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Halide-Induced Band Gap Modulation in $RbPbCl_{3-x}Br_x$ Perovskites: Insights from a First-Principles Study

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Abstract

First-principles calculations based on density functional theory (DFT) as implemented in Quantum ESPRESSO were used to systematically investigate the structural and electronic properties of inorganic halide perovskites $RbPbCl_{3-x}Br_x$ (x = 0.00, 0.25, 1.50, 2.75, and 3.00). The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional was employed to describe exchange correlation effects. The optimized lattice parameters reveal that bromine incorporation significantly influences the crystal structure, leading to variations in lattice constants, bond lengths, and unit cell volume due to the difference in atomic radii between Cl and Br atoms. The calculated bulk modulus indicates a reduction in mechanical stiffness with increasing bromine concentration, suggesting enhanced structural flexibility. Electronic band structure analysis shows that all compounds have a direct band gap at the Γ-point. Notably, the band gap values obtained were 2.22 eV, 1.87 eV, 1.62 eV, 1.32 eV, and 1.21 eV for $RbPbCl_{3-x}Br_x$ (x = 0.00, 0.25, 1.50, 2.75, and 3.00), respectively. The decrease in the band gap becomes prominent as the Br doping concentration increases. This indicates effective band gap tuning via halide substitution. The density of states (DOS) and partial density of states (PDOS) analysis reveal that the valence band is predominantly contributed to by halide p-orbitals, while the conduction band is mainly composed of Pb p-states with minor contributions from Rb states. These findings demonstrate that bromine doping effectively modulates the electronic properties of $RbPbCl_3$, making $RbPbCl_{3-x}Br_x$ a promising candidate for optoelectronic and photovoltaic applications.

Keywords: Halide perovskites; Density Functional Theory (DFT); Halide substitution; Electronic structure; Band gap engineering.

I. Introduction

Hybrid halide perovskites have attracted considerable research interest in recent years because of their outstanding optoelectronic properties and remarkable performance in photovoltaic applications [1]. Their attractive characteristics include direct band gaps [2], low charge-carrier recombination rates [3], low-cost fabrication, high optical absorption coefficients [4-5], and excellent defect tolerance [6]. Despite these advantages, the long-term stability of

organic–inorganic hybrid halide perovskites remains a major challenge. Their susceptibility to heat, moisture, and atmospheric degradation significantly limits their practical application and large-scale commercialization [7].

To address these stability issues, increasing attention has been directed toward fully inorganic halide perovskites, which generally exhibit superior thermal and environmental stability compared with their hybrid counterparts [8–10]. In hybrid perovskites, the presence of organic cations introduces molecular dipoles that can distort the crystal lattice and contribute to current–voltage hysteresis, thereby reducing the operational stability and power conversion efficiency (PCE) of perovskite solar cells (PSCs) [11–13]. In contrast, inorganic perovskites possess relatively stable crystal structures because their inorganic cations are less volatile and do not introduce molecular dipoles. Consequently, they exhibit reduced hysteresis and improved charge-carrier transport, making them promising candidates for next-generation photovoltaic devices [14-15].

Among inorganic halide perovskites, the $RbPbX_3$ (X = Cl, Br, I) family has emerged as a promising class of materials owing to its excellent structural stability and tunable electronic properties. Reference [16] demonstrated that $CsPbX_3$ (X = I, Br, Cl) exhibits excellent thermal stability while maintaining photovoltaic performance comparable to that of the widely studied hybrid $MAPbI_3$ perovskite. Their study also showed that halide substitution strongly influences carrier transport and optical absorption. Similarly, [17] reported that variations in halide composition significantly affect electron mobility, while [18] demonstrated that the ionic radius and Goldschmidt tolerance factor of Rb^+ favor the formation of stable perovskite structures. In general, halide perovskites with tolerance factors in the range of 0.7–1.0 are considered structurally stable.

Halide engineering has become an effective strategy for tailoring the structural, electronic, and optoelectronic properties of perovskite materials. For example, [19] reported that $MAPbI_{3-x}Cl_x$ exhibits enhanced air stability compared with pristine $MAPbI_3$. Reference [20] demonstrated that partial bromine substitution substantially improves the stability of $MAPbI_3$ without significantly compromising its photovoltaic efficiency. Furthermore, halide substitution has been shown to enhance charge-carrier mobility and diffusion length. Reference [21] reported longer carrier diffusion lengths in $MAPbI_{3-x}Cl_x$ than in $MAPbI_3$, while [22] observed improved carrier mobility and reduced recombination rates in both $MAPbI_{3-x}Br_x$ and $MAPbBr_{3-x}Cl_x$. In addition to improving stability and charge transport, halide substitution provides an effective means of tuning the electronic band gap, thereby enabling the optimization of perovskite materials for various optoelectronic applications [22].

