Quaternary semiconductors Cu$_2$MgSnS$_4$ and Cu$_2$MgSnSe$_4$ as potential thermoelectric materials

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Abstract
In this paper, we have systematically explored the thermoelectric properties of quaternary semiconductor Cu$_2$MgSnS$_4$/Se$_4$ along with their structural and electronic properties in two possible phases namely kesterite and stannite by employing first-principles calculations. Although stannite phase is found to be more stable but difference in energy from kesterite phase is marginal (∼75/62 meV per unit cell for CMTS/CMTSe). Both these systems are found to be direct band gap semiconductors with gap ranging from 0.55 to 1.10 eV. The bands are comparatively flat near the top of the valence band, which led to very high Seebeck coefficient ∼300 μV K$^{-1}$ in the entire temperature range of study. The estimated Seebeck coefficient is found to be very close to the experimentally reported value for the case of Cu$_2$ZnSnSe$_4$. Calculated power factor and figure-of-merit for both these systems in both possible phases are found to be comparable with state of art thermoelectric materials which are commercially in use. Therefore, these quaternary semiconductors under study are potential candidate materials for thermoelectric applications owing to their additional advantages being non-toxic, inexpensive and earth abundant.

1. Introduction

Recently, considerable efforts have been made toward the generation of electricity from sustainable sources. Devices such as thermoelectric generators convert waste heat into electricity by using the Seebeck effect. The efficiency of these devices is governed by figure-of-merit, $ZT = S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is electrical conductivity, $T$ is absolute temperature and $\kappa$ is thermal conductivity [1, 2]. However, it is very challenging to optimize $ZT$ as $S$, $\sigma$, and $\kappa$ are dependent on each other. Thus lot of research has been focused, to develop new bulk thermoelectric materials with improved thermoelectric performance over a wide range of temperature. It has been advocated that materials with complex crystal structures [3–5], impurities and heavy elements show potential in thermoelectricity [6]. Among the materials that have been synthesized, chalcogenides have drawn considerable interest as they are easy to synthesize. Chalcogenides such as, Bi$_2$Se$_3$, Bi$_2$Te$_3$, TeAgGeSb and their complexes are known to be good thermoelectric materials. Recently, complex chalcogenides such as quaternary Cu$_2$CdSnSe$_4$, Cu$_2$ZnGeSe$_4$, Cu$_2$ZnSnS$_4$ and Cu$_2$ZnSnSe$_4$ have received great interest as they show promising thermoelectric properties despite being large band gap materials. The presence of wide band gap ($E_g = 1−1.5$ eV) in these materials is considered to reduce the bipolar effect and therefore improve the thermoelectric figure of merit $ZT$ [7].

Due to the presence of non-toxic and abundant elements: Cu, Zn, Sn, S, and Se; Cu$_2$ZnSnS$_4$ and Cu$_2$ZnSnSe$_4$ members of quaternary chalcogenides family, have been widely studied for photovoltaic and thermoelectric applications. Materials belonging to quaternary chalcogenides family such as Cu$_2$ABX (A = Cd, Mg; B = Sn, Ge; X = S, Se) have been suggested to crystallize either in kesterite (KS) or stannite (ST) phases, having space groups $\bar{I}4$ and $\bar{I}4$ 2 $m$, respectively [8–13]. In KS phase four Cu atoms occupy the Wyckoff positions 2a and 2c, two Sn atoms on position 2d, two Sn atoms on position 2b and eight S/Se atoms on the 8g position. On the other hand ST phase has four equivalent Cu atoms on Wyckoff position 4d, two Zn atoms on 2a, two Sn atoms on 2b and
eight S/Se atoms on the 8i position. In these structures, the anion 8g or 8i positions are undefined and represented by \((x, y, z)\).

Recently, it has been shown experimentally that \(\text{Cu}_2\text{AsSnSe}_4\) (A = Zn, Cd) in ST phase show fairly good thermoelectric performance when doped with indium [14] and copper [15], attributed to the generation of hole carriers which results in increased electrical conductivity and at the same time reducing thermal conductivity, which led to the significant increase in ZT at high temperature. However, the quest for new abundant bulk thermoelectric materials with low thermal conductivity is still ongoing. In a recent report, it has been shown that indium doped \(\text{Cu}_2\text{MgSnSe}_4\) stabilized in ST phase, as a promising thermoelectric material [16]. On the other hand similar systems synthesized by Wei et al [17] are found to be in KS phase. By using density functional calculations Zhong et al [18] found that the ground-state structure of \(\text{Cu}_2\text{MgSnS}_4\) (CMTS) and \(\text{Cu}_2\text{MgSnSe}_4\) (CMTSe) is stabilized in ST phase instead of KS as in case of Zn-based compounds and the energy difference between two phases is 40.2 and 42.1 meV per unit cell, respectively for CMTS and CMTSe. The previous studies suggest that these systems may be prepared in both phases; therefore, it becomes pertinent to explore and understand the thermoelectric properties of these systems in both possible phases for the potential future applications.

