCuTe\(_2\) [18]. Surprisingly, they mentioned that the room temperature resistivity and the band gap energy are much larger than that of the parent compound [19]. Here, the [K] layers even provide excess electrons to the [Cu\(_{0.5}\)Zn\(_{0.5}\)Te] layers in KCuZnTe\(_2\). As a result, the Fermi level is shifted on top of the valence band. Moreover, the extra layers of [K] impede the hole transmission like in parent host, which reduces the electrical conductivity. From the calculated band structure, we can see that the top of the valence band and the bottom of the conduction band are placed at the same k-point Γ', indicating direct-transition type semiconductor with the calculated energy gap of 1.5 eV. Finally, the band structure result in KCuZnTe\(_2\) is exactly consistent with Heulings et al prediction [15] and also similar with the results found in [18].

![Figure 1.](image)
Table 1. Crystallographic information, nearest neighbor atomic bond distances (Å) and bond angles (°) of proposed CuZnTe$_2$ and KCuZnTe$_2$ with tetragonal system.

| Chemical formula | Space group | Z | Lattice parameters | Volume $V_0$ (Å$^3$) | Bonding information | Ref. |
|------------------|-------------|---|--------------------|-----------------------|---------------------|------|
|                  |             |   | a (Å) | c (Å) | Axial angle (°) | Atomic bond | Bond length (Å) | Bond type | Bond angle (°) |
| CuZnTe$_2$       | P4/mnm (no. 129) | 1 (Primitive lattice) | 4.029 | 5.631 | $\alpha = \beta = \gamma = 90$ | Cu/Zn-Te | 2.555 | Te-Cu/Zn-Te | 53 (1) | Calc. |
|                  |             |   |        |       |            | Cu/Zn-Cu/Zn | 2.892 | Cu/Zn-Te-Cu/Zn | 53 (1) |          |
| CuFeTe$_2$ [8, 19, 28] |             | 3.930 | 6.078 |        |            | Cu/Fe-Te | 2.621 | Te-Cu/Fe-Te | 115 (1) | Expt. |
|                  |             |   |        |       |            | Cu/Fe-Cu/Fe | 2.821 |           | 99 (2) |          |
| KCuZnTe$_2$      | I4/mmm (no. 139) | 2 (Body-centered lattice) | 4.181 | 14.48 | 253.24 | Cu/Zn-Te | 2.619 | Te-Cu/Zn-Te | 111 (1) | Calc. |
|                  |             |   |        |       |            | Cu/Zn- Cu/Zn | 2.957 |           | 106 (2) |          |
|                  |             |   |        |       |            | K-Te | 3.594 | Cu/Zn-Te-Cu/Zn | 69 (1) |          |
|                  |             |   |        |       |            | K-K | 4.181 |           | 106 (2) |          |
| KCuZnTe$_2$ [15] |             | 4.269 | 14.91 | 271.76 |   | Cu/Zn-Te | 2.681 | Te-Cu/Zn-Te | 112 (1) | Expt. |
|                  |             |   |        |       |            | Cu/Zn- Cu/Zn | 3.018 |           | 106 (2) |          |
|                  |             |   |        |       |            | K-Te | 3.679 | Cu/Zn-Te-Cu/Zn | 69 (1) |          |
|                  |             |   |        |       |            | K-K | 4.269 |           | 106 (2) |          |
In the right panel of figures 3 and 4, the valence band is contributed by Cu/Zn 3d and Te 5p orbitals, while the conduction band is mainly from the Cu/Zn 4s and Te 5s states. The calculated values of DOS at around Fermi level due to the crossing of Te 5p orbital are shown in table 2. The unexpected values of DOS found in both of these chalcogenides is indicating the degeneracy behavior of a semiconductor [32–34].

![Figure 2](image1.png)

**Figure 2.** The structural variation in 2-dimension of a CuZnTe2 (left) and an intercalated KCuZnTe2 (right) compounds. The interatomic distances and the bond angles are displayed without and with intercalation.

![Figure 3](image2.png)

**Figure 3.** The energy band structure of a new layered ternary CuZnTe2 (left). The right panel shows the calculated density of states for the corresponding band structure. The Fermi level is adjusted to zero.

The electron or hole effective masses $m_e^*$ or $m_h^*$ at the band extremes can also be computed from the band structure by [35]

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k^2},$$

where, $\hbar$ is the reduced Planck constant and $E(k)$ is the dispersion of energy in $k$-space. By fitting with the parabolic equation of the energy in terms of wave vector near the band extremes, the effective masses of electrons $m_e^*$ and holes $m_h^*$ were calculated in units of the rest mass of an electron $m_0$ and also presented in the above table 2. Lower value of hole effective mass in parent compound indicates the $p$-type conductivity [36].

