

Electronic Structure of Sr-doped CsPbCl₃ Crystal: First Principles Investigation

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Introduction

Organic-inorganic perovskites, particularly CsPbCl₃, are significantly interested in designing electronic devices like light-emitting diodes and solar cells due to their low cost and application feasibility. The efficiency of solar cell materials changes with their band gap, while the band gap depends on different physical parameters separately, such as a phase transition. As is well known, CsPbCl₃ is a direct band gap semiconductor that absorbs visible and ultraviolet light. Hence, this compound is used in photovoltaic and optoelectronic devices such as solar cells, photonic crystals, and light-emitting diodes. A promising strategy to expand properties is the impurity doping of perovskite materials. For some metal ions (e.g., Zn²⁺, Cr³⁺, Nd³⁺, Er³⁺, Ce³⁺), doping has been checked to be a hopeful way to improve the optical and electrical performance of perovskite materials, including the decrease of trap density and the boosts of stability, carrier mobility, and photoluminescence quantum yield. For example, Sr²⁺ dopants in CsPbI₃ perovskite nanocrystals enhance their stability and optical properties by increasing defect formation energy [1]. However, a mechanism of how doping influences the optical properties in perovskite nanocrystals is unobvious, and with it, no generalizable understanding is available that captures all observed effects. There are also no first-principles studies of the electronic structure of doped perovskites, which would make it possible to interpret the existence of experimental data.

Aim and objectives

In this study, we report first-principles investigations of pure and Sr-doped CsPbCl₃ electronic properties.

Models and Methods

All theoretical calculations are completed using the density functional theory (DFT). We apply the Perdew-Burke-Ernzerhof (PBE) parametrization for generalized gradient approximation (GGA) to describe the exchange-correlation functional. The cut-off energy was set as 450 eV; the convergence tolerance for energy was set as 5×10^{-6} eV/atom, and the tolerance for maximum force was 0.01 eV/Å. A 2×2×2 supercell was used to simulate the substitutional doping CsPbCl₃ system. First, we provide the geometry optimization of undoped CsPbCl₃ crystal using effectively Broyden-Fletcher-Goldfarb-Shanno algorithm. Next, we substituted the Pb atom for the Sr atom, and the optimization procedure was repeated. For a more accurate description of electronic spectra, Hubbard correction was applied to GGA, the so-called GGA+U method.

Results and discussion

To understand the changes in electronic properties of Sr-doped CsPbCl₃ crystal, we initially performed calculations of structural and electronic properties for undoped ones. Fig. 1 presents the optimized structure of pure CsPbCl₃ crystal in cubic phase.

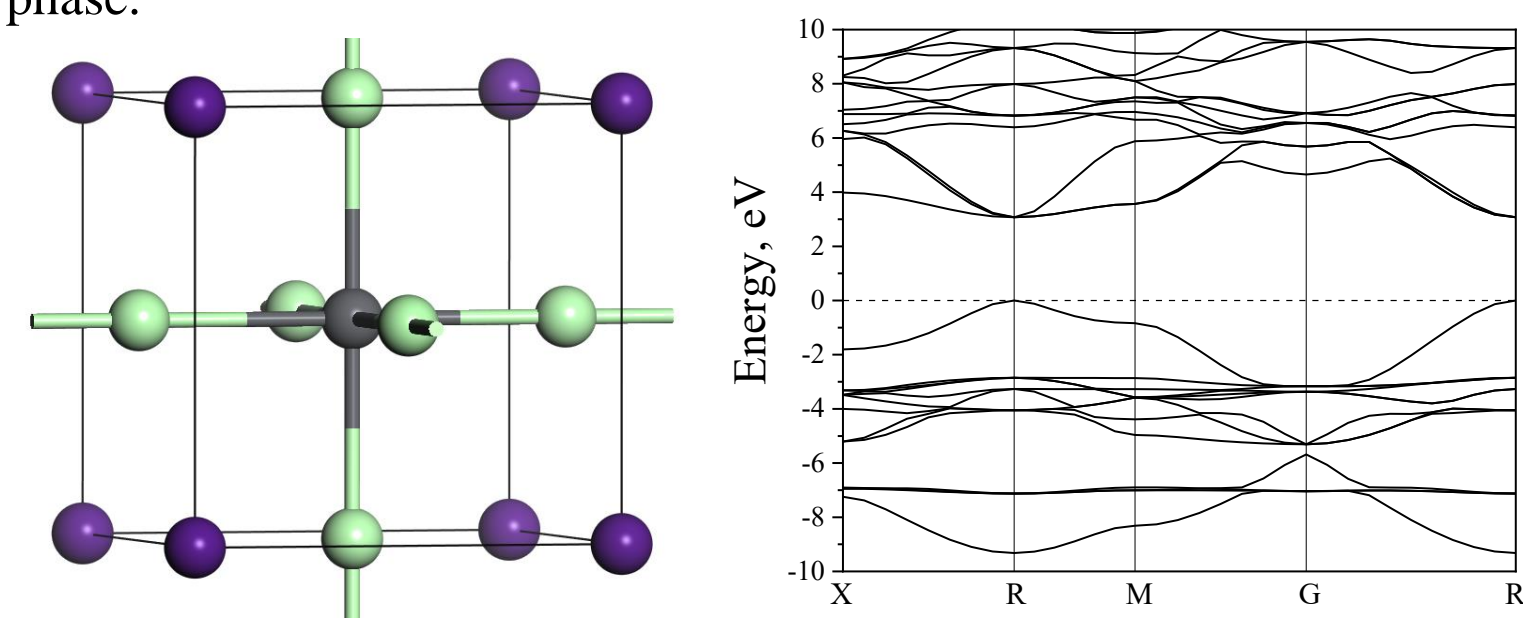


Fig. 1. The optimized structure and band structure of cubic CsPbCl₃ perovskite.

