The effect of B-site alloying on the electronic and opto-electronic properties of RbPbI₃: A DFT study

Anupriya Nyayban* and Subhasis Panda†

Department of Physics
National Institute of Technology Silchar, Assam, 788010, India

Avijit Chowdhury‡

Department of Physics
National Institute of Technology Silchar, Assam, 788010, India
and
Department of Condensed Matter Physics and Material Sciences,
S.N. Bose National Centre for Basic Sciences, JD Block,
Sector III, Salt Lake City, Kolkata 700106, India

(Dated: January 31, 2022)

Divalent cations mixed lead halide perovskites with enhanced performances, high stabilities, and reduced toxicity are requisite to make persistent progress in perovskite solar cells. However, the mixing strategy is not reported extensively in search of a lead reduced structure. Herein, we report the structural, electronic and optical properties of RbPb₁₋ₓMₓI₃ (where, M={Sn,Ge} and x={0.25, 0.50, 0.75}) by alloying the B-site with Sn and Ge, using the density functional theory. The formation enthalpy is estimated for all RbPb₁₋ₓMₓI₃ (with x = 0.25, 0.50, 0.75), which confirms stability for all the structures. The energy bandgap and density of states (DOS) have been thoroughly investigated. The energy bandgap decreases with the increasing Sn/Ge contents, the lowest bandgap of 1.850 eV is observed at x = 0.50 in the case of RbPb₁₋ₓGeₓI₃ systems. Further, the effective masses and the binding energy of excitons and spectroscopic limited maximum efficiency (SLME) are also estimated for all the mixed systems. The exciton type is observed to change from Mott-Wannier to Frenkel type with increasing the contents of both Sn and Ge at the B-site. The maximum efficiency of 23% is achieved using an active layer containing an equal admixture of Sn/Ge and Pb. The estimated parameters of both the mixed systems are consistent with the available literature of similar types.

I. INTRODUCTION

The burgeoning photo conversion efficiency (PCE) toward the Shockley–Queisser limit makes perovskites a game-changing material in photovoltaic technology over a short time frame. The perovskite materials possess a few notable features, such as suitable energy band edge positions [1], high mobilities of photogenerated charge carriers [2], the lower binding energy of excitons [3], etc., which are perfect for solar cell applications [4–10]. The rapid progress of perovskite materials inspires researchers to look at ways to make a more stable and less hazardous ABX₃ structure, where A, B, and X are the organic or inorganic monovalent cations, inorganic divalent cations, and halides, respectively. Despite their great success, perovskites are still suffering from a few drawbacks, e.g., the device instability due to heat and moisture [11, 12], the toxicity due to Pb, etc. Therefore, further attempts to resolve these issues are required to shape the solar cell research based on perovskites materials. The inorganic halide perovskites have emerged as one of the hotspots in perovskite photovoltaics due to their higher thermal stability as compared to the organic-inorganic hybrid perovskites [13–15]. Among the inorganic perovskites, CsPbX₃ was studied earlier [16–19] and found to exhibit the most promising photovoltaic properties. In another study [20], CsSnI₃ is reported to have a direct energy bandgap (1.3 eV) and mobility as 400 cm⁻²/Vs. However, very few studies are available for Rb-based inorganic perovskites [21–24].

Despite their exceptional features and application scopes, several concerns, such as stability and toxicity, continue to hamper their performance at the device level. Hence, alloying the B-site with suitable group materials, such as Sn and Ge, is a popular trend to deal with the toxicity issue of perovskites without compromising the performance [25, 26]. Both the materials pose the same oxidation state and structure, which facilitates the possible partial substitution of Pb in MAPbI₃ [25–29]. Better photoconversion efficiency and stability have been observed experimentally for the partial Sn substitution in the Pb site of the MAPbI₃ [25, 26]. It has been theoretically investigated [29] and reported...
that the partial Ge substituted MAPbI$_3$, i.e., MAGe$_x$Pb$_{1-x}$I$_3$, exhibits better photovoltaic properties and higher absorption. Ming-Gang Ju et al. [30] have predicted that the energy bandgap and the absorption of RbSn$_{0.5}$Ge$_{0.5}$I$_3$ are suitable for PSC and its performance is comparable to that of MAPbI$_3$. B-site doping in CsPbI$_3$ with Sn$^{2+}$ are also reported [31] theoretically to improve the bandgap and the structural stability. CsPb$_{0.7}$Sn$_{0.3}$I$_3$ based solar cell is experimentally reported [32] to achieve a PCE of 9.41 % and high $J_{sc}$ (short circuit current density) of 20.96 mAm$^{-2}$. Recently, the cubic phase of CsPb$_{0.8}$Ge$_{0.2}$I$_3$ are experimentally [33] formed at 90$^\circ$C, showing PCE of 3.97 %, external quantum efficiency of 40 – 70 % and poses stability at room temperature. To the best of our knowledge, no literature describes the partial substitution of either Sn or Ge in the divalent cation-site of RbPbI$_3$. Therefore, in this work, we have partially substituted Sn or Ge in the divalent cation-site of RbPbI$_3$ and theoretically studied their electronic and optoelectronic properties using density functional theory. The structural, electronic, and optical properties are systematically investigated for both RbPb$_{1-x}$Sn$_x$I$_3$ and RbPb$_{1-x}$Ge$_x$I$_3$ with $x = 0.25, 0.50$ and 0.75. The computational details are described in Section II. The structural properties, lattice parameters, and formation energies are calculated and described in Section III-A. The energy band structure and density of states (DOS) under the electronic properties are investigated in detail and discussed in Section III-B. The optical properties, e.g., the imaginary part of the dielectric function and the absorption spectra for all the mixed systems, are described in Section III-C. Furthermore, the effective masses, exciton binding energies, and the spectroscopic limited maximum efficiencies are also studied and sectioned in III-C, followed by a brief conclusion in section IV.

