Mixed-Cation Mixed-Metal Halide Perovskites for Photovoltaic Applications: A Theoretical Study

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ABSTRACT: Perovskite solar cells based on multiple cations have shown excellent optoelectronic properties with high power conversion efficiency. Herein, the structural, electronic, and optical properties of mixed-cation mixed-metal perovskites MA$_{1-x}$Cs$_x$Pb$_{0.25}$Sn$_{0.75}$I$_3$ were studied by employing the first-principles calculations for the first time. Our calculated results reveal that these perovskite materials possess direct band gaps in the range of 1.0—1.3 eV. Moreover, these compounds show excellent photovoltaic performance in terms of strong optical absorption coefficients compared with MAPbI$_3$. Particularly, they also exhibit good structural stability and decrement of lead content. These results demonstrated that mixed-cation mixed-metal perovskites may be potential candidates for high-efficiency light-absorbing materials.

INTRODUCTION

Lead halide perovskites have emerged as highly promising materials for photovoltaic applications in the past 10 years because of their excellent properties such as suitable band gap, strong optical absorption, high carrier mobility, and long charge-carrier diffusion length. The certified power conversion efficiency (PCE) was rapidly increased from 3.8% in 2009 to 25.2% in 2019, which is comparable to conventional silicon solar cells. The perovskite structure has a general chemical formula of ABX$_3$, where A is usually occupied by monovalent cations such as Cs$^+$, CH$_3$NH$_3$ $^+$ (MA$^+$), or CH(NH$_2$)$_2$ $^+$ (FA$^+$), B is occupied by divalent metal cations such as Pb$^{2+}$, Sn$^{2+}$, or Ge$^{2+}$, and X is occupied by halide anions such as Cl$^-$, Br$^-$, or I$^-$. Unfortunately, the perovskite solar cells with high PCE usually contain the toxic lead and the poor stability, which seriously restricts their commercial applications. The development of stable lead-free hybrid perovskites is still a big challenge to obtain high photovoltaic performance.

With regard to the all-inorganic lead perovskite CsPbX$_3$, CsPbI$_3$ is the best candidate because of the improved stability and suitable band gap (1.73 eV). However, α-CsPbI$_3$ is unstable below 634 K, and it can easily transform to a yellow nonperovskite δ-phase under room temperature. A theoretical study showed that a two-dimensional layered Ruddlesden—Popper perovskite Cs$_x$Pb$_{1-x}$I$_4$ may not be a good material for photovoltaic applications owing to its low carrier mobility and poor optical absorption. CsPbBr$_3$ was shown to have good charge transport properties, and it has significant potential in ferroelectric applications. Moreover, the Mo$_2$/CsPbBr$_3$ heterostructure can effectively retain some of the excellent properties of individual MoS$_2$ and CsPbBr$_3$.

A series of Ge-based halide perovskites have been synthesized, and the theoretical results indicate that Ge is a suitable substitution to replace the toxic Pb. MAPb$_{0.25}$ Ge$_{0.75}$I$_3$ can become a promising candidate for perovskite solar cells because of the proper band gap, lower effective masses, and better optical absorption. The photovoltaic performance of the mixed halide perovskite MAGeI$_3$—Cl$_x$ was investigated, and the transport and optical properties can be improved by increasing the concentration of I. The geometrical, electronic, and optical properties of the mixed metal perovskite RbGe$_{1-x}$Sn$_x$I$_3$ were systematically studied. The results found that RbGe$_{0.50}$Sn$_{0.50}$I$_3$ has superior transport and optical properties. Some investigations have been carried out to explore alternative lead-based hybrid perovskites, involving analogous Sn-based perovskites. Sn is an ideal candidate element to replace lead, which is located in the same periodic table. Moreover, they have similar ionic radius. However, the Sn$^{2+}$ ion is highly unstable and can be easily oxidized to Sn$^{4+}$, which leads to a great reduction in photovoltaic performance. The PCE of Sn-based perovskite solar cells is reported to be about 6%. Recently, the use of mixed MAPb$_{1-x}$Sn$_x$I$_3$...
perovskites for photovoltaic applications has been reported by experimental and theoretical works.\textsuperscript{20–23} The results have revealed that partial replacement of Pb with Sn can reduce the band gap, extending the absorption spectra toward the mid-infrared region of the solar spectrum.\textsuperscript{20} The higher PCE of 9.8\% has been reported for such perovskite materials, which leads to the consideration of their application to reduce the use of toxic Pb in perovskite solar cell devices.\textsuperscript{25}

