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Design of $(C_3N_2H_5)_{(1-x)}Cs_xPbI_3$ as a novel hybrid perovskite with strong stability and excellent photoelectric performance: A theoretical prediction

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ABSTRACT

Due to its unique properties, such as long carrier diffusion length and adjustable optical band gap, organicinorganic hybrid perovskite has been a potentially strong photoelectric material for solar cells. However, the challenge of insufficient stability of perovskite materials has not been solved, which in turn, limits its commercial application. Inspired by the strong stability of C3N2H5PbI3 (ImPbI3), we present an innovative doped system, $Im_{(1-x)}Cs_xPbI_3$ (x = 0.25, 0.5, 0.75), based on the cation-doped strategy, to obtain both strong stability and excellent photoelectric performance. A new perovskite phase ImPbI₃ is proposed and verified rationality of existence through formation energy, ab initio molecular dynamics (AIMD), mean square displacement (MSD), and X-ray diffraction (XRD) based on density functional theory (DFT) calculations. For analyzing the photoelectric properties of $Im_{(1-x)}Cs_xPbI_3$, the bandgap, charge distribution of the frontier molecular orbital, and projected density of states are investigated. To study the stability of $Im_{(1,x)}Cs_xPbI_3$, geometric configuration, tolerance factor, crystal orbital Hamilton populations (COHP), and AIMD simulations are performed. The results show that the perovskite phase ImPbI₃ has strong thermodynamic stability and structural stability, and its optical bandgap value is lower than that of the hexagonal system. When the content of doped Cs does not exceed 50%, the stability of the perovskite phase ImPbI3 is significantly improved. Comprehensive analysis shows that Im_{0.5}Cs_{0.5}PbI₃ exhibits encouraging performance with strong stability and high optical absorption coefficient. This theoretical study opens a new avenue for the design of robust organic-inorganic hybrid perovskite materials with strong stability and excellent photoelectric performance based on our findings from perovskite phase ImPbI₃ system.

1. Introduction

After $CH_3NH_3PbI_3$ (MAPbI₃) was first used in photovoltaic solar cells achieving an efficiency of 3.8% [1], organic-inorganic hybrid perovskites have been considered a promising photoelectric material. Due to its easy preparation and low cost, as well as adjustable optical bandgap, high carrier mobility, and high optical absorption coefficient, hybrid perovskites are very suitable as light-absorbing materials for application in solar cells [2–6]. However, organic-inorganic hybrid perovskite easily decomposes during use [7,8] demonstrating poor long-term stable solar cell power conversion efficiency (PCE). Therefore, extensive study has been conducted on material design and preparation for developing new

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materials with high stability through both experimental research and density functional theory (DFT) calculations [9–14].

In prior work to improve the stability of hybrid perovskite materials, it was found that HC(NH₂)₂PbI₃ (FAPbI₃) perovskite prepared by replacing MA⁺ with organic cation FA⁺ improved the thermodynamic stability and reduced the optical bandgap [15-17]. However, experimental studies revealed that FAPbI3 easily reacts with water [17] and the vellow non-perovskite phase at room temperature transforms to a stable black perovskite phase at about 430 K [6,18]. Zhou et al. showed that the use of the inorganic cation Cs^+ instead of MA^+ can eliminate enhanced ion mobility and improve material stability [19-23]. However, CsPbI₃ exhibits different phase transitions when the temperature changes yielding a stable black perovskite phase at high temperatures, which causes great fluctuations of the PCE [24,25]. Taya et al. [26] partially replaced the MA with Cs. Their results showed 12.5% Cs-doping slightly enhanced the absorption coefficient of MAPbI₃ with prevention of the compositional degradation of the MAPbI₃. Luo et al. [27] revealed that partially doped Cs increased the moisture resistance of the material with improvement of the PCE. Therefore, A-site doping with Cs was found to be an effective method to improve material properties. However, development of new materials that exhibit the required stability and performance to be practically applied is required. Therefore, it is necessary to explore new materials to provide another option for photovoltaic solar cells.

The tolerance factor and octahedron factor [27,28] are used to measure whether ABX_3 (A = monovalent metal cation or organic cation; B = divalent metal cation; X = halogen anion) is a perovskite-structure material. Recently, experimental studies have shown that the thermal stability of hexagonal C₃N₂H₅PbI₃ (ImPbI₃) is better than that of MAPbI₃ but that it has a wider optical bandgap, which in turn, is not conducive to the efficient absorption of sunlight [29]. For ABX₃, when the tolerance factor (*t*) is within the interval 0.8 < t < 1 and the octahedral factor (μ) is within the range 0.44 $< \mu <$ 0.90, it is a three-dimensional perovskite [30,31]. When t approaches 1, it indicates that a densely packed cubic structure of stable perovskite is formed. The t and μ of ImPbI3 are 0.99 and 0.54, respectively, suggesting that ImPbI3 should exist with a cubic structure [32]. However, the cubic system of ImPbI₃ has not been proposed before for application as an optoelectronic material in any published experimental and theoretical studies. Therefore, inspired by the tolerance factor and potential thermal stability of ImPbI₃, herein, we explore the potential application of ImPbI₃ as an optoelectronic material.

In this work, the stable existence of the perovskite phase ImPbI₃ was verified, and cation doping engineering was used to improve the stability and optical properties of the perovskite phase ImPbI₃ via DFT calculations. First, X-ray diffraction (XRD) and ab initio molecular dynamics (AIMD) simulated at 300-800 K over 10 ps were used to determine the structural and thermodynamic stability of perovskite phase ImPbI₃. Second, the Cs⁺ is doped at the A-site, and the doping concentration is controlled between 25% and 75%. Third, the electronic structure properties of $Im_{(1-x)}Cs_xPbI_3$ (x = 0, 0.25, 0.5, 0.75, 1) were analyzed to study the effect of A-site doping on the energy band and projected density of states. Fourth, crystal orbital Hamilton populations (COHP) analysis was used to calculate the bonding mechanism of chemical bonds to analyze the stability of Pb-I octahedron. All doped systems were simulated using AIMD simulation at a different temperature over 10 ps to evaluate the thermodynamic stability. Finally, the materials with relatively good stability and optoelectronic properties in the doped system $Im_{(1-x)}Cs_xPbI_3$ (x = 0.25, 0.5, 0.75) were screened out. As far as we know, this work is the first study on the properties and performance improvement of the perovskite phase ImPbI₃ system.

