CsPd$_{0.875}$Cr$_{0.125}$I$_3$: PROMISING CANDIDATE FOR THERMOELECTRIC APPLICATIONS

We study the electronic structure, magnetization, and thermoelectric properties of CsPd$_{0.875}$Cr$_{0.125}$I$_3$ obtained by doping CsPdI$_3$ with atoms of the 3$d$ transition metal Cr. By applying the generalized-gradient-approximation (GGA) and the GGA $+ U$ one, we found that CsPd$_{0.875}$Cr$_{0.125}$I$_3$ alloy exhibits a completely metallic characteristic. Changes in the thermoelectric properties of the alloy are determined with the use of the BoltzTrap code. The electronic thermal conductivities ($k/\tau$), Seebeck coefficients (S), power factors (PF), and electrical conductivities ($\sigma/\tau$) are calculated. The value of the ZT merit factor is near 1 at room temperature, by indicating that CsPd$_{0.875}$Cr$_{0.125}$I$_3$ is a good candidate for thermoelectric applications at high and low temperatures.

Keywords: thermoelectric, perovskite, solar cell, DFT, magnetic materials.

1. Introduction

Perovskites are vastly studied materials due do their extensive variety of propitiusd physical properties, including those for spintronics and superconductivity (CH$_3$NH$_3$PbI$_3$–$x$Cl$_x$) [1], solar cells (FA)$_y$(MA)$_{1-y}$PbBr$_2$I$_3$–$x$) [2], multiferroicity (BiFe$_{1-y}$Sc$_y$O$_3$) [3], and colossal magnetoresistance (RE$_{1-x}$AE$_x$MnO$_3$ (RE = La, Pr, Sm, etc. and AE = = Cu, Sr, Ba,Pb)) [4].

The power conversion efficiency of perovskite-based solar cells is now becoming comparable to that of silicon photovoltaics, which is employed in the first successful experimental implementation of halide perovskite materials in solar cells by Kojima et al. [5]. Compared to other twenty-eight conventional solar cell materials, they provide the lowest cost in the solar energy technology [6–8]. In 2012, researchers first discovered how to make a stable, thin-film perovskite solar cell with light photon-to-electron conversion efficiencies over 10%, using lead halide perovskites as the light-absorbing layer. Since then, the sunlight-to-electrical-power conversion efficiency of perovskite solar cells has skyrocketed, with the laboratory record standing at 25.2% [9]. Researchers are also combining perovskite solar cells with conventional silicon solar cells, whose record efficiencies for these “perovskite on silicon” tandem cells are currently 29.15% [10] (surpassing the record of 27% for conventional silicon cells) and rise rapidly. With this rapid surge in cell efficiency, perovskite solar cells and perovskite tandem solar cells may soon become cheap, highly efficient alternatives to conventional silicon solar cells [10–12].

Perovskite semiconductors offer an option that has the potential to rival the efficiency of multijunction solar cells [13], but can be synthesized under more common conditions at a greatly reduced cost. Rivaling the double, triple, and quadruple solar cells, there are all-solar cells with a max power conversion efficiency of 31.9% [14], all-perovskite triple-junction cell
Fig. 1. Crystal structure of CsPd$_{0.875}$Cr$_{0.125}$I$_3$.

Fig. 2. Band structure for high-symmetry directions in the Brillouin zone for CsPd$_{0.875}$Cr$_{0.125}$I$_3$ using the GGA + $U$ method.

reaching 33.1% [15]. These multijunction perovskite solar cells, in addition to being available for cost-effective synthesis, also maintain a high power conversion efficiency under varying weather extremes making them utilizable worldwide [16].

Until now, due to their extraordinary features, the perovskite groups are received much attentions, particularly by theoretician workers [17–28]. Nevertheless, although large efforts were spent on different perovskite compounds [29–37], we need the clarification and identification of the fundamental physical characteristics of alloys. For that purpose, the current contribution reports on the electronics, magnetism, and thermoelectric properties of Cr-doped CsPdI$_3$. The computations are performed using $ab$ initio calculations based on the density functional theory (DFT) within the GGA-PBE and GGA + $U$. More details about the methods used are given in the following section.

