Revealing the Optoelectronic Properties of Tin-Based Vacancy Ordered Double Perovskites: K$_2$SnBr$_6$ and Rb$_2$SnBr$_6$

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Abstract: In the field of photovoltaics and optoelectronics, perovskites have drawn significant interest due to their high-power conversion efficiency of 22%. This drives the researchers to search for new lead-free stable materials that can show good performance to use in optoelectronic devices specially in the photovoltaic field. In the present work, we focused to find out the electronic and optical properties of two tin based vacancy ordered double perovskites, K$_2$SnBr$_6$ and Rb$_2$SnBr$_6$. The primary purpose of this work is to provide fundamental understanding on the physical properties of the considered two compounds by calculating its electronic structure and optical characteristics accurately. The calculations are performed by using the Vienna ab-initio simulation package (VASP) based on the density functional theory. We used hybrid functional (Heyd-Scuseria-Ernzerhof) method to account for exchange and correlation effects which provides accurate band gap values. From the electronic property calculation, it can be seen that the compounds have direct band gap nature with optimal band gap energy suitable for photovoltaic applications. For understanding the electronic states and nature of chemical bonding, we calculated the total and partial density of states. In order to obtain a better insight on these material for photovoltaic applications, we simulated excited state spectra and plotted the optical functions such as the absorption coefficient, extinction coefficient, conductivity and reflectivity.

INTRODUCTION

Solar energy generation is one of the suitable approaches to achieve clean and sustainable energy. Perovskite lead halides are a class of materials which have shown great promise as good solar absorbers and also can be used in other optoelectronic devices than solar cell [1]. However, the materials still face a huge challenge in the large-scale commercialization because of the structural instability against moisture/air and temperature as well as the toxicity of lead (Pb). Therefore, there is a great demand to find stable and nontoxic perovskites for further development of perovskites solar cells. Recently the inorganic lead-free vacancy ordered perovskite Cs$_2$SnI$_6$ [2] attracts much attention to use in the photovoltaic cell because of its high PCE. There are many studies reported based on the compound Cs$_2$SnI$_6$ and other compounds which consist of A$_2$BX$_6$ structure [3]. It is always advantageous to find materials which are less-expensive and the non-toxic in nature. In this study, we report the optoelectronic properties of a two non-toxic lead-free inorganic vacancy-ordered halide double perovskites K$_2$SnBr$_6$ and Rb$_2$SnBr$_6$.

Even though there are a few studies available on K$_2$SnBr$_6$ and Rb$_2$SnBr$_6$, the important optical coefficients rather than absorption coefficient, have not been analysed so far. Therefore, it is necessary to examine those optical coefficients along with the structural and electronic properties. To address this interest, in this work, we investigate the structural, electronic and optical properties of the considered compounds by using first-principle calculations. The rest of this paper is organized as follows. In Section 2, we present computational parameters used. In Section 3, we present our calculated structural, electronic and optical properties. Finally, we gave a brief conclusion in Section 4.
COMPUTATIONAL DETAILS.

Vienna Ab-initio simulation package (VASP) \[4,5\] is used to perform density function theory (DFT) based calculations on the proposed materials. The exchange–correlation potential was calculated within the local density approximation (LDA) developed by Ceperly and Alder and parameterized by Perdew and Zunger \[6\] as well as the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof. We used an energy cut off of 520 eV for all the calculations. The tolerance for geometry optimization were set as the difference of total energy within \(10^{-6}\) eV atom\(^{-1}\), maximum ionic Hellmann–Feynman force within 0.01 eV Å\(^{-1}\). The k-points were generated using the Monkhorst Pack method for structural optimization while the Gamma centred grid for electronic structure calculations. For obtaining accurate band structure and band gap value, we have performed Heyd-Scuseria-Ernzerhof (HSE06) \[7\] hybrid functional in the electronic band structure calculations.

