A First-Principles Study on ABBR₃ (A = Cs, Rb, K, Na; B = Ge, Sn) Halide Perovskites for Photovoltaic Applications

Dibyajyoti Saikia, Mahfooz Alam, Jayanta Bera, Atanu Betal, Appala Naidu Gandi, and Satyajit Sahu*

Perovskite solar cells (PSCs) have received intensive attention and demonstrated power conversion efficiency (PCE) as high as 25.8%. Concerning Pb toxicity and the instability of organic elements, all inorganic lead-free perovskites (ILPs) have been extensively studied to achieve comparable or greater photovoltaic performance. To develop ILPs as an alternative for solar cell (SC) applications, first-principles calculations of ABBR₃ perovskites (A = Cs, Rb, K, and Na, and B = Sn, and Ge) is performed. Structural, electronic, and optical properties are systematically studied to probe the potential for photovoltaic applications. These ILPs exhibit a direct bandgap in the range of 1.10–1.97 eV, which is highly beneficial for absorbing solar energy. Furthermore, these ILPs demonstrated significant optical absorption (over 10⁵ cm⁻¹) in the UV–Vis spectrum. These results will help design high-performance lead-free PSCs.

1. Introduction

Organic–inorganic halide perovskites (OIHPs) have gained notable attraction as potential candidates in the field of photovoltaics (PV) industry due to the ease of fabrication and optoelectronic properties.[1–4] Within a decade or more, the PCE of PSCs has reached certified values of over 25%.[5,6] Nevertheless, the organic elements (methylammonium and formamidinium) present in the OIHPs showed inferior stability under several environmental conditions,[7–9,10] limiting the application. Replacement of these organic species with inorganic alkali cations (Cs⁺ and Rb⁺) overcome this problem.[11] All inorganic CsPbX₃ perovskites are potential candidates for efficient PSCs due to their high thermal stability and improved optoelectronic characteristics.[12] However, the toxicity that arises from Pb element causes serious environmental concern and constrains in large-scale commercialization.[13,14]

Replacement of Pb²⁺ cation with another less toxic element could be considered an efficient tool for the practical implementation of PSCs. Recently, the substitution of Pb with other divalent cations like Sn²⁺, Ge²⁺, Zn²⁺, Cu²⁺, Mn²⁺, etc., and other elements such as Bi, Sb, Ag, etc. have been extensively studied to explore their potential in photovoltaics as well as optoelectronics.[15–19] Among them, Sn and Ge are key Pb replacements due to similar electronic characteristics.[18] Chen et al. reported 4.92% PCE on lead-free PSCs by synthesizing CsGeX₃ perovskite quantum rods,[20] while mixed tin-germanium (CsSn₀.₅Ge₀.₅I₃) based PSCs delivered 7.11% PCE.[19] Meanwhile, CsSnI₃ based PSCs achieved over 10% PCE.[21] It was demonstrated that perovskite materials (ABX₃) with Br in the X-site position has shown superior stability compared to their iodine counterpart.[22] Upon substituting I with Br, orthorhombic phase CsSnI₃ changes to cubic phase CsSnBr₃. In addition, Br addition improves the Voc of mixed CsSnIₓBrₙ PSCs.[23] In another work, Song et al. developed Sn-based PSCs in a reducing vapor atmosphere. The fabricated CsSnBr₃ based device delivered 3.04% PCE, while for the CsSnI₃ based device PCE was 1.83%.[24] However, the PCE of all inorganic lead-free PSCs is still quite lower than the state-of-the-art OIHP-based PSCs. It could be expected that the replacement of Cs with Rb in the A-site position improves the quality of perovskite film and, thus, suitability in PSCs.[25,26] However, to our knowledge, except for a few theoretical investigations, no experimental work has been performed on RbBBR₃ (B = Sn, Ge), although there are several experimental and theoretical investigations on CsBBR₃ perovskites. Thus, a great deal of insight is required to further develop ILPs.

Here, an investigation of ABBR₃ perovskites has been performed using first-principles calculations to examine their potential as photovoltaic materials. The structural, electronic, and optical properties have been comprehensively studied.