II. COMPUTATIONAL METHODS

All the first principle based calculations for $2 \times 2 \times 2$ supercell of both RbPb$_{1-x}$Sn$_x$I$_3$ and RbPb$_{1-x}$Ge$_x$I$_3$ (where $x = 0.25, 0.50$ and 0.75) are performed using WIEN2k [34] within the full potential linearized augmented plane wave (FP-LAPW) method. The supercell is created from the optimized orthorhombic RbPbI$_3$ [23] of NH$_4$CdCl$_3$ type structure having Pnma space group. Each supercell is relaxed and optimized. The Muffin tin radius of 2.50 Å is set for all the atoms in all the mixed systems. $R_{K_{max}}$ of 8 is considered for both RbPb$_{0.50}$Sn$_{0.50}$I$_3$ and RbPb$_{0.50}$Ge$_{0.50}$I$_3$ whereas it is set to 7 for all other systems. PBE (Perdew-Burke-Ernzerhof)-GGA (generalized gradient approximation) [35] is used to treat the exchange correlation functional. Spin orbit coupling (SOC) effect is not included here due to the fact that PBE without SOC estimate the bandgap accurately for the hybrid perovskites [36–39] and even PBEsol [40, 41] and hybrid functional [36] are reported to overestimate the bandgap. Moreover, PBE with SOC does not change the band structure pattern for both RbSnI$_3$ and RbGeI$_3$ [24], rather it reduces the bandgap. The electronic structure is calculated over the kmesh of $1 \times 6 \times 13$ and $8 \times 7 \times 2$ for $x = 0.50$ and others in RbPb$_{1-x}$Sn$_x$I$_3$ systems. In case of RbPb$_{1-x}$Ge$_x$I$_3$, kmesh of $1 \times 5 \times 11$ and $7 \times 3 \times 3$ are set to calculate the electronic structure for $x = 0.50$ and all other values of $x$. TB-mBJ (Tran-Blaha modified Becke-Johnson) [42] potential is reported to estimate the bandgap accurately [43, 44] with less computations as compared to that with the hybrid functionals. Therefore, TB-mBJ potential is considered to find the bandgap for all the treated systems. Later, the higher kmesh of $15 \times 14 \times 4$, $3 \times 11 \times 25$ and $15 \times 7 \times 8$ are set to evaluate all the optical properties for $x = \{0.25, 0.75\}$ in RbPb$_{1-x}$Sn$_x$I$_3$, $x = 0.50$ in both the mixed cases and $x = \{0.25, 0.75\}$ in RbPb$_{1-x}$Ge$_x$I$_3$, respectively.

III. RESULTS AND OBSERVATIONS

A. Structural and electronic properties

The optimized lattice parameters for all the supercells, obtained using the Birch-Murnaghan equation of state [45], are represented in TABLE I. The variation of total energy with volume fitted to the second order Birch-Murnaghan equation of state for all are represented in FIG. S1 in the Supporting Information.

| M  | x  | a (Å) | b (Å) | c (Å) | $\alpha$ | $\beta$ | $\gamma$ | $H$ (eV) |
|----|----|-------|-------|-------|----------|--------|---------|---------|
| Sn | 0.25 | 9.785 | 10.530 | 35.601 | 90.000° | 90.000° | 90.000° | -1.932 |
| Sn | 0.50 | 35.478 | 10.494 | 4.876 | 90.000° | 90.000° | 90.000° | -3.312 |
| Sn | 0.75 | 9.784 | 10.529 | 35.598 | 90.000° | 90.000° | 90.000° | -3.070 |
| Ge | 0.25 | 9.702 | 20.883 | 21.074 | 119.701° | 103.309° | 90.000° | -1.562 |
| Ge | 0.50 | 34.943 | 10.336 | 4.802 | 90.000° | 90.000° | 90.000° | -2.448 |
| Ge | 0.75 | 9.496 | 20.438 | 20.625 | 119.701° | 103.309° | 90.000° | -1.922 |

TABLE I: Lattice parameters for RbPb$_{1-x}$M$_x$I$_3$ systems
All the optimized supercells are also depicted in FIG. S2 in the supporting information. TABLE I also suggests that there is a decreasing trend in the lattice parameters for both RbPb$_{1-x}$Sn$_{3}$I$_3$ and RbPb$_{1-x}$Ge$_{1-x}$I$_3$ when the concentration of Sn and Ge increases, respectively. This is attributed to the smaller ionic radii of Sn and Ge compared to that of Pb. The volume of the supercell also decreases more with the increase of Ge concentration than that of Sn owing to the smaller Ge-ionic radii. The lowest volume is observed for the equal mixture of both Pb-Sn and Pb-Ge cases. A material can be destabilized by the external effects e.g. heat, oxygen, and moisture. Therefore, it is necessary to find the enthalpy of the formation, which plays a significant role in determining the chemical as well as the thermodynamic stability of the material. A ABX$_3$-type structure generally decomposes into AX and BX$_2$. Hence, the formation energy (H) for Pb-Sn and Pb-Ge mixing systems are calculated using the following reactions:

$$ H_{Sn} = E(RbPb_{1-x}Sn_{x=0.75}) - E(RbI) - xE(SnI_2) - 2(1-x)E(I) - (1-x)E(Pb) $$

