Electronic and Optical Properties of CsGeX₃ (X = Cl, Br, and I) Compounds

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ABSTRACT: We used first-principles calculations to investigate the electrical and optical properties of CsGeX₃ (X = Cl, Br, and I) compounds. These materials present rich and unique physical and chemical phenomena, such as the optimal geometric structure, the electronic band structure, the charge density distribution, and the special van Hove singularities in the electronic density of states. The optical properties cover a slight red shift of the optical gap, corresponding to weak electron-hole interactions, strong absorption coefficients, and weak reflectance spectra. The presented theoretical framework will provide a full understanding of the various phenomena and promising applications for solar cells and other electro-optic materials.

1. INTRODUCTION

Nowadays, solar cell devices have become one of the outstanding systems in engineering applications and basic science research studies because they can provide eco-friendly and renewable energy and are efficient by using a special route to convert photon energy into electricity. The principal architectures of the perovskite solar cell include the absorber layer sandwich between the electron-transporting and hole-transporting layers, in which the first component is very important since it absorbs the electromagnetic wave and generates the electron–hole pairs. Apparently, the geometric, electronic, and optical features of these components are regarded as very important characteristics. These factors should be critical in determining the efficiency of light-generated currents and finding the best combination of the three kinds of core components.

Up to now, inorganic perovskite materials, such as CsPbX₃ (X = Cl, Br, and I), have attracted more and more research attention for energy harvesting applications due to their excellent photoelectronic properties. However, there are still many disadvantages, for example, the limit of large-scale applications owing to the toxicity of the lead element. Currently, the lead-free CsGeX₃ (X = Cl, Br, and I) compounds are other candidates to replace CsPbX₃ perovskites for solar cell and other applications. In fact, such compounds cover many interesting properties/novel features and have been investigated by both previous theoretical and experimental methods.

On the experimental side, Li et al. have successfully synthesized the CsGeI₃ compound and demonstrated that this material processes a high photocurrent (6 mA cm⁻²), which means that it is suitable for photovoltaic applications. To enhance the photocurrent generation of WS₂ nanoflakes, WS₂/CsGeBr₃ has been fabricated, with an external quantum yield and a responsivity of about 151% and 6.4 (A/W), respectively. The absorption edges of CsGeCl₃ and CsGeBr₃ are very sensitive and significantly red-shift under applied external hydrostatic pressure. This phenomenon was verified by the experiment of Schwarz and his co-workers. Besides, photoluminescence and absorption measurements of CsGeCl₃, CsGeBr₃, and CsGeI₃ have been reported.

On the theoretical aspects, the fundamental electrical and optical properties of the CsGeCl₃, CsGeBr₃, and CsGeI₃ materials have been investigated with various approaches, such as first-principles calculations, the effective mass approximation, and the tight-binding model; among them, the first-principles calculations are the most effective approach to identify the optimal geometric, electronic, and optical properties of these compounds. According to current theoretical predictions, CsGeCl₃ belongs to the direct gap semiconductor materials, with their gap values ranging from 0.82 to 7.91 eV, depending on the approximations. For example, using the Perdew–Burke–Ernzerhof (PBE)-sol functional, Jong et al. provided the energy band gaps of CsGeI₃, CsGeBr₃, and CsGeCl₃, respectively.

Received: April 4, 2022
Accepted: June 29, 2022
Published: July 13, 2022
respectively. The accuracy of the energy gap could be improved with the typical values of 1.64, 2.34, and 3.24 eV for CsGeI₃, CsGeBr₃, and CsGeCl₃, respectively, when adopting the hybrid functional (HSE) approximation.

