Interface of Sn-doped AgAlTe$_2$ and LiInTe$_2$: A theoretical model of tandem intermediate band absorber

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ABSTRACT

Designing a new absorber to overcome the Shockley–Queisser limit for single-junction solar cells is of great importance for solar cell advancements. Here, a theoretical model of tandem intermediate band absorber is proposed based on the interface of Sn-doped AgAlTe$_2$ and LiInTe$_2$. Sn-doped AgAlTe$_2$ and LiInTe$_2$ are imminent to produce ideal heterojunctions as they possess similar lattice constants and the type-II band offset, providing an approach to overcome the Shockley–Queisser limit.
doping a suitable element with a high concentration in the host semiconductor is regarded as the feasible way to induce an IB in the original bandgap. Several doped semiconductors like Ti-12, Cr-13, Fe-14, and Sn-doped15 CuGaS2, Ti-16 and V-doped17 SnS2, V-doped InSb18, O-doped ZnTe19,20 etc., have been studied experimentally in which distinct sub-gap absorptions related to the IB have been observed. Interestingly, no study has been reported to couple these two approaches (i.e., tandem and intermediate band) to design a tandem intermediate band absorber, which is clearly expected to absorb more photons with less absorber layers.

To design a tandem intermediate band absorber, first, we need to find two different semiconductors, which can form a half-filled and delocalized IB after a heavy doping. Second, the IB position and then the sub-bandgaps of the intermediate band absorbers should be suitable to absorb the photons with different energies to cover the solar light spectrum effectively. Third, the two host semiconductors should possess similar crystal structures and lattice constants to avoid serious lattice mismatch. Fourth, a type-II band offset between the two adopted host semiconductors is required to facilitate light-generated electron and hole separation. In our earlier work,21 we found that Sn is easily doped at the Al site in AgAlTe2 and reaches a large doping concentration to form an IB. Due to the ideal IB position resulting from Sn doping, the values of the main bandgap and sub-bandgaps have a reasonable distribution and then the absorption coefficient of Sn-doped AgAlTe2 can cover the solar light spectrum effectively. Moreover, with the Sn-doping concentration increasing in AgAlTe2, the center of the intermediate band would not have a significant change while the width of the intermediate band and the absorption coefficient will have an increase. Therefore, Sn-doped AgAlTe2 with a chalcopyrite structure has been suggested as a promising intermediate band absorber.21 We notice that LiXTe2 (X = Al, Ga, In) compounds have the same chalcopyrite structure and similar lattice constants to AgAlTe2 and it is possible to design a tandem intermediate band absorber from the heterojunction by these compounds.

In this letter, we have theoretically studied the electronic structure of LiXTe2 (X = Al, Ga, In) and found interestingly that LinTe2 possesses a type-II band offset with AgAlTe2 and an isolated and half-filled IB when doped with Si, Ge, or Sn at In sites. Further studies reveal that Sn-doped LinTe2 is a promising intermediate band absorber capable of high doping concentration. As the type-II band offset is preserved between Sn-doped AgAlTe2 and LinTe2, the corresponding tandem intermediate band absorber is proposed for high efficiency solar cells. Of note, our proposed tandem model is based on connecting two intermediate band absorbers other than two solar cells. This is different from usual tandem solar cells, where a tunneling layer is required to connect the different solar cells (multiply p–n junctions).10

We notice that LiXTe2 (X = Al, Ga, and In) and AgAlTe2 have similar lattice constants (c.f. Table S1). In particular, the differences of a and b between LiXTe2 (X = Al, Ga, and In) and AgAlTe2 are all less than 2%. Heterojunctions between LiXTe2 (X = Al, Ga, and In) and AgAlTe2 along the [001] direction are expected to avoid serious lattice mismatch. In addition to the crystal structure, the electronic structure of LiXTe2 (X = Al, Ga, and In) is another criterion to single out the component of the heterojunction to match AgAlTe2. All the calculated band structures of LiXTe2 (X = Al, Ga, and In) possess direct bandgaps (c.f. Fig. S1). The HSE06 calculated bandgaps are 3.112, 2.497, and 2.223 eV for LiAlTe2, LiGaTe2, and LinTe2, respectively, in line with the experimental results22–25 and available theoretical results based on advanced methods,25–21 as listed in Table S1. It is well known that the traditional calculation methods like local density approximation (LDA), generalized gradient approximation (GGA), and GGA+U (correction with an on-site Coulomb interactions) underestimate the bandgaps of semiconductors.22 After adopting advanced methods like modified Becke-Johnson exchange potential (mbJ) and hybrid functional (HSE06 and B3PW91), one can obtain reasonable bandgaps compared with experiment. Therefore, the bandgaps from HSE06 calculations are adopted for further studies in this work. The bandgap of LiAlTe2 is not suitable for the host of the IBSC, while the bandgaps of LiGaTe2 and LinTe2 are close to the ideal values of bandgaps (2.40 eV at one sun concentration and 1.93 eV at full concentration)23 for the IBSC.