1.1. Computational methods

In this study, all DFT calculations were performed on the Vienna *ab initio* simulation software package (VASP5.4.4) [33,34].

Perdew-Burke-Ernzerhof (PBE) functional with generalized gradient approximation and projector augmented wave (PAW) basis were used [35]. To determine the precise hydrogen bonding interaction between the organic cation Im⁺ and I⁻, Van der Waals force correction was used considering the influence of spin polarization [36]. Since the PBE functional underestimates the bandgap, the hybrid nonlocal Heyd-Scuseria-Ernzerhof (HSE) exchange-correlation functional is used to accurately simulate the electronic structure [37]. Gaussian broadening is set equal to $\sigma = 0.05$ eV. For the $2 \times 2 \times 1$ perovskite phase ImPbI₃ supercell, after k-point testing (Figure S1), a 3 \times 3 \times 6 Γ -centered k-point grid was used for sampling during geometric structure optimization, and the cutoff energy of the plane wave basis set was set equal to 520 eV. The force on each atom is set to be below 0.05 eV/Å as the threshold to stop structure optimization. For structural optimization and electronic self-consistent iterative calculations, the convergence accuracy criterion for electronic energy is equal to 10^{-5} eV.

To explore the bonding mechanism of chemical bonds in the system, the Crystal Orbital Hamilton Population (COHP) method [38,39] is used, which is calculated by using the Local Orbital Basis Suite towards Electronic-Structure Reconstruction (LOBSTER) software package [40, 41]. In the projection process, the reference basis for the valence electron of the atom is as follows: $C_2s^22p^2$; $N_2s^22p^3$; H_1s^1 ; Pb,6s²6p²; I, $5s^25p^5$; Cs, $5s^25p^66s^1$, and the basis set given by Koga [42,43].

When calculating the optical properties, the spectral properties of materials are described by dielectric functions. A $4 \times 4 \times 8$ Γ -centered k-point grid is selected for calculation. The imaginary part of the dielectric function is derived from the momentum matrix element between the occupied and unoccupied wave functions under the selection rule. The real part can be obtained from the imaginary part using the Kramer-Kronig relationship. The imaginary part is of great significance for insights into the electron transition law and light absorption characteristics. The expression of the dielectric function is as follows:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \tag{1}$$

where $\varepsilon_1(\omega)$ is the real part of the dielectric function, $\varepsilon_2(\omega)$ is the imaginary part, and ω is the frequency of the photon. The real and imaginary parts of the dielectric function affect the optical properties of the material. To determine the optical properties of the material, the absorption coefficient (α), refractive index (n), and reflectivity (R) of the material were calculated. Their relationship is determined according to the following formula [44]:

$$\alpha(\omega) = \sqrt{2}\omega\sqrt{-\varepsilon_1(\omega) + \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}}$$
(2)

$$n(\omega) = \frac{1}{\sqrt{2}} \sqrt{\varepsilon_1(\omega) + \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}}$$
(3)

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2 \tag{4}$$

To understand the conductive properties of the material, we further calculated the effective mass according to the following equation:

$$m^* = \frac{h^2}{\left(\frac{\partial^2 E(k)}{\partial k^2}\right)} \tag{5}$$

where E(k) is the energy band structure, k is the magnitude of the wave vector in the momentum space, and h is the Planck constant.

2. Results and discussion

2.1. Crystal structure

First, the perovskite phase $ImPbI_3$ was optimized and the result is displayed in Fig. 1a. Taking into account the influence of the initial



Fig. 1. Atomic systems of bulk $(C_3N_2H_5)_{(1-x)}Cs_xPbI_3$ (x = 0, 0.25, 0.5, 0.75, 1) crystals: (a) $C_3N_2H_5PbI_3$; (b) $(C_3N_2H_5)_{0.75}Cs_{0.25}PbI_3$; (c) $(C_3N_2H_5)_{0.5}Cs_{0.5}PbI_3$; (d) $(C_3N_2H_5)_{0.25}Cs_{0.75}PbI_3$; (e) CsPbI_3. Color code: purple, I; dark grey, Pb; green, Cs; pink, H; brown, C; and light blue, N; (g) Tolerance factor and volume change of $(C_3N_2H_5)_{(1-x)}Cs_xPbI_3$ (x =0, 0.25, 0.5, 0.75, 1); (h) The X-ray diffraction evolution of $C_3N_2H_5PbI_3$ triclinic system with the temperature from 300 K to 800 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

position of the organic cations on the properties of the system [45], eight different organic cation orientation systems were designed for optimization. Under different orientations of organic cations, the calculations reveal that the differences of the system energies are less than -0.1 eV, indicating that the influence of organic cation orientation on the system formation energy can be ignored. Therefore, the system with the smallest energy was selected for further analysis. The optimization result is shown in Fig. 1b. The optimized energy of the perovskite phase ImPbI₃ is -291.53 eV with an average energy of -72.88 eV. The optimized energy of hexagonal phase ImPbI₃ from weber et al. [56] is -437.76 eV with an average energy of -72.96 eV. The energy difference of the two systems is only 0.08 eV, indicating that the ImPbI₃ in the hexagonal phase and perovskite phase both exist. To further compare the stability of ImPbI₃ in the view of energy, the formation energy was calculated using the following formula:

$$E_{\rm f} = E(\rm{ImPbI}_3) - E(\rm{ImI}) - E(\rm{PbI}_2)$$
(6)

where *E*(ImI), *E*(PbI₂), and *E*(ImPbI₃) are the total energies of each reactant, for which PbI₂ is treated with a bulk crystal structure while ImI and PbI₂ are put into a 20 Å \times 20 Å \times 20 Å supercell, and treated as a

molecule for energy calculations. The more negative is the formation energy, the more stable is the system. We calculate that the formation energy of the perovskite phase ImPbI₃ is -1.04 eV, and the hexagonal phase ImPbI₃ is -1.12 eV. The formation energy of the perovskite phase ImPbI₃ is negative, which is very close to the formation energy of the hexagonal phase, indicating that the perovskite phase should be formed.