In light of the potential applications of mixed Sn–Pb hybrid perovskites in replacing lead-based materials, it is valuable to explore good stability and lead-less perovskite materials and to improve the photovoltaic performance. In this work, we employed first-principles calculations to investigate the electronic and optical properties of mixed-cation mixed-metal halide perovskites. The choice of mixed Pb–Sn perovskites is motivated by the fact that these materials have broader optical absorption in the visible light region. Moreover, the amount of toxic Pb would be greatly reduced in these materials. Interestingly, our calculated results indicate that the band gaps of the mixed perovskites are slightly decreased by doping the Cs cation. The optical absorption can be further enhanced in the long-wavelength region of 600–1000 nm. In addition, these mixed perovskite materials possess better structural stability.

## RESULTS AND DISCUSSION

Geometry optimization of MA$_{1-x}$Cs$_x$Pb$_{0.25}$Sn$_{0.75}$I$_3$ compounds has been carried out using the MAPbI$_3$ tetragonal I4/mcm experimental cell parameters.\textsuperscript{18} The optimized structures of the MA$_{1-x}$Cs$_x$Pb$_{0.25}$Sn$_{0.75}$I$_3$ series are shown in Figure 1. The Goldschmidt tolerance factor ($t$) is usually used to evaluate the crystallographic stability of perovskites. The formula is as follows:\textsuperscript{26}

$$t = \frac{R_A + R_X}{\sqrt{2 (R_B + R_X)}}$$  \hfill (1)

where $R_A$, $R_B$, and $R_X$ are effective ionic radii for A, B, and X, respectively. The value of the tolerance factor $t$ should be in the range of 0.81–1.11.\textsuperscript{27} Our calculated $t$ values are variable from 0.84 to 0.87. These results preliminarily show that these mixed halide perovskites are stable.

To further examine the effect of Cs substitution, we have evaluated the formation energy of the mixed halide perovskites according to the following equation:

$$\Delta H = E(MA_{1-x}Cs_xPb_{0.25}Sn_{0.75}I_3) - (1 - x)E(MAI) - xE(CsI) - 0.25E(PbI_2) - 0.75E(SnI_2)$$  \hfill (2)

where $E(MA_{1-x}Cs_xPb_{0.25}Sn_{0.75}I_3)$, $E(MAI)$, $E(CsI)$, $E(PbI_2)$, and $E(SnI_2)$ are the energy of MA$_{1-x}Cs_xPb_{0.25}Sn_{0.75}I_3$, MAI, CsI, PbI$_2$, and SnI$_2$, respectively. $x$ is the ratio of Cs$^+$ doping, and we adopted the x value of 0, 0.25, 0.50, and 0.75, respectively. Our calculated ($\Delta H$) value for MAPbI$_3$ is 0.01 eV/f.u., which is well consistent with the previous theoretical values of −0.01\textsuperscript{28} and −0.02 eV/f.u.\textsuperscript{29} The results indicate that MAPbI$_3$ is marginally stable and it can decompose to MAI and PbI$_2$ under ambient condition. The calculated formation energies of the predicted perovskites are shown in Figure 2. It can be seen that all of our predicted mixed perovskites are highly stable.