In order to estimate the band edge positions of LiXTe2 (X = Al, Ga, and In) with respect to the vacuum, we adopt the ionization potential of AgAlTe2 (6.05 eV) from our earlier work21 and then calculate the band offsets between AgAlTe2, LiAlTe2, LiGaTe2, and LinTe2. Figure 1 presents band edge positions relative to vacuum of AgAlTe2, LiAlTe2, LiGaTe2, and LinTe2. One observes that the valence band position of AgAlTe2 is higher than those of LiGaTe2 (X = Al, Ga, and In). The conduction band positions of LiAlTe2, LiGaTe2, and LinTe2 decrease sequentially. In particular, LinTe2 forms a type-II band offset with AgAlTe2, where the offsets are 0.229 and 0.197 eV for valence and conduction bands, respectively. This indicates that the light-generated electrons and holes can be separated efficiently at the interface between AgAlTe2 and LinTe2. In addition, our calculated carrier effective masses for LinTe2 are m∗100 = 0.25 m0, m∗100 = 0.21 m0, and m∗110 = 0.22 m0 for electrons, which should be correlated with the isotropy of In-s state at CBM, and m∗100 = 0.19 m0, m∗100 = 0.59 m0, and m∗110 = 0.59 m0 for holes, which should be related to the anisotropy of Te p-states at the VBM (as shown in the PDOS in Fig. S2). The small effective carrier masses are beneficial for an effective optical response and carrier separation. Based on the criteria of ideal main bandgap for the IBSC, light carrier effective masses, lattice constant, and band offset matching with AgAlTe2, LinTe2 is selected as the
component of the heterojunction to match AgAlTe$_2$ for the design on the tandem intermediate band absorber in this work.

As in the AgAlTe$_2$ case, doping of group-IV (Si, Ge, and Sn) elements at the In site is considered as the defects to produce a partially filled intermediate band in the main bandgap of LiInTe$_2$ since each of these atoms has one residual delocalized $s$ electron and may form a band when heavily doped. Fortunately, the half-filled and isolated IBs are introduced in the bandgap of LiInTe$_2$ when any of these group-IV (Si, Ge, and Sn) elements are doped, as shown in Figs. 2(a) and S3. Unlike the flat intermediate band originated from $d$-orbitals, the intermediate bands in Si, Ge, and Sn-doped LiInTe$_2$ are broad and show delocalized characteristic. As listed in Table I, the widths of the IBs are close to the optimal width (0.825 eV) of the intermediate band according to the balance between the positive effect of recombination suppression and the negative effect of optical absorption reduction. Figures 2(b)–2(f) show the PDOS of Li, In, Te, Sn, and the crystal orbital overlap populations (COOP) between Sn-$s$ and Te-$p$ states in Sn-doped LiInTe$_2$. The components of the original VB and CB do not change remarkably after Sn-doping in AgAlTe$_2$. The IB in the main bandgap mainly comes from Sn-$s$ and Te-$p$ states. Based on the analysis of COOP, we have learned that the IB results from the antibonding states between Sn-$s$ states and Te-$p$ states, while the corresponding bonding states are located around $-8$ eV below the Fermi level, as shown in Fig. 2(f). This is in line with the origin of the IB in Sn-doped AgAlTe$_2$. The wave function square of the IB in Sn-doped LiInTe$_2$ also shows antibonding and delocalized characters (c.f. Fig. S4), in line with the analyses of PDOS and COOP. Therefore, the IBs in different doped systems have a similar shape and are all delocalized, although the detailed position of IBs shifts from each other in the main bandgap for the various group-IV dopants (as shown in Fig. 5). The IB induced by Sn-doping is higher in energy than those from Ge- and Sn-doping. The IB relative energy positions can be explained by our earlier illustrations based on bonding/antibonding attribution and atomic orbital energy as for group-IV (Si, Ge, and Sn)-doped AgAlTe$_2$. The sub-bandgaps in various doped systems possess different widths (c.f. Table I) due to different IB positions, thus affecting the theoretical efficiency of the IBSC directly. The main bandgap of pure LiInTe$_2$.