### 3.3. Optical absorption and energy band gap

We investigate the absorption spectrum in terms of photon energy in an intercalated KCuZnTe2 by using first-principles calculation. Before going to observation given in figure 5, first we make $2 \times 2$ supercell with the random
After optimizing the geometry made by supercell, we measured the optical absorption as a function of energy analyzed for the unpolarized light. As illustrated in figure 5, the absorption, starts from ∼1.50 eV, curve reveals the semiconductor behavior that exactly consistent with the electronic band structure result shown in the above figure 4. Two major absorption peaks in such spectrum are found at ∼7.5 eV and at ∼22 eV. In this context, we can say that the strong absorption will be occurred in the ultraviolet region. Inset (figure 5) shows the optical band gap energy ($E_g$) estimated by Wood-Tauc theory, given by the relation

$$\alpha \propto (h \nu - E_g)^2,$$

where $\alpha$ is an absorbance, $h$ is the Planck’s constant, $\nu$ is the frequency and $k$ is a constant associated with the different transitions, obtained for the best linear relation for a value of 2 [34]. The optical band gap using this theory is calculated to be 1.49 eV, which is exactly identical with the electronic band gap shown in figure 4.

### 3.4. Elastic moduli and mechanical stability

The elastic behaviors of a crystal lattice can be expressed by its matrix of second-order elastic/stiffness constants,

$$C_{ij} = \frac{1}{V_0} \frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j},$$

where $E$ is the energy of the crystal, $V_0$ is its equilibrium volume and $\varepsilon$ denotes a strain [37]. Out of these 21 nonzero components of stiffness tensor, only six of them are independent in tetragonal system due to the additional symmetry constraints. We present, for the first time, the calculated stiffness constants ($C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, $C_{44}$ and $C_{66}$) of CuZnTe$_2$ and KCuZnTe$_2$ in table 3. Depending on the stiffness matrix, the following four necessary conditions for mechanical stability in tetragonal crystal [37],

$$C_{11} \geq |C_{12}|, \quad 2C_{13}^2 < C_{33}(C_{11} + C_{12}), \quad C_{44} > 0 \text{ and } C_{66} > 0$$

The values of stiffness constants, shown in table 3, satisfy the above criteria except the larger value of $C_{12}$ compared with $C_{11}$ in the proposed host of CuZnTe$_2$. Although the first condition is unusual in the host but not
so sensitive to find the other moduli in this system like hexagonal [37]. Moreover, both compounds are mechanically anisotropic and especially favorable for shear deformation because of $C_{11} > C_{33}$ as well as $C_{33} > C_{44}$ and $C_{66}$ [38].

We also evaluated the modulus of elasticity e.g. the bulk modulus ($B_H$) and the shear modulus ($G_H$) using the average approximations given by Hill [39] and Young’s modulus ($E$) and Poisson’s ratio ($\nu$) using the relationships found in [40]. The calculated values of $B_H$, $G_H$, $E$ and $\nu$ are listed in table 3. The value of either bulk modulus or shear modulus can indirectly measure the hardness of a material. Using Hill’s approximation, the values of shear modulus obtained in both of these compounds are much smaller than the bulk modulus, reflecting the shear deformation is easier as already discussed in the earlier. The value of Pugh’s ratio ($B_H/G_H$) distinguishes the ductile ($>1.74$) and brittle ($<1.74$) nature of materials [41]. Depending on the values of Pugh’s ratio, most malleable behavior is seen in host compared with intercalated KCuZnTe$_2$. The malleability can also be correlated with the Poisson’s ratio. A material will be ductile if $\nu > 0.26$, otherwise it will be brittle [41]. The calculated values of Poisson’s ratio, shown in table 3, of both compounds ensure the malleable character.

Generally, Young’s modulus measures the stiffness of an elastic material. Within this context, KCuZnTe$_2$ is the stiffest due to the higher Young’s modulus in comparison with CuZnTe$_2$. The crystal is completely isotropic, when the value of the universal anisotropy factor ($A_U$) is exactly zero [42]. Any deviation from this represents the degree of anisotropy. In this case, both chalcogenides possess anisotropic behavior identical with the result already mentioned in the above conditions of stiffness tensor.