(1)

$$ H_{Ge} = E(RbPb_{1-x}Ge_{x=0.75}) - E(RbI) - xE(GeI_2) - 2(1-x)E(I) - (1-x)E(Pb) $$

(2)

where x and E symbolize the concentration percentage of Sn/Ge and the total energy corresponding to each compound, respectively. The calculated total energy for RbPb$_{1-x}$Sn$_{3}$I$_3$, RbPb$_{1-x}$Ge$_{x}$I$_3$, SnI$_2$, GeI$_2$, PbI, Pb and I are listed in TABLE SI in the Supporting Information. Further, the enthalpy of formation per formula unit for both the systems are also calculated using relation (1)-(2) and listed in TABLE I. It is observed that the negative values of the enthalpy of formation is increasing with the concentration of Sn and Ge excepts the highest enthalpies are for x = 0.50 for both RbPb$_{1-x}$Sn$_{3}$I$_3$ and RbPb$_{1-x}$Ge$_{x}$I$_3$. These values suggest the stability of all the structures whereas the highest stability is observed at x = 0.50. Additionally, the formation energy can be explained by the bond strength of B-I. The stronger bond again is determined from the smaller bond length and the higher electronegativity difference between B and I. The difference of electronegativities between Pb-I, Sn-I and Ge-I are 0.33, 0.70 and 0.56 respectively. The higher electronegativity difference for Sn-I (for RbPb$_{1-x}$Sn$_{3}$I$_3$) indicates the stronger bonds and the higher enthalpies as compared with RbPb$_{1-x}$Ge$_{x}$I$_3$. Therefore, the calculated enthalpy of formation and B-I bond strength both follow the condition of a stable structure.

### B. Electronic Properties

The electronic bandgap values are crucial for an absorber used in solar cell owing to the fact that it makes a solar cell suitable to absorb photons and achieve maximum efficiency with minimum optical losses. Therefore, the calculated values of the bandgaps for all are listed in TABLE II.

#### TABLE II: The bandgap $E_g$ in eV for all Pb-Sn and Pb-Ge mixed systems

|                  | RbPb$_{1-x}$Sn$_{3}$I$_3$ | RbPb$_{1-x}$Ge$_{x}$I$_3$ |
|------------------|---------------------------|---------------------------|
| x=0.25 x=0.50    |                           |                           |
| PBE              | 2.056                     | 2.153                     |
| TB-mBJ           | 2.450                     | 2.581                     |

The bandgap values calculated with PBE decrease gradually with the increase of Sn concentration for Pb-Sn mixed systems. The Fermi level is fixed to zero for all the structures. The DOS estimated with PBE and the bandstructures estimated with both PBE and TB-mBJ potentials are shown for Pb-Sn mixed systems and RbPb$_{0.5}$Ge$_{0.5}$I$_3$ in FIG. 1 while it is shown in FIG. 2 for RbPb$_{0.75}$Ge$_{0.25}$I$_3$ and RbPb$_{0.25}$Ge$_{0.75}$I$_3$.

The FIG. 1 suggests that the conduction band minimum (CBM) and the valence band maximum (VBM) are observed at Y, S, T and U, Z, X for RbPb$_{1-x}$Sn$_{3}$I$_3$ when x values are 0.25, 0.50 and 0.75, respectively. The CBM are observed at Z, Y, Γ while the VBM are found at X, Z high symmetry k-points for RbPb$_{1-x}$Ge$_{x}$I$_3$ when Ge concentration increases from 0.25, 0.50 to 0.75, respectively. This confirms that all the structures have the indirect bandgaps. The bandgap does not decrease linearly (Vegard’s law) with x rather it follows an anomalous behavior for both RbPb$_{1-x}$Sn$_{3}$I$_3$ and RbPb$_{1-x}$Ge$_{x}$I$_3$. The similar behavior is also observed for MAPb$_{1-x}$Sn$_{3}$I$_3$ [46]. This is owing to the variation of the symmetry for both RbPb$_{1-x}$Sn$_{3}$I$_3$ and RbPb$_{1-x}$Ge$_{x}$I$_3$ structures with the changing x values. The calculated bandgap values cannot be compared with any experimental values due to the unavailability of the reported data in the literature. Although PBE without SOC are reported [36–39] to estimate the bandgaps accurately, more advanced TB-mBJ potential is also used to estimate the band structures. TB-mBJ is reported [44] to estimate the bandgap for the hybrid organic-inorganic perovskites efficiently with the affordable computational cost as compared to that with both hybrid functionals and GW method. The TB-mBJ estimated band structures show that the bandgaps are increased by 0.394, 0.504, 0.483 eV as compared to that with PBE for x = 0.25, 0.50 and 0.75, respectively in the case of Pb-Sn mixed systems. In case of RbPb$_{1-x}$Ge$_{x}$I$_3$, the bandgaps are widened by 0.468, 0.426 and 0.431 eV.
for Ge concentrations of 0.25, 0.50 and 0.75, respectively. The CBM are mainly shifted to the higher energy region whereas no significant changes are observed in the VBM for all the structures. The similar nature of bandstructures calculated with PBE and TB-mBJ potentials are also observed for pristine RbPbI₃ [23], RbSnI₃ and RbGeI₃ [24].