Generally, the geometric and electronic properties of CsGeX₃ have been studied; however, the critical factors, such as the orbital hybridizations in the chemical bonds, have not been discussed in detail. Only a few studies have been performed on the optical properties so far; most theoretical investigations are based on the density functional theory (DFT), and thus, the theoretical predictions on optical properties of CsGeX₃ compounds do not accommodate the experimental results. Note that the operation of a solar cell is highly dependent on the formation of excitons since the charge separations are hugely influenced by these electron–hole bound states. Although the excitonic effects in the broad energy range of materials, including CsGeX₃, have been qualitatively estimated by effective mass models, the quantitative description of these bound states is rather limited. There are few works that relied on ab initio Bethe–Salpeter equation (BSE) calculations; however, the formation as well as the nature of the excitonic states has not been elucidated yet. In this work, the first-principles calculations were utilized to investigate the geometric and electronic properties and effects of the electron–hole interactions on the optical properties of the CsGeX₃ (X = Cl, Br, and I) compounds. The theoretical framework is based on the examination of the geometric structure, the accurate quasi-particle energy band structure, the special van Hove singularities on the electronic density of states (DOS), the band decomposed charge densities, the dielectric functions in the case of presence/absence of excitonic effects, the exciton wave functions, and other related optical properties. As a result, the influences of excitonic effects on the optical absorption spectrum and its nature have been clarified. The CsGeCl₃, CsGeBr₃, and CsGeI₃ compounds are excellent candidates for solar cell and opto-electronic applications. The presented theoretical studies in this work are useful for solar cells and other materials.

2. COMPUTATIONAL DETAILS

We investigated the DFT based on the VASP Package to present the optimized structure of the CsGeCl₃, CsGeBr₃, and CsGeI₃ compounds. The related problems to exchange–correlation functions were solved by adopting the PBE form of the generalized gradient approximation (GGA). To treat the core issues, the projector augmented wave (PAW) pseudopotential was used. The cutoff energy of 500 eV was used for the expansion of the plane wave. The Brillouin zone was integrated with a sufficient k-point mesh of 20 × 20 × 20 in the Γ-centered sampling technique for optimizing the geometric structure. Between two successive simulation steps, the ground state’s convergence condition was set to 10⁻⁶ eV. During the geometric optimization, all atoms and the cell could fully relax until the Hellmann–Feynman force acting on each atom was smaller than 0.01 eV/Å.

In the current research, the electronic properties of CsGeCl₃, CsGeBr₃, and CsGeI₃ were studied by using the GW method (G stands for Green’s function and W represents the screened Coulomb potential), in which the quasi-particle energies were obtained within the G3W0 approximation (three self-consistent updates for the quasi-particle Green’s function for the self-energy), the response function’s cutoff energy was set to 200 eV, and 12 × 12 × 12-centered k-points sampling was used to represent reciprocal space. The quasi-particle band structure was plotted by using the Wannier 90 code. Simultaneously, the DFT electronic band structures in the case of with/without spin–orbit coupling (SOC) are also calculated for comparison. However, the SOC effects have been ignored in our GW calculations due to the extremely expensive many-body effects. Based on the electronic wave functions, the single-particle excitations were described by Fermi’s golden rule.

$$e_{\omega}(\omega) = \frac{8\pi e^2}{\omega} \sum_{\mathbf{k}} |c(\mathbf{k})|^2 \delta(\omega - (E_{\mathbf{k}} - E_{\mathbf{k}}^0)),$$

in which the intensity of the excitation peaks is described by the matrix element, while the available transition channels are defined by the joined DOS, $\delta(\omega - (E_{\mathbf{k}} - E_{\mathbf{k}}^0))$.

In addition to the independent particle excitations, the presence of exciton states may have a significant impact on the optical responses. The wave functions related to these bound states of electrons and holes could be expressed by using the following expression

$$|S\rangle = \sum_{k_s} \sum_{v} \sum_{c} A^S_{vk}(w_k);$$

where $E^{QP}_{\mathbf{k}}$ and $E^{QP}_{\mathbf{k}}$, respectively, are the quasi-particle energies of the valence and the conduction states as obtained with the GW method. $K^{eh}$ is the kernel describing the correlated electron–hole pairs, and $\Omega$ is the energy of the excited states. The imaginary part of the dielectric function $e_{\omega}(\omega)$ is calculated from the excitonic states as

$$e_{\omega}(\omega) \propto \sum_S \sum_{\mathbf{k}} A^S_{vk}(w_k) |\delta(\omega - \Omega)|.$$
neously, which can improve the separation of charge carriers and the electronic and optical properties.