To explore the thermodynamic stability of the perovskite phase ImPbI₃, AIMD were performed at temperatures between 300 and 800 K with the canonical ensemble (NVT) with a time step of 1.0 fs, together with the Nosé thermostat. The total simulation time is 10 ps (results shown in Figure S2). The energy and Pb–I bond length of the system vary within a reasonable range, indicating that the perovskite phase ImPbI₃ has good thermodynamic stability over the temperature range from 300 to 800 K. From Fig. 1h, the position of each peak in the XRD pattern is roughly the same over the range from 300 to 800 K, implying the structural stability of the system versus temperature. On the other hand, MAPbI₃ undergoes a phase change at about 330 K [6], further proving that the perovskite system of ImPbI₃ is more stable than MAPbI₃. Based on the simulation results, the mean square displacement (MSD) measurement was also taken to evaluate the system stability of C₃N₂H₅PbI₃

in the view of dynamics. We calculated the diffusion coefficient (D) [57] according to:

$$D = \lim_{t \to \infty} \left[\frac{1}{2dt} [\vec{r}(t)]^2 \right]$$
(7)

where *d* is the dimension (d = 3), $\vec{r}(t)^2$ is the mean square displacement, and *t* is simulation time [58]. The calculation results are shown in Figure S8. The results show that the diffusion coefficients of 300 K–800 K are in the orders of 10^{-6} , which proves that the system is stable.

To further improve the stability and photoelectric performance of perovskite phase ImPbI₃, we doped the system with A-site cations, as shown in Fig. 1(c-e). Considering the influence of the chain order, for the Im_{0.75}Cs_{0.25}PbI₃ system, we have established a $2 \times 2 \times 2$ supercell, in which Im and Cs are alternatively arranged in the lattice, using HSE hybrid functionals for band structure calculation. The calculation results are shown in Figure S9. From Figure S9, the calculated bandgap of the Im_{0.75}Cs_{0.25}PbI₃ system is 2.15 eV, which is consistent with the calculation result of $2 \times 2 \times 1$ supercell. The calculation results show that the influence of the chain order on the electronic structure of the system can be ignored. Therefore, $2 \times 2 \times 1$ supercell was adopted to reduce the computational cost. The doping system is Im_(1-x)Cs_xPbI₃ (x = 0.25, 0.5, 0.75). When x = 1, it is a cubic crystal phase of CsPbI₃ (Fig. 1f). Due to

the different interaction forces between Cs^+/Im^+ and the surrounding inorganic framework and the large difference of the radius, the addition of Cs causes the lattice tilt angle to decrease and the Pb–I–Pb bond angle to deform, which is consistent with previous research results [46]. The tolerance factors and volume statistics of $Im_{(1-x)}Cs_xPbI_3$ (x = 0, 0.25, 0.5, 0.75, 1) are listed in Fig. 1g. The tolerance factors of doped systems vary within the range of 0.8–1 ensuring that the system is a stable three-dimensional perovskite. Due to the radius of Cs^+ being 1.67 Å, and Im^+ equal to 2.58 Å [47], the replacement of Cs^+ leads to a reduction of the tolerance factor accompanied by volume shrinkage.

2.2. Electronic structure analysis

2.2.1. Bandgap

To explore photoelectric performance, the bandgap was calculated by using the HSE functional, as shown in Fig. 2(a-e). The optical band gap determined for the perovskite phase ImPbI₃ is equal to 2.28 eV, which is much lower than that of hexagonal ImPbI₃ (2.94 eV). This suggests that the perovskite system is more promising for photovoltaic applications than the hexagonal system. In addition, our calculated band gap for the hexagonal ImPbI₃ (2.94 eV) is very close to that of an experimentally obtained value (3.1 eV [48]), which indicates that our calculated results are reliable. The band gap of CsPbI₃ is 1.70 eV, which



Fig. 2. Band structure of (a) $C_3N_2H_5PbI_3$; (b) $(C_3N_2H_5)_{0.75}Cs_{0.25}PbI_3$; (c) $(C_3N_2H_5)_{0.5}Cs_{0.5}PbI_3$; (d) $(C_3N_2H_5)_{0.25}Cs_{0.75}PbI_3$; (e) C_3PbI_3 ; (f) Fitted line between HSE-Bandgap and Cs doping concentration.

is in good agreement with the experimentally determined band gap value of 1.73 eV [49]. As the concentration of Cs increases, the band gap of the doped systems drops from 2.16 to 1.99 eV. Due to a decrease of the lattice constant, the expansion of the conduction band increases, resulting in a decrease in the forbidden bandwidth. All systems are direct band gaps, which reduces unnecessary energy loss during electron transition.

To explore the relationship between doping concentration and band gap, Fig. 2f plots the HSE band gap versus the Cs concentration as well as a regressed quadratic function which achieves a correlation coefficient equal to $R^2 = 0.97$. This result proves that the doping concentration and the band gap follow a quadratic curve distribution [50], further demonstrating that our calculation results are reliable. The fitting equation is $y = 2.25-0.08x-0.45x^2$ and therefore, the bowing parameter b [50] of the system is equal to 0.45 eV. The relatively small bowing parameter of this system means that CsPbI₃ and ImPbI₃ are miscible [51], 52], which is convenient for adjusting the desired bandgap material.