RESULTS AND DISCUSSION

Structural properties:

\(\text{K}_2\text{SnBr}_6\) and \(\text{Rb}_2\text{SnBr}_6\) stabilize into the face-centered-cubic (fcc) with the space group \(\text{Fm} \overline{3} \text{m}\) (the anti-fluorite structure) and the structure type of \(\text{K}_2\text{PtCl}_6\). As shown in Fig. 1, the unit cell is composed of eight \(\text{A}^2+\) cations at the tetragonal interstitials and four \([\text{SnBr}_6]\)\(^2-\) octahedra at the corners and at the face centres. The calculated equilibrium lattice constants for \(\text{K}_2\text{SnBr}_6\) are \(a=b=c=7.6468\) and volume is \(316.17\ \text{Å}^3\). And for \(\text{Rb}_2\text{SnBr}_6\) the lattice parameters are \(a=b=c=7.7881\) and volume is \(333.12\ \text{Å}^3\). It is to be added that the lattice parameters and the volume for the two considered compounds show good agreement with the experimental data \[8\].

Electronic Properties

Using their respective optimized structure, the band structures of \(\text{K}_2\text{SnBr}_6\) and \(\text{Rb}_2\text{SnBr}_6\) are computed using the HSE functional along high symmetry direction W–Γ–L–X–W for energy range from −5 eV to 5 eV. The Fermi level is set at 0 eV. In Fig. 2 a and b, the HSE calculated band structures for \(\text{K}_2\text{SnBr}_6\) and \(\text{Rb}_2\text{SnBr}_6\) are displayed respectively. From the structure of the bands, it is found that one band is present alone in the conduction band and more bands are localised in the 4.98 eV energy after the valence band maximum. This indicates the presence of an intermediate band in the two compounds. It is worth noting that the VB to IB transitions and IB to CB transition can improve the performance of these materials \[9\]. This is the advantage of using the materials with intermediate band gap. The valence band maximum (VBM) and the conduction band minimum (IBM) are located at \(\Gamma\) point, resulting in a direct energy band gap. To the best of our knowledge, there are no experimental measurements of the band gaps of these compounds. The calculated energy band profiles of both the compounds are quite similar but only difference is in the energy band gap values. \(\text{K}_2\text{SnBr}_6\) acquires a VB-IB direct band gap value of 1.69 eV while the band gap value is 1.74 eV for \(\text{Rb}_2\text{SnBr}_6\). From the top of the intermediate band and bottom of the conduction band, two materials possess indirect band gap and the band gap values are 1.95 eV and 2.2 eV for \(\text{K}_2\text{SnBr}_6\) and \(\text{Rb}_2\text{SnBr}_6\) respectively.

In order to elucidate the nature of the electronic band structures, we have calculated the total and partial densities of states (TDOS and PDOS, respectively) for these compounds. Since the DOS plots for both the compounds show a
significant amount of similarity, we have displayed the DOS plot in general in Fig.3. The similarity in DOS indicating similarity in chemical bonding. The top of the valence band for both the compounds mainly arise from Br-p states. The nearest band above the fermi level, that is the intermediate band is mainly composed of the 5s orbitals of Sn and halogen p orbitals. And it can be understood from the structure itself that the Sn cation is octahedrally coordinated with the halogen atom thus points their covalent bonding. The DOS plot also confirms the covalent bonding between Sn and Br as the electronic states of the elements are energetically degenerate to each other. Also, due to the difference in the electronegativity between the comprising elements, some ionic character can be expected between Br and A(K,Rb). The bonding character may be described as a mixture of covalent–ionic.

