A first-principles study of the unsynthesized Indium halide perovskites RbInX₃ (X= F, Cl, Br, I) for photovoltaic and photocatalytic applications

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Abstract. Due to their relevant properties, lead-free halide perovskites have attracted wide attention in the scientific community. This study investigates the structural, mechanical, electronic, optical, and photocatalytic properties of the Indium-based halide perovskites RbInX₃ (X= F, Cl, Br, I) based on the density functional theory (DFT) using the WIEN2k package. The results show that RbInI₃ exhibits a metallic behavior, while RbInBr₃, RbInCl₃, and RbInF₃ exhibit semiconducting behavior with bandgap energies of 0.67, 1.43, and 2.45 eV, respectively. The high optical absorption and corresponding band gap energies make them good candidates for photovoltaic applications. In addition, the RbInF₃ compound exhibits good photocatalytic performance since it satisfies the thermodynamic requirements needed to trigger the water-splitting reaction. This study also allows us to analyze the influence of halogen substitution on the properties of the compound RbInX₃. Moreover, it will open the way to the experimental community as it is the first to study the properties of these perovskites.

1 Introduction

Perovskite compounds are materials whose chemical formula is ABX₃, where A and B are two cations, and X is a halogen [1]; these materials are good candidates for use as photovoltaic applications in PV solar panels, thanks to their ideal combination between performance and price [2,3]. The power conversion efficiency (PCE) of perovskite solar cells has increased over the last few years from 3.8 to 26% [4], making them competitive with those based on silicon (Si). Despite this high performance, the presence of lead, known for its toxicity, is holding back the commercialization of this type of solar cell [5,6]. Then, the solution is to find alternative elements to substitute the lead (Pb). Tin (Sn) and germanium (Ge) elements have been the most widely studied in this context. However, Sn oxidizes rapidly, making the compound unstable [7]; on the other side, germanium-based perovskites generally have very high band gap energies, making them unsuitable for photovoltaic applications [8,9]. Indium (In) is another substituent, and several indium-based compounds have been developed and studied, such as NaInX₃, LiInX₃, CsInX₃, and KInX₃ [10,11]. This work aims to determine the structural, mechanical, electronic, and optical properties of four In-based perovskites RbInX₃ (X= Cl, Br, I, F).
A material with good photovoltaic performance can also be used for water splitting using sunlight if it satisfies the thermodynamic conditions required to initiate this reaction. Therefore, the photocatalytic performance of the treated materials has been discussed in this paper, which is structured into two main sections: the first section explains the method used to establish this first-principles study. Furthermore, the second section presents and analyzes the results obtained, starting with the volume optimization, mechanical properties, and the electronic study, then the compounds' optical properties comparison, and concluding with a discussion of their photocatalytic properties.

To the best of our knowledge, there are no previous research studies on these compounds. This paper enables the experimental community to focus on these compounds, with their relevant and encouraging properties as substituents for lead-based perovskites whose effect is harmful.

2 Calculation method

The WIEN2k code [12], based on the Full Potential Linearized Augmented Plane Wave (FP-LAPW) method [13], was used in this study to perform first-principles simulations on RbInX₃ (X = F, Cl, Br, I) compounds based on density functional theory (DFT) [14]. The exchange-correlation function was determined using the Perdew–Burke–Ernzerhof (PBE) Generalized Gradient Approximation (GGA) [15] to ensure the different properties. Iterations were conducted until the total energy reached a minimum of 10⁻⁴ Ry. The cut-off energy, the maximum number of plane waves (lₘₐₓ), the product of the smallest muffin tin radii, and the maximum modulus of the K-vector in the reciprocal space (RₘₜKₘₙₐₓ) were set to -7 Ry, 10, and 9, respectively. The calculations were performed with 5000 K points over the Brillouin zone for elastic properties and 1000k points for the other properties. The charge density was Fourier expanded to GMAX= 12, and the muffin-tin radii Rₘₜ were taken as 2.3, 2, 2, 4, 2.45, and 2.5 a.u for Rb, In, F, Cl, Br, and I, respectively.

