Insight into the Improved Phase Stability of CsPbI₃ from First-Principles Calculations

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ABSTRACT: The effect of organic cation doping with aziridinium (Az⁺) on the material properties of CsPbI₃ was investigated by applying first-principles calculations. The results showed that the phase stability is greatly improved by incorporating the organic cation Az⁺ at the A site of CsPbI₃. However, the band gap of CsPbI₃ is further enlarged from 1.76 to 2.27 eV when 12.5% of Az doping is used. The optical absorption coefficient of Cs₀.₈₇₅Az₀.₁₂₅PbI₃ is also decreased in the visible light region. The reasons of the improved phase stability and the enlargement of band gap arising from the organic cation doping are revealed. Our calculated results can provide theoretical guidance for improving the phase stability of halide perovskites.

INTRODUCTION

Lead halide perovskites have attracted extensive attention as promising photovoltaic candidates for solar cell applications during the past 10 years. The reason that makes halide perovskites suitable for photovoltaic applications is their excellent optoelectronic properties, such as tunable band gaps, high absorption coefficients, small effective masses, high carrier mobilities, and long electron–hole diffusion lengths. Since their first successful implementation in dye-sensitized solar cells in 2009, the power conversion efficiencies (PCE) have rapidly increased from 3.8% in 2009 to 25.2% in 2019. Methylammonium lead iodide (MAPbI₃) and formamidinium lead iodide (FAPbI₃) are the most promising photovoltaic materials. However, in view of the nature of the organic cations, the structural stability of hybrid perovskites is usually poor, which is the main factor for hindering commercial applications. An alternative approach to solve this issue is the replacement of these organic cations with an inorganic Cs cation for developing all-inorganic halide perovskites. The cubic phase of CsPbI₃ possesses a direct band gap of 1.73 eV, making it a promising photovoltaic material. However, the cubic phase can only be stable at temperatures over 300°C, and it can easily convert to an undesirable nonperovskite δ-phase at room temperature.

Great efforts have been made to improve the stability of CsPbI₃. Partial substitution of the iodine ion with the smaller bromine ion has been proven to be a feasible method for improving the phase stability. However, the incorporation of Br can lead to an increase in the band gap of CsPbI₃, which is undesirable for solar cell applications. Our previous study has indicated that the band gap of CsPbI₃ can be effectively tuned from 1.03 to 2.14 eV by applying strain. Recently, the phase stability of the CsPbI₃ perovskite can be significantly improved via organic cation doping. The results suggested that dimethylammonium cation (DMA⁺) is a more efficient dopant in stabilizing CsPbI₃ than ethylammonium (EA⁺) and guanidinium (GA⁺). A moderate amount of DMA⁺ can substitute partial Cs⁺ of CsPbI₃ forming the double-cation Cs₁₋ₓDMAₓPbI₃. The calculated results have revealed that 12.5% of Cs doping can slightly enhance the optical absorption of MAPbI₃, which makes it a possible candidate for highly efficient perovskite solar cells. A three-membered cyclic organic cation-based lead halide perovskite (CH₂)₂NH₂PbI₃ was proposed to be a potential absorber material for photovoltaics due to its good stability and lower band gap. The ionic radius of aziridinium ((CH₂)₂NH₂, Az) is between those of MA and FA. The previous calculated results further suggested that substitution of the Az cation at the A site can enhance the stability of the MA₁₋ₓAzₓPbI₃ perovskite and tune the band gap. Therefore, it is important to investigate whether Az doping can increase the stability of CsPbI₃ and the effect of Az cation on the structural stability and electronic and optical properties of the CsPbI₃ perovskite needs to be further explored for evaluating the photovoltaic performance.
In this work, the effect of cation replacement with Az on the properties of CsPbI$_3$ was investigated by applying first-principles calculations. The results show that Az doping can apparently improve the phase stability of CsPbI$_3$. The results indicate that the structural distortion of CsPbI$_3$, arising from Az doping is the main factor for the enhanced phase stability. At 12.5% dopant content, CsPbI$_3$ exhibits an apparently blue-shifted band gap from 1.76 to 2.27 eV and reduced the optical absorption in the visible light region.