The Debye temperature ($\Theta_D$) can also be defined in terms of the average elastic wave velocity ($v_w$) as [43]

$$\Theta_D = \frac{\hbar}{k_B} \left( \frac{3\pi n}{4\pi V_0} \right)^{1/3} v_w,$$

where $h$ is the Plank’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 per unit cell. The average sound velocity in the polycrystalline material is given by

![Figure 5](image.png)

**Figure 5.** The optical absorption curve as a function of energy of an intercalated KCuZnTe$_2$. Inset shows the optical band gap using the Wood-Tauc theory.

---

**Table 3.** Elastic stiffness constants (GPa), elastic moduli (GPa), universal anisotropy factor, wave velocities (ms$^{-1}$) and Debye temperature (K) of CuZnTe$_2$ and KCuZnTe$_2$ at ambient condition.

|               | CuZnTe$_2$ | KCuZnTe$_2$ | CuZnTe$_2$ | KCuZnTe$_2$ |
|---------------|------------|-------------|------------|-------------|
| $C_{11}$      | 25         | 56          | 25         | 56          |
| $C_{12}$      | 56         | $-5$        | 8          | 14          |
| $C_{13}$      | 12         | 4           | 0.43       | 0.33        |
| $C_{33}$      | 17         | 19          | $-3$       | $-54$       |
| $C_{44}$      | 2          | 8           | 623        | 966         |
| $C_{66}$      | 7          | 0.2         | 1871       | 1943        |
| $B$           | 21         | 14          | 709        | 1084        |
| $G$           | 3          | 5           | 74         | 110         |
| $\Theta_D$    |            |             |            |             |

---

[37]: https://www.example.com
[38]: https://www.example.com
[39]: https://www.example.com
[40]: https://www.example.com
[41]: https://www.example.com
[42]: https://www.example.com
[43]: https://www.example.com
where \( v_t = \sqrt{G/\rho} \) and \( v_l = \sqrt{(3B + 4G)/3\rho} \) are the transverse and longitudinal sound velocities, respectively and \( \rho \) is the density of the material \([43]\). The estimated value of Debye temperature in an intercalated compound is comparatively higher than the parent host.

### 3.5. Thermal properties

We studied the thermal characteristics at finite pressure and temperature, for the first time, in an intercalated KCuZnTe\(_2\) by using the quasi-harmonic Debye model found in the literature \([22]\). Applying this model, we computed the Debye temperature, specific heats at constant pressure and at constant volume and volume thermal expansion coefficient (VTEC) as a function of temperatures and pressures.

First, we measure the pressure dependence of Debye temperature \( (\Theta_D) \) at room temperature, which is displayed in figure 6. It is seen that \( \Theta_D \) increases exponentially with increasing the pressure. Inset shows the variation of Debye temperature at zero pressure. Here, \( \Theta_D \) decreases exponentially with the increase of temperature. The calculated Debye temperature from the elastic parameters is almost reasonable with the value of \( \Theta_D (\sim 96 \text{ K}) \) at constant room temperature and zero pressure using the Debye model. Recently, another groups have been experimentally estimated the values of Debye temperature in other quaternary compounds \([44, 45]\). In comparison with the experimental results, the underestimation is on account of the familiar complication with the LDA calculation \([46]\). It is well-known that the highest thermal vibrational frequency of a solid is directly related to the Debye temperature. Thus, the change of \( \Theta_D \) with respect to temperature and pressure also describes the variable vibrational frequency in KCuZnTe\(_2\).

Another significant parameter in thermal properties is the specific heat capacity which is independent on the amount of substance. Generally, phonons and free electrons in the solid are main agent for the transfer of heat. The thermal conductivity in pure metal is dominated only by the electronic contribution but in the semiconductor or insulator, the phonon dominates the most. The variation of specific heat at constant pressure \( (C_P) \) with temperature at zero pressure is shown in figure 7. At low temperature, \( C_P \) increases sharply but the increment slows down like classical behavior when the temperature reaches at around 300 K. The change of \( C_P \) with pressure at constant room temperature is illustrated in the inset of figure 7. The specific heat \( C_P \) decreases exponentially as a function of pressure. At room temperature with constant zero pressure, the value of \( C_P \) is around \( \sim 108 \text{ Jmol}^{-1}\text{K}^{-1} \), almost consistent with the classical values satisfying the Dulong-Petit law found in \([44, 45]\).