To discuss the structural and thermodynamic stability, we have calculated the Goldschmidt factor and the formation energy using these two equations [16,17]:

\[ t'_G = \frac{r_{Rb} + r_X}{\sqrt{2} \times (r_{In} + r_X)} \]  \hspace{1cm} (1)

Where r_{Rb}, r_{In}, and r_{X} are the ionic radius of Rb, In, and the halogen, respectively.

\[ E_f = \frac{1}{5} \times (E_{RbInX}^{tot} - (E_{Rb} + E_{In} + 3E_{X})) \]  \hspace{1cm} (2)

Where E_{RbInX}^{tot} is the total energy of the RbInX₃ compound, and E_{Rb}, E_{In}, and E_{X} are the total energies of Rb, In, and the halogen, respectively.

On the other hand, the stability in the cubic phase can be verified by the Born stability conditions [18]

\[ (C_{11} - C_{12}) > 0, \quad (C_{11} + 2C_{12}) > 0, \quad C_{11} > 0 \]  \hspace{1cm} (3)

The optical properties depend on the electrical constant defined as follows:

\[ \varepsilon = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \]  \hspace{1cm} (4)

With \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) are the real and the imaginary parts of the dielectric function, respectively, and \( \omega \) is the photon frequency.

Optical absorption \( \alpha \), optical conductivity \( \sigma \), and reflectivity \( R \) were calculated using the equations shown below.

\[ \alpha(\omega) = \frac{2\omega}{c}k(\omega) \]  \hspace{1cm} (5)
\[ \sigma(\omega) = \frac{\omega}{4\pi} \varepsilon_2(\omega) \]  
(6)

\[ R(\omega) = \frac{(1-n)^2 + k^2}{(1+n)^2 + k^2} \]  
(7)

Where \( k \) and \( n \) are the extinction coefficient and the refractive index, respectively [19]:

\[ k(\omega) = \left[ \frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) - \varepsilon_1(\omega)}}{2} \right]^2 \]  
(8)

\[ n(\omega) = \left[ \frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) + \varepsilon_1(\omega)}}{2} \right]^2 \]  
(9)

To understand photocatalytic properties, it is necessary to calculate the CBM and VBM potentials using these two formulas [20]:

\[ E_{\text{CBM}} = -\frac{1}{2} E_g + \chi + E_0 \]  
(10)

\[ E_{\text{VBM}} = E_g + E_{\text{CBM}} \]  
(11)

Where \( E_g \) is the band gap energy, \( E_0 = -4.5 \text{ eV} \), is the energy level of the Normal Hydrogen Electrode (NHE), and \( \chi \) is the compound’s electronegativity calculated as below [20]:

\[ \chi_{\text{RbInX}_3} = \left( \chi_{\text{Rb}} \chi_{\text{In}} \chi_{\text{X}} \right)^{\frac{1}{3}} \]  
(12)

Where the \( \chi_{\text{RbInX}_3} \) is the absolute electronegativity of RbInX\(_3\), \( \chi_{\text{Rb}} \), \( \chi_{\text{In}} \), \( \chi_{\text{X}} \) are the absolute electronegativities of Rb, In, and the halogen X (F, Cl), respectively, which values have been determined by Bartolotti [21].

3 Results and discussion

3.1 Structural Properties

The RbInX\(_3\) materials possess a cubic structure with the Fm-3m (No. 225) space group, as shown in Figure 1. As in the ABX\(_3\) perovskite structure, each Rb cation (A site) is surrounded by 12 Cl anions, and each In cation (B site) by 6 Cl anions.

Fig. 1. The investigated structure of RbInX\(_3\).
The lattice parameters (Table 1) were determined for each compound by structure optimization using the GGA approximation, as shown in the following curves (Fig. 2). These values were obtained by applying the Murnaghan equation of states.

![Energy vs Volume Graphs](image)

**Fig. 2.** Volume optimization curves.

**Table 1.** Formation energies and structural properties of RbInX₃ compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>Formation energy (eV/atom)</th>
<th>t₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbInF₃</td>
<td>9.4192</td>
<td>-2.42</td>
<td>1.00</td>
</tr>
<tr>
<td>RbInCl₃</td>
<td>11.1045</td>
<td>-1.40</td>
<td>0.96</td>
</tr>
<tr>
<td>RbInBr₃</td>
<td>11.6081</td>
<td>-1.52</td>
<td>0.94</td>
</tr>
<tr>
<td>RbInI₃</td>
<td>12.3875</td>
<td>-1.13</td>
<td>0.92</td>
</tr>
</tbody>
</table>