Although considerable progress has been made in understanding mixed-halide perovskites, systematic first-principles investigations of bromine substitution in $RbPbCl_3$ remain relatively limited. Understanding how bromine incorporation modifies the structural and electronic properties of this material is important for the rational design of stable inorganic perovskites with tunable band gaps for photovoltaic and optoelectronic applications.

In this work, first-principles density functional theory (DFT) calculations were performed to systematically investigate the influence of bromine substitution in $RbPbCl_{3-x}Br_x$ (x = 0.25, 1.50, 2.75, and 3.00). Emphasis was placed on evaluating the effects of halide substitution on the structural properties, electronic band structure, density of states (DOS), partial density of states (PDOS), and band-gap modulation. The findings provide further insight into the potential of mixed-halide $RbPbCl_{3-x}Br_x$ perovskites for future optoelectronic and photovoltaic applications.

II. Computational Details

First-principles calculations were performed to compute the total energy based on density functional theory (DFT) as implemented in Quantum ESPRESSO with periodic boundary conditions. The projector-augmented wave (PAW) method was used for characterizing the interaction of the ions. The total energies are obtained by solving the Kohn–Sham equations self-consistently. The generalized gradient approximation (GGA) was used as an exchange correlation functional with its underlying Perdew–Burke–Ernzerhof (PBE) variant. PAW pseudopotentials were sourced from the Quantum ESPRESSO Pseudopotential Library (PSLibrary). The electronic self-consistent field (SCF) calculations were deemed converged when the total energy difference between successive iterations was less than 1.0×10^{-8} Ry. The atomic positions and internal forces were fully relaxed until the energy was 0.01 eV/Å. A plane wave kinetic energy cut-off of 550 eV was set. Both the atomic positions and crystal lattices were fully optimized by relaxation using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-Newton algorithm. The occupation scheme was set to 'fixed' for semiconducting systems, and the k-point mesh was set as $10 \times 10 \times 10$ for the structural optimization, and was increased to $12 \times 12 \times 12$ to compute the density of states (DOS). The electronic band structure was calculated in the high symmetry directions of the Brillouin zone $M - \Gamma - R - X - M$. The cubic crystal structure for Pb-based perovskites $RbPbCl_{3-x}Br_x$ (x= 0, 0.25, 1.50, 2.75, and 3.00) with space group Fm-3m is shown in Fig. 1 (see next page).

III. Results and Discussion

A. Structural properties

The optimized crystal lattice parameter of $RbPbCl_3$ was obtained to be a = b = c = 11.58 Å and $\alpha = \beta = \gamma = 90^0$. The introduction of Br into the lattice was found to influence both the lattice dimensions and unit cell volume, as summarized in Table I. The calculated cell volume slightly decreased from 155.20 Å³ for pristine $RbPbCl_3$ to 154.80 Å³ for $RbPbCl_{0.25}Br_{2.75}$, followed by a gradual increase to 161.80 Å³ for $RbPbBr_3$ with increasing Br concentration. This increase

in volume with higher Br compositions may be associated with the difference in ionic radii and the structural relaxation induced by halide substitution.

Similarly, the bond lengths were observed to vary with the composition. The Pb–Cl bond length in pristine $RbPbCl_3$ was calculated as 2.63 Å, while the Pb–Br bond lengths in the doped compounds ranged from 3.26 Å to 3.31 Å. These structural modifications indicate that bromine substitution significantly alters the local bonding environment and lattice configuration of the perovskite structure.

Furthermore, the bulk modulus decreases with increasing Br incorporation, suggesting reduced structural rigidity and enhanced compressibility in the mixed-halide compounds. The observed changes in structural parameters confirm that halide substitution effectively tunes the crystal properties of $RbPbCl_3$ perovskites.