Again, the heat capacity \( C_V \) exhibits the Debye \( T^3 \) power-law behavior in the low temperature limit and at high temperature \((>300 \text{ K})\), \( C_V \) approaches the classical asymptotic limit of \( 3NR \), where \( N \) is the number of atoms per formula unit and \( R (= N \varepsilon R) \) is the gas constant. As shown in figure 8, the estimated classical value of \( C_V (\sim 100 \text{ Jmol}^{-1}\text{K}^{-1}) \) is exactly identical with the result, indicated by the red solid line, obtained by quasi-harmonic Debye model. As mentioned above, similar trend of \( C_P \) with temperature was observed experimentally......
in other quaternary chalcogenides [44, 45]. The classical value based on Dulong-Petit law at 300 K in these materials is almost reasonable compared to our result. The pressure dependence of $C_V$ at constant room temperature is also illustrated in the inset of figure 8. Slight difference of $C_p$ and $C_V$ in KCuZnTe$_2$ is basically due to the thermal expansion caused by anharmonicity effects.

The basic difference between $C_p$ and $C_V$ can be explained in terms of the volume thermal expansion coefficient ($\alpha_V$) caused by anharmonicity effects and also be defined as [47]

$$C_p - C_V = \alpha_V^2(T) BTV_m,$$

where $B$, $T$ and $V_m (=N_V V_0/Z)$ are the bulk modulus, absolute temperature and molar volume, respectively. The temperature dependence of the volume expansion coefficient (VTEC), inverse of bulk modulus, at constant zero pressure for KCuZnTe$_2$ is displayed in figure 9. The VTEC with temperature rapidly increases initially but the increment gradually slows down at comparatively high temperature. At constant room temperature, the VTEC decreases exponentially with the increase of pressure as in the inset of figure 9. The value of VTEC is theoretically estimated to be $\sim 15.8 \times 10^{-5}$ K$^{-1}$ at 300 K in KCuZnTe$_2$ using the above equation (3). The calculated value is almost identical with the observed value $\sim 17.1 \times 10^{-5}$ K$^{-1}$ at 300 K using this model but unfortunately there is

**Figure 7.** The specific heat capacity $C_p$ varies with temperature at constant zero pressure in an intercalated KCuZnTe$_2$. Inset shows the pressure dependence of $C_p$ at 300 K.

**Figure 8.** The change of heat capacity at constant volume with temperature at constant zero pressure in KCuZnTe$_2$. The red solid line indicates the classical value obeying Dulong-Petit law at high temperature. Inset shows the pressure dependence of $C_V$ at room temperature.
no measured value available in the literature to compare the reliability of present calculation. Nevertheless, our estimation in association with the observed one would put some confidence in this model we are using for intercalated KCuZnTe₂.

4. Summary

We investigate a new layered ternary CuZnTe₂ and quaternary KCuZnTe₂ chalcogenides by using an ab-initio method based on density functional theory (DFT). The optimized lattice parameters and the bonding information presented in the structural analysis reflect the effect of K intercalation in the ternary parent host of CuZnTe₂ and also agree well with the other experimental data. The parent compound in the band structure result shows p-type conductivity with the indirect gap of 0.7 eV but quaternary KCuZnTe₂, a direct-transition type semiconductor, interestingly reduces the conductivity (1.5 eV), identical with the optical band gap energy (1.49 eV) by Wood-Tauc theory, though the Fermi level is on top of the valence band. In both of these compounds, the atom projected contribution of Cu/Zn 3d and Te 5p orbitals dominates the valence band DOS but the contribution of Cu/Zn 4s including Te 5s mainly in the conduction band DOS. The DOS values at Fermi level in these chalcogenides indicate the degeneracy behavior. Both compounds possess mechanical stability, anisotropy as well as malleability. The change of ΘD with temperature and pressure reveals the variable vibrational frequency in KCuZnTe₂. The estimated values of heat capacities as well as VTEC are almost consistent with the observed results using this model.

Acknowledgments

Authors thank Prof. Fahmida Parvin and Dr Monira Jannatul Kobra for their support to perform Gibbs program operated by Linux. Fruitful discussion with Prof. Fahmida Parvin are gratefully acknowledged. This work was supported in part by JSPS KAKENHI Grant Number JP18K04683.

ORCID iDs

M S Islam https://orcid.org/0000-0002-7023-4705

References

[1] Aldakov D, Lefrancois A and Reiss P 2013 Ternary and quaternary metal chalcogenide nanocrystals: synthesis, properties and applications J. Mater. Chem. C 1 3756
[2] Han Y, Li W Y, Cao X, Wang X Y, Xu B, Zhao B R, Guo Y Q and Yang J L 2010 Superconductivity in iron telluride thin films under tensile stress Phys. Rev. Lett. 104 017003
[3] Zhao L D, Berardan D, Peyi Y L, Byl C, Pinsard-Gaudart I and Dragoe N 2010 Bi₁₋ₓSrₓCuSeO oxyselenides as promising thermoelectric materials Appl. Phys. Lett. 97 092118
[4] Wang C, Tan M-Q, Feng C-M, Ma Z-F, Ji Liang S, Xu Z-A, Cao G-H, Matsubayashi K and Uwatoko Y 2010 La_{2-x}Co_{x}Se_{2}: a quasi-two-dimensional Mott insulator with unusual cobalt spin state and possible orbital ordering J. Am. Chem. Soc. 132 7069