2. Computational Details

First-principles calculations were performed using the pseudopotential-based density functional theory as implemented in the Quantum Espresso package.[27] Ultrasoft pseudopotentials...
have been employed for electron–ion interactions using Perdew–Burke–Ernzerhof (PBE)\cite{28} within the generalized gradient approximation. The electronic kinetic energy cut-off energy was set to 520 Ry. For the structural relaxation $10 \times 10 \times 10$ k-grids were employed and for the electronic structure calculations denser k-grids of $15 \times 15 \times 15$ were used. All the structures were fully relaxed until the residual forces on atoms were less than 0.01 eV Å$^{-1}$ and energy values were converged within $10^{-6}$ eV. The optical properties were calculated using VASP package.\cite{29} In the VASP calculation, the interaction between electron and the ions were described by the projector-augmented wave (PAW) potentials\cite{30} within PBE-GGA formalism. The electronic kinetic energy cutoff is set as 300 eV to make the plane wave basis finite. Structural relaxation was continued until the energies are converged within $10^{-3}$ eV. All the compounds except NaSnBr$_3$ have a $t$ value of 0.832–1.009. As NaSnBr$_3$ has a $t$ value of 0.774, it does not stabilize in the perovskite phase. Hence, the NaSnBr$_3$ is not considered in further calculations. The octahedral distortion exists if the $B^{2+}$ ion is not likely to be well fitted with the $X_6$ octahedral cage, accountable for structural distortion. The calculated $\mu$ values are found to be in the range of 0.372–0.561, as listed in Table S3, Supporting Information. The lower values of $\mu$ for the Ge-based materials compared to the Sn-based halides indicate more octahedral distortion of Ge-based halides because of the smaller ionic radius of the Ge$^{2+}$ ions (0.73 Å) in comparison to the Sn$^{2+}$ ion (1.10 Å). This leads to more Ge$^{2+}$ cation off-centering.

The calculated lattice constants, bond lengths, and bond angles for all the relaxed structures are shown in Table 1. The lattice constants for CsSnBr$_3$ and CsGeBr$_3$ were calculated to be 5.89 and 5.75 Å, showing good agreement with the previously computed results.\cite{37,38} Calculations slightly overestimated the lattice constants for CsSnBr$_3$ and CsGeBr$_3$.
parameters compared with the experiments (≈1.4% for CsSnBr₃ and ≈2.0% for CsGeBr₃). As the A-site cation changes from Cs to K for Sn-based and from Cs to Na for Ge-based perovskite compounds, the lattice constant decreases slightly due to the reduction of ionic radius from Cs to Na.

To investigate the thermodynamic stability, the formation energies were evaluated by employing the relation

\[ H_f = E(ABBr₃) - [E(ABr) + E(BBr₂)] \]  

where \( E(ABBr₃) \), \( E(ABr) \) and \( E(BBr₂) \) represent the total energies of \( ABBr₃ \), \( ABr \) and \( BBr₂ \) compounds, respectively. According to Equation (1), a negative value of \( H_f \) indicates loss of energy during the formation of \( ABBr₃ \) (exothermic process), validating the thermodynamic stability of these compounds. A more negative value of \( H_f \) leads to more thermodynamic stability and vice-versa. The calculated formation energies for all the compounds are depicted in Figure 2. It was observed that CsGeBr₃ exhibits a lower \( H_f \) value compared to other materials. In contrast, KGeBr₃, NaGeBr₃, and KSnBr₃ showed positive \( H_f \) similar to previous findings, indicating they are not energetically favorable. It should be noted that thermodynamic stability increases in the order of Na, K, Rb and Cs for both Ge- and Sn-halides, supporting the rise of tolerance factor from Na, K, Rb to Cs-based compounds.

### 3.2. Electronic Properties

The band gap of a material is a key quantity that influences the efficiency of PV materials. Semiconducting materials with suitable band gap is crucial for the fabrication of SCs. As most Sun radiations that reach the surface of the Earth have an energy of <2 eV, photovoltaic materials with band gaps >2 and <0.9 eV are less effective. In addition, materials with band gaps in the range of 0.9–2.0 eV are effective for single single-junction SCs and top and bottom cells in the tandem structure. To probe the electronic properties band structures were calculated along paths connecting the high symmetry points \( \Gamma (0 0 0) \), \( X (0.5 0.0 0.0) \), \( M (0.5 0.5 0.0) \), \( R (0.5 0.5 0.5) \) and \( \Gamma (0 0 0) \) for the Sn-based; and \( \Gamma (0 0 0) \), \( Z (0.5 0.5 0.5) \), \( F (0.5 0.5 0.0) \) and \( \Gamma (0 0 0) \) for the Ge-based compounds. As shown in Figure 3, all the studied materials showed direct band gaps having both the valence band maximum (VBM) and the conduction band minimum (CBM) at \( \Gamma \) point in the case of Sn-based compounds, and \( Z \) point in the case of Ge-based compounds. The horizontal dashed line in the band structure represents the mid-point of the band gap and it is set to 0 eV. The band gap values for CsSnBr₃ and CsGeBr₃ were computed to be 0.64 and 1.37 eV, respectively, which agrees well with other calculated results. However, these band gap values are quite smaller in comparison to experimental results as PBE functional results in underestimated bandgaps except from some Pb-based halide perovskites. More accurate electronic density of states (DOS) computed using the HSE06 functionals are shown.