Furthermore, the slightly non-uniform environment demonstrates the rather complex hybridizations of orbitals in the chemical bonds, which are responsible for the essential electronic and optical properties.

The CsGeX₃ perovskite compounds sketch unique electronic properties which are entirely reflected in the energy band structure along the high symmetry points in the first Brillouin zone, named Γ–Z–F–I. The effective energy which is related to the main electronic features of these compounds lies mostly in the energy range of −8.0 to −6.0 eV (left panel in Figure 3). Obviously, a lot of sub-bands are formed by specific atoms with numerous orbitals in the unit cell. The energy dispersions of these states reveal the parabolic, saddle, and camelback shapes (−5 to −2 eV). Many maximum and minimum points in the wave-vector space generate van Hove singularities in the DOS. The CsGeX₃ compounds belong to direct band gap semiconductors, in which the lowest unoccupied states and the highest occupied ones locate on the same Z point. The effects of SOC make a minor reduction of the gap; these effects are significantly smaller than that of CsSnX₃ or CsPbX₃ due to the lighter Ge atom. In addition, the relativity effects also cannot create the higher spin degeneracy breaking in the electronic state vicinity of the Fermi level, and thus, the dark excitons due to spin-forbidden transitions are totally absent. The gap values of the DFT calculations in the absence and presence of SOC are summarized in Table 2 and Figure S1 (Supporting Information), and these results are in accordance with previous works. After the GW approximations are adopted, the band gap values are increased to 4.01, 3.05, and 1.88 eV, respectively, for CsGeCl₃, CsGeBr₃, and CsGeI₃ compounds. The slightly over-estimated band gap values originate from the absence of SOC.

The effective mass of the hole/electron, being inversely proportional to the second-order derivative of energy, is able to reveal the carrier mobility. Since the carrier mobility in most indirect gap semiconductors such as CdS, SrTe, and PbS is related to the main electronic features of these compounds lies mostly in the energy range of −8.0 to −6.0 eV (left panel in Figure 3). Obviously, a lot of sub-bands are formed by specific atoms with numerous orbitals in the unit cell. The energy dispersions of these states reveal the parabolic, saddle, and camelback shapes (−5 to −2 eV). Many maximum and minimum points in the wave-vector space generate van Hove singularities in the DOS. The CsGeX₃ compounds belong to direct band gap semiconductors, in which the lowest unoccupied states and the highest occupied ones locate on the same Z point. The effects of SOC make a minor reduction of the gap; these effects are significantly smaller than that of CsSnX₃ or CsPbX₃ due to the lighter Ge atom. In addition, the relativity effects also cannot create the higher spin degeneracy breaking in the electronic state vicinity of the Fermi level, and thus, the dark excitons due to spin-forbidden transitions are totally absent. The gap values of the DFT calculations in the absence and presence of SOC are summarized in Table 2 and Figure S1 (Supporting Information), and these results are in accordance with previous works. After the GW approximations are adopted, the band gap values are increased to 4.01, 3.05, and 1.88 eV, respectively, for CsGeCl₃, CsGeBr₃, and CsGeI₃ compounds. The slightly over-estimated band gap values originate from the absence of SOC.

