Computational Modeling of Novel Bulk Materials for the Intermediate-Band Solar Cells

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ABSTRACT: Research communities have been studying materials with intermediate bands (IBs) in the middle of the band gap to produce efficient solar cells. Cells based on these materials could reach theoretical efficiencies up to 63.2%. In this comprehensive study, we investigate by means of accurate first-principle calculation the electronic band structure of 2100 novel compounds (bulk materials) to discover whether the IB is present in these materials. Our calculations are based on the density functional theory, using the generalized-gradient approximation for exchange and correlation terms and focusing on the band structure, the density of states, and the electron effective masses of the structures in the database. The IB structures are obtained by adding metallic or semimetallic atoms in the bulk material. By means of these calculations, we have clearly identified a number of compounds that may have high potential to be used as photovoltaic materials. We present here the numerical results for 17 novel IB materials, which could theoretically prove to be suitable for photovoltaic applications.

INTRODUCTION

Multi-band gap materials offer the possibility of increasing the efficiency of solar cells beyond the limit of traditional single-band gap solar-cell materials. Intermediate-band (IB) materials are characterized by the splitting of the main band gaps into two or more sub-band gaps by narrow IBs and have been the focus of recent studies.1–7. In IB solar cells, an IB material is sandwiched between two ordinary p-type and n-type semiconductors and used as discriminating contacts to the valence band (VB) and the conduction band (CB), respectively. In IB materials, an electron is promoted from the VB to the CB through the IB. Upon absorption of sub-band gap-energy photons, the electrons transit from VB to CB and later from IB to CB. It will add up to the transition of electrons from VB to CB through conventional VB-to-CB photon absorption.1,2 By adopting a hypothesis similar to that of Shockley and Queisser,3 it was shown in 1997 that balance-limiting efficiencies of 63.2% for IB solar cells and 41% for single-band gap solar cells can be achieved at a concentration of 46 050 suns at earth and sun temperatures of 300 and 6000 K, respectively.

The IB should be partially filled to permit the comparable rates for the low sub-band gap-energy photon absorption processes and should not overlap with either the VB or the CB to avoid fast transitions through thermalizations.5 We can consider the IB solar cells as a combination of three cells. Cells representing VB-to-IB and IB-to-CB transitions can be regarded as two cells in series, and the VB-to-CB transition can represent a parallel cell. The cell will have a high tolerance to changes in the solar spectrum.

In the mid-20th century, researchers7–10 suggested the concept of creating intermediate levels in the middle of a forbidden band gap to increase the maximum photocurrent by doping the semiconductor with a large concentration of impurities. At an early stage, it was believed that these IBs would cause nonradiative recombination. It has been later shown that the nonradiative recombination can be suppressed by using a sufficiently high concentration of dopants.10–13

Two major approaches are considered in fabricating IB solar cells, namely, quantum-dot IBs (QDIBs) and bulk IB solar cells. By using quantum dots with different shapes and sizes, the IB levels can be tuned. The first QDIB was produced in 2004 on the basis of the InAs/GaAs QD material with an efficiency of 15.3%. Energy levels of the confined states in a quantum dot can be used as IB in QDIBs. However, there are many challenges with QDIBs as quantum dots are very small and do not absorb a significant amount of light. With an increasing number of QDs, the cell structure can be damaged, and strain will cause severe damages. At room temperature, the Shockley–Read–Hall recombination is a dominant mechanism that leads to low efficiency in QDIB solar cells due to deeper impurities.