### Table 1. Calculated structural parameters of \( ABBr₃ \) perovskites using the PBE functionals.

| Compound | Lattice parameter [Å] | Bond length [Å] | Bond angle [°] |
|----------|-----------------------|----------------|--------------|
|          | This work | Expt. | Others | This work | Expt. | Others |
| CsSnBr₃  | 5.89     | 5.804 | 5.881,[19] 5.90,[18] 5.882,[40] | 2.945 | 90   |
| RbSnBr₃  | 5.87     | –     | 5.85,[41] 5.863,[42] 5.891,[41] | 2.935 | 90   |
| KSnBr₃   | 5.85     | –     | 5.873,[41] 5.758,[17] 5.78,[41]  | 2.925 | 89.23 | 88.74 | 88.35[45] |
| CsGeBr₃  | 5.75     | 5.635[33,44] | 5.758,[17] 5.78,[41] | 2.5773–3.1875 | 89.23 | 88.74 | 88.35[45] |
| RbGeBr₃  | 5.66     | –     | 5.53,[46] (PBEsol) | 2.5947–3.0782 | 89.40 | 87.99[46] |
| KGeBr₃   | 5.61     | –     | 2.6060–3.0159 | 89.49   |
| NaGeBr₃  | 5.59     | –     | 2.6144–2.9969 | 89.30   |

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Figure 2. Calculated tolerance factor (t), octahedral factor (µ), and formation energy of \( ABBr₃ \) perovskites (black diamonds represent t and µ, while red squares represent formation energy).
Figure 3. Band structures of a) CsSnBr$_3$, b) RbSnBr$_3$, c) KSnBr$_3$, d) CsGeBr$_3$, e) RbGeBr$_3$, f) KGeBr$_3$, and g) NaGeBr$_3$ (blue and yellow curves represent band structures with and without SOC using PBE functional).

In the Figure 4. The computed band gap values obtained from the DOS showed good agreement with the experimental findings compared to PBE computed band gaps. As we replace the Cs$^+$ with other alkali cations, the lattice constant varies in descending order from Cs to Na because of the reduction of ionic radius, resulting strengthening of p–p hybridization due to the smaller distance between atoms. Consequently, VBM shifts upward while CBM shifts downward, resulting in the band gap reduction. However, for NaGeBr$_3$ band gap value obtained from HSE is much higher than the PBE computed one. To study the significance of spin-orbit coupling (SOC), band structures were computed using PBE under SOC consideration. It was observed that under SOC consideration (PBE + SOC), band gaps for all the compounds decrease because of the splitting and downshifting of CBM. Furthermore, the $\Delta_{soc}$ values for Ge-halides (0.04–0.06 eV) are very small compared to Sn-halide perovskites (0.36–0.37 eV). This indicates that Ge-based perovskites showed a weak SOC effect compared to Sn-based compounds as Ge is lighter than Sn. Obtained band gap values of the studied compounds are shown in Table 2. The results are consistent with the previous findings.

In order to gain a better understanding of the electronic properties, the projected density of states (PDOS) were computed and are depicted in Figure 5. All of the studied compounds showed similar trends of electronic orbital behavior. The valence band is predominantly contributed by Br 4p states, while the conduction band is mainly contributed by 4p/5p states of Ge/Sn elements with a little contribution from Br 4p states. In addition, below the VBM a small superposition of B-site element p states and Br p states was observed, implying a marginal hybridization of B–Br bond. It should be noted that Br 4p and Ge/Sn 4s/5s states constitute the VBM while the CBM is formed by Br 4s and Ge/Sn 4p/5p states. Like the prototype halide perovskite MAPbI$_3$, band edges are not directly contributed by A-site elements indicating the electronically inert behavior. However, the A-site cation indirectly impacts the overall electronic structure of the compound by inducing distortion of BX$_6$ octahedron due to their difference in ionic radii. Moreover, charge densities at CBM and VBM were computed to obtain further insight of electronic structure. As seen from Figure 6, electron densities of VBM are located on Br and B-site elements, while for CBM the densities...
Figure 4. Calculated density of states (DOS) of a) CsSnBr₃, b) RbSnBr₃, c) KSnBr₃, d) CsGeBr₃, e) RbGeBr₃, f) KGeBr₃, and g) NaGeBr₃ perovskites.

