First Principles Analysis of Crystal Structure, Electronic and Optical Properties of $\text{CsSnI}_{3-x}\text{Br}_x$ Perovskite for Photoelectric Applications

D. D. Nematov^{a,*}, A. S. Burhonzoda^a, M. A. Khusenov^a, Kh. T. Kholmurodov^{b,c,**}, and T. Yamamoto^{d,***}

^a Osimi Tajik Technical University, Dushanbe, 724000 Tajikistan

^b Joint Institute for Nuclear Research, Dubna, Moscow Region, 141980 Russia

^c Dubna State University, Dubna, Moscow Region, 141980 Russia

^d Waseda University, Shinjuku, Tokyo, 169-8555 Japan

*e-mail: dilnem@mail.ru

**e-mail: mirzo@jinr.ru

***e-mail: tymmt@waseda.jp

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Abstract—The crystal structure, electronic and optical properties of lead-free mixed halide inorganic perovskites, $\text{CsSnI}_{3-x}\text{Br}_x$ ($x = 0, 1, 2, 3$), were studied within the framework of density functional theory. The effective electron-electron exchange correlation functional and, modified Becke–Johnson potential, were used for calculations of electronic and optical properties. The calculated optical parameters and the density of electronic states indicate that the $\text{CsSnI}_{3-x}\text{Br}_x$ system has a property favorable for application in solar cells.

Keywords: perovskite solar cell, band gap, electronic structure, density functional theory, modified Becke–Johnson potential

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INTRODUCTION

In recent years, photovoltaic devices such as solar panels and inverters have been considered the best way to inexpensively convert light to electricity as a renewable energy source. Silicon composites are widely used to create solar cells because of their unique electrical properties, such as the size of the area required and the ability to absorb sunlight. Moreover, the technology of manufacturing traditional silicon-based solar cells has been improved to increase the efficiency of Si based solar cells to 26.7% [1]. Nevertheless, some problems should be stressed out, such as high cost and pollution of Si-based solar cells. Therefore, in modern technologies, new types of photovoltaic devices are associated with sensitized solar cells, such as quantum dot and perovskite solar cells. Among them, perovskite solar cells have an advantage of low-cost fabrication and structurally adjustable materials. Recently, perovskite solar cells, referred to as “third generation solar cells”, have emerged and have been widely promoted as economically and environmentally viable and renewable technologies over traditional solar cell technologies to address global energy, safety and environmental concerns [2]. Moreover, the latest perovskite-based solar cells can convert energy with an efficiency of up to 25.5% [1]. Recently, the theoretical achievement of an

efficiency of more than 46% of solar inverters based on perovskite materials by focusing with a light lens in a small photocell has been pointed out [3]. The conversion efficiency of solar cells depends on the optical properties of the materials, the so-called ability to absorb light, which in turn is highly dependent on the band gap of the materials. Presumably, halide perovskites of $\text{CsSnI}_{3-x}\text{Br}_x$ family have a narrow band gap in the range from 1.0 to 1.8 eV, which corresponds to the maximum ability to absorb light as excellent converters. Such materials are suitable for use in solar cells.

In this work, the crystal structure, electronic and optical properties of the $\text{CsSnI}_{3-x}\text{Br}_x$ family were investigated by first principles calculations within the framework of density functional theory (DFT) for their applications as candidate materials for non-toxic light absorbers in solar cell panels and batteries.

COMPUTATION METHODS

The crystal structure of the orthorhombic $\text{CsSnI}_{3-x}\text{Br}_x$ with the perovskite structure was investigated within the framework of DFT using the projector augmented wave package with the plane-wave basis VASP [4]. Geometry optimization was carried out by allowing

Table 1. Comparison of calculated structural parameters with experimental ones for $\text{CsSnI}_{3-x}\text{Br}_x$

System	$a, b, c, \text{\AA}$		$V, \text{\AA}^3$		Error in volume, %
	this work	experiment	this work	experiment	
CsSnI_3	8.9081, 12.4354, 8.4355	8.688, 12.378, 8.643 [9]	934.4653	929.4687 [9]	0.52
CsSnI_2Br	8.46708, 12.5517, 8.4675	—	899.9003	—	—
CsSnIBr_2	8.2064, 12.6192, 8.2046	—	849.6717	—	—
CsSnBr_3	8.3557, 11.7306, 8.2055	8.3634, 11.7609, 8.1782 [10]	804.2926	804.4168 [10]	0.015

the relaxation of all atomic positions in the cell and the cell shape. Electron-electron correlation was expressed by the generalized gradient approximation proposed by Perdew, Becke and Ernzerhof (GGA-PBE) [5]. A $3 \times 3 \times 2$ $\mathbf{k}$ -point mesh was selected in the Brillouin zone according to Monkhorst-Pack (MP) scheme [6]. The plane-wave cutoff was chosen to be 400 eV.

Electronic structure calculations for perovskite models after geometry optimization with VASP were performed using the full-potential augmented plane wave plus local orbit package, WIEN2k [7], where the modified Becke-Johnson potential refined by Tran and Blaha (TB-mBJ) [8] was employed for the electron-electron correlation functional. The muffin-tin radii for Cs, Sn and I were set equal to 2.5 a.u., and that for Br was to 2.07 a.u. The plane wave cutoff K_{max} was chosen to be $3.0 \text{ Ry}^{1/2}$. The $\mathbf{k}$ -point mesh was $3 \times 3 \times 2$ for all calculations using the MP scheme.

