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Theoretical Study on Optical Absorption of Lead-Free Double Perovskites $Cs_2AgBiBr_6$ and $Cs_2InBiBr_6$

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We have studied the optical absorption of lead-free double perovskites $Cs_2AgBiBr_6$ and $Cs_2InBiBr_6$ using the solutions of the Dirac-Kohn-Sham equations. It is found that the absorption coefficient of $Cs_2AgBiBr_6$ in the high-energy part of the solar spectrum is considerably large and that the absorption spectrum of $Cs_2InBiBr_6$ shows strong similarity to that of $CH_3NH_3PbI_3$ in the main part of the solar spectrum.

During the last decade, organic-inorganic lead halide perovskite $MAPbI_3$ (MA = CH_3NH_3) has been extensively studied as a promising material for photovoltaic applications.[1] However, the toxicity issue of lead is still an unsolved problem. Many studies have been carried out to find lead-free perovskite materials by substituting lead with other non-toxic elements.[2] Slavney *et al*. reported that the double perovskite $Cs_2AgBiBr_6$ shows a long photoluminescence lifetime of about 660 ns, which indicates that the material is a promising candidate.[3] However, they also noted that owing to its wide indirect band gap of 1.95 eV the application may be restricted to the optical absorber in a tandem solar cell. Another candidate is $Cs_2InBiBr_6$ and its family.[4,5] Nakajima *et al*. reported using first-principles calculations that $Cs_2InBiBr_6$ is one of promising materials, showing a direct band gap of 1.45 eV.[4] Volonakis *et al*. studied $A_2InBiBr_6$ (A = Cs, MA, $CH(NH_2)_2$) and proposed that the mixed-cation double perovskite $(Cs/MA/CH(NH_2)_2)_2InBiBr_6$ is a potential replacement for $MAPbI_3$.[5] Although their synthesizability is under investigation, it is worth studying the electronic and optical properties of $Cs_2InBiBr_6$ for gaining insight into the related class of lead-free perovskite materials. Interestingly, the band structures of $Cs_2AgBiBr_6$ and $Cs_2InBiBr_6$ are considerably different from each other although both the Ag and In atoms play the role of monovalent cation.[6] It thus seems also important to study the differences between their optical properties. For understanding the optical properties of $Cs_2AgBiBr_6$ and $Cs_2InBiBr_6$ in more detail, it is important to calculate their absorption coefficients quantitatively. In particu-

lar, since these materials contain heavy element Bi, it is indispensable to take into account all the relativistic effects including spin-orbit coupling (SOC). Note that the relativistic effects should be taken into account not only for one-electron energies but also for transition matrix elements. In this work, we study the optical absorption of $Cs_2AgBiBr_6$ and $Cs_2InBiBr_6$ as well as that of $MAPbI_3$ for comparison using the four-component spinors obtained as the solutions of the Dirac-Kohn-Sham equations for calculating the transition matrix elements within the independent particle approximation combined with a phenomenological approach.

We carried out all-electron calculations based on the density functional theory.[7–10] The generalized gradient approximation (GGA) to the exchange-correlation energy functional was adopted using the Perdew-Burke-Ernzerhof form.[11] The lattice constants and the atomic positions were optimized with the scalar relativistic full-potential linear-combination-of-atomic-orbitals method.[9] The double perovskites crystallizes in space group $Fm\bar{3}m$ while the crystal structure of MAPbI3 is assumed to be of space group $P1$ with a cube-shaped unit cell containing 12 atoms. Using the optimized structures, the band structures and the absorption coefficients were calculated with the fully relativistic full-potential linear-combination-of-atomic-orbitals method.[8] The absorption coefficients were obtained from the optical conductivity calculated within the independent particle approximation combined with a phenomenological approach.[10] The transition matrix elements were calculated using the four-component spinors obtained as the solutions of the Dirac-Kohn-Sham equations. Also, the phenomenological relaxation-time parameter $\hbar/\tau$ was introduced to simulate the lifetime of excitations; for all the materials studied in this work $\hbar/\tau = 0.3$ eV was used. The calculated absorption spectra were smoothed with gaussian of width 0.1 eV. The Brillouin zone sampling for the structure optimization were performed using a $4 \times 4 \times 4$ $\boldsymbol{k}$ point grid. We used 185 $\boldsymbol{k}$ points generated with the good-lattice-point method for calculating the self-consistent potential.[12] For calculating the absorption coefficients, we employed several sets of $\boldsymbol{k}$ points generated with the good-lattice-point method; we used 418 $\boldsymbol{k}$ points for $Cs_2AgBiBr_6$ and $Cs_2InBiBr_6$ while we used 4044 $\boldsymbol{k}$ points for $MAPbI_3$ to obtain well converged results. The atomic orbitals used in this work are of the same quality as used in our previous studies.[7–10]