![Diagram](image-url)

**FIG. 2.** The calculated band structure of Sn-doped LiInTe$_2$ (a) and the corresponding partial density of states (PDOS) of Li (b), In (c), Te (d), and Sn (e) and the COOP (f) between Sn-$s$ and Te-$p$ states. The Fermi energy level is set to zero.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Original main bandgap (eV)</th>
<th>Sub-band gap1 (VBM-$E_f$)</th>
<th>Sub-band gap2 ($E_f$-CBM)</th>
<th>Width of the IB (eV)</th>
<th>Theoretical efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiInTe$_2$</td>
<td>2.223</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>21%</td>
</tr>
<tr>
<td>Si-doped</td>
<td>2.329</td>
<td>1.926</td>
<td>0.403</td>
<td>0.733</td>
<td>30%</td>
</tr>
<tr>
<td>Ge-doped</td>
<td>2.304</td>
<td>1.396</td>
<td>0.908</td>
<td>0.737</td>
<td>45%</td>
</tr>
<tr>
<td>Sn-doped</td>
<td>2.286</td>
<td>1.540</td>
<td>0.746</td>
<td>0.888</td>
<td>43%</td>
</tr>
</tbody>
</table>
LiInTe$_2$ is a little too large as the absorber for the single-junction solar cell and its theoretical efficiency is just 21%. Ge- and Sn-doped LiInTe$_2$ have a suitable IB position and then the corresponding widths of sub-bandgap and main bandgap (c.f. Table I) can have a suitable distribution in the range of the solar light spectrum. The theoretical efficiencies of Ge- and Sn-doped LiInTe$_2$ are estimated to be 45% and 43%, respectively, close to the maximum (46%) of the theoretical efficiency of the IBSC with one IB. Figure 3 shows the absorption coefficient of pure and (Si, Ge, and Sn)-doped LiInTe$_2$. Obviously, the absorption coefficients of the doped systems can fulfill the absorption of photons with different energies and are enhanced in the visible light region and then cover the solar radiation spectrum effectively.

Therefore, Ge and Sn are suitable dopants for LiInTe$_2$ to produce an IB, according to the induced IB position and widths of sub-bandgaps.

In order to produce an IB other than the localized impurity level in the doped systems, the samples generally need to be heavily doped. To give an estimation on the possibility of realizing a large doping concentration of group-IV dopants in LiInTe$_2$, the defect formation energies on Si, Ge, or Sn substituting at the In site are calculated. The details on the calculations of defect formation energy are described in the supplementary material. Figure 4 shows the formation energies of Si, Ge, and Sn substituting at the In site in LiInTe$_2$ as a function of the chemical potential at points A, B, C, D, and E, which represent five extreme conditions in the allowed chemical potential ranges (in FIG. S5) for a stable LiInTe$_2$ with consideration of competing compounds.

The band edge positions are expected to change compared to the pure system when various elements are doped heavily in LiInTe$_2$. The band offsets among the undoped and doped LiInTe$_2$ are calculated by the traditional approach, i.e., aligned by the average potentials of host elements far away from the dopant. Combined with the band offset between pure AgAlTe$_2$ and LiInTe$_2$ (in Fig. 1), we can get the band offsets of various hosts with different dopants in Fig. 5. Following our samples can be prepared by non-equilibrium processes such as implantation and molecular beam epitaxy. Therefore, we expect that the IB can be realized by Sn doping at the In site in LiInTe$_2$.

FIG. 3. Absorption coefficients of pure LiInTe$_2$ and (Si, Ge, and Sn)-doped LiInTe$_2$. The reference air-mass 1.5-solar spectral irradiance is plotted in yellow.

FIG. 4. Formation energies of Si, Ge, and Sn substituting at the In site in LiInTe$_2$ as a function of the chemical potential at points A, B, C, D, and E, which represent five extreme conditions in the allowed chemical potential ranges (in FIG. S5) for a stable LiInTe$_2$ with consideration of competing compounds.