After structure optimization using the GGA+U method, the lattice parameter is 5.706 Å and slightly bigger than the experimental one [2]. The band structure shows the bandgap of pure CsPbCl₃ crystal was 3.07 eV at R-point (see Fig.1), which agrees with experimental data [3].

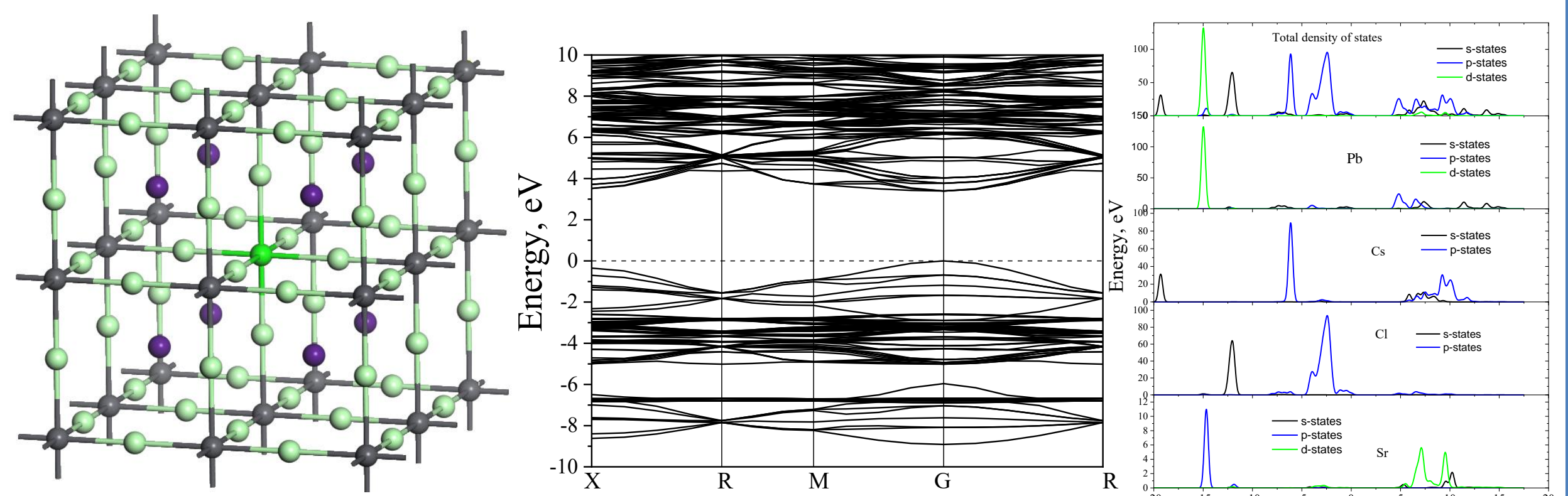


Fig. 2. The optimized structure, band structure and PDOS of cubic Sr-doped CsPbCl₃ perovskite.

Adding a Sr atom slightly changes the lattice parameters of CsPbCl₃ crystal to 5.722 Å (Fig. 2), mainly due to a lengthening of Pb–Cl and Sr–Cl bond length. The calculated formation energy of Sr-doped CsPbCl₃ shows the value of –1.74 eV, indicating the thermodynamically favorable position of the dopant. The presence of the Sr atom changes the doped crystal's electronic structure and leads to the band gap widening to 3.39 eV compared with the pure one. It should be noted, that the highly symmetric point of the band changes from R to Γ after doping (Fig. 2). The change in the energy band shows that the atomic orbitals overlap of Sr-doped CsPbCl₃ is different from undoped crystal. To explain the difference, we calculated the partial density of states presented in Fig. 2. The contribution of Sr to the bottom of the conduction band and the top of the valence band is weak, but the d-orbitals contribute at ~6 eV is large, indicating that they affect the atomic orbital overlap at the conduction band, and cause the conduction band move up, increasing the band gap value.

Conclusions

In this work, we studied the structural stability and electronic properties of Sr-doped CsPbCl₃ using first-principles calculations and compared them with those of undoped perovskite. The structure analysis shows that doping of Sr leads to a slight increase in lattice parameters compared with undoped ones due to a lengthening of Pb–Cl and Sr–Cl bond length. The formation energy values demonstrate that Sr doping can improve the stability of the material. Furthermore, the electronic properties show a change in the band gap for Sr-doped CsPbCl₃ perovskite, which is attributed to the influence of the doped element d-orbitals on the original orbitals. Our investigation provides a helpful reference for the deep understanding and further development of Sr-doped CsPbCl₃ perovskites.

Acknowledgments

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References

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