The optimized lattice constants are 11.58, 12.03, and 6.41 Å for $Cs_2AgBiBr_6$, $Cs_2InBiBr_6$, and $MAPbI_3$, respectively. The experimental lattice constants are available for $Cs_2AgBiBr_6$ and $MAPbI_3$: 11.25 and 6.391 Å, respectively.[3,13] In Fig. 1, the band structures of $Cs_2AgBiBr_6$ and $Cs_2InBiBr_6$ are shown. $Cs_2AgBiBr_6$ shows an indirect band gap.[6] The GGA band gap is 1.08 eV, which is smaller than the band gap of 1.79 eV calculated with a hybrid exchange-correlation energy functional.[6] The large separation between the lowest and the
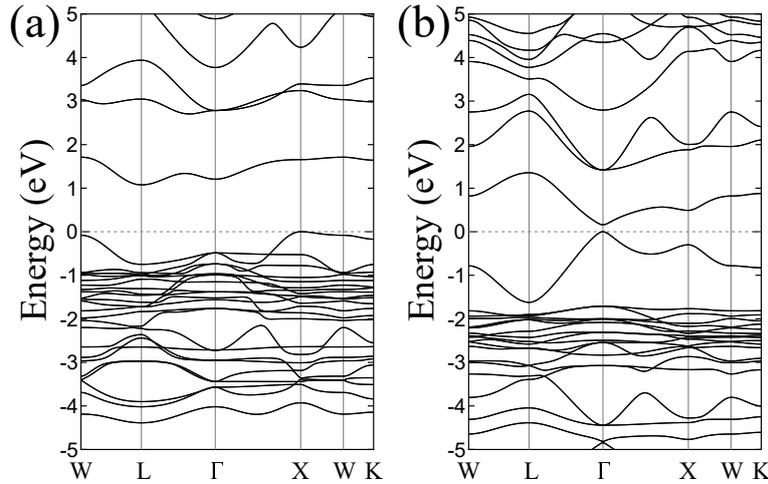
Fig. 1. Band structures of (a) $Cs_2AgBiBr_6$ and (b) $Cs_2InBiBr_6$. The zero of the energy is taken at the top of the valence bands.

second lowest conduction bands is due to SOC; the magnitude of the separation exceeds 1 eV. Moreover, the dispersion of the lowest and second lowest conduction bands is small. Our calculated band structure of $Cs_2AgBiBr_6$ is in good agreement with that reported by Filip *et al*.[14] On the other hand, $Cs_2InBiBr_6$ shows a direct band gap. The GGA band gap is 0.16 eV, which is smaller than the band gap of 1.45 eV calculated with a hybrid exchange-correlation energy functional.[4] The lowest and the second lowest conduction bands are also separated due to SOC. The dispersion of the lowest and the second lowest conduction bands as well as the highest valence band of $Cs_2InBiBr_6$ is larger than that of $Cs_2AgBiBr_6$.

In Fig. 2(a), the calculated absorption coefficients of $Cs_2AgBiBr_6$, $Cs_2InBiBr_6$, and $MAPbI_3$ are shown. Also, in Fig. 2(b), the calculated absorption coefficients of $MAPbI_3$, GaAs, and CdTe are shown together with the experimental ones.[15] For all the calculated absorption spectra, the scissors correction is used to correct the underestimation of the GGA band gaps; for $Cs_2AgBiBr_6$ and $Cs_2InBiBr_6$, we used the band gaps of 1.79 and 1.45 eV mentioned above, respectively, while, for $MAPbI_3$, GaAs, and CdTe, we used the experimental band gaps of 1.61, 1.43, and 1.44 eV, respectively.