The density of states (DOS) are also estimated to gain a brief understanding of the behavior of atomic orbitals into the electronic structures. PDOS for RbPb₁₋ₓSnₓI₃ (where, x = 0.25, 0.50 and 0.75) and RbPb₀.₅₀Ge₀.₅₀I₃ are plotted to the right hand column in FIG. 1 whereas FIG. 2c represents the PDOS for both RbPb₀.₇₅Ge₀.₂₅I₃ and RbPb₀.₂₅Ge₀.₇₅I₃. The orbitals of Rb⁺ cation contribute to the energy region far below the bandgap region and they are found to be well localized. Hence, Rb atom does not contribute to the to the active region of both the structures. Thus, the contribution of Pb, Sn, I orbitals for RbPb₁₋ₓSnₓI₃ and the orbitals of Pb, Ge, I in case of RbPb₁₋ₓGeₓI₃ are represented and discussed to get a clear understanding near the bandgap. PDOS plot suggests that the uppermost region of the first valence band is dominated by the I-5p and Pb-6s orbitals. Since Sn and Ge are of similar electronic structures as Pb, it also shows a similar behavior in the uppermost region of the first VB for both RbPb₁₋ₓSnₓI₃ and RbPb₁₋ₓGeₓI₃. The lower region of the first VB is mainly contributed by I-5p with a minor population of Sn-5p and Pb-6p in case of RbPb₁₋ₓSnₓI₃ whereas Ge-4p and Pb-6p for RbPb₁₋ₓGeₓI₃. The first VB energy levels are extended from 0 to −3.063, −3.158 and −3.114 eV with the increasing x values (0.25, 0.50 and 0.75) for RbPb₁₋ₓSnₓI₃. In case of RbPb₁₋ₓGeₓI₃, the first VB ranges from 0 to −2.954, −3.152 and −3.433 eV when Ge concentration changes to 0.25, 0.50 and 0.75, respectively. The more or less similar contribution of I-5p are observed for all the systems. The contribution of Sn-5s (Ge-4s) in the first VB region is decreasing when the concentration of Sn (Ge) increases. The
second VB are dominated by Sn-5s and it increases with the increase of Sn content in RbPb$_{1-x}$Sn$_x$I$_3$. Similarly, the contribution of Pb-6s and Ge-4s are observed for the second VB where Pb-6s is dominant and the contribution of Ge-4s is increased with the increasing Ge concentration. Again, the conduction band is predominantly occupied by Pb-6p and Sn-5p (Ge-4p) orbitals for RbPb$_{1-x}$Sn$_x$I$_3$ (RbPb$_{1-x}$Ge$_x$I$_3$). The contribution of Sn-5p and Ge-4p to the CB increases with the increasing Sn and Ge content for the Sn and Ge mixed systems, respectively. The upper region of CB also shows a minor contribution of I-5s and I-5p orbitals for all the mixed systems under consideration. The CB energy levels ranges from 2.025 to 3.957, 1.957 to 3.944 and 1.920 to 3.906 eV when Sn concentrations are 0.25, 0.50.
and 0.75, respectively for Sn mixed systems. Similarly, the CB in RbPb$_{1-x}$Ge$_x$I$_3$ extends from 2.119 to 4.295, 1.855 to 4.304 and 2.243 to 4.310 eV with the Ge concentration of 0.25, 0.50 and 0.75, respectively. The similar behavior are also reported [29] for the mixed MAGe$_x$Pb$_{1-x}$I$_3$ systems. Therefore, the hybrid states of Pb$^{2+}$ and Sn$^{2+}$ (Ge$^{2+}$) mainly determine the photovoltaic properties whereas it is determined by Pb$^{2+}$ states in pristine RbPbI$_3$ [23].

The total density of states (TDOS) for $x$ =0.25, 0.50 and 0.75 are plotted in FIG. 3a and FIG. 3b for the all Sn and Ge mixed systems. The figure shows the rise in VB edge is more compared to that of CB edge for all the mixed systems whereas the rise in the VB edge is highest for Sn mixed systems. The calculated TDOS also indicates the increase in the no of states are more for RbPb$_{0.75}$Sn$_{0.25}$I$_3$ and RbPb$_{0.25}$Sn$_{0.75}$I$_3$ compared to RbPb$_{0.50}$Sn$_{0.50}$I$_3$. Similar behavior is observed for Ge mixed systems where the lesser no of states are found for $x$ = 0.50. Hence, a large no of states are observed for the smaller and higher concentration of Pb for all the mixed systems. Therefore, the probability of higher carrier concentration is observed at $x$ = 0.25 and $x$ = 0.75 for both the mixed systems and this can enhance the transport as well as the device properties.