Table 2. Calculated bandgap values of ABBr₃ perovskites studied in this work in the unit of electronvolts.

| Compounds  | PBE     | Others  | PBE + SOC | HSE     | Others  | Expt.  |
|------------|---------|---------|-----------|---------|---------|--------|
|            | This work |         |           | This work |         |        |
| CsSnBr₃    | 0.64    | 0.64[41] | 0.28      | 1.10    | 1.11[51] | 1.75   |
| RbSnBr₃    | 0.60    | 0.556[43] | 0.24      | 1.05    | 1.10[51] |        |
| KSnBr₃     | 0.56    | 0.57[41] | 0.19      | 1.00    |         |        |
| CsGeBr₃    | 1.37    | 1.44[45] | 1.33      | 1.97    | 1.97[51] | 2.38[52] |
| RbGeBr₃    | 1.08    | 1.57[46] | 1.03      | 1.64    | 1.65[51] | 2.32[53] |
| KGeBr₃     | 0.91    | 0.85     | 1.55      |         | 1.47[51] |        |
| NaGeBr₃    | 0.78    | 0.73     |           |         |         |        |
are essentially located at the B-site atom with a little presence on Br atoms. No charge accumulation around the A-site element was observed, consistent with the PDOS findings.

To study the charge (electron and hole) transport characteristics, we have calculated the effective masses which are closely related to the mobility of carriers. The lower the effective mass of carriers the higher will be the carrier mobility. The effective masses of electrons and holes were obtained by fitting their energy dispersion curve to parabolic function at CBM and VBM, respectively, along two different k-paths: Γ to Z and Z to F for the Ge-based perovskites; and from M to R and R to Γ for the Sn-based perovskites. The calculated effective masses of the carriers are given in Table S4, Supporting Information. The effective masses of holes for the Sn-based perovskites have been found to be smaller compared to Ge-based perovskites, consistent with the high hole mobility of Sn-halides found in previous theoretical investigations.[18,50] In addition, CsGeBr₃ showed a very low effective mass for electrons compared to the other investigated compounds, suggesting high electron mobility of CsGeBr₃. The change of A-site cation does not play a significant role in the effective mass of carriers; the values of effective masses are more or less unchanged. To evaluate the exciton binding energy ($E_b$) of the studied materials, the reduced effective mass $m^* \left( \frac{1}{m^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*} \right)$ were calculated. In SC applications, A lower value of $E_b$ is highly favourable for the minimization of energy loss. Within the effective mass approximation, $E_b$ was calculated by using the formula $E_b = \frac{2\hbar^2}{m^* a_0^2}$; $a_0$ is the effective exciton Bohr radius, given as $a_0 = \frac{2\hbar^2 \epsilon_{\infty}}{m_e^* \epsilon_{\infty}}$.[56] Here $\epsilon$ and $\epsilon_{\infty}$ being the electronic charge and high frequency dielectric constant, respectively. The computed values of $E_b$, $a_0$, and $E_b$ are listed in Table S5, Supporting Information, and showed good agreement with previous theoretical results.[57,58] RbSnBr₃ perovskite exhibits the smallest $E_b$ of 44 meV, comparable to that of prototype perovskite MAPbI₃ ($\approx 50$ eV).[59]

3.3. Optical Properties

Optical properties like absorption coefficient, dielectric constant, etc., are also very important quantities that directly impact the
Figure 6. Charge densities of the VBM (bottom) and CBM (upper) of CsSnBr$_3$ (a,c) and CsGeBr$_3$ (b,d), respectively.

PCE of PSCs. Large dielectric constants with high optical absorption around a broad range of solar spectrums are critical for better photovoltaic performance.