In this paper, we have systematically investigated the possible ground state structures and their effects on the electronic and transport properties of \(\text{Cu}_2\text{MgSnS}_4\) and \(\text{Cu}_2\text{MgSnSe}_4\) compounds, using first-principles calculations within the density functional formalism. The ground state structure is found to be ST, however, the difference in energy between ST and KS is marginally small ~75 and 62 meV/unit cell for CMTS and CMTSe, respectively. This clearly suggests that both these phases are possible to synthesize and may even coexist, as has been reported for other members of quaternary chalcogenides family. For ST-CMTSe the experimentally reported band gap is \(\sim 1.7\) eV [16] which is larger than our theoretical value in both phases. We note that theoretical band gap values should be considered as a guidance, but at the same time we also note the measured band gap is for disordered sample of ST-CMTSe and measurements were done at room temperature which may additionally contribute to band gap by ~0.1–0.2 eV. The power factor and figure-of-merit for both these systems in both possible phases are found to be comparable with state of art thermoelectric materials. Therefore, suggesting that these quaternary semiconductors under study can be used as potential candidates for thermoelectric applications in wide temperature range.

2. Computational details and crystal structure

To study the electronic properties of CMTS and CMTSe, we have applied the full potential linearized augmented plane-wave method as implemented in WIEN2k code [19]. For exchange-correlation potentials, the localized density approximation (LDA) and generalized gradient approximation (GGA) based on Perdew et al [20] have been applied. However, LDA and GGA usually underestimate the band gap of semiconductors [21], the modified Becke-Johnson potential (mBJ), with new parametrization for semiconductors [22], was also employed to obtain better band gaps. The muffin-tin radii were fixed to 2.32, 2.19, 2.41 and 1.90 Bohr \((a_0)\) for Cu, Mg, Sn and S atoms of CMTS and 2.25, 2.07, 2.31, 2.14 Bohr \((a_0)\) for Cu, Mg, Sn and Se atoms of CMTSe. \(R_{\text{MT}} K_{\text{MAX}}\) was set equal to 7, where \(R_{\text{MT}}\) is the smallest atomic sphere radii in the unit cell and \(K_{\text{MAX}}\) is the plane wave cut-off. The self-consistency was achieved by demanding the convergence of the total energy/cell and charge/cell of the system to be less than \(\sim 10^{-5}\) Ry and \(\sim 10^{-3}\) electronic charge, respectively. A denser \((40 \times 40 \times 40)\) \(k\)-mesh was used in the calculations of transport coefficients. The thermoelectric properties were studied by using the BoltzTraP code [23] under the constant relaxation time approximation for the charge carriers.

3. Results and discussions

The crystal structures for KS and ST phases are shown in figure 1. The total energy calculations show that ST is the ground state structure for both CMTS and CMTSe compounds, opposed to Zn based compounds which are found to be stabilized in KS phase [13]. In CMTS and CMTSe, the energy difference between ST and KS is about 75 and 62 meV/unit cell, respectively. In order to determine the theoretical equilibrium crystal structures for the kesterite and stannite phases of CMTS and CMTSe, we performed a full geometry optimization of the lattice constants and the non-equivalent fractional parameters using LDA and GGA functionals. In table 1, we compare the lattice parameters and non-equivalent fractional parameters with the experimental data and previous theoretical results. The lattice constants \(a/c\) of the KS structure are slightly larger/smaller than that of ST structure for both the compounds under LDA and GGA. Compared to the experimentally measured lattice constants in ST phase of CMTSe, our LDA calculations slightly underestimate \(a\) by 0.2% and overestimate \(c\) by 0.7% while GGA calculations overestimate \(a\) and \(c\) by ~2% and 4%, respectively. The computed values of lattice
parameters are fairly in good agreement with the earlier reported values for both the S and the Se-based compounds. It is also clear from the table 1, that both LDA and GGA yield very comparable atomic positions for both compounds.