2. Computational Method

The considered CsPdI$_3$ is presumed to have the ideal cubic perovskite structure ($\bar{4}2m$). The computations are based on the super cell (i.e., $2 \times 2 \times 2$) in which the Pb atom that is at $(0.5, 0.5, 0.5)$ site in the super cell cubic structure of CsPdI$_3$ is replaced by Cr atoms, respectively. We have established an elementary crystal structure which contains 40-atoms. The positions of the atoms during the relaxation are established to correspond to the cubic symmetry of the space group PM-3M(n221). The structure of the crystal for the Pd$_{0.875}$Cr$_{0.125}$I$_3$ material is shown in Fig. 1. We have used the full-potential linearized augmented plane wave (FP-LAPW) as implemented in the WIEN2K code [38]. To include the exchange-correlation part in the total electronic energy, the revised Perdew–Burke–Ernzerhof scheme within the GGA [39] is used. The Cr 3$d$ is described through the use of the GGA + $U$ approach [40]. This method uses an effective parameter, $U_{\text{eff}} = U + J$, in which $U$ represents the Hubbard parameter, and $J$ represents the exchange parameter. The Hubbard parameter approach, which includes the exchange-correlation potential, is also very efficient to study strongly correlated electrons, in which the band-gap of the given materials could be found more precisely. Then, for such cases, we took the core electrons as relativistic, while the valence electrons are taken to be semirelativistic. These assumptions seem to be more accurate for the present method and for the full potential system. We considered the $U_{\text{eff}}$ value as 4.97 eV. This is similar to those found in Refs. [41, 42].

The thermoelectric properties of CsPd$_{0.875}$Cr$_{0.125}$I$_3$ materials have been obtained, when we apply the theory of Boltzmann transport and use a BoltzTraP code [43, 44].

3. Results and Discussion

The electronic band structure and the density of states are computed using GGA and GGA + $U$ for CsPd$_{0.875}$Cr$_{0.125}$I$_3$ along high-symmetry directions in the Brillouin zone as indicated in Figs. 2 and 3. The non-existence of a forbidden gap at the Fermi level...
Individual and net magnetic moment ($\mu_B$)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Approximations</th>
<th>$m_{Pd}$</th>
<th>$m_{Cr}$</th>
<th>$m_I$</th>
<th>$m_{Cs}$</th>
<th>$m_{int}$</th>
<th>$m_{total}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsPd$<em>{0.875}$Cr$</em>{0.125}$I$_3$</td>
<td>GGA + $U$</td>
<td>0.0957</td>
<td>3.9214</td>
<td>-0.03</td>
<td>0.0055</td>
<td>0.1752</td>
<td>4.6021</td>
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<tr>
<td></td>
<td>GGA</td>
<td>0.1608</td>
<td>3.8756</td>
<td>-0.03</td>
<td>0.0001</td>
<td>0.2835</td>
<td>4.5961</td>
</tr>
<tr>
<td>BiCrO$_3$ [45]</td>
<td>EXP</td>
<td>-</td>
<td>3.87</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.161</td>
</tr>
<tr>
<td>Ba$_2$CrTaO$_6$ [46]</td>
<td>GGA + $U$</td>
<td>-</td>
<td>2.391</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.00</td>
</tr>
<tr>
<td>PrCrO$_3$ [47]</td>
<td>GGA + $U$</td>
<td>-</td>
<td>2.34734</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.00003</td>
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![Fig. 3. Total density of states (TDOS)](image)

Fig. 3. Total density of states (TDOS)

oh the studied material confirms its metallic behavior indicating the existence of conductor features.

The obtained interstitial, atom-resolved and total magnetism moment of CsPd$_{0.875}$Cr$_{0.125}$I$_3$ are given in Table. The main thing, namely the total magnetic moment, is due to the Cr atoms. Small contributions come from interstitial regions and the moments of Cs, Pd, and I are negligible. The obtained data regarding the magnetic moment for Cr atoms are in agreement with those of experiment and theory cited in Refs. [45–47].