C. Optical Properties

The higher absorption and larger dielectric constant are crucial for the better performance of a solar cell. Therefore, the optical properties are estimated with the linear response method using the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. The imaginary part of the dielectric function $\epsilon_2(\omega)$ is estimated using the momentum matrix involving the occupied and unoccupied states. FIG 4a and 4c represent $\epsilon_2(\omega)$ for RbPb$_{1-x}$Sn$_x$I$_3$ and RbPb$_{1-x}$Ge$_x$I$_3$, respectively. The first and the strongest peaks are observed at 3.741, 3.959, 4.068; 4.122, 4.013, 3.768; and 3.659, 4.013, 4.040 eV for RbPb$_{0.75}$Sn$_{0.25}$I$_3$, RbPb$_{0.50}$Sn$_{0.50}$I$_3$ and RbPb$_{0.25}$Sn$_{0.75}$I$_3$ along x, y and z polarization directions whereas the second stronger peak is found near a photon energy of 7.000 eV. On the other hand, the first strongest peaks are observed at the photon energy of 3.796, 4.014, 4.095; 4.259, 4.041, 3.878; 3.769, 4.204, 4.231 along different directions (x, y and z) eV when the Ge concentration in RbPb$_{1-x}$Ge$_x$I$_3$ increases as 0.25, 0.50 and 0.75, respectively. The bandgap reduction associated with the increase of Sn/Ge concentration (except at $x$ = 0.50 for RbPb$_{1-x}$Ge$_x$I$_3$) is responsible for such trend of peaks observed in all the mixed systems.

The real part of the dielectric function $\epsilon_1(\omega)$ is estimated using $\epsilon_2(\omega)$ and the Kramer-Kronig relation. The variation of $\epsilon_1(\omega)$ with the photon energy for all the mixed systems are shown in FIG. S3a and S3b in the supporting information whereas the values of the static dielectric constants are provided in the TABLE III. The average static dielectric constants ($\epsilon_1(0)$) are found to be 5.137, 5.232 and 5.300 for RbPb$_{1-x}$Sn$_x$I$_3$ at the Sn-concentrations of 0.25, 0.50 and 0.75, respectively, while these values are 5.174, 5.377 and 5.299 for all the Ge mixed systems. A large static dielectric constant induces the higher charge screening. This will reduce the charge defect levels which will again reduce the radiative electron hole recombination. Thus, the large values of $\epsilon_1(0)$ for all the mixed systems will help the material to be used as an efficient photovoltaic absorber.

Moreover, all other optical properties such as extinction coefficient ($k(\omega)$), absorption coefficient ($\alpha(\omega)$), reflectivity
(a) The imaginary part of the dielectric function for RbPb$_{1-x}$Sn$_x$I$_3$.

(b) The absorption coefficients for RbPb$_{1-x}$Sn$_x$I$_3$.

(c) The imaginary part of the dielectric function for RbPb$_{1-x}$Ge$_x$I$_3$.

(d) The absorption coefficients for RbPb$_{1-x}$Ge$_x$I$_3$.

FIG. 4: The variation of $\epsilon_2$ and $\alpha$ with the photon energy along three different polarization direction for $x = 0.25$, 0.50 and 0.75, respectively.

TABLE III: The static dielectric constant, reflectivity, refractive index, binding energy of excitons and the radius of the lowest bound states for all the systems.

| M  | x   | $\epsilon_1(0)$ | $R(0)$ | $n(0)$ | $E_b$ | $a^*$ |
|----|-----|-----------------|--------|--------|-------|-------|
|    |     | (100)           | (010)  | (001)  | (100) | (010) | (001) | (100) | (010) | (010) | (meV) | Å    |
| Sn | 0.25| 5.408           | 4.943  | 5.061  | 0.159 | 0.144 | 0.148 | 2.326 | 2.223 | 2.250 | 54.629 | 25.637 |
| Sn | 0.50| 5.143           | 5.035  | 5.519  | 0.151 | 0.147 | 0.162 | 2.268 | 2.244 | 2.349 | 46.702 | 29.444 |
| Sn | 0.75| 5.622           | 5.093  | 5.186  | 0.165 | 0.149 | 0.152 | 2.371 | 2.257 | 2.278 | 333.101 | 4.075  |
| Ge | 0.25| 5.436           | 5.004  | 5.081  | 0.160 | 0.146 | 0.149 | 2.332 | 2.237 | 2.254 | 49.279 | 28.217 |
| Ge | 0.50| 5.177           | 5.143  | 5.810  | 0.152 | 0.151 | 0.171 | 2.275 | 2.268 | 2.410 | 57.858 | 23.125 |
| Ge | 0.75| 5.486           | 5.160  | 5.252  | 0.161 | 0.151 | 0.154 | 2.342 | 2.272 | 2.292 | 96.384 | 14.086 |

$R(\omega)$ and refractive index $n(\omega)$ are estimated using the following formulae:
of photon energy from the solar spectrum compared to the pristine RbPbI$_3$ to both visible and ultraviolet regions. Therefore, Sn and Ge mixed systems show the ability to absorb the wide range respectively. In case of Ge mixed systems, the first strong absorption peaks are observed at 4.

transitions from the mixed valence state of I-5p, Pb-6s and Sn-5s to the mixed conduction state of Sn-5p and Pb-6p Ge-concentrations of 0 systems that the absorption regions are widened as compared to that of pristine RbPbI$_3$ system compared to the cubic one. Yet, it is interestingly observed from the absorption spectra for all the mixed conduction state occupied by Pb-5p and Ge-4p for the all the Ge mixed states. It is difficult to analyze the interband absorption intensities are also higher than that of pristine RbPbI$_3$ highest absorption in the near infrared region. For all the Pb-Sn and Pb-Ge mixed systems, the average integrated intensities over the energy range of 0