2.2.2. Electronic density of states

To determine the electronic distribution of the system, the projected density of states (PDOS) and the partial charge density distribution of the valence band maximum (VBM) and conductive band maximum (CBM) are plotted in Fig. 3. From Fig. 3, alpha and beta are completely symmetrical, there is no obvious influence of spin polarization in the system of $Im_{(1-r)}Cs_rPbI_3$. Subsequently, we added spin-orbit coupling (SOC) correction without considering the spin-polarized, combined with the HSE hybridization functional to calculate the bandgaps of the doped systems. The calculation results are shown in Figure S10. Due to the large spin-orbit coupling constant of Pb atoms, the spin-orbit coupling has a significant influence on the band structure of ImPbI₃. From the band structure of Figure S10, the bandgaps of $Im_{(1-x)}Cs_xPbI_3$ (x = 0.25, 0.5, 0.75) systems have been reduced from 2.16 eV, 2.10 eV, 1.99 eV-1.10 eV, 1.05 eV, 0.95 eV, respectively. The band structure with SOC in the calculation is denser than that without SOC. These results show that the SOC effect leads to a reduction in the electronic bandgap by



Fig. 3. The projected density of state of (a) $C_3N_2H_5PbI_3$; (b) $(C_3N_2H_5)_{0.75}Cs_{0.25}PbI_3$; (c) $(C_3N_2H_5)_{0.5}Cs_{0.5}PbI_3$; (d) $(C_3N_2H_5)_{0.25}Cs_{0.75}PbI_3$; (e) $CsPbI_3$; (f) The charge density maps of CBM and VBM with $(C_3N_2H_5)_{0.5}Cs_{0.5}PbI_3$ and $(C_3N_2H_5)_{0.25}Cs_{0.75}PbI_3$ system.

inducing a large atomic energy level-splitting [59]. In particular, the energy reduction at the bottom of the conduction band is more significant, whose main contribution is from the Pb 6p orbitals. This phenomenon of the underestimated band gap is consistent with the results of the cubic CsPbI₃ and the pseudocubic MAPbI₃ systems [60].

In this work, the SOC correction will cause the bandgap to be underestimated, which leads to a significant difference between the calculated results and the experimental results. From our calculation results, the research results without considering the SOC are more consistent with the experiment. As we all know, the HSE hybrid functional calculation with SOC correction will be very time-consuming. Therefore, the HSE hybrid functional was selected to calculate the $Im_{(1-x)}Cs_xPbI_3$ systems.

As for the cationic A part, the PDOS results in Fig. 3(a–e) show that the contribution of organic cations is far away from the Fermi level, and it gradually decreases with the addition of Cs. Cs has no electron orbit contribution to the entire energy level. These results indicate that adjusting the A-site cation composition has no direct effect on the optical band gap of the system. As shown in Fig. 3f, there is no electron distribution at the A-site, indicating that the A-site is only providing charge to

the Pb–I octahedron keeping the system as an electrically neutral material. As the Pb–I part, from Fig. 3(a–e), the energy contribution of the band edge is mainly occupied by the electron orbits of Pb and I. The valence band is mainly occupied by the 5*p* orbital of I and the 6*s* orbital of Pb. The conduction band is mainly occupied by the 6*p* orbital of Pb. These results are also consistent with the electron distribution at CBM and VBM (Fig. 3f, other systems shown in Figure S3). The 5*p* orbital of I and the 6*s* orbital of Pb are strongly coupled but there is no interaction between Im⁺ and I⁻, which proves that the strong covalent interaction between Pb²⁺ and I⁻ is higher than the hydrogen bond between Im⁺ and I⁻. The stability of the Pb–I octahedron is a very important leading factor in the system.

2.3. Analysis of structural stability

Since the stability of Pb–I octahedrons is related to the stability of the system, the integrated crystal orbital Hamilton population (ICOHP) integral value of the Pb–I bond is calculated based on the crystal orbital Hamilton population (COHP) method, and its bonding mechanism is described in Fig. 4. As shown in Fig. 4e, there are four Pb–I octahedrons



Fig. 4. (a–d) The change graph of the integral value of all Pb–I bonds in the system; (1)–(16) is the atomic number in the system (see Figure S7); (e) Line chart of the weakest Pb–I bond change in the system; (f) The crystal orbital Hamilton population (COHP) analysis of the Pb–I bond in perovskite phase ImPbI₃.

in the system, and each octahedron has six Pb-I bonds. The ICOHP integral value of each Pb-I bond in the four octahedrons is calculated and presented in Fig. 4(a-d). As shown in Fig. 4(a-d), as the Cs concentration increases, the -ICOHP integral difference of the Pb-I bond in each system gradually decreases. However, it is shown from the integral value statistics chart (Fig. 4(a-d)) that when the Cs^+ concentration is 50%, the integral value of the Pb-I bond in the system changes very little when it is raised to 75%. The bond strength of each Pb-I in the octahedron of CsPbI₃ is close to each other and higher than the weakest Pb–I bond in C₃N₂H₅PbI₃, which may be one of the reasons that doping of Cs⁺ into organic cations enhances the stability. We count the Pb-I bond with the smallest -ICOHP integral value in each system in Fig. 4e. With the addition of Cs⁺, the weakest bond gradually strengthens, but the difference between the values at 50% and 75% is very small. These results indicate that the addition of Cs⁺ helps to improve the stability of the Pb–I octahedron, but it should be controlled within 50%. The interaction between Cs and the inorganic framework Pb-I octahedron is ionic bonding interaction, and the interaction between Im and Pb-I octahedron is hydrogen bonding interaction. Therefore, as the amount of Cs increases, the interaction between the A-site and the octahedron increases, improving the stability of the system. Fig. 4f shows the bonding mechanism of the Pb–I bond in perovskite phase ImPbI₃ (see Figure S4 for other systems). The stability of the Pb–I bond is decomposed into the contribution of different orbitals, which is mainly reflected in the contribution of the 6p orbital of Pb and the 5p orbital of I. In the valence band, the 6s anti-bonding orbital of Pb and the 5p anti-bonding orbital of I are hybridized, which corresponds to the electron density diagram of Fig. 3(a-e).