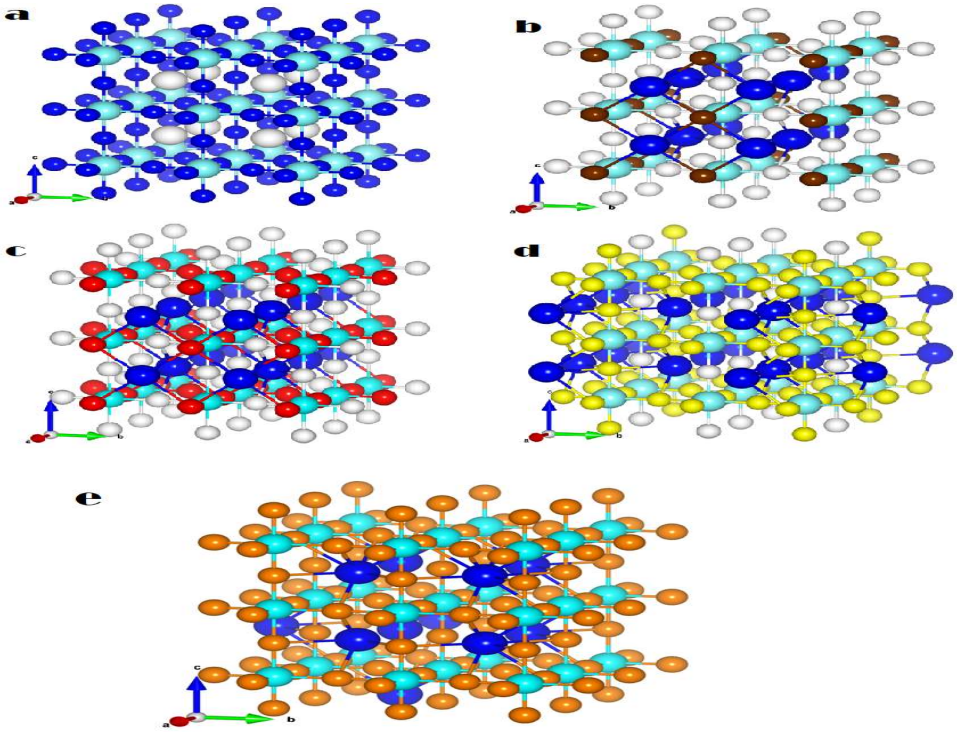

Fig. 1. Optimized Crystal Structure for $RbPbCl_{3-x}Br_x$ (a) $x = 0.00$ (b) $x = 0.25$ (c) $x = 1.50$ (d) $x = 2.75$ (e) $x = 3.00$.

Table I. Calculated Lattice Parameters (a), Volume, Bond Length, Energy Band Gap (Eg), Bulk Modulus B_0, and Derivative of the Bulk Modulus B′ for $RbPbCl_{3-x}Br_x$ (x= 0, 0.25, 1.50, 2.75, and 3.00).

Compound	Lattice distance a (Å)	Volume (Å³)	Bond length (Å)	Band gap Eg (eV)	Bulk modulus B_0 (GPa)	Derivative of bulk modulus (B')
$RbPbCl_{3-x}Br_x$	11.58	155.20	(Pb-Cl) 2.93	2.22	27.62	5.00
$RbPbCl_{3-x}Br_x$	11.34	154.80	(Pb-Br) 3.26	1.87	20.90	4.69
$RbPbCl_{3-x}Br_x$	11.21	160.50	(Pb-Br) 3.22	1.62	19.10	6.97
$RbPbCl_{3-x}Br_x$	11.29	161.30	(Pb-Br) 3.11	1.32	17.10	5.52
$RbPbCl_{3-x}Br_x$	11.26	161.80	(Pb-Br) 3.31	1.21	23.30	8.18

B. Electronic Properties

The electronic band structures of pristine and Br-substituted $RbPbCl_{3-x}Br_x$ were calculated using the PBE-GGA exchange-correlation functional, and the results are presented in Fig. 2. The band structures were computed along the high-symmetry path M–Γ–R–X–M of the Brillouin zone within an energy window of −4 to 4 eV, with the valence band maximum (VBM) aligned to 0 eV for all compositions. As shown in Fig. 2, the conduction band minimum (CBM) and the VBM occur

at the Γ-point for all investigated compositions, confirming the direct band-gap nature of the compounds.