To understand the thermoelectric properties of compounds it is crucial to study their electronic structures also. The electronic band structures of CMTS and CMTSe computed using mBJ along high symmetry directions in the Brillouin zone are shown in figure 2. It is clear from the figure that these materials are direct band gap semiconductors at Γ-point and have similar band structures. In KS phase, at X-point there are three non-degenerate bands near the top of the valence band (VB) and these bands remain non-degenerate on going from X to Γ-point. At Γ-point the top most VB band remains non-degenerate while other two become doubly degenerate. This degeneracy again lifted completely along Γ to N-direction. However, in ST phase top most first
and second VBs become doubly degenerate at $\Gamma$ and third VB becomes non-degenerate. The band structures of these compounds show that the top of the VB is split by the crystal field $\Delta_{cf}$. We define $\Delta_{cf} > 0$ for case when the doubly degenerate VB is energetically higher than the non-degenerate band. It is clear from dispersion plots that for KS phase $\Delta_{cf}$ is negative and small, while for ST phase it is positive and large, which is consistent with earlier calculations based on Zn based compounds [11, 13]. The calculated value of $-\Delta_{cf}$ is about 0.08/0.04 eV for CMTS/CMTSe in KS structures and in ST structures $\Delta_{cf}$ is nearly 0.14/0.08 eV for CMTS/CMTSe. Also band structures of these compounds in both phases show comparatively flat bands near the top of the valence band, which suggest very high Seebeck coefficient in these materials.

The estimated band gaps under different approximations and their comparison with the earlier reported and experimental values are given in table 2. The estimated LDA/GGA band gaps are $E_g = 0.35/0.22$ eV for KS-CMTS and 0.25/0.11 eV for ST-CMTS. For the case of CMTSe under LDA as well as GGA approximations we could not get any band gap suggesting the underestimation of band gaps within these approximations. Further, for the case of CMTS in both phases the estimated band gaps are smaller than the experimental values. Generally, LDA and GGA underestimate the values of band gap for some systems and one way to overcome this inadequacy is to use the modified Becke–Johnson potential (mBJ). The band gaps obtained using mBJ show a significant improvement over LDA and GGA values and are closer to the experimental values. Band gap in CMTS system is always higher than CMTSe, owing to larger extension of Se orbitals, also when the size is reduced as in the case of nano-system, the band gap is expected to increase because of confinement. We note that experimental reported value of $E_g$ in case of CMTSe [16] is even higher than nano-particles of CMTS [17]. The possible reason for the

![Figure 2. Electronic band structures of (a) Cu$_2$MgSnS$_4$ (KS), (b) Cu$_2$MgSnS$_4$ (ST), (c) Cu$_2$MgSnSe$_4$ (KS) and (d) Cu$_2$MgSnSe$_4$ (ST) using mBJ.](image-url)
large reported gaps in CMTSe may be disorder in the measured systems and also measurements were done at room temperature, which may give additional contribution of $\sim 0.1$–0.2 eV to the $E_g$. We find that $E_g(KS) - E_g(ST) \approx 0.04$ eV and $E_g(S) - E_g(Se) \approx 0.5$ eV. It has been noticed in different families of Chalcogenides that difference in $E_g(S) - E_g(Se)$ is $\sim 0.5$ eV. In our calculations, we also find similar magnitude of difference in band gaps.

Table 2. The calculated band gap, $E_g$ (eV), for CMTS/Se in their kesterite (KS) and stannite (ST) phases under different approximations (LDA, GGA and mBJ) and comparison with the previous work and experimental measurements.

| System      | LDA  | GGA  | mBJ  | Expt. | Others calculated |
|-------------|------|------|------|-------|-------------------|
| CMTS (KS)   | 0.35 | 0.22 | 1.07 | 1.6 [17] | —                 |
| CMTS (ST)   | 0.25 | 0.11 | 0.96 | —     | 0.19 [18]        |
| CMTSe (KS)  | No gap at $E_g$ | No gap at $E_g$ | 0.58 | — | —                 |
| CMTSe (ST)  | No gap at $E_g$ | No gap at $E_g$ | 0.54 | 1.7 [16] | — 0.05 [18] |

Figure 3. Variation of (a) Seebeck coefficient ($S$), (b) electrical conductivity ($\sigma/\tau$), (c) electronic thermal conductivity ($\kappa_e/\tau$) and power factor (PF) with temperature for Cu$_2$MgSnS$_4$ in KS and ST phases.