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Several research groups have produced QDIB solar cells, and efficiencies over 18% have been reported by Blokhin et al. The second type of IB solar cells is based on bulk materials. The IB was detected through photoreflectance measurements in some bulk materials, and this formation was attributed to band anticrossing and heavily mismatched alloys. The first of these bulk materials, ZnMnTeO, was developed by Walukiewicz and co-workers. Later, numerous quantum-accurate calculations have been performed on VInS bulk material, characterized by an IB containing Fermi levels. Phillips and co-workers developed bulk IB solar cells using ZnTe doped with an oxygen atom and obtained higher efficiencies and short-circuit current than QDIB solar cells. The band gap properties of bulk materials are widely studied, and the technologies are well verified by researchers. However, the search for intermediate-band gap materials continues, to model high-efficiency IB solar cells. Figure 1 shows the band diagram of an IB solar cell with $E_v$ the total band gap between the top of the VB and the bottom of the CB. In the figure, $E_v$ is the energy gap between the top of the VB and the bottom of an IB, $E_i$ is the energy gap between the top of the IB to the bottom of the CB, and $\Delta E_i$ is the width of the IB. Furthermore, the electronic transitions of (V, I), (I, I), (I, C), and (V, C) are also explained.

Table 1. Calculated Selected Narrow-Band Gap Semiconductors with IBs and Band Gap Type

| serial no. | chemical formula | Pearson symbol | space group number | band gap ($E_v$) | band gap ($E_i$) | width of IB ($\Delta E_i$) | total band gap ($E_g$) | band gap type |
|------------|------------------|----------------|--------------------|-----------------|-----------------|--------------------------|----------------------|--------------|
| 1.         | K$_8$C$_{60}$    | cI132          | 204                | 0.61            | 0.28            | 0.33                     | 1.28                 | ID           |
| 2.         | Au$_2$Cs$_4$I$_4$ | tI20           | 139                | 0.64            | 1.01            | 0.65                     | 1.08                 | ID           |
| 3.         | Ag$_2$GeBaS$_4$  | tI16           | 121                | 0.90            | 0.35            | 1.60                     | 1.15                 | ID           |

Table 2. Wide-Band Gap 1 Semiconductors with IB Ranging from 2.62 to 3.15 eV

| serial no. | chemical formula | Pearson symbol | space group number | band gap ($E_v$) | band gap ($E_i$) | width of IB ($\Delta E_i$) | total band gap ($E_g$) | band gap type |
|------------|------------------|----------------|--------------------|-----------------|-----------------|--------------------------|----------------------|--------------|
| 1.         | Cu$_2$AgPO$_4$   | oP56           | 61                 | 1.27            | 0.61            | 0.74                     | 2.62                 | DB           |
| 2.         | Ag$_2$ZnSnS$_4$  | tI16           | 121                | 0.47            | 0.57            | 1.13                     | 2.70                 | DB           |
| 3.         | Au$_2$Cs$_4$Br$_4$ | tI20           | 139                | 0.67            | 1.23            | 0.64                     | 2.67                 | DB           |
| 4.         | Ag$_2$AsS$_4$    | oP16           | 31                 | 0.73            | 1.04            | 0.71                     | 2.77                 | DB           |
| 5.         | Ag$_2$KSbS$_4$   | tI16           | 121                | 0.81            | 1.08            | 0.72                     | 2.93                 | DB           |
| 6.         | Na$_2$Se$_3$Sb   | cI16           | 217                | 1.02            | 1.24            | 0.81                     | 2.71                 | DB           |
| 7.         | Ag$_2$K$_2$Sb$_4$ | oP32           | 118                | 1.52            | 1.03            | 0.72                     | 2.97                 | DB           |
| 8.         | AsRb$_3$Se$_4$   | oP32           | 62                 | 1.32            | 0.98            | 0.72                     | 3.15                 | DB           |

Several research groups have produced QDIB solar cells, and efficiencies over 18% have been reported by Blokhin et al. The second type of IB solar cells is based on bulk materials. The IB was detected through photoreflectance measurements in some bulk materials, and this formation was attributed to band anticrossing and heavily mismatched alloys. The first of these bulk materials, ZnMnTeO, was developed by Walukiewicz and co-workers. Later, numerous quantum-accurate calculations have been performed on VInS bulk material, characterized by an IB containing Fermi levels. Phillips and co-workers developed bulk IB solar cells using ZnTe doped with an oxygen atom and obtained higher efficiencies and short-circuit current than QDIB solar cells. The band gap properties of bulk materials are widely studied, and the technologies are well verified by researchers. However, the search for intermediate-band gap materials continues, to model high-efficiency IB solar cells. Figure 1 shows the band diagram of an IB solar cell with $E_v$ the total band gap between the top of the VB and the bottom of the CB. In the figure, $E_v$ is the energy gap between the top of the VB and the bottom of an IB, $E_i$ is the energy gap between the top of the IB to the bottom of the CB, and $\Delta E_i$ is the width of the IB. Furthermore, the electronic transitions of (V, I), (I, I), (I, C), and (V, C) are also explained.

