First-Principles Study on Optic-Electronic Properties of Charge-Ordered Indium Halide Perovskite Cs$_2$In(I)In(III)Cl$_6$ at High Pressure

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Using the first principle method we studied, theoretically and in detail, the structural, optical, and electronic properties of a charge-ordered indium halide perovskite Cs$_2$In(I)In(III)Cl$_6$ at high pressure. In this structure, In1, In2, and In3 are octahedrally coordinated, whereas In4 is at the center of a pentagonal bipyramid. The charge of In on In1 and In2 sites can be assigned to 3+, while In+ occupies In3 and In4 sites. The results indicated that the band gap decreases, and the electron excitation produces the red-shift of peak value of optical absorption coefficient in visible and infrared regions with increasing pressure, and the reflectivity decreases in visible and infrared regions with increasing pressure. These theoretical results provide a basis for designing related inorganic halide perovskites.

Keywords: halide perovskites, band structure, charge-ordered indium, optic-electronic properties, high pressure

INTRODUCTION

Halide perovskites with various compositions, dimensionalities, and morphologies, have been greatly developed over the last decade. The class of materials have a wide range of potential applications, such as photovoltaics, light-emitting diodes, photodetectors, and lasers, due to their remarkable optoelectronic properties (Dreizler and Gross, 1990; Retuerto et al., 2013; Yin and Kotliar, 2013; Filip et al., 2014; Amgar et al., 2016; He et al., 2017; Kovalenko et al., 2017; Vargas et al., 2017; Volonakis et al., 2017; Zhao et al., 2017; Han et al., 2018; Jeong et al., 2018; Lin et al., 2018; Lin et al., 2019; Lin et al., 2019b; Tan et al., 2019; Chen et al., 2020; Li et al., 2020). Halide perovskites have the general formula ABX$_3$ (Lin et al., 2019a), and the crystal symmetry and phase stability can be determined using the Goldschmidt’s tolerance factor t (Zhao et al., 2017). In the perovskite structure, a site can be occupied by either an inorganic ion (e.g., Cs$,^+$, Rb$,^+$, K$^+$) or an organic ion [e.g., CH$_3$NH$_3$$^+$ (MA$^+$), HC(NH$_2$)$_2$$^+$ (FA$^+$)]; B is a divalent metal cation (e.g., Pb$^{2+}$, Sn$^{2+}$, or Ge$^{2+}$) and X is a halide anion (e.g., I$^-$, Br$^-$, Cl$^-$). The B cation has six nearest-neighbored anions X, and the A cation occupies a vacancy formed by eight corner-sharing [BX$_6$]$^{14-}$ octahedrons (Lin et al., 2019a). Among the perovskite-type structure materials, the charge ordered materials Cs$_2$B$^+$$^+$B$^{3+}$X$_6$, such as Cs$_2$Au$^+$Au$^{3+}$X$_6$ and Cs$_2$TI$^+$$^+$TI$^{3+}$X$_6$ (X = Cl, Br, I), show unique properties, including potential high-$T_c$ superconducting behaviors and semiconductor-metal transition at high pressures (Yin and Kotliar, 2013; Lin et al., 2019). For example, Cs$_2$TI$^+$$^+$Cl$_6$ and Cs$_2$TI$^+$$^+$I$_6$ perovskites were theoretically predicted to be potential superconductors if they were optimally doped and indicated high-$T_c$ ~20 and ~30 K superconduction under reasonably high pressures (Yin and Kotliar, 2013).
These two compounds, together with a complete characterization of the samples were synthesized (Retuerto et al., 2013). Cs₂Tl⁺Tl³⁺Cl₆ is obtained as orange crystals in two different polymorphs: a tetragonal (I₄/m) and a cubic (Fm-3m) phase. Cs₂Tl⁺Tl³⁺F₆ is formed as a light brown powder, also as a double cubic perovskite (Fm-3m). In all three Cs₂Tl⁺Tl³⁺X₆ phases, Tl⁺ and Tl³⁺ were located in two different crystallographic positions that accommodate their different bond lengths. Recently, polycrystalline samples of Cs₁.₁₇In₀.₈₁Cl₃ were prepared by annealing a mixture of CsCl, InCl, and InCl₅, stoichiometric for the targeted CsInCl₃ (Tan et al., 2019). The composition Cs₁.₁₇In₀.₈₁Cl₃ with both corner-sharing and edge-sharing InCl₆ octahedra and InCl₇ pentagonal bipyramids, is isostructural with tetragonal Cs₂Tl⁺Tl³⁺Cl₆ (I₄/m). Subsequently, the In⁺/In³⁺-based charge-ordered halide perovskite compound Cs₂In⁺In³⁺Cl₆ \([\text{Cs}_2\text{In(I)In(III)Cl}_6]\) has also been successfully synthesized through a solid-state reaction method, which shows a semiconductor-to-metal phase transition under high pressures (Lin et al., 2019a).