FIG. 5. The band energy positions relative to vacuum in pure and group-IV (Si, Ge, and Sn)-doped AgAlTe$_2$ and LiInTe$_2$. Here, the width of the main bandgap of pure compounds and the widths of sub-bandgaps of the doped systems (unit: eV) are labeled. The main bandgap of the doped systems can be obtained by adding the two sub-bandgaps. The interface of Sn-doped AgAlTe$_2$ and LiInTe$_2$ is highlighted in the dashed black line.
earlier work.\(^{23}\) Sn-doped AgAlTe\(_2\) is set as primary part of the tandem intermediate band absorber according to the suitable sub-bandgaps and the low defect formation energy. Our former work\(^{23}\) also indicated that the band edge positions of AgAlTe\(_2\) would not show a remarkable change after IV-group atom doping. Then, the type-II band offset between AgAlTe\(_2\) and LiInTe\(_2\) can be maintained after IV-group atom doping. One can observe that the VB, IB, and CB from both Sn-doped LiInTe\(_2\) and Ge-doped LiInTe\(_2\) have lower energy positions than those from Sn-doped AgAlTe\(_2\). Since the positions of their Fermi energy levels do not show a significant variation, the partially filled IB can be preserved after the electron transfer when the heterojunction is formed. Therefore, from the band offset point of view, both Sn-doped LiInTe\(_2\) and Ge-doped LiInTe\(_2\) are suitable as another part of the heterojunction. Specifically, the conduction band offset and valence band offset between Sn-doped AgAlTe\(_2\) and Sn-doped LiInTe\(_2\) are 0.28 and 0.52 eV, respectively, which are slightly greater than those between rutile and anatase TiO\(_2\) (i.e., 0.22 and 0.39 eV, respectively).\(^{43}\) The band offsets are regarded to account for the efficient carrier separation and driving force for the increased photoactivity in rutile-anatase composite materials.\(^{43}\) Therefore, we expect that it can have an efficient electron-hole separation at the interface of Sn-doped AgAlTe\(_2\) and LiInTe\(_2\). In addition, thin films AgAlTe\(_2\),\(^{44}\) and LiInTe\(_2\),\(^{45}\) have been grown by different experimental groups and large Sn doping concentrations in chalcophyrite compounds like 25% in Sn-doped CuInSe\(_2\)\(^{46}\) 8% in Sn-doped CuIn\(_2\)Se\(_2\)\(^{47}\) and 6% in Sn-doped CuGaSe\(_2\)\(^{48}\) have been reported experimentally. Considering the reported experimental results, low defect formation energies of Sn\(_{\text{In}}\) in LiInTe\(_2\) and Sn\(_{\text{Al}}\) in AgAlTe\(_2\)(0.24 eV)\(^{21}\) and less dopant types in the heterojunction, Sn-doped AgAlTe\(_2\) and LiInTe\(_2\) are expected to be convenient for the heterojunction growth. Although it contains some rare elements like Te (0.001 ppm in Earth’s crust) and Ag (0.075 ppm in Earth’s crust)\(^{49}\) and some expensive elements like Li ($85.6/kg), In ($167/kg), and Ag ($521/kg),\(^{49}\) the thin film heterojunction would not need a large amount of raw materials in a single solar cell module and the cost is normally decreased substantially once a technology has been established (e.g., LED lamps\(^ {50}\) and Li batteries\(^ {51}\)). Therefore, Sn-doped AgAlTe\(_2\) and LiInTe\(_2\) heterojunctions, which will have two main bandgaps and four sub-bandgaps, are suggested as the tandem intermediate band absorber.

In summary, we have studied the electronic structures of Li\(_x\)Te\(_2\) (X = Al, Ga, and In) and group-IV (Si, Ge, and Sn)-doped LiInTe\(_2\) by first-principles calculations based on the hybrid HSE06 functional. It is found that LiInTe\(_2\) is suitable to form a heterojunction with Sn-doped AgAlTe\(_2\) as they have excellent lattice match and form a type-II band offset. It is also revealed that Sn is easily doped at the In site with a concentration up to ~5.6% and produce an IB. The absorption coefficient of Sn-doped LiInTe\(_2\) can cover the solar light spectrum effectively, with the estimated theoretical efficiency of 43%.\(^{22}\) Moreover, the type-II band offset is maintained between AgAlTe\(_2\) and LiInTe\(_2\) when both are heavily doped with Sn. Consequently, an absorber combining tandem and IB approaches was proposed to overcome the Shockley–Queisser limit, as exemplified with Sn-doped AgAlTe\(_2\) and LiInTe\(_2\). Moreover, our proposed model will stimulate the research interest to explore the tandem intermediate band absorber from low-cost and nontoxic compounds.

See the supplementary material for the calculated and referenced lattice parameters and bandgaps, the calculated band structures for LiAlTe\(_2\), LiGaTe\(_2\), and LiInTe\(_2\), the partial density states of LiInTe\(_2\), the band structures of Si- and Ge-doped LiInTe\(_2\), the wave function square of the IB in Sn-doped LiInTe\(_2\), and the calculation details of this work.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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