Moreover, the integrated absorption intensity are estimated using the integration over the absorption curves along different energy regions for all the mixed systems. TABLE IV shows the estimated integrated absorption intensities along the three most important energy regions of the solar spectrum (near-infrared, visible and ultraviolet). The integrated intensities over the energy range of 0 – 1.7 and 1.7 – 3.3 eV for Sn mixed systems increase with the increase of Sn concentration while the highest integrated intensity in the energy range of 0 – 1.7 and 1.7 – 3.3 eV are observed for RbPb$_{0.50}$Ge$_{0.50}$I$_3$ in the case of all Ge mixed systems. The near-infrared region is interesting due to the fact that 55% of the solar energy reaching the earth are of this region. RbPb$_{0.25}$Sn$_{0.75}$I$_3$ and RbPb$_{0.50}$Ge$_{0.50}$I$_3$ exhibit the highest absorption in the near infrared region. For all the Pb-Sn and Pb-Ge mixed systems, the average integrated absorption intensities are also higher than that of pristine RbPbI$_3$ in the near infrared and visible region.

FIG S3. of the supporting information provides the variation of the real part of the dielectric function $\epsilon_1(\omega)$, refractive index $n(\omega)$ and reflectivity $R(\omega)$ with the variation of the photon energy. The calculated static refractive index $n(0)$ and static reflectivity $R(0)$ for all are listed in TABLE III. The average static refractive indices for RbPb$_{1-x}$Sn$_x$I$_3$ systems are 2.266, 2.287 and 2.302 while these values are 2.274, 2.318 and 2.302 for RbPb$_{1-x}$Ge$_x$I$_3$ at $x = 0.25$, 0.50 and 0.75, respectively. The refractive index increases with the Sn concentration whereas the highest static refractive index is observed for RbPb$_{0.50}$Ge$_{0.50}$I$_3$ in Ge mixed systems. Similarly, the average static reflectivity increases from 15% to 15.5% and with the increase of Sn content while the highest 15.8% reflectivity is observed for all mixed systems.

The charge transport property is an important factor and the effective masses ($m_{e,f}$) of the charge carriers play a significant role in determining the mobility of the photogenerated electrons and holes. TABLE V shows the calculated effective mass for all the systems along three different crystallographic directions $\Gamma(0,0,0) \rightarrow X(0.5,0,0)$, $Y(0,0.5,0) \rightarrow \Gamma(0,0,0)$ and $\Gamma(0,0,0) \rightarrow Z(0,0,0.5)$. Effective masses $m_{e,f}$ of electrons and holes are estimated by

$$k(\omega) = \left(\frac{\sqrt{\epsilon_1(\omega)^2 + \epsilon_2(\omega)^2 + \epsilon_1(\omega)}}{\sqrt{2}}\right)$$

$$\alpha(\omega) = \frac{2\omega k(\omega)}{c}$$

$$R(\omega) = \left(\frac{n(\omega) - 1}{n(\omega) + 1}\right)^2 + k(\omega)^2$$

$$n(\omega) = \frac{\sqrt{\epsilon_1(\omega)^2 + \epsilon_2(\omega)^2 - \epsilon_1(\omega)}}{\sqrt{2}}$$

FIG. 4b and 4d show the behavior of the absorption coefficients at different energy for all the Sn and Ge mixed systems. The first strong absorption peaks of RbPb$_{1-x}$Sn$_x$I$_3$ are found at the photon energy of 4.422, 4.340 and 4.694 eV for $x = 0.25$; 4.694, 4.395 and 4.340 eV for $x = 0.50$; 4.068, 4.340 and 4.694 eV for $x = 0.75$ along x, y, z directions, respectively. In case of Ge mixed systems, the first strong absorption peaks are observed at 4.503, 4.476 and 4.667; 4.640, 4.390 and 4.449; 4.449, 4.422 and 4.640 eV of photon energy along x, y and z polarization directions for the Ge-concentrations of 0.25, 0.50 and 0.75, respectively. The first strong peaks are appeared due to the electronic transitions from the mixed valence state of I-5p, Pb-6s and Sn-5s to the mixed conduction state of Sn-5p and Pb-6p for RbPb$_{1-x}$Sn$_x$I$_3$ whereas it is due to the transition from the valence state consisting I-5p, Pb-6s and Ge-4s to the conduction state occupied by Pb-5p and Ge-4p for all the Ge mixed states. It is difficult to analyze the interband transitions exactly corresponding to the critical point as the large number of bands are involved for the orthorhombic system compared to the cubic one. Yet, it is interestingly observed from the absorption spectra for all the mixed systems that the absorption regions are widened as compared to that of pristine RbPbI$_3$ case [23] and this is expanded to both visible and ultraviolet regions. Therefore, Sn and Ge mixed systems show the ability to absorb the wide range of photon energy from the solar spectrum compared to the pristine RbPbI$_3$ [23].

| Energy range (eV) | M = Sn | M = Ge |
|------------------|--------|--------|
| $0 - 1.7$        | 1.7 - 3.3 | 3.3 - 5.0 | 0 - 1.7 | 1.7 - 3.3 | 3.3 - 5.0 |
| $x = 0.25$       | 2.907  | 112.347 | 1224.86 | 2.839 | 103.477 | 1283.39 |
| $x = 0.50$       | 3.051  | 133.66  | 1205.98 | 3.073 | 129.155 | 1227.267 |
| $x = 0.75$       | 3.267  | 162.843 | 1217.186 | 2.823 | 107.949 | 1099.527 |