Despite the tremendous progress which has been made, challenges still remain with perovskites, which call for a better understanding of the fundamental mechanisms of halide. Pressure, a thermodynamic variable, provides a powerful tool to tune structures and properties (Li et al., 2020). On one hand, in combination with in situ characterization methods, high-pressure research could experimentally provide a better fundamental understanding. On the other hand, the properties of materials could be theoretically predicated at high pressure. In this work we shall discuss, theoretically and in detail, the structural, optical, and electronic properties of Cs₂In⁺In³⁺Cl₆ at high pressure.

### COMPUTATIONAL METHODS

In this study, all structure optimizations are calculated by the generalized gradient approximation (GGA) with density functional theory (DFT) (Dreizler and Gross, 1990). The Perdew–Burke–Ernzerhof (PBE) functional is applied to describe the electron exchange correlation. At the present calculations, energy cutoff of plane-wave was set to be 400 eV, the special points sampling integration over the Brillouin zone were performed using a k-mesh of dimensions 4×4×4 k-points mesh according to a Monkhorst-Pack scheme. Geometrical optimization...
FIGURE 2 | (Color online) Band structure and lattice constants at different pressure for Cs$_2$In(I)In(III)Cl$_6$: (A) 0 GPa, (B) 3 GPa, (C) 9 GPa, (D) 22 GPa, (E) 32 GPa. (F) variation of band gaps at different pressures, and (G) variation of lattice constants at different pressures.
was conducted using the convergence of thresholds of $5 \times 10^{-6}$ eV/atom for the total energy, all forces on atoms were converged to less than 0.01 eV/Å. The crystal structures have been energy-optimized by the above calculation method.

The linear optical properties for Cs$_2$In(I)In(III)Cl$_6$ can be obtained from the frequency-dependent complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the dielectric function, and $\omega$ is the photon frequency. The frequency-dependent linear optical spectra, e.g., refractive index $n(\omega)$, extinction coefficient $\kappa(\omega)$, absorption coefficient $\alpha(\omega)$, energy-loss function $L(\omega)$, and reflectivity $R(\omega)$ can be calculated from the real part $\varepsilon_1(\omega)$ and the imaginary part $\varepsilon_2(\omega)$. Refractive index is formulated as

$$n(\omega) = \left(\frac{\varepsilon_1(\omega) + \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}}{2}\right)^{\frac{1}{2}},$$

(1)

Similarly, extinction coefficient is denoted by $\kappa(\omega)$ and is calculated as

$$\kappa(\omega) = \left(\frac{-\varepsilon_1(\omega) + \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}}{2}\right)^{\frac{1}{2}},$$

(2)

General formula of reflectivity to find the reflection from surface of any material is given as

$$R(\omega) = \frac{(n - 1)^2 + \kappa^2}{(n + 1)^2 + \kappa^2},$$

(3)

In the same way, absorption coefficient $\alpha(\omega)$ has been determined by using the following relation:

$$\alpha(\omega) = 4\pi\kappa(\omega)/\lambda,$$

(4)

RESULTS AND DISCUSSIONS

The calculations were conducted on the Cs$_2$In(I)In(III)Cl$_6$ version of the structural model as shown in Figure 1, that is,
without considering the apparent presence of Cs in the In sites or attendant vacancies in the crystal structure of Cs2In(I)In(III)Cl6. The crystallographic data of Cs2In(I)In(III)Cl6, according to the structural model described in Table 1. The structure of the Cs2In(I)In(III)Cl6 sample is very similar to that of CsTlCl3 (Retuerto et al., 2013). In this structure, there are two Cs sites, four In sites, and seven Cl sites. In1, In2, and In3 are octahedrally coordinated, whereas In4 is at the center of a pentagonal bipyramid. The charge of In on In1 and In2 sites can be assigned to 3+. The remaining two nominal In sites indicate a lower oxidation state on In3 and In4 sites. One would conclude that In+ occupies In3 and In4 sites.