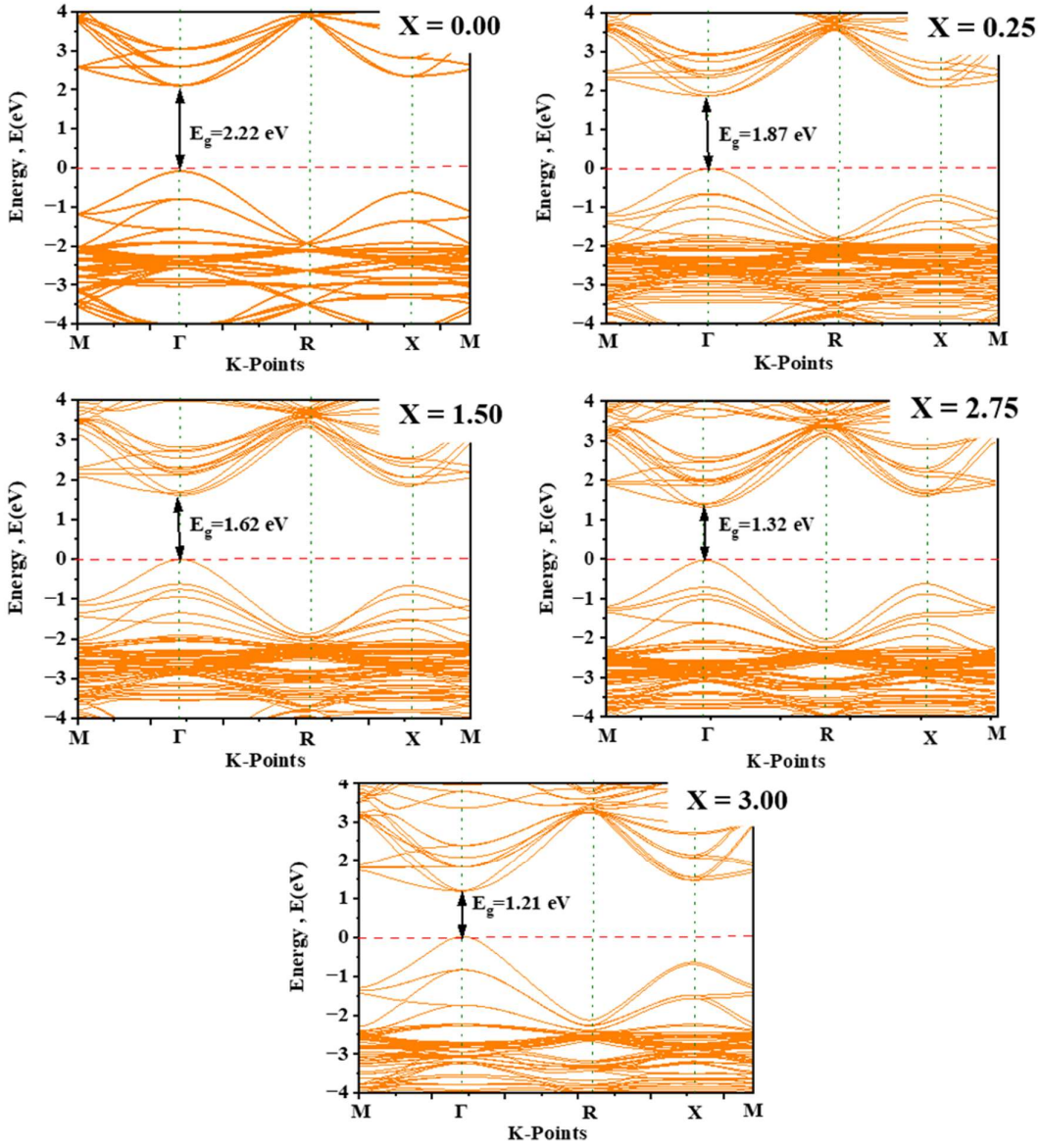

Fig. 2. Calculated band structure for $RbPbCl_{3-x}Br_x$ (x=0, 0.25, 1.50, 2.75, and 3.00).

The calculated band gap of pristine $RbPbCl_3$ is 2.22 eV, which agrees well with previously reported theoretical values of 2.13 and 2.19 eV [24-25], thereby validating the computational approach employed in this study. Minor discrepancies between the calculated values and those reported in the literature may arise from differences in computational parameters, including pseudopotentials, plane-wave cutoff energies, k-point sampling, structural optimization procedures, and exchange-correlation functionals. Furthermore, the progressive reduction in band gap with increasing bromine concentration is consistent with the behavior previously reported for mixed-halide perovskites.