TABLE IV: The calculated average integrated absorption intensity in 10$^3$ eV/cm for RbPb$_{1-x}$M$_x$I$_3$
TABLE V: Effective masses for RbPb$_{1-x}$M$_x$I$_3$ when $x = 0.25$, 0.50 and 0.75.

| Directions | $x=0.25$ | $x=0.50$ | $x=0.75$ |
|------------|-----------|-----------|-----------|
|            | Electron  | Hole      | Electron  | Hole      | Electron  | Hole      |
| $\Gamma \rightarrow X$ | 0.052     | 0.225     | 1.294     | 0.039     | 0.051     |
| Sn         | 0.179     | 0.620     | 0.176     | 0.175     | 0.220     | 0.088     |
| $\Gamma \rightarrow Z$ | 2.662     | 0.053     | 0.059     | 3.376     | 4.635     |
| $\Gamma \rightarrow X$ | 0.155     | 0.438     | 1.334     | 0.058     | 0.365     |
| Ge         | 0.154     | 0.075     | 0.223     | 0.165     | 0.977     | 0.232     |
| $\Gamma \rightarrow Z$ | 0.097     | 0.073     | 0.370     |           |           |

The parabolic fitting of the bottom and top of CB and VB, respectively, using the relation:

$$m_{\text{eff}} = \frac{\hbar^2}{\partial^2 E(k)}$$

where, $E(k)$ and $k$ are the band energy and the wave vector, respectively. For RbPb$_{1-x}$Sn$_x$I$_3$ systems, the average effective masses of electrons and holes are 0.116, 1.169; 0.115, 0.509; and 1.212, 1.591 for $x$ values of 0.25, 0.50 and 0.75, respectively. On the other hand, 0.155, 0.160 and 0.518 are the average effective masses of electrons while 0.257, 0.524 and 0.322 are holes’ average effective masses corresponding to $x = 0.25$, 0.50 and 0.75, respectively. Later, the reduced effective masses ($\mu$) are calculated using $\mu = \frac{m_{\text{eff}} m_{\text{h}}}{m_{\text{e}} + m_{\text{h}}}$. The estimated reduced effective masses are 0.0160, 0.094, 0.688 for Sn mixed systems and 0.097, 0.123, 0.199 for Ge mixed systems corresponding to $x = 0.25$, 0.50 and $x = 0.75$, respectively. The effectiv masses increase with the increase of Sn/Ge concentration. Effective masses also can help an exciton to dissociate into electron and hole. Hence, the binding energy ($E_b$) and the radius ($a^*$) of the lowest bound state are estimated using the relations $E_b = 13.6 \frac{\mu}{\epsilon_{\text{(1)}}} \sigma$ and $a^* = \frac{\epsilon_{\text{(1)}}}{\mu} a_0$, respectively. The estimated values of the binding energies and radii of the lowest bound state are listed in TABLE III. The binding energies of Sn and Ge mixed systems are 54.629, 46.702, 333.101 and 49.279, 57.858, 96.384 meV when Sn/Ge concentration changes to 0.25, 0.50 and 0.75, respectively. The binding energy increases with the increase of Sn/Ge concentrations. The radius of the lowest bound state varies from 29.444 to 4.075 Å in RbPb$_{1-x}$Sn$_x$I$_3$ and 28.217 to 14.086 Å in RbPb$_{1-x}$Ge$_x$I$_3$ systems. The lower binding energy and the larger radius of the lowest bound state for all the systems at $x = 0.25$ and $x = 0.50$, make the exciton to be weak and Mott-Wannier type. On the other hand, the excitons in both RbPb$_{0.25}$Sn$_{0.75}$I$_3$ and RbPb$_{0.25}$Ge$_{0.75}$I$_3$ are of Frenkel type. Therefore, excitons are found to be weak and strong for the lower and higher concentrations of Sn/Ge. This is consistent with the fact that the excitons in pristine RbPbI$_3$ are of Mott-Wannier type [23] whereas for both the pristine RbSnI$_3$ and RbGeI$_3$ it is of Frenkel type [24].

![FIG. 5: The SLME for both Pb-Sn and Pb-Ge mixed systems at a temperature of 300 K](image-url)
Furthermore, the spectroscopic limited maximum efficiency (SLME) are estimated for all the mixed systems and it is shown in FIG 5. SLME is estimated as the ratio between the maximum power density ($P_m$) and the incident power density ($P_i$). All the required formulae to estimate the maximum power density are provided in the supporting information. The first principle estimation of the absorption coefficient, direct and indirect bandgap with PBE are used to find SLME for all the systems and these values are listed in TABLE S3 in the supporting information. The FIG. 5 shows that SLME increases with the increase of thickness at the temperature of 300 K. At a thickness of 500 nm and temperature of 300 K, SLME are estimated as 17.250 %, 21.897 % and 22.057 % for Pb-Sn mixed systems while 15.079 %, 23.248 % and 17.358 % for RbPb$_{1-x}$Ge$_x$I$_3$ systems with the increase of Sn and Ge content, respectively. RbPb$_{0.50}$Ge$_{0.50}$I$_3$ exhibits the highest efficiency among all the investigated mixed systems due to the higher absorption width and the smaller bandgap.