In the present work, we study 2100 structures with the aim of identifying ideal candidates for solar-cell materials. We employ density functional theory (DFT) calculations to verify the presence of an IB, isolated in the band gap of the semiconductor compounds of bulk material compounds with different substitutional impurities forming ternary alloys. The calculated band gap values are used to identify the most suitable compounds for solar-cell applications. We also present density of states (DOS) and effective mass calculations for the selected IB materials.

**RESULTS AND DISCUSSION**

The main focus of the present work is to find the potential IB materials from the selected 2100 compounds. Because of the very high computational cost, we mainly focused on the electronic structure, the DOS and effective mass calculations. The hybrid electronic structure and optical properties of the selected IB compounds are under investigation, and the results will be published in a forthcoming work. We employ the DFT method to elucidate the band structure arrangement of 2100 compounds.
bulk materials, vital for the interaction of IB and could be potent solar cells with sufficient band gap. The DFT approaches to reveal the significant and computational features of the bulk materials and these features can be used as virtual screenings of band structures of the 2100 compounds to identify the novel IB compounds. From the first screening, we observed 312 compounds having an IB with the maximum of the VB at the Fermi level. Among these, 282 compounds were selected for further analysis and 30 compounds were found as heavy elements. After carrying out a detailed analysis, we found out that only 17 compounds among the starting 282 would be acceptable semiconductor materials for photovoltaic applications. The rest were found to be perfect insulators, with band gap values larger than 3.51 eV. The electronic properties of these 17 compounds are presented in Tables 1−3. It is well known that the band gap ($E_g$) values of solids obtained from usual DFT calculations are systematically underestimated due to discontinuity in the exchange-correlation potential. Thus, the calculated $E_g$ values are typically 30−50% smaller than those measured experimentally. It is recognized that the theoretically calculated $E_g$ for semiconductors and insulators are strongly dependent on the approximations used, particularly on the exchange and correlation terms of the potential. In the present work, because of the large number compounds involved in the screening process, we have used only generalized-gradient approximation. However, the overall structure is not going to change except the band gap value irrespective of the approximation.

We have chosen to divide the 17 compounds with IBs into three groups depending on the magnitude of their band gap values. The first group of three compounds is named as narrow-band gap semiconductors, which is characterized by band gaps varying from 1.2 to 2.5 eV. The second group of eight compounds is named wide-band gap 1 semiconductors, which includes materials with band gaps varying from 2.6 to 3.15 eV. Finally, the third group is named as wide-band gap 2 semiconductors. In this case, the band gap values vary from 3.15 to 3.5 eV. The band structures of these compounds are presented in Figures 2a−c, 3a−d, and 4a−d, and we calculate the total band gaps, band gaps $E_{vi}$ and $E_{ci}$ and the widths of the IB ($\Delta E_i$) bands for all of the compounds. The electronic structure properties of these compounds are presented in Tables 1, 2, and S1.