Although advanced approaches such as hybrid functionals (HSE06) and GW approximations generally provide more accurate band-gap predictions, the GGA-PBE functional remains suitable for investigating compositional trends and qualitative electronic properties in halide perovskites. The calculated band-gap values are summarized in Table I, showing a systematic decrease from 2.22 eV for pristine $RbPbCl_3$ to 1.21 eV for fully substituted $RbPbBr_3$. This reduction is attributed to modifications in the electronic structure resulting from halide substitution. The incorporation of Br atoms alters the hybridization between Pb and halide orbitals, leading to changes in the positions of the valence

band maximum and conduction band minimum. Similar band-gap modulation resulting from halide substitution has been widely reported for mixed-halide perovskites, attributed to changes in orbital interactions and local lattice environments [7], [14-15], [26]. Consequently, the observed band-gap narrowing is associated with compositional tuning of the electronic structure rather than the formation of impurity states. Further investigations using hybrid functionals, charge-density analysis, or many-body perturbation methods would provide additional insight into the underlying electronic transitions and improve the quantitative prediction of electronic properties.

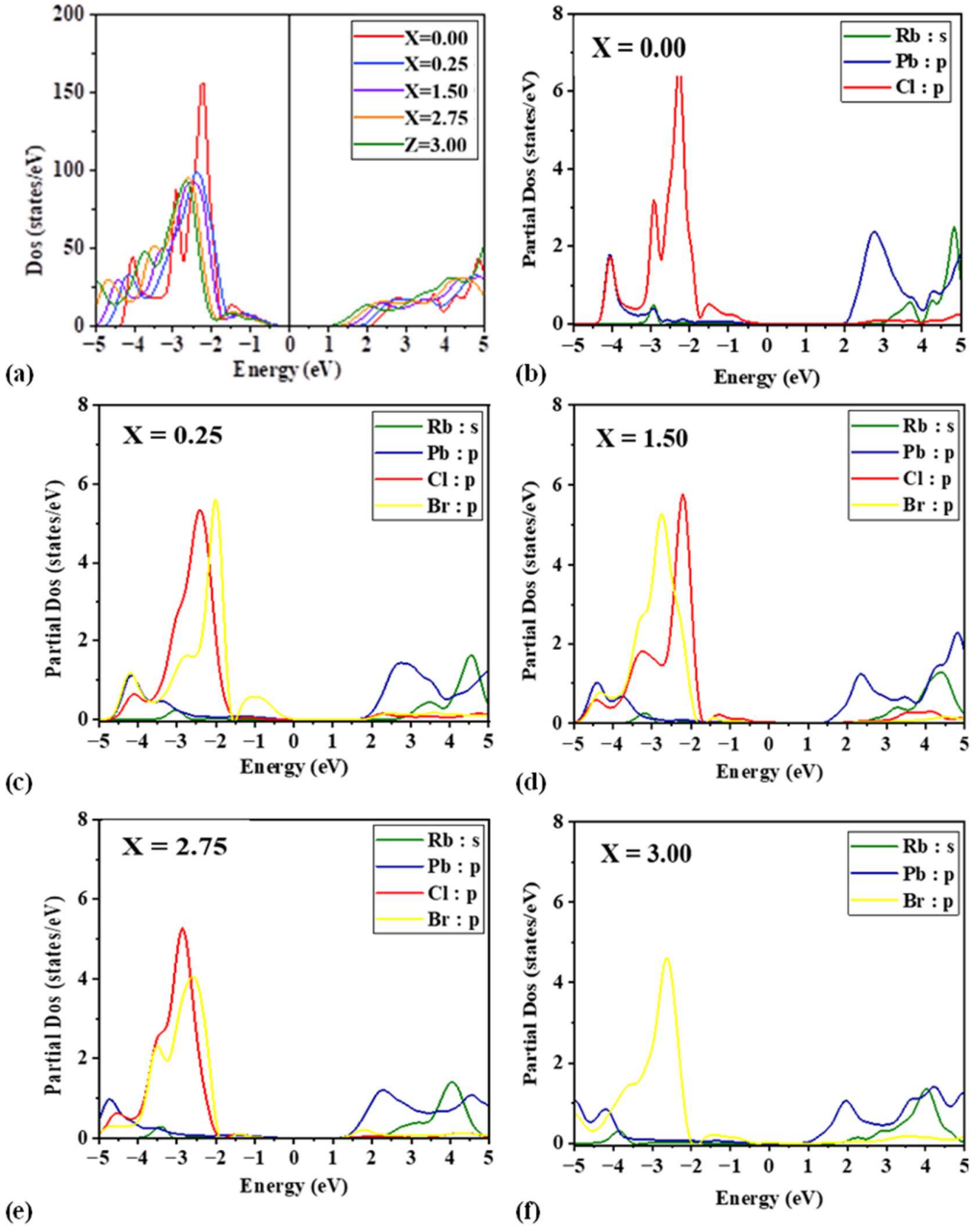

Fig. 3. Calculated (a) DOS of $RbPbCl_{3-x}Br_x$ (b – e) PDOS of $RbPbCl_{3-x}Br_x$ (x=0, 0.25, 1.50, 2.75, and 3.00).

The total density of states (DOS) and partial density of states (PDOS) for the investigated compositions are presented in Fig. 3. The DOS spectra confirm the semiconducting nature of all compounds, characterized by a well-defined band gap

separating the valence and conduction bands. The dominant DOS peaks are located within the valence band region, indicating that the occupied electronic states are primarily concentrated below the Fermi level.

The PDOS analysis provides further insight into the orbital contributions responsible for the electronic structure. For pristine $RbPbCl_3$, the valence band is predominantly composed of Cl *p* states, whereas the conduction band is mainly derived from Pb *p* states with minor contributions from Rb *s* orbitals. As the Br concentration increases, Br *p* orbitals progressively contribute to the valence band while the contribution from Cl *p* states decreases accordingly. Throughout the substitution range, the conduction band remains largely dominated by Pb *p* states with relatively small contributions from Rb orbitals. These results indicate that bromine substitution primarily modifies the valence-band electronic states while preserving the overall conduction-band character, thereby accounting for the gradual reduction in band gap observed across the series.