![Figure 1. Optimized structures of (a) MAPb$_{0.25}$Sn$_{0.75}$I$_3$, (b) MA$_{0.75}$Cs$_{0.25}$Pb$_{0.25}$Sn$_{0.75}$I$_3$, (c) MA$_{0.50}$Cs$_{0.50}$Pb$_{0.25}$Sn$_{0.75}$I$_3$, and (d) MA$_{0.25}$Cs$_{0.75}$Pb$_{0.25}$Sn$_{0.75}$I$_3$.](https://dx.doi.org/10.1021/acsomega.9b04484)

As a photovoltaic material for solar cells, the band gap is crucial to the optical absorption in the visible light region. We have calculated the band structure to explore the electronic properties of predicted perovskites by using the optB86b-vdW and HSE06 functionals. The band gaps of perovskites calculated by the two functionals are shown in Figure 3. The band gap value of MAPb$_{0.25}$Sn$_{0.75}$I$_3$ with the optB86b-vdW functional is 0.71 eV, which is much lower than its experimental value. The band gap value of MAPb$_{0.25}$Sn$_{0.75}$I$_3$ with the HSE06 functional is 1.24 eV, which matches well with the previous theoretical value of 1.20 eV\textsuperscript{23} and reaches the experimental values of 1.25\textsuperscript{21} and 1.17 eV.\textsuperscript{20} The results of two methods demonstrate clearly the same tendency that the values of band gaps slightly decrease when the proportion of Cs$^+$ increases. The band gaps of mixed-cation halide perovskites are in the range of 1.0–1.3 eV. Moreover, both the valence band maximum (VBM) and conduction band minimum (CBM) of these perovskite materials are located at the same high symmetry point in the Brillouin region from optB86b-vdW calculations, indicating that these materials exhibit a direct

![Figure 2. Calculated formation energies of MA$_{1-x}$Cs$_x$Pb$_{0.25}$Sn$_{0.75}$I$_3$.](https://dx.doi.org/10.1021/acsomega.9b04484)
band gap feature. MA$_{1-x}$Cs$_x$Pb$_{0.25}$Sn$_{0.75}$I$_3$ with ideal band gaps in the visible absorption region can be potential candidates of lead-less photovoltaic materials.

It is important to explore the intrinsic reason for the variation of band gaps in halide perovskites. The band gaps of halide perovskites are mainly affected by structural distortion, and the key factor is the Pb−I−Pb bond angle.$^{30}$ The B−I−B (B = Pb or Sn) bond angles of these mixed perovskites are listed in Table 1. The larger distortion of the B−I−B bond is from the $ab$ plane. For MAPb$_{0.25}$Sn$_{0.75}$I$_3$ and MA$_{0.75}$Cs$_{0.25}$Pb$_{0.25}$Sn$_{0.75}$I$_3$, the $ab$ plane distortion may play an important role in tuning the band gap compared with MAPbI$_3$. However, both the $ab$ plane and the $c$-axis distortion should be crucial to tune the band gap for MA$_{0.50}$Cs$_{0.50}$Pb$_{0.25}$Sn$_{0.75}$I$_3$ and MA$_{0.25}$Cs$_{0.75}$Pb$_{0.25}$Sn$_{0.75}$I$_3$.

Figure 4 illustrates the density of states (DOS) and projected DOS for these mixed perovskites, calculated by the HSE06 functional. The results show that the compositions of DOS for the four materials are very similar. The VBM is mainly constituted by I-5p orbitals, while the CBM is mainly constituted by Sn-5p orbitals. The Cs/MA cations cannot affect the electronic states because they are far from the band edges.

The optical absorption is important to photovoltaic material in applications. The optical spectra of these mixed perovskites can be calculated through the complex dielectric function by the following equation$^{31}$

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$$  \hspace{1cm} (3)

Here, $\epsilon_1$ and $\epsilon_2$ are the real and imaginary parts of dielectric function, respectively, and $\omega$ represents the frequency of light. The absorption coefficient $I(\omega)$ was given below$^{32}$

$$I(\omega) = \frac{\omega}{2a}\left[\sqrt{\epsilon_1(\omega)^2 + \epsilon_2(\omega)^2} - \epsilon_1(\omega)\right]^{1/2}$$  \hspace{1cm} (4)