As presented in Table 1, narrow-band gap semiconductors $K_6C_{60}$ (alkali fullerides), $Au_2Cs_2I_6$, and $Ag_2GeBaS_4$ had total indirect band gaps of 1.28, 2.35, and 2.41 eV, respectively. From Figure 2a, the calculated values for $K_6C_{60}$ are: The total indirect band gap is 1.28 eV, band gaps $E_{vi}$ and $E_{ci}$ are 0.61 and 0.28 eV, respectively, and the width of the IB, $\Delta E_i$ is 0.39 eV. The band gap of 1.28 eV makes an optimal compound for the PV applications as their light responses are in the infrared region. Also, the IB will help the material to absorb additional photons with lower energy. It should be noted that $K_6C_{60}$ is already known as a semiconductor and the nature of the band structure is not well explained about the IB. However, they explained that the electronic structure of crystalline $K_6C_{60}$ is indirect band gap of 0.48 eV. The DOS around the VB maximum is very similar to that of the isolated $C_{60}$ molecule, and the K atoms are almost completely ionized.

Similarly, from Figure 2b, the calculated values for $Au_2Cs_2I_6$ are as follows: The total indirect band gap is 2.35 eV, band gaps $E_{vi}$ and $E_{ci}$ are 0.64 and 1.01 eV, respectively, and the width of the IB, $\Delta E_i$ is 0.70 eV. The band gap of 2.35 eV for $Au_2Cs_2I_6$ shows that the material has its response to light in the visible region.
For Au$_2$Cs$_2$I$_6$, the IB region has the optimal thickness to balance the absorption rate and recombination rate. In Figure 2b, Au$_2$Cs$_2$I$_6$ has a broad band dispersion of IB, enough to produce an optical depth for subgap light, ensuring the compound to absorb subgap light so that it can be considered as a potential PV material.

From Figure 2c, the calculated values for Ag$_2$GeBaS$_4$ are:
- The total indirect band gap is 2.41 eV, band gaps $E_{vi}$ and $E_{ci}$ are 0.90 and 0.35 eV, respectively, and the width of the IB is 1.16 eV. The band gap of 2.35 eV for Ag$_2$GeBaS$_4$ shows that the material has its response to light in the visible region. Here, we observe that the width of the IB, $\Delta E_{i}$ in Ag$_2$GeBaS$_4$ is much higher than $E_{ci}$ and $E_{vi}$. Because of the broadness of the IB, photons can also be absorbed by the electrons from lower-energy states of the IB to excite to higher-energy states of IB. When the IB broadens, the absorption of photons for the transition of electrons from the VB to lower-energy states of IB as well as from the higher-energy states of IB to CB will be reduced. These effects will lead to lower efficiencies of the solar cell based on Ag$_2$GeBaS$_4$. It has been shown that the efficiency limit for an IB solar cell is reduced from higher to lower efficiencies if the width is infinitesimally significant. It is important to note that all of these three materials, K$_6$C$_{60}$, Au$_2$Cs$_2$I$_6$, and Ag$_2$GeBaS$_4$ present indirect band gaps.

As presented in Table 2, the wide-band gap semiconductors CuAgPO$_4$, Ag$_2$ZnSnS$_4$, Au$_2$Cs$_2$Br$_6$, Ag$_3$AsS$_4$, Ag$_2$KSbS$_4$, Na$_3$Se$_4$Sb, AgK$_2$SbS$_4$, and AsRb$_3$Se$_4$ had the total band gaps of 2.62, 2.70, 2.71, 2.77, 2.93, 2.97, and 3.15 eV, respectively. Figures 3a–d and 4a–d show the calculated band structures of CuAgPO$_4$, Ag$_2$ZnSnS$_4$, Au$_2$Cs$_2$Br$_6$, Ag$_3$AsS$_4$, Ag$_2$KSbS$_4$, Na$_3$Se$_4$Sb, AgK$_2$SbS$_4$, and AsRb$_3$Se$_4$ with IB, respectively. The calculated values of $E_{vi}$, $E_{ci}$, and the total band gaps are presented in Table 2. The band gap type of the above eight compounds is direct band gap except for Ag$_2$KSbS$_4$ (indirect band gap). From Figure 2c, the calculated values for Ag$_2$ZnSnS$_4$ are:
- The total direct band gap is 2.70 eV, band gaps $E_{vi}$ and $E_{ci}$ are 0.47 and 0.57 eV, respectively, and the width of the IB is 1.66 eV. The band gap of 2.70 eV for Ag$_2$ZnSnS$_4$ shows that the material has its response to light in the visible region. Here, we observe that the width of the IB, $\Delta E_{i}$ in Ag$_2$ZnSnS$_4$ is much higher than $E_{ci}$ and $E_{vi}$. The increase in the IB width leads to a decrease in efficiency; however, it is still significantly higher than that of a single-band gap solar cell. The band gaps associated with optimum efficiencies are constant for all IB solar cells when the IB width exceeds 2 eV.