[5] Neilson R, Llobet A, Stier A V, Wu L, Wen J I, Tao J, Zhou Y M, Tesanovic Z B, Armitage N P and McQueen T M 2012 Mixed-valence-driven heavy-fermion behavior and superconductivity in KNi_{2}Se_{2} Phys. Rev. B 86 054512

[6] Reiss P, Protiere M and Lin L 2009 Core shell semiconductor nanocrystals Small 5 154

[7] Shen F, Que W, Liao Y and Yin X 2011 Photocatalytic activity of TiO_{2} nanoparticles sensitized by CuInS_{2} quantum dots Ind. Eng. Chem. Res. 50 9131

[8] Kradinova L V, Polubotko A M, Popov V V, Prochukhan V D, Rud Yu V and Skorukhin V E 1993 Novel zero-gap compounds, magnetics: CuFeS_{2} and CuFeTe Se. S. Sci. Tech. 8 1616

[9] Knight S K 1992 The crystal structures of CuInS_{2} and CuInTe_{2} Mat. Res. Bull. 27 161

[10] Delgado J M, Delgado D G, Quintero M and Woolley J C 1992 The crystal structure of copper iron selenide CuFeS_{2} Mater. Res. Bull. 27 608

[11] Rincon C, Waisim S M, Marin G, Hernandez E and Galibert P 2001 Raman spectra of the chalcopyrite compound CuGaTe_{2} Phys. C 342 23

[12] Wang B, Guo Z, Sun F, Deng J, Lin J, Wu D and Yuan W 2019 The transition between antiferromagnetic order and spin-glass state in layered chalcogenides KFeAg_{2} (Ch = Se, S) J. Solid State Chem. 272 126

[13] Islam M S, Kabir H, Inagaki Y and Sarker A R 2020 Comparative study of the conductivity of synthesized bivalent vanadates CaV_{2}O_{6} and MnV_{2}O_{6} J. Alloys Compd. 829 15449

[14] Kittel C 2005 Introduction to Solid State Physics eighth ed. (New York: John Wiley & Sons, Inc)

[15] Sarmadian N, Saniri R, Partoens B and Lamoen D 2016 Easily doped p-type, low hole effective mass, transparent oxides Sci. Rep. 6 20446

[16] Mouhat F and Coudert F-X 2014 Necessary and sufficient elastic stability conditions in various crystal systems Phys. Rev. B 90 241404

[17] Zhou M, Gao X, Cheng Y, Chen X and Cai L 2015 Structural, electronic and elastic properties of CuFeS_{2}: first-principles study Appl. Phys. A 118 1145

[18] Hill R 1932 The elastic behaviour of a crystalline aggregate Proc. Phys. Soc. A 65 349

[19] Islam M S, Amir M A K and Amir M A K 2012 Structural, elastic electronic and optical properties of a new layered-ternary T_{x}S_{x}C_{y} compound Physica B 406 275

[20] Pugh S F 1954 NCII. Relations between the elastic moduli and the elastic properties of polycrystalline pure metals Philos. Mag. 45 823

[21] Anderson O L 1963 A simplified method for calculating the Debye temperature from elastic constants J. Phys. Chem. Solids 24 909

[22] Wang B, Guo Z, Sun F, Deng J, Lin J, Wu D and Yuan W 2019 The transition between antiferromagnetic order and spin-glass state in layered chalcogenides KFeAg_{2} (Ch = Se, S) J. Solid State Chem. 272 126

[23] Lei H, Bozin E S, Wang K and Petrovic C 2011 Antiferromagnetism in semiconducting KFe_{0.8}Ag_{0.2}Te_{2} single crystals Phys. Rev. B 84 060506

[24] Zhang H, Jin S, Guo L, Shen S, Lin Z and Chen X 2016 Bandgap narrowing in the layered oxysulfide semiconductor Ba_{2}Fe_{2}O_{4}Se_{2}: role of FeO_{x} layer Chin. Phys. B 25 026101

[25] Hasan M Z, Hossain M M, Islam M S, Parvin F and Islam A K M A 2012 Elastic, thermodynamic and optical properties of U_{2}Ti Comput. Mater. Sci. 63 236