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Table 1. Number of Bonds, the Bond Length of Chemical Bonding of Cs–Cl/Cs–Br/Cs–I and Ge–Cl/Ge–Br/Ge–I Bonds, and the Lattice Constant of the CsGeX₃ (X = Cl, Br and I) Compounds

| space group (R3m) | atom–atom | number of bonds | bond length (Å) | lattice constant α (Å) | α (deg) |
|------------------|-----------|-----------------|----------------|------------------------|--------|
| CsGeCl₃         | Cs–Cl    | 12              | 3.90, 3.91, 3.97 | 5.53                   | 89.66  |
|                  | Ge–Cl    | 6               | 2.41, 3.14      | 5.53                   | 89.63  |
|                  | CsGeBr₃  | Cs–Br           | 12              | 4.03, 4.09, 4.17       | 5.77   | 88.61 |
|                  | Ge–Br    | 6               | 2.58, 3.21      | 5.78                   | 88.35  |
|                  | CsGeI₃   | Cs–I            | 12              | 4.30, 4.40             | 6.10   | 88.61 |
|                  | Ge–I     | 6               | 2.79, 3.30      | 5.94                   | 88.68  |

The lattice parameters were determined from the PBE functional from ref 33. The lattice parameters were determined from the PBE functional from ref 20. These values are from experiments.60
properties as well as the orbital hybridizations in the chemical bonds. As clearly indicated in the right panels in Figure 3, the DOS of three-dimensional CsGeX$_3$ compounds exhibits a lot of symmetric/asymmetric and shoulder structures arising from the parabolic, saddle, and dispersionless energy sub-bands in the band structure. The van Hove singularities of different orbitals mixed with each other are evidence of the complicated orbital hybridizations in the chemical bonds. Around the Fermi level, the DOS disappears and creates a sizable energy band gap of 4.01, 3.05, and 1.88 eV for CsGeCl$_3$, CsGeBr$_3$, and CsGeI$_3$, respectively. According to the orbital-projected DOS, the occupied states around the Fermi level can be divided into three paths, for example, for CsGeCl$_3$, (i) $-8 \text{ eV} < E' < -5 \text{ eV}$ is due to the strong orbital hybridizations of Ge-4p and Cl-3p states and (ii) $-5 \text{ eV} < E' < -2 \text{ eV}$ is co-dominated by the Ge-4s and Cl-3p orbitals. Apparently, due to the very high ionization energy, the contributions of the Cl-3s orbital lie very deep and thus do not hybridize with the others. As for the CsGeBr$_3$ and CsGeI$_3$ cases, these states move farther up, reflecting the higher atomic energy levels in the latter elements of the periodic table. For the unoccupied states, (iii) $2 \text{ eV} < E' < 6 \text{ eV}$ is mainly dominated by Cl-3p and Ge-4p orbitals and only has slight contributions to the Cs-6s states. Similar phenomena are also observed for the CsGeBr$_3$ and CsGeI$_3$ compounds. The relationship between the energy band structures, the projected DOS, and the band decomposed charge densities (discussed later) can identify the orbital hybridizations in all Cs–Cl/Cs–Br/Cs–I and Ge–Cl/Ge–Br/Ge–I bonds of the 3D CsGeCl$_3$, CsGeBr$_3$, and CsGeI$_3$ compounds, respectively.

To further comprehend the orbital hybridizations of the Cs–Cl/Cs–Br/Cs–I and Ge–Cl/Ge–Br/Ge–I chemical bonds, we have constructed the band decomposed charge densities (Figure 4a–c) for three parts of the valence and conduction states for the CsGeCl$_3$, CsGeBr$_3$, and CsGeI$_3$ compounds. Since the plots for the CsGeCl$_3$ compound look so similar to those of CsGeBr$_3$ and CsGeI$_3$, we only present the figures for CsGeCl$_3$ as an example. As seen in Figure 4a, the lower portion of the occupied states ($-8 \text{ eV} < E' < -5 \text{ eV}$) clearly presents the π bonding character of the Ge-4p and Cl-3p orbitals, in which the Cl-3p charge density exhibits an important contribution. The charge density on the top of the

In addition to quasi-particle energy band structures, the DOS could provide complete information about the electronic

![Figure 3](http://pubs.acs.org/journal/acsodf)

**Figure 3.** Left panels show the GW quasi-particle band structures of the CsGeCl$_3$, CsGeBr$_3$, and CsGeI$_3$, compounds (solid black). The green arrows at the Z point indicate the direct gaps. In addition, DFT electronic band structures are also added for comparisons (dash red). Right panels indicate the van Hove singularities in the DOS of CsGeCl$_3$, CsGeBr$_3$, and CsGeI$_3$, compounds.