In general, the electrochemical potentials of the electrons in the different bands are close to the edges of the bands. The
open-circuit voltage of any solar cell is the difference between the CB minimum at the electrode in contact with the n-type side and the VB maximum at the electrode in contact with the p-type side. Thus, the maximum photovoltage of IB solar cells on the materials presented in Tables 1 and S1 is limited to 2.41 and 3.51 eV, respectively. Ag₅GeBaS₄ is still capable of absorbing energy photons above 0.28 eV in Table 1 and Ag₅SiSO₄ of 0.47 eV in Table 2. IB solar cells can deliver a maximum photovoltage by absorbing two sub-band gap
photons to produce one high-energy electron; the laws of thermodynamics would be violated if this were not the case.1

All of the 17 semiconductor compounds presented in this work have properties that make them suitable for PV applications; we show here the DOS analysis for three compounds, namely, Au2Cs2I6, Ag2GeBaS4, and Ag2ZnSnS4. The band gaps of 1.28 and 2.41 eV, respectively, make Au2Cs2I6, Ag2GeBaS4, and Ag2ZnSnS4 optimal PV materials. Solar cells based on Ag2ZnSnS4 materials are interesting as a high energy gap semiconductor for PV applications; we show here the DOS analysis for three compounds, namely, Au2Cs2I6, Ag2GeBaS4, and Ag2ZnSnS4. We observed excellent IB peaks between CB and VB in the three materials, which report on the possibilities to integrate Ag2ZnSnS4 in the Cu-based solar cells as an additional absorption layer.40 The total DOS of Au2Cs2I6 in Figure 5 shows that the IB is formed in the energy region between 0.47 and 2.13 eV, and the IB composed of the Sn 5s band and the S 2p band as shown in Figure 7. The IB region has the optimal energy region between 0.90 and 2.06 eV of the total DOS of Ag2GeBaS4. We have also plotted the PDOS at the IB mainly composed of the S 2p band and the Ge 4s band as well as the smaller mixing of the Ba 4d band. For Ag2ZnSnS4, the IB is formed in the energy region between 0.47 and 2.13 eV, and the IB composed of the Sn 5s band and the S 2p band is shown in Figure 7. The IB is formed in the energy region between 0.47 and 2.13 eV, and the IB composed of the Sn 5s band and the S 2p band is shown in Figure 7.

Figure 6. Total and site PDOS of Ag2GeBaS4. The Fermi level is set to zero and marked by a vertical dotted line.

The PDOS at the IB mainly composed of electron density, as shown in Figure 7. In Figures 5–7, broadening of IB indicates a highly parabolic dispersion relationship that induces lower values for the DOS.41 From Tables 3 and 4, the electron effective masses of Au2Cs2I6, Ag2GeBaS4, and Ag2ZnSnS4 are 0.095 m0, 0.021 m0, and 0.025 m0, respectively. Lower values for the electron effective mass are expected because the effective mass is directly related to the values of DOS. In addition, the IB region has the optimal thickness to balance the absorption rate and the recombination rate.37 We may expect the effective IBSC to have IB thickness enough to ensure these materials to absorb sufficient subgap light. We conclude that the conversion efficiency of bulk IBSC strongly depends not only on the band gap but also on the position and thickness of IB and DOS.37,41