We used the optB86b-vdw functional along with the scissor correction in band gap calculation to gain as accurate as that of the HSE06 functional. The band gap is usually underestimated in Perdew–Burke–Ernzerhof (PBE) calculations and overestimated for the dielectric properties. Based on the scissor correction, we compare the optical absorption of Cs-doped MAPb$_{0.25}$Sn$_{0.75}$I$_3$ with that of the pure structure MAPbI$_3$, as shown in Figure 5a. When the wavelength is located in the range of 200−300 nm, the optical absorption of the studied perovskite materials is stronger than that of MAPbI$_3$, and the optical absorption coefficient can reach over $10^{-6}$ cm$^{-1}$. Moreover, their light absorption is also considerable in the

Table 1. B−I−B (B = Pb or Sn) Bond Angles of the Mixed MA$_{1-x}$Cs$_x$Pb$_{0.25}$Sn$_{0.75}$I$_3$ Perovskites

| B−I−B (B = Pb or Sn) | Bond angles (deg) |
|----------------------|------------------|
| in the $ab$ plane     | along the $c$-axis |
| MAPbI$_3$            | 150.0            | 176.0            |
| MAPb$_{0.25}$Sn$_{0.75}$I$_3$ | 155.3            | 175.7            |
| MA$_{0.75}$Cs$_{0.25}$Pb$_{0.25}$Sn$_{0.75}$I$_3$ | 155.7            | 176.3            |
| MA$_{0.50}$Cs$_{0.50}$Pb$_{0.25}$Sn$_{0.75}$I$_3$ | 158.5            | 172.2            |
| MA$_{0.25}$Cs$_{0.75}$Pb$_{0.25}$Sn$_{0.75}$I$_3$ | 159.6            | 171.8            |

Figure 3. Calculated band gap trends with different methods of MA$_{1-x}$Cs$_x$Pb$_{0.25}$Sn$_{0.75}$I$_3$ with the experimental value.

Figure 4. DOS of MA$_{1-x}$Cs$_x$Pb$_{0.25}$Sn$_{0.75}$I$_3$ at the HSE06 functional.
Figure 5. (a) Calculated optical absorption coefficients for MA$_{1-x}$Cs$_x$Pb$_{2x}$Sn$_{1-2x}$I$_3$ compared with that MAPbI$_3$. (b) Calculated optical absorption coefficients for MA$_{1-x}$Cs$_x$Pb$_{0.25}$Sn$_{0.75}$I$_3$ in the wavelength region between 600 and 1000 nm.

CONCLUSIONS

In summary, we have systematically studied the structural stability, electronic structures, and optical properties of MA$_{1-x}$Cs$_x$Pb$_{0.25}$Sn$_{0.75}$I$_3$ by employing the first-principles calculations to reveal their photovoltaic applications for the first time. These four compounds are direct band gap semiconductors and have good structural stability. The band gap values of these materials are in the range of 1.0–1.3 eV, which are suitable for photovoltaic devices. It should be noted that these compounds show excellent optical absorption coefficients in the visible light region. The above-mentioned performances clearly show that mixed-cation mixed-metal perovskite materials can serve as potential candidates for perovskite solar cells. Our calculations can provide theoretical guidance for the development of novel lead-less and stable perovskites for photovoltaic applications.

COMPUTATIONAL METHODS

The structural optimization and electronic properties of perovskite materials were calculated using density functional theory as implemented in the Vienna ab initio simulation package.33 The interaction between electron and ion was described by the projector-augmented wave method,34 while the generalized gradient approximation (GGA) of the PBE functional was used to describe the electron exchange correlation.35 The kinetic energy cutoff was 550 eV. The energy and force convergence criteria were set to 10$^{-5}$ eV and 0.01 eV/Å, respectively. The Monkhorst–Pack $k$ points used in the structural optimization and electronic properties were $6 \times 6 \times 6$ and $8 \times 8 \times 8$, respectively. The optB86b-vdW functional was applied to account for dispersion interactions in all calculations.36 It is well known that GGA–PBE usually underestimates the band gaps of halide perovskites. In order to obtain more accurate band gaps, we used Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional calculations.37 The precise Hartree–Fock exchange contribution for the hybrid functional was set to 30% in order to repeat the experimental value.

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Notes
The authors declare no competing financial interest.

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