### RESULTS AND DISCUSSION

The CsPbI$_3$ perovskite is a cubic structure with space group $Fm\overline{3}m$ at high temperatures. The calculated lattice parameter of CsPbI$_3$ is 6.26 Å, which agrees with the experimental value (6.29 Å). Therefore, the optB86b-vdW functional can give an accurate lattice parameter for CsPbI$_3$. In order to obtain 12.5% of Az doping, a 2 × 2 × 2 supercell containing eight formula units of CsPbI$_3$ was used, and one Cs$^+$ ion was replaced by Az$^+$, as shown in Figure 1. Az has a larger ionic radius than Cs; the substitution of Cs by Az should lead to the expansion of the volume. Interestingly, the volume contraction is observed when Cs is replaced by Az, as listed in Table 1. Moreover, the volume contraction is observed in Figure 1. Az has a larger ionic radius than Cs; the volume with respect to the pure CsPbI$_3$. In addition, the absorption in the visible light region.

Az-doped CsPbI$_3$ may be an ideal material for tandem solar cells due to its larger band gap.

### Table 1. Lattice Parameter and Volume of Pure and Az-Doped CsPbI$_3$ Supercell

| Perovskite       | A (Å) | B (Å) | C (Å) | V (Å$^3$) | Pb—I (Å) | Pb—I—Pb (°) |
|------------------|-------|-------|-------|-----------|----------|-------------|
| CsPbI$_3$        | 12.56 | 12.56 | 12.56 | 1981.79   | 3.14     | 180         |
| Cs$_{0.875}$Az$_{0.125}$PbI$_3$ | 12.49 | 12.31 | 12.35 | 1895.63   | 3.20—3.24| 144.3—151.6|
valence band maximum of pure and Az-doped CsPbI3 is mainly dominated by the I-5p orbital, while the conduction band minimum is contributed by the Pb-6p orbital.

We also compared the optical absorption of Az-doped CsPbI3 at a doping content of 12.5% with that of the pure CsPbI3. We used an optB86b-vdW functional along with the scissors correction to obtain an accurate band gap as that of the HSE06 functional. The band gap is usually underestimated in PBE calculations and overestimated for the dielectric properties. Based on the scissors correction, we compared the optical absorption of Az-doped CsPbI3 with that of the pure structure CsPbI3, as shown in Figure 4. Due to the larger band gap, Cs0.875Az0.125PbI3 exhibits a blue-shifted onset with respect to the pure CsPbI3. Although the optical absorption coefficient is apparently decreased in the visible spectrum, a slight absorption advantage for ultraviolet light can be observed. The reduced optical absorption can be ascribed to the wider band gap. In general, considering the improved phase stability, the photovoltaic performance of Cs0.875Az0.125PbI3 is expected to be further improved.

CONCLUSIONS

In conclusion, our calculated results indicate that the structural stability of CsPbI3 can be improved by Az doping. However, the Az-doped CsPbI3 shows blue-shifted band gap and reduced optical absorption in the visible spectrum. Further analyses reveal that the structural distortion of a perovskite material is the main reason for the improved phase stability and decreased optical properties. Our work can provide theoretical insight to further explore better phase stability of the CsPbI3 perovskite.

COMPUTATIONAL METHODS

Our calculations were carried out by employing density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP).28 The Perdew–Burke–Ernzerhof (PBE) version of the generalized gradient approximation29 (GGA)-based DFT methods using the projector augmented plane wave (PAW) was adopted.30 The energy cutoff of the plane wave basis was set to 500 eV. The optB86b-vdW functional was used to account for dispersion interactions in the halide perovskites.31,32 The criterion of $1 \times 10^{-5}$ eV for the total energy convergence was required. The atomic coordinates were fully optimized until the residual forces were smaller than 0.01 eV/Å. For CsPbI3, a $6 \times 6 \times 6$ k-point mesh was used for structural optimization. A $3 \times 3 \times 3$ k-point mesh was used for the CsPbI3 supercell. It is well known that the GGA-PBE functional usually underestimates the band gaps of halide perovskites. In order to obtain the band gap more accurately, Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional was applied.33,34 In the HSE06 method, the screened parameter was set to 0.2 Å$^{-1}$, and 20% of the screened Hartree–Fock (HF) exchange was used with the PBE functional.

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Notes
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