The variation in lattice parameters between compounds is explained by differences in the halogen ionic radii (F, Cl, Br, and I); larger ion radius results in higher lattice parameters. The negative sign of the formation energy (Eₖ) indicates the possibility of developing the compound experimentally, and the smaller the value, the more thermodynamically stable the compound. The structural stability was verified by calculating the Goldschmidt factor (t₆), which should be between 0.8 and 1 for halide perovskites [22]. Then, from the obtained values, we can conclude that the four structures are stable and realizable experimentally and that the RbInF₃ is the most stable structure.
3.2 Mechanical properties

The elastic constants determination is necessary to explore the mechanical properties of the studied compounds. Since these compounds have a cubic structure, they possess three independent constants: \( C_{11} \), \( C_{12} \), and \( C_{44} \). The values found are grouped in Table 2. According to those results, all four compounds satisfy the Born stability conditions [18], confirming their stability in the cubic phase.

Table 2. Elastic constants of the studied compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{RbInF}_3 )</th>
<th>( \text{RbInCl}_3 )</th>
<th>( \text{RbInBr}_3 )</th>
<th>( \text{RbInI}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{11} )</td>
<td>108.787</td>
<td>51.966</td>
<td>46.119</td>
<td>17.375</td>
</tr>
<tr>
<td>( C_{12} )</td>
<td>19.410</td>
<td>13.915</td>
<td>9.412</td>
<td>12.597</td>
</tr>
<tr>
<td>( C_{44} )</td>
<td>16.603</td>
<td>5.452</td>
<td>3.339</td>
<td>1.698</td>
</tr>
</tbody>
</table>

Fundamental mechanical properties such as bulk modulus (B), shear modulus (G), Pugh ratio (B/G), Young modulus (E), and Poisson ratio (\( \nu \)) can be computed from the elastic constants via the relations detailed by Ali et al. [23] (Table 3 and Fig 3).

Fig. 3. Pugh’s and Poisson’s ratios of the investigated compounds.

Table 3. Mechanical properties of the studied compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{RbInF}_3 )</th>
<th>( \text{RbInCl}_3 )</th>
<th>( \text{RbInBr}_3 )</th>
<th>( \text{RbInI}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B (GPa)</td>
<td>49.20</td>
<td>26.5986</td>
<td>21.647</td>
<td>14.189</td>
</tr>
<tr>
<td>G (GPa)</td>
<td>25.007</td>
<td>9.255</td>
<td>7.1539</td>
<td>1.9472</td>
</tr>
<tr>
<td>B/G</td>
<td>1.96</td>
<td>2.8739</td>
<td>3.02</td>
<td>7.28687</td>
</tr>
<tr>
<td>E</td>
<td>64.152</td>
<td>24.8793</td>
<td>19.33</td>
<td>5.586</td>
</tr>
<tr>
<td>( \nu )</td>
<td>0.2826</td>
<td>0.34</td>
<td>0.351</td>
<td>0.43</td>
</tr>
<tr>
<td>A</td>
<td>0.37</td>
<td>0.2865</td>
<td>0.18192</td>
<td>0.7107</td>
</tr>
</tbody>
</table>
The bulk modulus measures a material's resistance to a change in volume when subjected to an external pressure. Then, a low value of B means that the material is flexible, which is the case for RbInI$_3$, RbInBr$_3$, and RbInCl$_3$, whereas RbInF$_3$ is the least flexible material. Similar to the discussion about the bulk modulus, a low shear modulus indicates that a material is more flexible and can deform under shear stress. Poisson and Pugh ratios are other vital parameters to explore a material's ductile/brittle nature. The material is ductile if its Poisson and Pugh ratios are higher than 0.26 and 1.75, respectively [24], which is the case for all RbInX$_3$ compounds, showing that they can undergo significant deformation before fracture. A represents elastic anisotropy, i.e., the directional dependence of elastic properties. For the value A=1, the material is said to be isotropic. The table above shows that the materials studied are elastically anisotropic.

### 3.3 Electronic Properties

The band structures of the different compounds were plotted (Fig. 4) to identify their behavior (metal, semiconductor, or insulator) and determine the value of the bandgap energy and the nature of this forbidden band.