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**Table 2.** Electronic Properties of CsGeX$_3$ Compounds: Fundamental Electronic Band Gap from DFT, DFT + SOC, HSE, HSE + SOC, and GW Approximations$^a$

| systems  | DFT  | DFT + SOC | HSE  | HSE + SOC | GW   | EX  |
|----------|------|-----------|------|-----------|------|-----|
| CsGeCl$_3$ | 2.12 | 2.05      | 2.81 | 2.28$^b$  | 4.01 | 3.40$^d$ |
|          | 2.13$^b$ | 2.08$^b$  | 3.24$^b$ | 2.28$^b$ | 4.37$^c$ |     |
|          | 2.07$^c$ | 2.01$^c$  |      |          |      |     |
|          | 1.97$^c$ |          |      |          |      |     |
| CsGeBr$_3$ | 1.40 | 1.35      | 1.98 | 1.77$^b$  | 3.05 | 2.39$^d$ |
|          | 1.46$^b$ | 1.42$^b$  | 2.34$^b$ | 1.77$^b$ | 2.69$^c$ |     |
|          | 1.44$^c$ | 1.39$^c$  |      |          |      |     |
|          | 1.09$^d$ |          |      |          |      |     |
| CsGeI$_3$  | 1.05 | 0.88      | 1.44 | 1.52$^b$  | 1.88 | 1.63$^c$ |
|          | 1.19$^b$ | 1.06$^b$  | 1.64$^b$ | 1.52$^b$ | 1.69$^c$ |     |
|          | 1.14$^c$ | 0.99$^c$  |      |          |      |     |
|          | 0.80$^d$ |          |      |          |      |     |

$^a$The experimental (EX) results are also listed for comparison. $^b$The electronic band gap estimated from ref 33 $^c$The electronic band gap estimated from ref 20 $^d$These values are from experiments. $^{20} $Reference. $^{61}$

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Table 3. Effective Mass of Electrons, Holes, and Reduced Mass Calculated with the PBE Functional$^a$

| systems  | $m_e^*$ | $m_h^*$ | $\mu$ | $\varepsilon_1(0)$ | $E_g$(eV) |
|----------|--------|--------|-------|-------------------|-----------|
|          |        |        |       | DFT               | GW        | GW + BSE       |
| CsGeCl$_3$ | 0.272  | 0.284  | 0.139 | 3.36              | 1.70      | 2.45           | 0.28       |
|          | 0.450  | 0.306  | 0.140 | 3.24$^a$          |           |                |            |
|          | 0.270  | 0.280  |       |                   |           |                |            |
| CsGeBr$_3$ | 0.176  | 0.181  | 0.089 | 4.29              | 1.97      | 2.85           | 0.25       |
|          | 0.191  | 0.197$^a$ | 0.09$^a$ | 3.88$^a$          |           |                |            |
|          | 0.180  | 0.190  |       |                   |           |                |            |
| CsGeI$_3$ | 0.157  | 0.143  | 0.070 | 5.86              | 2.53      | 4.19           | 0.14       |
|          | 0.176$^a$ | 0.186$^a$ | 0.080$^a$ | 4.83$^a$          |           |                |            |
|          | 0.150$^a$ | 0.160$^a$ |       |                   |           |                |            |

$^a$The static dielectric constants of with and without excitonic effects and exciton binding energy calculated from the GW + BSE method. $^b$The effective mass of electrons and holes was calculated with the DFT method.$^{61, 62}$