**OPTICAL PROPERTIES**

Optical properties are necessary to calculate before applying any material as solar cell absorbers. To investigate the optical behaviour of the two compounds, we have calculated the optical dielectric function \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \). With the help of imaginary part of dielectric function, we have calculated all other optical coefficients [10]. The most relevant optical parameters for PV application are absorption coefficient, reflectivity, extinction coefficient and optical conductivity. These coefficients for the two compounds are displayed in Fig.4(a), (b), (c) and (d) respectively. All the spectra are seen in black in colour for K\(_2\)SnBr\(_6\) while those are present in red colour for Rb\(_2\)SnBr\(_6\). The artificial shift technique has been applied to account for the underestimation of bandgap by PBE in all calculated optical spectra by taking the corresponding accurate band gap value obtained from the hybrid functional calculation. Since the crystal structure of K\(_2\)SnBr\(_6\) and Rb\(_2\)SnBr\(_6\) are cubic in nature, their optical properties are isotropic i.e. same along the crystallographic a, b and c axes. So, for the analysis, only one of the dielectric tensor components, \( \varepsilon_{xx} (=\varepsilon_{yy} = \varepsilon_{zz}) \) is sufficient for finding the other optical properties.

The absorption coefficients of K\(_2\)SnBr\(_6\) and Rb\(_2\)SnBr\(_6\) are presented in Fig. 4a. The energy band gap is the one at which absorption starts for any material. And it is worth noting that the absorption coefficient is in the order of 105 cm\(^{-1}\) in the visible region. Here the spectra in black colour start from 1.69 eV represents that the absorption in K\(_2\)SnBr\(_6\) begins at 1.69 eV. This value is at 1.74 eV for Rb\(_2\)SnBr\(_6\). This is due to the electronic transition from the VBM to IBM. The peaks observed are almost at the similar energy ranges for both the compounds. An electronic transition from IBM to CBM corresponds to the first small peak at 2.2 eV, which is well suited for solar applications. The next two peaks are at 4.8 eV and around 7 eV for the two compounds. These peaks may arise due to the electronic transitions from VBM to CBM.

The reflectivity, R(\(\omega\)), is one of the important optical parameters, which shows how much light is reflected from a surface. Figure 4(b) presents the reflectivity spectra computed for K\(_2\)SnBr\(_6\) and Rb\(_2\)SnBr\(_6\) in the black and red lines respectively. In the visible range, the reflectivity is lower than 5% and which indicates that the compounds are transparent for photons in the visible region. Due to the absorptive nature of k(\(\omega\)) (shown in Fig.4(c)), the line shape of k(\(\omega\)) spectra shows same spectral distribution as the absorption spectra with peak values also. Same as the extinction coefficient, the spectra of the absorptive part of conductivity (shown in Fig.4(d)) of these compounds...
have similar frequency dependent features like the corresponding absorption spectra. More highest peaks are observed in the UV region in all the three absorption, extinction and optical conductivity spectra. So, these two compounds are more useful in tandem solar cells where many cells of different band gap are fabricated one over the other in order to avail the complete solar spectrum.

CONCLUSION

First principles calculations have been performed on cubic lead-free vacancy-ordered double for photovoltaic applications. The structural parameters of the considered compounds are found and the equilibrium lattice constants and optimised volume of the two materials are in good agreement with the corresponding available experimental data. The nature of the band gap is found as direct band gap from the electronic structure analysis. From the improved band gap method (HSE06), energy band gap values for the three compounds obtained are close to the optimum band gap values 1.69 eV and 1.74 eV for K$_2$SnBr$_6$ and Rb$_2$SnBr$_6$ respectively. Using electronic structure, the bonding mechanism of the compounds are discussed. From the optical property calculation, it is found that the two compounds show relatively high absorption in the visible region. Since we are able to consider VB-IB and IB-CB transition in the single band gap material, the absorption is relatively higher when we compare with materials without intermediate band gap. Also, the two compounds show higher extinction coefficient, optical conductivity and low reflectivity in the visible region which are well suited for photovoltaic applications. As peaks are at higher energy (UV) regions, they can be used as possible shields for ultraviolet radiation and thus they are applicable to use in tandem solar cells where many cells of different band gaps are attached in order to avail the complete solar spectrum. The material system is accessible by chemical synthesis, consisting of abundant and non-toxic elements and so is potentially suitable for large-scale deployment as a promising new candidate for high-performance photovoltaic devices.

![Figure 4](image-url)
REFERENCES

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