Figure 2 represents electronic band structures of Cs2In(I)In(III)Cl6 under different pressures. It has been observed that under ambient conditions, the top of the valence band (VB) and bottom of the conduction band (CB) are located at X and N symmetry points, respectively, and the band-gap Eg calculated under ambient pressure is 2.02 eV (Figure 2A). Hence, Cs2In(I)In(III)Cl6 is regarded as an indirect band-gap semiconductor. Interestingly, while increasing the pressure, shifting the top of VB at P symmetry points toward the Fermi level was observed. Contrary to this, other symmetry points were observed to move away from the Fermi level. With the increasing pressure, the band-gap decreases and becomes zero at ~27.5 GP, as shown in Figure 2F, which indicates the semiconductor-metal transition with the increasing pressures. The lattice constant $a$ ($a = b$) ranges from 17.5779 Å (ambient pressure) to 14.5797 Å (32 GPa), and $c$ ranges from 11.3175 to 9.5625 Å (Figure 2G). It is well known that GGA functional underestimates in calculating the electronic band-gap, but the use of hybrid exchange-correlation functionals, such as HSE06 and mBJ, provides better results (Tan et al., 2019). In addition, the calculated band gap here is much larger than the literature report (<1 eV) of theoretical CsInCl3 (Körbel et al., 2016). This is possibly attributed to the calculations carried out based on the experimental crystal structure. Meanwhile, we observe the semiconductor-metal transition appears at ~27.5 GPa in our theoretical result, which is larger than experimental result (~22 GPa) (Lin et al., 2019a). This could be attributed to the removal of some disorder components in our model, compared with the crystal structure shown in the
Reference Lin et al. (2019a). The large indirect band gap suggests that this nonstoichiometric perovskite-derived phase is not a good candidate for photovoltaic application. These theoretical and experimental results, however, provide a basis for designing related inorganic halide perovskites for potential photovoltaic functions or superconductivity.

To further reveal the factors controlling the bandgap trends, density of states (DOS) and partial density of states (PDOS) based on variable control approaches were carried out. Firstly, to study the effect of In cations on bandgap trend, DOS and PDOS of Cs$_2$In(I)In(III)Cl$_6$ were calculated at 0 GPa, and shown in Figure 3. The calculation results indicated that In on In2 and In3 sites do not contribute to the basic electronic structures. The valence band maximum (VBM) is derived from the p orbitals of In on In4 sites and p orbitals of Cl, and their overlapping indicates the significant hybridization. The s orbitals of In on In1 sites, p orbitals of In on In4 sites and p orbitals of Cl constitute the conduction band minimum (CBM). The trend of difference value between VBM and CBM for Cs$_2$In(I)In(III)Cl$_6$ is consistent with the change of calculated bandgaps. With the increase in pressure from 0 to 27.5 GPa, the s and p orbitals of In on In1 sites, and the s and p orbitals of In on In4 sites lowered the bottom of conduction band (see Figure 4), and the metal–insulator transition occurs in the Cs$_2$In(I)In(III)Cl$_6$.

The real and imaginary parts of dielectric function for Cs$_2$In(I)In(III)Cl$_6$ are shown in Figure 5. The complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ completely describes the optical properties of a medium for different photon energies. The peak value of real part of the dielectric constant is related to the electron excitation. The real part can be derived from the imaginary part $\varepsilon_2(\omega)$ by the Kramers–Kronig relation. With an increase in pressure from 0 to 32 GPa, the peak value of the real part $\varepsilon_1(\omega)$ of the dielectric function increases in visible and infrared regions, while imaginary dielectric function decreases.

The absorption coefficient determines the solar energy conversion efficiency and it indicates how far light of a specific energy (frequency) can penetrate into the material before absorption. With increasing pressure, the peak value of the absorption coefficient increases in visible and infrared regions as shown in Figure 6A. The electron excitation produces the red-shift of the peak value of the optical absorption coefficient. The reflectivity spectrum as a function of photon energy is shown in Figure 6B. We have observed that the reflectivity decreases with increasing pressure in visible and infrared regions.

**CONCLUSION**

In conclusion, using the first principle method, we studied theoretically and in detail the structural, optical, and electronic properties of a charge-ordered indium halide perovskite Cs$_2$In(I)In(III)Cl$_6$ at high pressure, based on the experimental crystal structure. With increasing pressure, the band gap of Cs$_2$In(I)In(III)Cl$_6$ decreases, which shows a semiconductor-to-metal phase transition under high pressures 27.5 GPa. The theoretical result is larger than the experimental result.
(~22 GPa) due to the removal of disorder in the model. The peak value of optical absorption coefficient produces red-shift, and the reflectivity decreases in visible and infrared regions with increasing pressure. Meanwhile, the results show that high-pressure research provides a powerful tool to tune structures and properties. Thus, the properties of materials could be better understood by the method.

**DATA AVAILABILITY STATEMENT**

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

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**AUTHOR CONTRIBUTIONS**

LP proposed the research idea and analysis; YW and SY performed theoretical calculations and manuscript; All authors reviewed the manuscript, have given approval to the final version of the manuscript, and confirmed the authorship to this work.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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