RESULTS AND DISCUSSION

The optimized structural parameters of $\text{CsSnI}_{3-x}\text{Br}_x$ are summarized in Table 1. The experimental cell parameters of the end members, i.e., CsSnI_3 and CsSnBr_3 , were quantitatively well reproduced by current calculations within the typical GGA errors. Since the ionic radius of the Br ion is less than that of I ion, the calculated cell volume, as shown in Fig. 1, decreases linearly with increasing Br concentration, which suggests that the volume change obeys Vegard's law.

The calculated total density of electronic states of the structurally optimized models of $\text{CsSnI}_{3-x}\text{Br}_x$ described above is shown in Fig. 2. The calculated band gaps of these materials are summarized in Table 2. Since the GGA approximation typically underestimates the band gap, in the current calculations of the electronic structure, we used the TB-mBJ potential for the electron-electron exchange correlation functional. The calculated band gaps are plotted in Fig. 3, which suggest that the band gap increases linearly with

Fig. 1. Calculated cell volume as a function of Br concentration for $\text{CsSnI}_{3-x}\text{Br}_x$ ($x = 0, 1, 2, 3$). **Fig. 2.** Total density of electronic states (TDOS) for CsSnI_3 (black, 0), CsSnI_2Br (red, 1), CsSnIBr_2 (blue, 2) and CsSnBr_3 (green, 3).

Table 2. Comparison of calculated band gap with other theoretical and experimental ones

System	Band gap, eV		
	this work (mBJ)	experiment	other calculations
CsSnI ₃	1.307	1.30 [11]	0.885 [12], 0.561 [13], 1.71 [13]
CsSnI ₂ Br	1.486	—	—
CsSnIBr ₂	1.635	—	—
CsSnBr ₃	1.725	1.720 [12]	1.01 [14]

increasing Br concentration x in CsSnI_{3-x}Br_x. The least squares fitting to the calculated band gap shown by the solid line in Fig. 2 is expressed by the following formula: $E_{BG} = 0.1403x + 1.3278$, from which one can estimate the band gap value in CsSnI_{3-x}Br_x for any Br concentration, i.e., $0 < x < 3$.

The electronic band structures of the CsSnI_{3-x}Br_x are shown in Fig. 4. Overall band structures have similar profiles, although the band gap increases with increasing Br concentration. It should be noted here that all of these materials have a direct transition band structure, which implies that all of these compounds are quite suitable for use as optical materials of interest.

Then the optical properties were calculated using the use italic font code implemented in the WIEN2k package. Figures 5a, 5b show the real and imaginary parts of the dielectric constants, ϵ_1 and ϵ_2 , respectively, for entire family of the systems under study. Figure 5a shows that materials exhibit a metallic behavior at sufficiently high incident photon energies. A negative value of ϵ_1 indicates that the system has a metallic

nature. On the other hand, the imaginary part, ϵ_2 , represents the absorption capacity; the behavior of the ϵ_2 function for materials should exhibit an increase in energy, which is suitable for the photovoltaic applications.

Finally, the calculated absorption coefficients, α , are shown in Fig. 6 for all investigated materials. Although the absorption edge shifts toward higher energies as the Br concentration increases, as expected due to the change in the band gap, all of these materials seem to be suitable for the photovoltaic applications.

CONCLUSION

In this work, the crystal structure, electronic and optical properties were investigated for orthorhombic CsSnI_{3-x}Br_x ($x = 0, 1, 2, 3$) with a perovskite structure by first principles calculations using DFT. The crystal structures of the end members, CsSnI₃ and CsSnBr₃, are quantitatively well reproduced by our current calculations. Electronic and optical studies have shown that doping with Br can lead to an increase and an optimization of the band gap value. The calculated optical properties strongly indicate absorption in the visible and infrared regions. Based on the above characteristics, it can be concluded that these materials may be suitable for photovoltaic applications. The results of the first principles calculation satisfy the criteria for Br-doped CsSnI₃ materials necessary for sensitized solar cells targets. The studied new perovskite systems, lead-free mixed halide inorganic perovskites, CsSnI_{3-x}Br_x ($x = 0, 1, 2, 3$), can prove the criteria of search for candidate materials favorable for the photovoltaic design. We focused on CsSnI_{3-x}Br_x ($x = 0, 1, 2, 3$) perovskite systems as alternative lead-free materials for photovoltaic applications and devices. It should be noted that such materials will have several important advantages, i.e., lower toxicity, structural stability, favorable optical characteristics, etc., which makes

Fig. 3. Calculated band gap as a function of Br concentration for CsSnI_{3-x}Br_x ($x = 0, 1, 2, 3$).

Fig. 4. Top of the valence band at Gamma point should be zero of (a) CsSnI₃, (b) CsSnI₂Br, (c) CsSnIBr₂ and (d) CsSnBr₃.

Fig. 5. Calculated (a) real (b) and imaginary parts of the dielectric constant of CsSnI_{3-x}Br_x for $x = 0, 1, 2$ and 3 .

Fig. 6. Calculated absorption coefficient of CsSnI_{3-x}Br_x for $x = 0, 1, 2$ and 3 .

them attractive materials for photovoltaic devices and solar cell batteries. Presumably, comparing to Pb-based perovskites, lead-free materials will have high conversion efficiency, high carrier mobility, long diffusion length, etc., necessary for inexpensive conversion of light into electricity. It is found that for the $\text{CsSnI}_{3-x}\text{Br}_x$ system, the band gap increases with increasing Br content. The calculated optical properties were the sum of the real and imaginary parts of the dielectric constant and absorption coefficients. For the $\text{CsSnI}_{3-x}\text{Br}_x$ system, a high absorption rate and direct band gaps are predicted, which means that these materials may be quite suitable for use in solar cell technology [9–14].

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