### EFFECTIVE MASS CALCULATION

The calculation of the effective mass is important for a detailed study of energy levels in solar devices. The conductivity effective masses of electrons and holes affect the mobility, electrical resistivity, and free-carrier optical response of photovoltaic applications.32 To investigate the electron/hole conduction properties of the identified IB materials, we have computed the electron/hole effective mass at the VB/CB. For an excellent IB, a low effective mass corresponds to a high mobility of the electrons/holes at the VB/CB and consequently high conductivity. For the EM calculation, we have employed the effective mass calculator (EMC).43 EMC implements the calculation of the effective masses at the bands extreme using the finite difference method (FDM) (not the band-fitting method). The effective mass (m*) of charge carriers is defined as3

\[
\left( \frac{1}{m^*} \right)_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 E_k}{\partial k_j}, \quad i, j = x, y, z
\]

Figure 7. Total and site PDOS of Ag2ZnSnS4. The Fermi level is set to zero and marked by a vertical dotted line.

**Table 4. Effective Mass of Wide-Band Gap IB Compounds**

| serial no. | plane directions | compound | m*_{xx} | m*_{yy} | m*_{zz} | m*_{xy} | m*_{yz} | m*_{zx} |
|-----------|-----------------|----------|---------|---------|---------|---------|---------|---------|
| 1.        | 100             | CuAgPO4  | 3.875   | 4.969   | 14.229  |         |         |         |
| 2.        | 110             | Ag2ZnSnS4| 0.033   | 0.237   | 0.025   |         |         |         |
| 3.        | 110             | Au2Cs2I6 | 0.870   | 1.810   | 0.806   |         |         |         |
| 4.        | 100             | Ag2AsS4  | 0.200   | 0.234   | 0.012   |         |         |         |
| 5.        | 110             | Ag2KSBs4| 0.125   | 0.526   | 0.034   |         |         |         |
| 6.        | 110             | Na2Se5b  | 0.377   | 0.381   | 0.085   |         |         |         |
| 7.        | 100             | Ag2KBS4  | 1.524   | 12.025  | 1.007   |         |         |         |
| 8.        | 100             | AsRbS5b  | 6.213   | 84.330  | 2.595   |         |         |         |
| 9.        | 100             | AsCs5S4  | 8.213   | 24.794  | 3.561   |         |         |         |
| 10.       | 110             | Al2HgSe4 | 0.070   | 0.255   | 0.021   |         |         |         |
| 11.       | 100             | PdFbF4   | 0.391   | 0.592   | 0.094   |         |         |         |
| 12.       | 100             | C2TeF4   | 3.293   | 5.165   | 7.659   |         |         |         |
| 13.       | 100             | AlMoVO7  | 1.680   | 2.634   | 0.053   |         |         |         |
| 14.       | 110             | Ag6SiSO8 | 0.145   | 2.634   | 0.053   |         |         |         |
where $x$, $y$, and $z$ are the directions in the reciprocal Cartesian space $(2\pi/a)$, $E_i(k)$ is the dispersion relation for the $ith$ electronic band, and indices $i$ and $j$ denote reciprocal components. The explicit form of the symmetric tensor in the right-hand side of eq 1 is:

$$\frac{d^3E}{dk^2} = \left( \begin{array}{ccc}
\frac{d^2E}{dk_x^2} & \frac{d^2E}{dk_x dk_y} & \frac{d^2E}{dk_x dk_z} \\
\frac{d^2E}{dk_y dk_x} & \frac{d^2E}{dk_y^2} & \frac{d^2E}{dk_y dk_z} \\
\frac{d^2E}{dk_z dk_x} & \frac{d^2E}{dk_z dk_y} & \frac{d^2E}{dk_z^2}
\end{array} \right)$$

(2)

The effective mass components are the inverse of the eigenvalues of eq 2, and the principal directions correspond to the eigenvectors.\protect

To better understand the effective mass of semiconductors, it is not possible to fit the band to the quadratic polynomial. In this case, the results from the parabolic fitting can be reproduced with the FDM.\protect

The FDM employed to solve the effective mass approximation equations because the spurious solutions can be included in the formalism, and the FDM can be solved by the hard equation having a high degree of polynomial.\protect

This approach is quite reliable, and it was successfully applied for several classes of materials in the literature.\protect

We present the effective masses of 14 compounds in Tables 3 and 4. The effective mass of an electron was computed from the minimum of the CB; the effective mass of the heavy hole was computed from the maximum of the VB curvature, whereas the second VB curvature was used for the heavy hole, heavy hole, and electron, which are parabolic-fitted values with a step size of 0.05 (1/bohr). The three narrow-band gap compounds, $K_6C_60$, $Au_2Cs_4I_6$, and $Ag_2GeBaS_4$, have low effective masses, as presented in Table 3.