In addition, to further confirm the stabilities of $Im_{0.5}Cs_{0.5}PbI_3$, AIMD were conducted at 400 K and 800 K with the canonical ensemble (NVT) with a time step of 1.0 fs, together with the Nosé thermostat. The total simulation time is 10 ps with results displayed in Fig. 5. The results show that over the relatively long time period of 10 ps, the energy and average bond length of the Pb atom and I atom fluctuate over a small range suggesting that there is no significant variation of the structure geometry and the system should exhibit thermodynamic stability. The stability of $Im_{(1-x)}Cs_xPbI_3(x = 0.25, 0.75)$ was also studied via AIMD simulation (see Figure S5-6); similar conclusions were reached.



Fig. 5. Energy and Pb–I bond length of $(C_3N_2H_5)_{0.5}Cs_{0.5}PbI_3$ in the simulation of AIMD at T=(a) 400 K; (b) 800 K.

2.4. Optical properties

To further study the optical properties of materials studies here, the optical absorption coefficient, reflectivity, and refractive index were calculated from Equations (2-4). In Fig. 6a, the light absorption intensity of Im_{0.75}Cs_{0.25}PbI₃ material is higher than that of perovskite phase ImPbI₃. The greater the Cs concentration, the lower is the maximum wavelength absorption peaks for the $Im_{(1-r)}Cs_rPbI_3$ (x = 0.25, 0.5, 0.75) systems. The results also show that the results are much higher than that of CsPbI₃. The results in Fig. 6b show that CsPbI₃ has the highest reflectivity, which corresponds to the lowest refractive index in Fig. 6c: the CsPbI₃ has a good gloss. According to the carrier mobility formula $u = q\bar{t}/m^*$ (m^* is the effective carrier mass, q is the electric quantity, and \overline{t} is the mean free path), the effective masses of electrons (m_e^*) and holes (m_h^*) of the material are calculated according to Equation (5) and are shown in Fig. 6d. The smaller effective mass leads to higher conductivity, which facilitates the transfer and separation of charges. The effective masses of electrons and holes in perovskite phase ImPbI₃ are 0.31 m_e and 1.23 m_e (m_e is the static mass of a free electron), respectively, both being much higher than that of the CsPbI₃ perovskite. This may result in lowered carrier mobility of the perovskite phase ImPbI₃. When the concentration of Cs is 25%, the effective mass of holes decreases from 1.23 m_e to 0.64 m_e . With higher Cs, the effective mass of holes drops. When the concentration of Cs rises from 25% to 50%, the effective mass of electrons decreases from 0.26 m_e to 0.20 m_e . When the concentration of Cs rises above 50%, there is no change of the effective mass of the electron. The results show that the gradual increase of the Cs⁺ leads to a drop of the electron and hole effective masses and that the content of Cs⁺ need not exceed 50%. The gradual decrease of the electron and hole effective masses also agrees with the result of the gradual bending of the energy band (see Fig. 2(a-e)).

2.4.1. Band gap comparison

To compare $Im_{(1-x)}Cs_xPbI_3$ with other different systems in the literature, the band gap comparison was performed as shown in Table 1. Generally, $Im_{(1-x)}Cs_xPbI_3$, as shown in this work, has a smaller band gap, which is more suitable for application than other systems. Combined with the stability of the material and the comprehensive analysis of the optical properties, it shows that $Im_{0.5}Cs_{0.5}PbI_3$ is the most potential perovskite solar cell material, which has better light trapping ability in the visible light range and better charge carrier mobility.

3. Conclusions

In summary, the stable existence of the perovskite phase ImPbI₃ has been verified by DFT calculations in view of energy and dynamics. A novel doping system, $Im_{(1-x)}Cs_xPbI_3$ (x = 0.25, 0.5, 0.75), through which the A-site is doped with the inorganic cation Cs⁺, was examined for its stability and photoelectric performance. The AIMD simulation results for $Im_{(1-x)}Cs_xPbI_3$ (x = 0.25, 0.5, 0.75) over a temperature range from 300 to 800 K reveals that the perovskite phase ImPbI₃ has good structural and thermodynamic stabilities. The band gap of the perovskite phase ImPbI₃ is 2.28 eV, which is smaller than that of the hexagonal system which has been explored experimentally, indicating that the perovskite system is more suitable as a solar cell absorption material. Doping the inorganic cation Cs⁺ at the A-site not only enhances the stability of the system but also improves the optical properties of the system. The structural distortion due to doping increases the band broadening, which leads to a reduction of the band gap of the system. With the increase of the Cs content, the effective mass is also reduced, which improves the carrier mobility of the material. But when the concentration of Cs is greater than 50%, continuously increasing the concentration of Cs does not improve the stability of the system. Therefore, the amount of Cs added should be controlled to less than 50%. Combined with the stability of the doped systems and optical



Fig. 6. The optical performance of five optimized systems (a) optical absorption coefficient (b) reflectivity (c) refractive index (d) effective mass of electrons and holes.

Table 1

Bandgap of different systems.

| 3.1 [48] 2.33 [13] 2.31 [53] 2.30 [13] 2.30 [53] 2.29 [53] |
|---|
| 2.33 [13] 2.31 [53] 2.30 [13] 2.30 [53] 2.29 [53] |
| 2.31 [53] 2.30 [13] 2.30 [53] 2.29 [53] |
| 2.30 [13] 2.30 [53] 2.29 [53] |
| 2.30 [53] 2.29 [53] |
| 2.29 [53] |
| |
| 2.28 [13] |
| 2.27 [54] |
| 2.00 [55] |
| 1.62 [26] |
| 2.28 ^a |
| 2.16 ^a |
| 2.10 ^a |
| 1.99 ^a |
| |

Note.

^a This work.

analysis, it can be seen that $Im_{0.5}Cs_{0.5}PbI_3$ has a wider optical absorption range, higher carrier mobility, and stability, and is more suitable as a light absorption material for perovskite solar cells. We strongly call for efforts to improve the level of experimentation to synthesize this new class of perovskite material that we have designed with its potentially excellent photovoltaic performance.