In the calculated absorption spectrum of $Cs_2AgBiBr_6$, since the band gap, 1.79 eV, of $Cs_2AgBiBr_6$ is indirect, the absorption edge is located at a larger energy of 2.37 eV. The absorption spectrum shows a two peak structure. The first peak is at about 2.8 eV and the second peak at about 4.6 eV. The two peak structure is originated from the separation of the lowest and second lowest conduction bands due to SOC. The first peak corresponds to the optical transitions from the higher energy region of the valence bands to the lowest conduction bands.
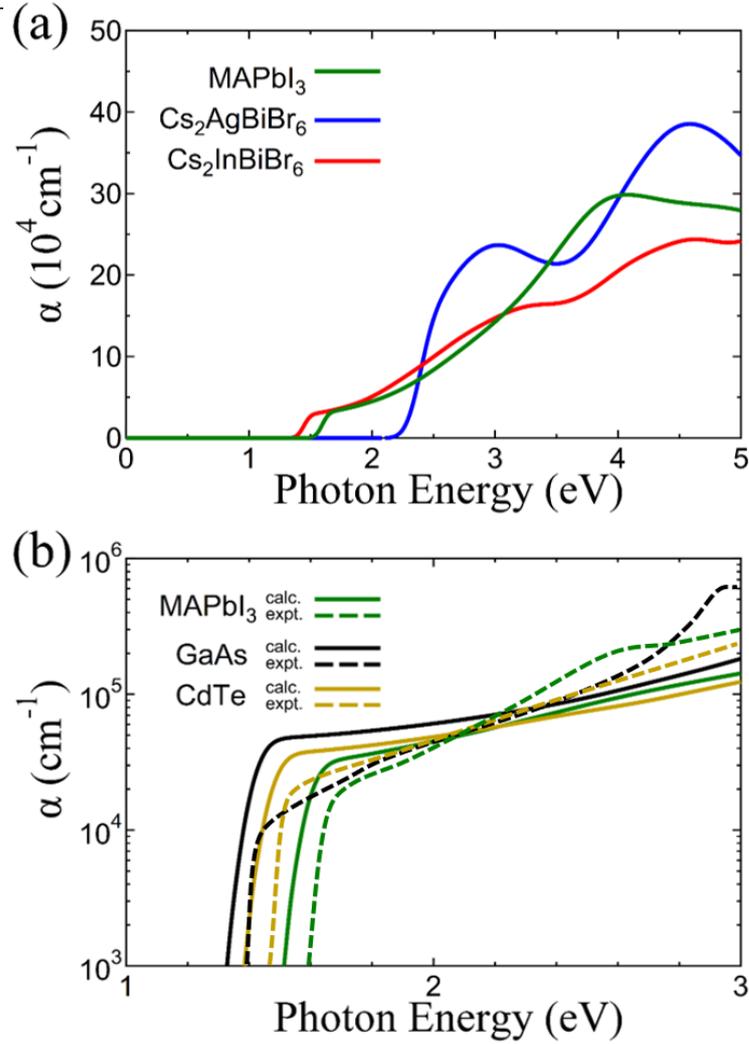
Fig. 2. (Color online) Calculated absorption coefficients α of (a) $Cs_2AgBiBr_6$, $Cs_2InBiBr_6$, and $MAPbI_3$ and (b) $MAPbI_3$, GaAs, and CdTe together with experimental ones. All the calculated absorption spectra are scissors-corrected.

The second peak corresponds to the optical transitions from the higher energy region of the valence bands to the second lowest conduction bands as well as those from the lower energy region of the valence bands to the lowest conduction bands. Note that owing to the small dispersion of the lowest and the second lowest conduction bands the two peak structure is clearly visible. It is also found that the absorption coefficient of $Cs_2AgBiBr_6$ increases more rapidly just above the absorption edge than those of $MAPbI_3$ and $Cs_2InBiBr_6$, exceeding 20×10^4 cm^{-1} at 2.8 eV. That is, $Cs_2AgBiBr_6$ shows very strong optical absorption in the high-energy part of the solar spectrum. Thus, the material is likely suited for a tandem solar cell.[3] The absorption spectrum of $Cs_2InBiBr_6$ shows a strong similarity to that of $MAPbI_3$ in the main part of the solar spectrum. Since the band gap of $Cs_2InBiBr_6$ is direct, the absorption edge is

located at 1.45 eV. The absorption spectrum of $Cs_2InBiBr_6$ also shows a two peak structure although the peaks are very broad; the first peak is at about 3.2 eV and the second peak at about 4.5 eV. The origin is again the separation of the lowest and the second lowest conduction bands due to SOC. However, since their dispersion is larger than that of $Cs_2AgBiBr_6$, the peaks are substantially broad. The strong similarity of the absorption spectrum of $Cs_2InBiBr_6$ to that of $MAPbI_3$ may indicate that $Cs_2InBiBr_6$ is a promising lead-free optical absorber alternative to $MAPbI_3$.[4,5]

Finally, we examine the reliability of the calculated absorption spectra in the main part of the solar spectrum, comparing them with the experimental ones as shown in Fig. 2(b) for $MAPbI_3$, GaAs, and CdTe.[15] We find an overestimation of the order of 10^4 cm^{-1} below 2 eV. On the other hand, the experimental absorption coefficients increase more rapidly than the calculated ones above 2 eV; the difference reaches the order of 10^5 cm^{-1} at 3 eV. Note that the agreement is better for $MAPbI_3$ and CdTe than for GaAs although the reason is not clear. Nevertheless, the general trend as well as the order of magnitude is reproduced in the main part of the solar spectrum. In view of this, the same level of reliability as $MAPbI_3$ is expected for the calculated absorption coefficients of $Cs_2AgBiBr_6$ and $Cs_2InBiBr_6$ because they are analogous materials to $MAPbI_3$.

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