The thirteen wide-band gap compounds in Table 4 have effective masses of electron lower than those of light holes and heavy holes except for CuAgPO$_4$. The effective masses of electron of photovoltaic materials silicon (Si), germanium (Ge), and gallium arsenide (GaAs) are 0.26$m_e$, 0.067$m_e$, and 0.12$m_e$, respectively. On the other hand, $Ag_2ZnSnS_4$ has 0.46$m_e$ and $CuAgPO_4$ has 0.26$m_e$. Hence, the effective masses of electron of narrow-band gap and wide-band gap materials are approximately equal to those of the photovoltaic materials. From Table 4, the effective mass of an electron is 0.025$m_e$ for $Ag_2ZnSnS_4$ in [110] plane direction. We observed from Jing et al. that the effective mass of an electron is 0.16$m_e$ for $Ag_2ZnSnS_4$ in [100] plane direction.\protect

Hence, we found a lower effective mass in [110] direction than in [100] direction. These effective masses are better described by the band structures of the most curved parabolic band, as shown in Figures 3–5. Because of the effective masses for the presented materials, in this article, the electron mobility from VB to CB will be higher and the recombination effect will be lower.

## CONCLUSIONS

We have carried out a comprehensive study of the electronic band structures of 2100 new bulk compounds using first-principle calculations with the DFT. Among these compounds, we have found that only 17 compounds have IBs. These compounds could be potentially used as photovoltaic materials based on the detailed studies of band structure, the DOS and effective mass calculations. Our effective mass calculations show that these compounds have high electron/hole conduction properties, which make them suitable for PV applications. Although we have studied 2100 new compounds from the ICSD database, our study clearly demonstrates the possibility of having more IB materials from the list of currently known compounds from the database. Thus, we are in the process of investigating more IB-compounds and results of the detailed analysis will be published in a forthcoming article.

## COMPUTATIONAL DETAILS

Total energies have been calculated by the projected augmented plane-wave (PAW) implementation of the Vienna ab initio simulation package.\protect

Ground-state geometries were determined by minimizing stresses and the Hellman–Feynman forces using the conjugate-gradient algorithm with a force convergence threshold if $10^{-3}$ eV Å$^{-1}$. Brillouin-zone integration was performed using the Monkhorst–Pack $k$-meshes with a Gaussian broadening of 0.1 eV. A 600 eV kinetic energy cutoff was used for the plane-wave expansion. All of these calculations usually set to use approximately the same density of $k$-points in the reciprocal space for all structures. Because a large variety of structures was considered in this study, both metallic and insulating, we ensured that the $k$-points mesh was dense enough to determine the total energy with meV/atom accuracy. All structures containing transition elements are treated using the spin-polarized approach. In some cases, the starting magnetization vanished as self-consistency was reached. For all of these computations, the starting structures were directly taken from the ICSD database and input parameters, and file generation was done automatically by locally developed code “_Tool”. For the calculation of band structure, the $k$-point files were generated again with the help of locally developed code “KPATH”. The information about the high symmetric points of the $k$-vector in the Brillouin zone was taken from the Bilbao Crystallographic Server.\protect

All of the calculated electronic structures of the studied systems are documented in the DFTBD database. For the transition metals, we have used exchange-correlation functional with the Hubbard parameter correction (GGA+U), following the rotationally invariant form. The full details about the computed $U$ and $J$ values are presented in the DFTBD database website.\protect

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