Presently, using thermoelectrics, it is possible to recapture some of the waste energy lost into the atmosphere and to convert it into electricity. The efficiency of a thermoelectric material in any power generator or cooler depends on the dimensionless constant $ZT = S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa$ designates the thermal conductivity, and $PF$ is a power factor. The thermoelectric transport parameters for both pristine and doped CsPd$_{0.875}$Cr$_{0.125}$I$_3$ materials are illustrated in Figs. 4–8. $T\sigma$ is related to the temperature effect with the essential thermoelectric parameters that are $(h/\tau), (\kappa/\tau)$, the power factor $PF = S^2\sigma/\tau$, and the $(ZT)$ factor. They have been considered in Refs. [48, 49]. The BoltzTrap code has been used to determine the thermoelectric properties; the efficiency of these properties is assessed by determining the transport parameters as functions of the temperature ($T$). The last coefficient characterizes the efficiency of this material, and the criterion $ZT \geq 1$ is retained in general for applications.

The Seebeck coefficient ($S$) for both pristine and doped CsPdI$_3$ at three constant temperatures is

shown in Fig. 4, at 300 K, CsPd$_{0.875}$Cr$_{0.125}$I$_3$ and CsPdI$_3$ compounds of interest are remarked to have high ($S$) values for $n$-type carriers which diminish, as the temperature grows; CsPd$_{0.875}$Co$_{0.125}$I$_3$ show larger $S$ than that of CsPdI$_3$ compound [50, 51].

The total thermal conductivity $\kappa_e$ (see Fig. 5) for both pristine and doped CsPdI$_3$ includes electron $\kappa_e$ and lattice $\kappa_{\text{lat}}$ thermal conductivities. The value of $\kappa_e$ is calculated by using $\kappa_e = LT\sigma$, where $L$ is the Lorenz number with the standard value. We remark also that the thermal conductivity is enhanced, when the temperature is increased for CsPd$_{0.875}$Cr$_{0.125}$I$_3$ in the positive range of the chemical potential. The maxima are localized at 14.6 (900 K), 9.4 (900 K) and 151.2 (900 K) for CsPd$_{0.875}$Cr$_{0.125}$I$_3$ (up) and CsPdI$_3$ (down), respectively. Meanwhile, we can clearly seen that the thermal conductivity at room temperature is smaller than those that correspond to 600 and 900 K. Thus, the thermal properties of the material of interest are completely sensitive to the energy of solar photons. The intrinsically low thermal conductivity ($\kappa_e \approx 0.70$ W/mK (up) and $\kappa_e \approx 0.96$ W/mK (down)) of CsPd$_{0.875}$Cr$_{0.125}$I$_3$ (up) and CsPdI$_3$ (down) is comparable to those of other materials such as Ag$_2$SbTe$_2$ ($\kappa \approx 0.73$ W/mK at 600 K) [52], Ag$_5$TI$_3$S$_3$ ($\kappa \approx 0.27$ W/mK at 600 K) [53], BiCuOSe ($\kappa \approx 0.45$ W/mK at 600 K) [54], $t_2$Bi$_2$Se$_3$ ($\kappa \approx 0.43$ W/mK at 600 K) [55], Ag$_4$Mo$_8$S$_{11}$ ($\kappa \approx 0.73$ W/mK at 600 K) [56], and ($\kappa \approx 0.67$ W/mK at 600 K) of both XBi$_4$S$_7$ (X = Mn, Fe) compounds [57].

The results for the electrical conductivity ($\sigma/\tau$) according to ($\mu$) are shown in Fig. 6. It is seen that, in all cases, the temperature $T = 300$ K induces the largest electric conductivity, depicting the mobility which becomes higher at the largest temperature, by diminishing the electrical conductivity. The variation of the coefficients with a change in the chemical potential is dramatic. This indicates that the smallest carrier concentration is sufficient for achieving the efficient thermoelectric performance. The calculated electrical conductivities ($\sigma/\tau$) for CsPd$_{0.875}$Cr$_{0.125}$I$_3$ (up) and CsPdI$_3$ (down) at 300 K are $10.14 \times 10^{19}$ and $8.30 \times 10^{19}$ $\Omega^{-1}$m$^{-1}$s$^{-1}$, respectively. By com-
paring the results on the electrical conductivity with those reported in [58–61], we found that the value of \(\sigma/\tau\) in our systems is higher than that found in \(\text{t}_2\text{gBiAg(Cl, Br)}\)\text{6} [58]. This may be due to the metallic character exhibited by these materials which show a lot of electron energy levels which are near the Fermi level. Some there exist a lot of electrons which are ready to move. The higher electrical conductivity for those materials induces a larger dielectric constant [62] that is important for reducing the exciton binding energy [63]. These materials can be used for solar cell applications.