![Band structures of RbInX$_3$ compounds.](image)

Band structures show that RbInF$_3$, RbInCl$_3$, and RbInBr$_3$ exhibit semiconducting behavior with gap energies of 2.452, 1.43, and 0.67 eV. The valence band maximum and conduction
band minimum appear at different symmetry points (W and L, respectively). However, RbInI₃ exhibits metallic behavior (Eₘₐₓ = 0.0 eV).

An in-depth understanding of electronic properties requires analysis of densities of states, as illustrated below in Fig. 5, within the energy range of −8 eV to 7 eV.

![Density of states](image)

**Fig. 5.** The RbInX₃ compounds density of states.
The densities of electronic states of the four compounds show almost the same pattern. In the valence band, the dominant contribution is that of the halogen occupying the X site (F, Cl, Br, I), essentially the p orbital. In-s has a small contribution from -1eV up to the near Fermi level. In the conduction band, a contribution from In-s and X-p is observed at the band minimum, and a similar contribution is noted for the three elements far from this minimum. The hybridization between the halogen and In orbitals leads to the formation of covalent bonds between these two elements, resulting in an overlap between their electron densities, as shown in Fig. 6 for RbInCl₃. On the other hand, the non-contribution of the element Rb explains the ionic nature of their bonds.

Fig. 6. The electronic density distribution of RbInCl₃.

3.4 Optical properties

3.4.1 Dielectric function

To predict how the material interacts with light, it is necessary to study its optical properties. \( \varepsilon_2 \) is the sum of all transitions from the valence band to the conduction one. Its high value indicates that more energy is being absorbed by the material, which can enhance its photovoltaic and photocatalytic performances. On the other side, the real part \( \varepsilon_1(\omega) \) represents the material’s ability for polarization and describes its dissipative behavior. A smaller real part of the dielectric function typically corresponds to lower reflection and higher light absorption, which is beneficial for photocatalytic and photovoltaic applications.

Fig. 7. Dielectric function of RbInX₃: (a) \( \varepsilon_1 \) and (b) \( \varepsilon_2 \).
In the infrared and the visible regions, the RbInF$_3$ and RbInCl$_3$ present the lower real part of the dielectric function with a small peak at 2.8 and 2 eV, respectively (Fig. 7-a). This low value makes the materials transparent to a larger range of wavelengths, allowing light to pass through, increasing the chances of photon absorption, and promoting efficient photocatalytic and photovoltaic behavior.

For the imaginary part (Fig. 7-b) of the complex dielectric function, we see that for RbInI$_3$, the value is different from 0 at 0 eV, which confirms that its metallic behavior since transitions are possible between the valence and conduction bands even in the absence of an external electric field. Transitions become possible for RbInBr$_3$ at 0.67 eV and show a peak in the infrared range. For RbInCl$_3$ and RbInF$_3$, despite their low $\varepsilon_2$ values, the latter show peaks in the visible range, which is the dominant part of solar radiation, making these two materials suitable for absorbing solar radiation in photovoltaic (PV) and photocatalytic (PC) applications.

### 3.4.2 Optical conductivity and absorption

Optical absorption $\alpha(\omega)$ is the process by which a material absorbs photons of light and converts them into electronic excitations. Optical conductivity $\sigma(\omega)$ describes the material’s electrical conductivity by absorbing electromagnetic radiation. When a material absorbs light, the number of free electrons and holes increases, increasing its electrical conductivity.

![Optical absorption and conductivity of RbInX$_3$ compounds.](image)

The optical conductivity and absorption of each material have the same allure (Fig. 8). $\alpha(\omega)$ and $\sigma(\omega)$ of RbInI$_3$ and RbInBr$_3$ present a peak in the Infrared region, with low values in the visible zone but high values in the UV range. However, $\sigma(\omega)$ and $\alpha(\omega)$ of RbInCl$_3$ and RbInF$_3$ are null in the Infrared region; they present a peak in the visible region and high values in the UV zone but lower than those of RbInI$_3$ and RbInBr$_3$.