CRediT authorship contribution statement

Zhengyang Gao: Conceptualization, Resources, Investigation. Min Wang: Investigation, Writing – original draft, Formal analysis. Hanwen Zhang: Investigation, Formal analysis. Shengyi Chen: Investigation, Formal analysis. Chongchong Wu: Validation, Writing – review & editing. Ian D. Gates: Validation, Writing – review & editing. Weijie Yang: Conceptualization, Writing – review & editing, Supervision. Xunlei Ding: Conceptualization, Writing – review & editing, Supervision. Jianxi Yao: Supervision, Project administration, Funding acquisition.

Declaration of competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.solmat.2021.111401.

References

- A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, Organometal halide perovskites as visible-light sensitizers for photovoltaic cells, J. Am. Chem. Soc. 131 (2009) 6050–6051, https://doi.org/10.1021/ja809598r.
- [2] W.J. Yin, T. Shi, Y. Yan, Unique properties of halide perovskites as possible origins of the superior solar cell performance, Adv. Mater. 26 (2014) 4653–4658, https:// doi.org/10.1002/adma.201306281.

- [4] S.D. Stranks, G.E. Eperon, G. Grancini, C. Menelaou, M.J. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, H.J. Snaith, Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber, Science 342 (2013) 341–344, https://doi.org/10.1126/science.1243982.
- [5] D.B. Mitzi, Synthesis, structure, and properties of organic-inorganic perovskites and related materials, Prog. Inorg. Chem. 48 (1999) 1–121, https://doi.org/ 10.1002/9780470166499.ch1.
- [6] C.C. Stoumpos, C.D. Malliakas, M.G. Kanatzidis, Semiconducting tin and lead iodide perovskites with organic cations: phase transitions, high mobilities, and near-infrared photoluminescent properties, Inorg. Chem. 52 (2013) 9019–9038, https://doi.org/10.1021/ic401215x.
- [7] B. Conings, J. Drijkoningen, N. Gauquelin, A. Babayigit, J. D'Haen, L. D'Olieslaeger, A. Ethirajan, J. Verbeeck, E. Mosconi, F.D. Angeli, H.G. Boyen, Intrinsic thermal instability of methylammonium lead trihalide perovskite, Adv. Energy Mater. 5 (2015) 1500477, https://doi.org/10.1002/aenm.201500477.
- [8] R.K. Misra, S. Aharon, B. Li, D. Mogilyansky, I. Visoly-Fisher, L. Etgar, E.A. Katz, Temperature-and component-dependent degradation of perovskite photovoltaic materials under concentrated sunlight, J. Phys. Chem. Lett. 6 (2015) 326–330, https://doi.org/10.1021/jz502642b.
- [9] M. Saliba, T. Matsui, K. Domanski, J.Y. Seo, A. Ummadisingu, S.M. Zakeeruddin, J. P. Correa-Baena, W.R. Tress, A. Abate, M. Grätzel, Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance, Science 354 (2016) 206–209, https://doi.org/10.1126/science.aah5557.
- [10] H. Zhang, R. Yuan, M. Jin, Z. Zhang, Y. Yu, W. Xiang, X. Liang, Rb⁺-doped CsPbBr₃ quantum dots with multi-color stabilized in borosilicate glass via crystallization, J. Eur. Ceram. Soc. 40 (2020) 94–102, https://doi.org/10.1016/j. jeurceramsoc.2019.09.020.
- [11] C.A. López, C. Abia, J.E. Rodrigues, F. Serrano-Sánchez, N.M. Nemes, J.L. Martínez, M.T. Fernandez-Díaz, N. Biškup, C. Alvarez-Galván, F. Carrascoso, A. Castellanos-Gomez, J.A. Alonso, Enhanced stability in CH₃NH₃PbI₃ hybrid perovskite from mechano-chemical synthesis: structural, microstructural and optoelectronic characterization, Sci. Rep. 10 (2020) 1–11, https://doi.org/10.1038/s41598-020-68085-0.
- [12] J. Zhang, L. Yang, Y. Zhong, H. Hao, M. Yang, R. Liu, Improved phase stability of the CsPbI₃ perovskite via organic cation doping, Phys. Chem. Chem. Phys. 21 (2019) 11175–11180, https://doi.org/10.1039/C9CP01211G.
- [13] R. Sa, Z. Ma, J. Wang, D. Liu, The effect of organic cation doping on the stability and optoelectronic properties of α-CsPbI₃, J. Solid State Chem. 290 (2020) 121577, https://doi.org/10.1016/j.jssc.2020.121577.
- [14] Z. Gao, S. Chen, Y. Bai, M. Wang, X. Liu, W. Yang, W. Li, X. Ding, J. Yao, A new perspective for evaluating the photoelectric performance of organic-inorganic hybrid perovskites based on the DFT calculations of excited states, Phys. Chem. Chem. Phys. 23 (2021) 11548–11556, https://doi.org/10.1039/D1CP01000J.
- [15] E. Smecca, Y. Numata, I. Deretzis, G. Pellegrino, S. Boninelli, T. Miyasaka, T. La Magna, A. Alberti, Stability of solution-processed MAPbI₃ and FAPbI₃ layers, Phys. Chem. Chem. Phys. 18 (2016) 13413–13422, https://doi.org/10.1039/ c6cp00721j.
- [16] J.W. Lee, D.J. Seol, A.N. Cho, N.G. Park, High-efficiency perovskite solar cells based on the black polymorph of HC(NH₂)₂PbI₃, Adv. Mater. 26 (2014) 4991–4998, https://doi.org/10.1002/adma.201401137.
- 4991–4998, https://doi.org/10.1002/adma.201401137.
 [17] T.M. Koh, K. Fu, Y. Fang, S. Chen, T.C. Sum, N. Mathews, S.G. Mhaisalkar, P. P. Boix, T. Baikie, Formamidinium-containing metal-halide: an alternative material for near-ir absorption perovskite solar cells, J. Phys. Chem. C 118 (2014) 16458–16462, https://doi.org/10.1021/jp411112k.
- [18] A. Binek, F.C. Hanusch, P. Docampo, T. Bein, Stabilization of the trigonal hightemperature phase of formamidinium lead iodide, J. Phys. Chem. Lett. 6 (2015) 1249–1253, https://doi.org/10.1021/acs.jpclett.5b00380.
- [19] V. Pawar, M. Kumar, P.A. Jha, S.K. Gupta, P.K. Jha, P. Singh, Cs/MAPbI₃ composite formation and its influence on optical properties, J. Alloys Compd. 783 (2019) 935–942, https://doi.org/10.1016/j.jallcom.2018.12.333.
- [20] R. Sedighi, F. Tajabadi, N. Taghavinia, Vapor assisted deposition of alkaline doped perovskites: pure phase formation of Cs_xMA_{1-x}PbI₃, Electrochim. Acta 259 (2018) 485–491, https://doi.org/10.1016/j.electacta.2017.10.185.
- [21] W. Zhou, Y. Zhao, X. Zhou, R. Fu, Q. Li, Y. Zhao, K. Liu, D. Yu, Q. Zhao, Lightindependent ionic transport in inorganic perovskite and ultrastable cs-based perovskite solar cells, J. Phys. Chem. Lett. 8 (2017) 4122–4128, https://doi.org/ 10.1021/acs.jpclett.7b01851.
- [22] C. Yi, J. Luo, S. Meloni, A. Boziki, N. Ashari-Astani, C. Grätzel, S.M. Zakeeruddin, U. Röthlisberger, M. Grätzel, Entropic stabilization of mixed A-cation ABX₃ metal halide perovskites for high performance perovskite solar cells, Energy Environ. Sci. 9 (2016) 656–662, https://doi.org/10.1039/c5ee03255e.
- [23] R.G. Niemann, L. Gouda, J. Hu, S. Tirosh, R. Gottesman, P.J. Cameron, A. Zaban, Cs⁺ incorporation into CH₃NH₃PbI₃ perovskite: substitution limit and stability enhancement, J. Mater. Chem. A. 4 (2016) 17819–17827, https://doi.org/ 10.1039/C6TA05869H.
- [24] A. Marronnier, G. Roma, S. Boyer-Richard, L. Pedesseau, J.M. Jancu, Y. Bonnassieux, C. Katan, C.C. Stoumpos, M.G. Kanatzidis, J. Even, Anharmonicity and disorder in the black phases of cesium lead iodide used for stable inorganic perovskite solar cells, ACS Nano 12 (2018) 3477–3486, https://doi.org/10.1021/ acsnano.8b00267.
- [25] A. Dutta, S.K. Dutta, S. Das Adhikari, N. Pradhan, Phase-stable CsPbI₃ nanocrystals: the reaction temperature matters, Angew. Chem. Int. Ed. 57 (2018) 9083–9087, https://doi.org/10.1002/ange.201803701.