The temperature dependence of Seebeck coefficient ($S$), electrical conductivity ($\sigma/\tau$), electronic thermal conductivity ($\kappa_e/\tau$) and power-factor (PF) in KS and ST phases are shown in figures 3 and 4 for CMCTS and CMTSe, respectively. The Seebeck coefficients (shown in figures 3(a) and 4(a)) are found to be very large and positive in the entire temperature range for both compounds. The maximum value of $S$ is $\sim 290 \mu V K^{-1}$ for KS-CMTS and KS-CMTSe compounds at 360 and 200 K, respectively. We note that this value is very close to the experimental value of 273.2 $\mu V K^{-1}$ reported for CMTSe (ST) at room temperature [16]. The electrical conductivities presented in figures 3(b) and 4(b) shows increment with increasing temperature as both compounds have semiconducting ground state. The electronic thermal conductivities for these compounds also show increment with increasing temperature (figures 3(c) and 4(c)). Both $\sigma/\tau$ and $\kappa_e/\tau$ are slightly larger for ST
phase than that of KS phase in CMTS compound. However, in CMTSe the $\kappa_e/\tau$ is almost same at temperature below 800 K in both phases. By using the value of $\tau = 10^{-14}$ s [25], the room temperature value of $\kappa_e$ is $\sim 0.3/0.5$ W m$^{-1}$ K$^{-1}$ for KS/ST-CMTS, respectively, while for KS/ST-CMTSe it is $\sim 0.4/0.5$, W m$^{-1}$ K$^{-1}$. The power-factors (PF) are shown in figures 3(d) and 4(d) for CMTS and CMTSe compounds, respectively. The ST-CMTS shows larger PF than the KS-CMTS for the entire temperature range, whereas it is almost same for CMTSe in both phases. The room temperature value of PF in these compounds for both phases is found to be about 10 $(\mu$W cm$^{-1}$ K$^{-2}$) which is more than the experimental value of 2 $\mu$W cm$^{-1}$ K$^{-2}$ reported for CMTSe (ST) [16]. The PF increases with increasing temperature and at higher temperature the PF is found to be similar as that of state-of-art Bi$_2$Te$_3$, which is known to be one of the best commercially available thermoelectric materials [23].

The dimensionless figure-of-merit (ZT) estimated from the calculated power-factor and electronic thermal conductivity, is presented in figure 5. The value of ZT is found to increase with increasing temperature till 400 K and after that it increases marginally with further increase in temperature. KS phase for both the systems show slightly larger ZT than ST phase and estimated room temperature value is $\sim 0.8$. The large value of ZT obtained for wide temperature range makes these systems as excellent thermoelectric materials. However, for the estimation of ZT, we have considered here only the electronic part of thermal conductivity but lattice part also contributes to the total thermal conductivity, which may further increase the ZT. Also the electronic contribution to the thermal conductivity is small as these materials have very large band gap. The experimentally measured value of total thermal conductivity for CMTSe (ST) is found in the range 2.2–1.0 W m$^{-1}$ K$^{-1}$ for temperature 300–700 K [16]. If we consider the room temperature value of total thermal conductivity equal to 2.2 W m$^{-1}$ K$^{-1}$, we get the value of ZT $\sim 0.15$, slightly larger than the experimental value of ZT [16]. Similar to experimental findings on CMTSe in ST phase, our calculations also predict that both these systems i.e CMTS and CMTSe are potential thermoelectric materials in both the experimentally reported phases and can be used as potential thermoelectric materials for a wide temperature range.

Figure 4. Variation of (a) Seebeck coefficient ($S$), (b) electrical conductivity ($\sigma/\tau$), (c) electronic thermal conductivity ($\kappa_e/\tau$) and power factor (PF) with temperature for Cu$_2$MgSnSe$_4$ in KS and ST phases.
4. Conclusions

In conclusion, first-principles calculations based on LDA, GGA and mBJ functionals have been carried for the potential thermoelectric materials CMTS and CMTSe in both possible phases. The energy difference between ST and KS phases is about 75 meV/unit cell for CMTS and 62 meV/unit cell for CMTSe. The Seebeck coefficient is found to be large and positive in the entire temperature range which suggests the presence of P-type charge carriers in these systems. The calculated room temperature value of Seebeck coefficient is found to be in good agreement with the experimental value reported for the case of CMTSe. We propose that CMTS, which has not been explored experimentally so far, will also be a potential thermoelectric material owing to its high PF and ZT. The large value of ZT predicts the applicability of these compounds as potential thermoelectric materials in a wide temperature range.

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