### 3.4.3 Reflectivity

The reflectivity is the ratio of the power reflected at the material’s surface, so high reflectivity limits the photovoltaic and photocatalytic performance. As presented in Fig. 8, it is shown that RbInCl$_3$ and RbInF$_3$ show lower reflectivity compared to that of RbInI$_3$ and RbInBr$_3$. The reflectivity of RbInCl$_3$ and RbInF$_3$ doesn’t exceed 0.26 and 0.2, respectively; they also
present low values in infrared and visible regions, the dominant waves in the sunlight radiations, which improve their performance for PV and PC applications.

![Optical Reflectivity of RbInX₃ compounds](image)

**Fig. 9.** Optical Reflectivity of RbInX₃ compounds.

In summary, RbInI₃ cannot be used as an absorber in photovoltaic solar cells due to its metallic nature, which leads to high heat loss and reflectivity. RbInBr₃, despite its semiconductor behavior, its optical properties make it unsuitable for photovoltaic applications. On the other hand, the gap energy of RbInCl₃ and RbInF₃ is located in the visible range, making them suitable for photovoltaic applications. It should also be noted that the gap energy value presented by RbInCl₃ (1.43 eV) is the ideal value for PV applications according to the Shockley-Queisser limit theory [25].

### 3.5 Photocatalytic Properties

Photocatalytic water splitting is a promising technology that utilizes a semiconductor photocatalyst material suspended in water. Light illumination of the suspended semiconductor material leads to electron-hole pairs creation due to the electrons’ excitation from the valence to the conduction band. The pairs can participate in redox reactions with adsorbed water molecules, producing di-oxygen (O₂) and dihydrogen (H₂) (Fig.10).

![Schematic description of photocatalytic water splitting process](image)

**Fig. 10.** Schematic description of photocatalytic water splitting process.
Two conditions are required for a material to be used as a photocatalyst [26]:
- A semiconductor behavior with a bandgap energy higher than 1.23 eV;
- The CBM and VBM potentials have to straddle the water redox levels to be utilized for water splitting. In other words, the CBM potential should be lower than the reduction one of $H^+/H_2 (E^0_{H^+/H_2} = 0 \text{ eV})$, and the VBM position should be higher than the oxidation potential of $O_2/H_2O (E^0_{O_2/H_2O} = 1.23 \text{ eV})$.

According to the first condition, only the two compounds, RbInCl$_3$ (1.43 eV) and RbInF$_3$ (2.45 eV), can operate as photocatalysts. It then remains to check the thermodynamic conditions by calculating the VBM and CBM potentials summarized in Table 4 and their alignments (Fig.11). The obtained results show that the CBM and VBM of RbInF$_3$ sandwich the water redox potentials so it can split water into $H_2$ and $O_2$. However, the VB of RbInCl$_3$ (0.785 eV) is under the water oxidation level (1.23 eV), which means its non-applicability in the photocatalytic application.

Fig. 11. The band gap alignment of RbInCl$_3$ and RbInF$_3$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>RbInF$_3$</th>
<th>RbInCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{CBM}}$ (eV)</td>
<td>-0.278</td>
<td>-0.645</td>
</tr>
<tr>
<td>$E_{\text{VBM}}$ (eV)</td>
<td>2.214</td>
<td>0.785</td>
</tr>
</tbody>
</table>

4 Conclusion

This paper investigates halide perovskites with the structure RbInX$_3$ (X= F, Cl, Br, I). From the study of the electronic properties, it is clear that RbInI$_3$ is a metal, while the other three compounds RbInX$_3$ (X=F, Cl, Br) exhibit semiconducting behavior with an indirect p-type band gap of 2.45, 1.43, and 0.67 eV. The optical properties of these compounds have also been analyzed and compared, proving that RbInCl$_3$ and RbInF$_3$ are good candidates for...
photovoltaic applications. Thanks to their band gap energies, they have been selected to discuss their photocatalytic properties, but only RbInF$_3$ meets the required thermodynamic criteria and can be used as a photocatalyst.

References


[17] Alqahtani SM, Alsayoud AQ, Alharbi FH. Structures, band gaps, and formation energies of highly stable phases of inorganic ABX3 halides: A = Li, Na, K, Rb, Cs, Ti; B = Be, Mg, Ca, Ge, Sr, Sn, Pb; and X = F, Cl, Br, I. RSC Adv 2023;13:9026–32. https://doi.org/10.1039/D3RA00185G.