It should be noted that spin–orbit coupling (SOC) was not included in the present calculations. In Pb-based halide perovskites, SOC significantly influences the conduction band edge through the splitting of Pb 6*p* states, generally leading to a reduction in the calculated band gap. Consequently, the band-gap values reported in this work may be slightly overestimated. Nevertheless, previous studies have shown that the omission of SOC has a relatively small effect on the qualitative description of the electronic structure and compositional trends. Therefore, the observed evolution of the electronic properties with increasing bromine concentration remains reliable, although future investigations incorporating SOC and hybrid exchange-correlation functionals would provide improved quantitative agreement with experimental measurements.

IV. Conclusion

A comprehensive first-principles investigation of the structural and electronic properties of Br-substituted $RbPbCl_{3-x}Br_x$ perovskites has been carried out to evaluate the influence of halide substitution on their fundamental properties. The results demonstrate that bromine incorporation significantly modifies the crystal structure through changes in lattice parameters, unit-cell volume, bond lengths, and mechanical properties. The reduction in bulk modulus with increasing Br concentration indicates enhanced structural flexibility and compressibility resulting from halide substitution.

Electronic structure calculations reveal that all investigated compositions retain a direct band gap at the Γ-point, while the band gap decreases progressively from 2.22 eV for pristine $RbPbCl_3$ to 1.21 eV for $RbPbBr_3$. This continuous band-gap reduction confirms that bromine substitution provides an effective route for tuning the electronic properties of the material. Analysis of the density of states further shows that the valence band is predominantly composed of halide p orbitals, whereas the conduction band is mainly derived from Pb p states, demonstrating that the observed band-gap modulation originates from changes in orbital hybridization induced by halide substitution.

Overall, the results indicate that Br substitution is an effective strategy for tailoring the structural stability and electronic characteristics of $RbPbCl_3$, highlighting the potential of $RbPbCl_{3-x}Br_x$ as a promising material for photovoltaic and other optoelectronic applications. Although spin–orbit coupling (SOC) was not considered in the present study, the calculated compositional trends remain physically meaningful and consistent with previous theoretical investigations. Future studies incorporating SOC, hybrid exchange-correlation functionals such as HSE06, and detailed optical and mechanical property analyses would provide improved quantitative accuracy and a more comprehensive understanding of the material's application potential.

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