Concerning the imaginary part, $\varepsilon_2(\omega)$, the optical gap (green color) is about 4.00, 3.03, and 1.89 eV, respectively, for the CsGeCl$_3$, CsGeBr$_3$, and CsGeI$_3$ compounds in the absence of the excitonic effects. These values are equal to the fundamental direct gap $E_g^0$ in Figure 3 owing to the conservation of the momentum. After taking into account the Coulomb interactions, the excitation strength is enhanced due to the enhancement of the electron–hole wave function overlap. Moreover, the presence of the excitonic effects also creates a slightly red-shifted threshold energy. The exciton binding is defined as the difference between the fundamental band gap and the optical gap after taking the Coulomb interaction into account; furthermore, the binding energy is also strongly proportional/inversely proportional to the effective mass of the carriers/dielectric screening constants. According to the delicate analysis, the typical exciton binding energy of CsGeCl$_3$ lies in the following order: Cl > Br > I atom (Table 3 and Figure 5g–i); this trend agrees well with the effective mass model.$^{53, 58}$ It is very important to note that the electron–hole interactions in CsGeI$_3$ are relatively weak and comparable with those in the CsPbI$_3$ solar cell;$^{35}$ the meta-stable exciton states easily break down to create free electron and hole carriers and thus efficiently generate the electrical currents.

Apparently, the first two peaks ($E_1$ and $E_2$) in Figure 6 are due to the excitonic effects since the excitation spectra without Coulomb attraction interactions nearly disappear in the ranges of 0 to 4 eV, 0 to 3 eV, and 0 to 2 eV for the CsGeCl$_3$, CsGeBr$_3$, and CsGeI$_3$ compounds, respectively. These sharp peaks originated from the coherent superposition of exciting electrons and holes. According to the exciton wave functions, as clearly depicted, the exciton states are located in the reciprocal space. Going from chlorine to iodine, the effective mass of carriers and the band gap decreases, and as a consequence, the extent of the exciton in $k$-space decreases. The first and second exciton states, respectively, arise from the vertical transitions from the last valence states to the first and second conduction states of the band extreme in the vicinity of the Z points (the blue and red circles in Figure 6), in which the excited holes and the excited electrons are characteristic for the Ge-4s, Cl-3p/Br-4p/I-5p, and Ge-4p orbitals, respectively. Obviously, owing to the high excitation strength around the meta-stable exciton states, the excitation strength is enhanced due to the enhancement of the electron–hole wave function overlap. Moreover, the presence of the excitonic effects also creates a slightly red-shifted threshold energy. The exciton binding is defined as the difference between the fundamental band gap and the optical gap after taking the Coulomb interaction into account; furthermore, the binding energy is also strongly proportional/inversely proportional to the effective mass of the carriers/dielectric screening constants. According to the delicate analysis, the typical exciton binding energy of CsGeCl$_3$ lies in the following order: Cl > Br > I atom (Table 3 and Figure 5g–i); this trend agrees well with the effective mass model.$^{53, 58}$ It is very important to note that the electron–hole interactions in CsGeI$_3$ are relatively weak and comparable with those in the CsPbI$_3$ solar cell;$^{35}$ the meta-stable exciton states easily break down to create free electron and hole carriers and thus efficiently generate the electrical currents.

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FIGURE 4. Band decomposed charge densities of CsGeCl$_3$: (a) lower portion of VBs ($\sim$8 eV $< E < \sim$5 eV), (b) upper portion of the VBs ($\sim$5 eV $< E < \sim$2 eV), and (c) bottom portion of the CBs (2 eV $< E < 6$ eV).

VBs ($\sim$5 eV $< E < \sim$2 eV) (Figure 4b) is dominated by $\sigma$ bonding states formed from the comparable contribution of the Cl-3p and Ge-4s states. On the other hand, the lower portion of the unoccupied states (2 eV $< E < 6$ eV) (Figure 4c) clearly shows the $\sigma$ bonding behavior originating from Cl-3p and Ge-4p states. The Ge states in this portion have a somewhat higher density than those on the top of the VBs because of the large contribution of Ge-4p orbitals. For the entire energy spectrum, the charge density associated with the Cs element is insignificant since it is related only to the 6s orbital. The band decomposed charge density, together with the energy band structure and the partial charge DOS, is useful for comprehending the orbital characters of the exciton states in the optical properties.