We define the power factor (PF) as \(PF = S^2\sigma/\tau\). Figure 7 depicts the change in PF versus \((\mu)\) and \(T\) (K). We note that the PF is augmented, when the temperature varies from 0 to 900 K. For temperatures which are smaller than 300 K, the PF rate of enhancement seems to be very moderate. However, beyond this temperature, it augments rapidly with augmenting the temperature. For PF which is lower than one, the voltage and current are not in phase. In fact, for the same amount of useful power transferred, a load with a low PF in an electric power system shows a higher current than with loads with a higher PF. By comparing the results on PF with those reported for SnSe. The PFs remain at a high value \(\sim 50.60 \times 10^{10}\) and \(30.34 \times 10^{10}\) (\(\text{Wm}^{-1}\text{K}^{-1}\)) around 773 K for \(\text{CsPd}_{0.875}\text{Cr}_{0.125}\text{I}_3\) (up) and \(\text{CsPdI}_3\) (down), which is twice higher than that of \(\sim 6.4 \text{ Wm}^{-1}\text{K}^{-2}\) at 773 K for the SnSe [64].

To know the efficiency of a thermoelectric material, it is necessary to determine the value of \(ZT\). In the present study, \(ZT\) contains the total thermal conductivity \(\kappa = \kappa_e + \kappa_{\text{lat}}\). Our calculated \(ZT\) for both pristine and doped \(\text{CsPdI}_3\) are plotted in Fig. 8. The value of \(ZT\) for \(\text{CsPd}_{0.875}\text{Cr}_{0.125}\text{I}_3\) (up) and \(\text{CsPdI}_3\) (down) is high and almost constant up to 300 K. Then it decreases slightly, as the temperature increases. We observe that the \(ZT\) value is about 0.976 and 0.325 at room temperature for \(\text{CsPd}_{0.875}\text{Cr}_{0.125}\text{I}_3\) (up) and \(\text{CsPdI}_3\) (down), respectively. It turns out that these values are very high as compared to the available thermoelectric materials, and we can explain this by the high Seebeck coefficients in the studied systems. The present results also indicate the maximum potential of the \(\text{CsPd}_{0.875}\text{Cr}_{0.125}\text{I}_3\) as a high temperature thermoelectric material, rather than the \(\text{CsPdI}_3\).
in view the above results on thermoelectric properties, we conclude that CsPd$_0.875$Cr$_{0.125}$I$_3$ shows a considerable thermoelectric performance accompanied by a significant $ZT$ which are than for many perovskite compounds reported till now. We cannot compare our results due to shortage of experimental or theoretical results. Nevertheless, these simulations can be considered as reference data for future investigations.

4. Conclusions

In the present work, the electronic, magnetic, and thermoelectric properties of CsPd$_0.875$Cr$_{0.125}$I$_3$ have been studied using the FP-LAPW method, in which we have applied GGA and GGA $+$ $U$ approximations. A metallic character has been shown by the electronic structures of the ferromagnetic configuration for CsPd$_0.875$Cr$_{0.125}$I$_3$ alloy. The main contribution to the magnetic moment is made by the Cr ions. High $ZT$ values of 0.976 and 0.988 were obtained for CsPd$_0.875$Cr$_{0.125}$I$_3$ (up) and CsPd$_0.875$Cr$_{0.125}$I$_3$(down), respectively. Our thermoelectric study predicts CsPd$_0.875$Cr$_{0.125}$I$_3$ as a probable thermoelectric material with considerable values of the $ZT$ factor at low temperatures. Finally, the investigated properties suggest the application of this material in thermoelectric devices.

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