The computed real ($\varepsilon_1(\omega)$) and imaginary ($\varepsilon_2(\omega)$) parts of dielectric constants for all studied materials are depicted in Figure 7. The Sn-halides have shown larger $\varepsilon_1(0)$ values compared to Ge-halide perovskites. Upon substituting Cs with other alkali atoms $\varepsilon_1(0)$ increases from Cs to K, while for NaGeBr$_3$ it decreases. The principal peak values of $\varepsilon_1(\omega)$ for CsSnBr$_3$, RbSnBr$_3$, KSnBr$_3$, CsGeBr$_3$, RbGeBr$_3$, KGeBr$_3$, and NaGeBr$_3$ were found to be 5.81, 5.60, 5.95, 5.00, 5.42, 5.57, and 4.25 at 1.01, 1.00, 0.83, 2.25, 2.05, 1.54 and 2.34 eV, respectively. The $\varepsilon_2(\omega)$ is related to the DOS of the material and describes the absorption characteristics.$^{[60]}$ It was observed that $\varepsilon_2(\omega)$ is red-shifted with the change of A-site cation from Cs to K for both Sn and Ge-based materials and it can be ascribed to the corresponding band gap reduction. However, NaGeBr$_3$ showed a blue shift of $\varepsilon_2(\omega)$ because of its larger band gap value. The critical onset points in the $\varepsilon_2(\omega)$ were found at 1.01, 1.00, 0.99, 1.85, 1.54, 1.37 and 2.03 eV for CsSnBr$_3$, RbSnBr$_3$, KSnBr$_3$, CsGeBr$_3$, RbGeBr$_3$, KGeBr$_3$, and NaGeBr$_3$, respectively, related to the corresponding calculated band gap values. Similar characteristics were observed for the K(\omega) spectra, as shown in Figure S3, Supporting Information.

In addition, other optical properties like $L(\omega)$, $n(\omega)$, and $R(\omega)$ also affect the performance of SC. The $L(\omega)$ describes the energy loss of electrons when they are propagated through the system, and the peaks in the $L(\omega)$ spectra (Figure S3, Supporting Information) represent the plasma resonance.$^{[61]}$ The most prominent peaks were found to be at 14.26, 18.71, 13.80, 15.01, 19.07, and 15.60 eV for CsSnBr$_3$, RbSnBr$_3$, KSnBr$_3$, CsGeBr$_3$, RbGeBr$_3$, and KGeBr$_3$, respectively. The refractive index is also an essential parameter of materials that represents the amount of light refracted. The computed $n(\omega)$ spectra are depicted in Figure S4, Supporting Information. The static refractive index $n(0)$ values were calculated to be 2.23, 2.26, 2.28, 1.97, 2.07, 2.11 and 1.82 for CsSnBr$_3$, RbSnBr$_3$, KSnBr$_3$, CsGeBr$_3$, RbGeBr$_3$, KGeBr$_3$, and NaGeBr$_3$, respectively. It should be noted that with the change of alkali elements, the static refractive index increases from Cs to K for both Sn- and Ge-based materials, respectively. On the contrary, NaGeBr$_3$ showed the lowest $n(0)$ value. As the energy increases, $n(\omega)$ increases and reaches a maximum value, and then decreases gradually and goes below unity for certain energy ranges for all the studied compounds. At these energy ranges the group velocity of the incident radiation surpasses the velocity of light.

The reflectivity $R(\omega)$ of a material determines the amount of incident radiation that would be reflected from it. As shown in
Figure 7. Spectra of dielectric constants: a,c) real and b,d) imaginary part of the studied materials.

Figure 8. Reflectance (a,b) and absorbance (c,d) spectra of the ABBr$_3$ perovskites.
Figure 8. In the low-energy range (<4 eV), reflectivity reaches 24.3% and 22.7% for Sn- and Ge-based perovskites, respectively, demonstrating good transparency in the visible and UV regions. Furthermore, for both Sn and Ge halides, the static reflectivity R(0) increases as the atomic radius of the A-site element decreases, except for the case of NaGeBr 3. The absorption coefficient is another crucial parameter that significantly influences SC performance. It is noted that excluding NaGeBr 3, for both Ge- and Sn-based perovskite materials, the absorption onset and the first peak of absorption are red-shifted as the atomic number of A-site elements decreases. These findings are remarkably consistent with the predicted band structures and DOS. All the studied materials exhibited strong absorption in the visible and UV range and are higher than that of the prototype perovskite material MAPbI 3 (3.8 × 10 4 cm −1) [62, 63]. In terms of A-site element, K-based perovskites exhibited maximum absorption compared to Rb and Cs-based materials for both Ge and Sn halide perovskites. Moreover, all the studied materials showed moderate absorption in the infrared region. The desirable absorption properties of all the investigated materials render them potential candidates for a solar cell absorber material.

4. Conclusions

In summary, the structural, electronic, and optical properties of eco-friendly ABBr 3 perovskites have been studied employing the first-principles calculations. The findings from this study demonstrate that both Cs and Rb-based perovskites are energetically favorable. All the studied compounds exhibit a direct band gap in the 1.00–1.97 eV range, desirable for SC application. Furthermore, all the ABBr 3 compounds exhibit strong photo-absorption in the whole UV–Vis range. We believe this study will encourage researchers to investigate these materials experimentally and enhance further research into alternative inorganic lead-free perovskite (ILP) materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

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