To understand the optical properties, the real part [$\varepsilon_1(\omega)$] and imaginary part [$\varepsilon_2(\omega)$] of the dielectric functions in the absence/presence of the excitonic effects of the CsGeX$_3$ systems were investigated (Figure 5). In the absence of hole and electron couplings, the real part of the dielectric function $\varepsilon_1(\omega)$ is weakly dependent on the energy in the inactive region, and the dielectric constant at zero energy $\varepsilon_1(0)$ is about 1.7, 2.0, and 2.7 eV, respectively, for the CsGeCl$_3$, CsGeBr$_3$, and CsGeI$_3$ compounds. These values increase after the excitonic effects have been adopted (details in Table 3). The ordering of the dielectric constant of CsGeX$_3$ is satisfied with its band gap values and strongly affects the exciton binding (discussed later). Moreover, the dispersionless feature of the real part at the low frequency is also an important factor to determine the vanishing range of the absorption coefficients $a(\omega)$ and the reflectance coefficient $R(\omega)$ in the low energy region.

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n(ω) and the reflectivity R(ω) have been calculated and are shown in Figure 7a–c to better elucidate the optical properties of the CsGeCl₃, CsGeBr₃, and CsGeI₃ compounds. Apparently, these compounds reveal strong absorption and weak reflectance coefficients. The α(ω) is equal to 0, and the R(ω) is almost independent of the energy in the visible region.
as they lack electronic excitation contributions. The fast increase of the absorption coefficient is contributed by the various inter-band transitions. The inverse values of the absorption coefficient are equal to 400, 200, and 100 Å for CsGeCl$_3$, CsGeBr$_3$, and CsGeI$_3$, respectively. These findings imply that photons propagating in the medium are easily absorbed by the rich electronic excitations. As for the reflectance coefficient, the static reflective index is $R(0) = 0.05$, 0.08, and 0.13 eV for the CsGeCl$_3$, CsGeBr$_3$, and CsGeI$_3$ compounds, respectively. A significant enhancement and a huge fluctuation are presented at a higher frequency. Obviously, these materials reveal low reflectivity and strong absorption, making them excellent candidates for solar cell applications.

4. CONCLUSION AND REMARKS

To summarize, accurate first-principles calculations were performed to calculate the rich and unique electronic and optical properties of CsGeX$_3$ (X = Cl, Br, and I) compounds. Consequently, the essential properties and potential applications for solar cell materials can be fully comprehended. The featured characteristics of these materials include an unusual geometric structure, unique electronic properties with a direct electronic band gap nature, the complicated orbital hybridizations comprehended from the electronic band structure, the band decomposed charge density, and the special van Hove singularities in the DOS. In addition, the exciton states and their nature have been qualitatively and quantitatively evaluated through delicate analysis on the mobility of carriers, the dielectric screening, orbital hybridizations in the initial and final states, and the exciton wave functions; other optical properties such as reflectance spectra and absorption coefficient are also achieved. Most importantly, the exciton binding of these materials is reliable to allow for the production of an electrical current upon sunlight adsorption.

As a result, CsGeX$_3$ (X = Cl, Br, and I) compounds emerge as promising candidates for solar cell and electro-optics applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02088.

Calculation results of the band structures by DFT and DFT + SOC corresponding to CsGeCl$_3$, CsGeBr$_3$, and CsGeI$_3$ compounds (PDF)

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N.T.H. designed the study and wrote the manuscript. V.K.D. performed the simulations and analyzed the results. M.-F.L. supervised this work. All authors discussed the results and revised the manuscript.

Notes
The authors declare no competing financial interest.
ACKNOWLEDGMENTS

This work was financially supported by the Hierarchical Green-Energy Materials (Hi-GEM) Research Center from The Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) and the Ministry of Science and Technology (MOST 110-2634-F-006 -017) in Taiwan.

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