- [26] A. Taya, P. Rani, J. Thakur, M.K. Kashyap, First principles study of structural, electronic and optical properties of Cs-doped CH₃NH₃PbI₃ for photovoltaic applications, Vacuum 160 (2019) 440–444, https://doi.org/10.1016/j. vacuum.2018.12.008.
- [27] P. Luo, S. Zhou, Y. Zhou, W. Xia, L. Sun, J. Cheng, C. Xu, Y. Lu, Fabrication of Cs_xFA_{1-x}PbI₃ mixed-cation perovskites via gas-phase-assisted compositional modulation for efficient and stable photovoltaic devices, ACS Appl. Mater. Interfaces 9 (2017) 42708–42716, https://doi.org/10.1002/cssc.201701779.
- [28] V.M. Goldschmidt, Die gesetze der krystallochemie, Naturwissenschaften 14 (1926) 477–485, https://doi.org/10.1007/BF01507527.
- [29] C. Seth, D. Khushalani, Non-perovskite hybrid material, imidazolium lead iodide, with enhanced stability, ChemNanoMat 5 (2019) 85–91, https://doi.org/10.1002/ cnma.201800375.
- [30] Z. Li, M. Yang, J.S. Park, S.H. Wei, J.J. Berry, K. Zhu, Stabilizing perovskite structures by tuning tolerance factor: formation of formamidinium and cesium lead iodide solid-state alloys, Chem. Mater. 28 (2016) 284–292, https://doi.org/ 10.1021/acs.chemmater.5b04107.
- [31] M.A. Green, A. Ho-Baillie, H.J. Snaith, The emergence of perovskite solar cells, Nat. Photonics 8 (2014) 506–514, https://doi.org/10.1038/NPHOTON.2014.134.
- [32] G. Kieslich, S. Sun, A.K. Cheetham, An extended tolerance factor approach for organic-inorganic perovskites, Chem. Sci. 6 (2015) 3430–3433, https://doi.org/ 10.1039/c5sc00961h.
- [33] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169, https:// doi.org/10.1103/PhysRevB.54.11169.
- [34] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci. 6 (1996) 15–50, https://doi.org/10.1016/0927-0256(96)00008-0.
- [35] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865, https://doi.org/10.1103/ PhysRevLett.77.3865.
- [36] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, J. Chem. Phys. 132 (2010) 154104, https://doi.org/10.1063/ 1.3382344.
- [37] J. Heyd, G.E. Scuseria, M. Ernzerhof, Hybrid functionals based on a screened coulomb potential, J. Chem. Phys. 118 (2003) 8207–8215, https://doi.org/ 10.1063/1.1564060.
- [38] V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, Crystal orbital Hamilton population (COHP) analysis as projected from plane-wave basis sets, J. Phys. Chem. A. 115 (2011) 5461–5466, https://doi.org/10.1021/jp202489s.
- [39] R. Dronskowski, P.E. Blöchl, Crystal orbital Hamilton populations (COHP): energyresolved visualization of chemical bonding in solids based on density-functional calculations, J. Phys. Chem. 97 (1993) 8617–8624, https://doi.org/10.1021/ j100135a014.
- [40] S. Maintz, V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, LOBSTER: a tool to extract chemical bonding from plane-wave based dft, J. Comput. Chem. 37 (2016) 1030–1035, https://doi.org/10.1002/jcc.24300.
- [41] S. Maintz, V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, Analytic Projection from plane-wave and PAW wavefunctions and application to chemical-bonding analysis in solids, J. Comput. Chem. 34 (2013) 2557–2567, https://doi.org/ 10.1002/jcc.23424.
- [42] T. Koga, K. Kanayama, T. Watanabe, T. Imai, A.J. Thakkar, Analytical Hartree-Fock wave functions for the atoms Cs to Lr, Theor Chem Acc 104 (2000) 411–413, https://doi.org/10.1007/s002140000150.
- [43] T. Koga, K. Kanayama, S. Watanabe, A.J. Thakkar, Analytical Hartree-Fock wave functions subject to cusp and asymptotic constraints: He to Xe, Li⁺ to Cs⁺, H⁻ to Γ, Int. J. Quant. Chem. 71 (1999) 491–497, https://doi.org/10.1002/(SICI)1097461X (1999)71:6<491::AIDQUA6>3.0.CO;2-T.
- [44] S. Saha, T.P. Sinha, A. Mookerjee, Electronic structure, chemical bonding, and optical properties of paraelectric BaTiO₃, Phys. Rev. B 62 (2000) 8828, https://doi. org/10.1103/PhysRevB.62.8828.
- [45] Q. Xu, A. Stroppa, J. Lv, X. Zhao, D. Yang, K. Biswas, L. Zhang, Impact of organic molecule rotation on the optoelectronic properties of hybrid halide perovskites, Phys. Rev. Mater. 3 (2019) 125401, https://doi.org/10.1103/ PhysRevMaterials.3.125401.
- [46] J. Liu, J. Kang, S. Chen, J.J. White, H. Yin, P. Liu, H. Zhao, Y. Wang, Effects of compositional engineering and surface passivation on the properties of halide perovskites: a theoretical understanding, Phys. Chem. Chem. Phys. 22 (2020) 19718–19724, https://doi.org/10.1039/D0CP02896G.
- [47] G. Kieslich, S. Sun, A.K. Cheetham, Solid-state principles applied to organicinorganic perovskites: new tricks for an old dog, Chem. Sci. 5 (2014) 4712–4715, https://doi.org/10.1039/C4SC02211D.
- [48] C. Seth, D. Jana, V. Jindal, D. Khushalani, S. Ghosh, One-dimensional behavior of imidazolium lead iodide, J. Phys. Chem. C 123 (2019) 16449–16455, https://doi. org/10.1021/acs.jpcc.9b03894.
- [49] G.E. Eperon, G.M. Paternò, R.J. Sutton, A. Zampetti, A.A. Haghighirad, F. Cacialli, H.J. Snaith, Inorganic caesium lead iodide perovskite solar cells, J. Mater. Chem. A. 3 (2015) 19688–19695, https://doi.org/10.1039/C5TA06398A.
- [50] R. Hill, Energy-Gap variations in semiconductor alloys, J. Phys. C Solid State Phys. 7 (1974) 521, https://doi.org/10.1088/0022-3719/7/3/009.
- [51] R. Venugopal, P.I. Lin, Y.T. Chen, Photoluminescence and Raman scattering from catalytically grown Zn_xCd_{1-x}Se alloy nanowires, J. Phys. Chem. B 110 (2006) 11691–11696, https://doi.org/10.1021/jp056892c.

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- [52] R. Hill, A.N. Casperd, Refractive indices of cadmium sulphide-telluride alloys, Solid State Commun. 17 (1975) 735–737, https://doi.org/10.1016/0038-1098(75) 90397-X.
- [53] X. Zhang, H. Liu, W. Wang, J. Zhang, B. Xu, K.L. Karen, Y. Zheng, S. Liu, S. Chen, K. Wang, X.W. Sun, Hybrid perovskite light-emitting diodes based on perovskite nanocrystals with organic-inorganic mixed cations, Adv. Mater. 29 (2017) 1606405, https://doi.org/10.1002/adma.201606405.
- [54] D. Liu, W. Zha, Y. Guo, R. Sa, Insight into the improved phase stability of CsPbI₃ from First-Principles Calculations, ACS Omega 5 (2019) 893–896, https://doi.org/ 10.1021/acsomega.9b03838.
- [55] W. Ke, I. Spanopoulos, C.C. Stoumpos, M.G. Kanatzidis, Myths and reality of HPbI₃ in halide perovskite solar cells, Nat. Commun. 9 (2018) 1–9, https://doi.org/ 10.1038/s41467-018-07204-y.
- [56] O.J. Weber, K.L. Marshall, L.M. Dyson, M.T. Weller, Structural diversity in hybrid organic-inorganic lead iodide materials, Acta Crystallogr B Struct Sci Cryst Eng Mater 71 (2015) 668–678, https://doi.org/10.1107/S2052520615019885.
- [57] K. Kobayashi, M.U. Salam, Comparing simulated and measured values using mean squared deviation and its components, Agron. J. 92 (2000) 345–352, https://doi. org/10.1007/s100870050043.
- [58] J. Kubečka, F. Uhlík, P. Košovan, Mean squared displacement from fluorescence correlation spectroscopy, Soft Matter 12 (2016) 3760–3769, https://doi.org/ 10.1039/C6SM00296J.
- [59] J. Kim, S.C. Lee, S.H. Lee, K.H. Hong, Importance of orbital interactions in determining electronic band structures of organo-lead iodide, J. Phys. Chem. C 119 (2015) 4627–4634, https://doi.org/10.1021/jp5126365.
- [60] G. Giorgi, J.I. Fujisawa, H. Segawa, K. Yamashita, Cation role in structural and electronic properties of 3D organic-inorganic halide perovskites: a DFT analysis, J. Phys. Chem. C 118 (2014) 12176–12183, https://doi.org/10.1021/jp504479c.