IV. CONCLUSIONS

In summary, the structural, electronic and optical properties of both RbPb$_{1-x}$Sn$_x$I$_3$ and RbPb$_{1-x}$Ge$_x$I$_3$ have been systematically investigated using the first principle calculations. The decrease in the volume is observed for the increase in both Sn and Ge content in the mixed structures except for $x = 0.50$. The highest stability is observed for RbPb$_{0.50}$Sn$_{0.50}$I$_3$ and RbPb$_{0.50}$Ge$_{0.50}$I$_3$ whereas all the systems under consideration exhibit stability. The bandstructure calculations show the indirect bandgaps for all the structures while the lowest bandgaps calculated with PBE are 1.951 and 1.850 eV for RbPb$_{0.25}$Sn$_{0.75}$I$_3$ and RbPb$_{0.50}$Ge$_{0.50}$I$_3$, respectively. The decrease in the bandgaps follow an anomalous behavior similar to the observed in MAGe$_x$Pb$_{1-x}$I$_3$ [29]. The comparatively highest absorption in the near infrared and visible spectra region is observed for both RbPb$_{0.25}$Sn$_{0.75}$I$_3$ and RbPb$_{0.50}$Ge$_{0.50}$I$_3$ structures. The lower effective masses of charge carriers and the binding energies of excitons are found upto $x = 0.50$ for both Pb-Sn and Pb-Ge mixed systems. The highest SLME of 22.057% and 23.248% are observed for $x = 0.75$ and Ge = 0.50 in case of Pb-Sn and Pb-Ge mixed systems. Among all the investigated structures, RbPb$_{0.50}$Ge$_{0.50}$I$_3$ exhibits the lowest bandgap, highest stability, high absorption and low exciton binding energy, thus, is the most suitable one for the photovoltaic application.

ACKNOWLEDGMENTS

A. N. would like to thank B. I. Sharma, Assam University, Silchar, India heartedly for the fruitful discussions and suggestions.

[1] T. Baikie, Y. Fang, J. M. Kadro, M. Schreyer, F. Wei, S. G. Mhaistarkar, M. Graetzel, and T. J. White, Synthesis and crystal chemistry of the hybrid perovskite CH$_3$NH$_3$PbI$_3$ for solid-state sensitised solar cell applications, Journal of Materials Chemistry A 1, 5628 (2013).
[2] Y. Shao, Z. Xiao, C. Bi, Y. Yuan, and J. Huang, Origin and elimination of photocurrent hysteresis by fullerene passivation in CH$_3$NH$_3$PbI$_3$ planar heterojunction solar cells, Nature communications 5, 1 (2014).
[3] V. D’innocenzo, G. Grancini, M. J. Alcocer, A. R. S. Kandada, S. D. Stranks, M. M. Lee, G. Lanzani, H. J. Snaith, and A. Petrozza, Excitons versus free charges in organo-lead tri-halide perovskites, Nature communications 5, 1 (2014).
[4] W. S. Yang, B.-W. Park, E. H. Jung, N. J. Jeon, Y. C. Kim, D. U. Lee, S. S. Shin, J. Seo, E. K. Kim, J. H. Noh, et al., Iodide management in formamidinium-lead-halide–based perovskite layers for efficient solar cells, Science 356, 1376 (2017).
[5] J. Seo, J. H. Noh, and S. I. Seok, Rational strategies for efficient perovskite solar cells, Accounts of chemical research 49, 562 (2016).
[6] W. A. Dunlap-Shohl, Y. Zhou, N. P. Padture, and D. B. Mitzi, Synthetic approaches for halide perovskite thin films, Chemical reviews 119, 3198 (2018).
[7] X. Meng, X. Cui, M. Rager, S. Zhang, Z. Wang, J. Yu, Y. W. Harn, Z. Kang, B. K. Wagner, Y. Liu, et al., Cascade charge transfer enabled by incorporating edge-enriched graphene nanoribbons for mesostructured perovskite solar cells with enhanced performance, Nano Energy 52, 123 (2018).
[8] H. Dong, J. Xi, L. Zuo, J. Li, Y. Yang, D. Wang, Y. Yu, L. Ma, C. Ran, W. Gao, et al., Conjugated molecules “bridge”: Functional ligand toward highly efficient and long-term stable perovskite solar cell, Advanced Functional Materials 29, 1808119 (2019).
[9] N. Arora, M. I. Dar, A. Hinderhofer, N. Pellet, F. Schreiber, S. M. Zakeeruddin, and M. Grätzel, Perovskite solar cells with cusc hole extraction layers yield stabilized efficiencies greater than 20%, Science 358, 768 (2017).
[38] M. Pazoki, T. J. Jacobsson, A. Hagfeldt, G. Boschloo, and T. Edvinsson, Effect of metal cation replacement on the electronic structure of metalorganic halide perovskites: Replacement of lead with alkaline-earth metals, Physical Review B 93, 144105 (2016).

[39] M. Shirayama, H. Kadowaki, T. Miyadera, T. Sugita, M. Tamakoshi, M. Kato, T. Fujiseki, D. Murata, S. Hará, T. N. Murakami, et al., Optical transitions in hybrid perovskite solar cells: ellipsometry, density functional theory, and quantum efficiency analyses for CH$_3$NH$_3$PbI$_3$, Physical Review Applied 5, 014012 (2016).

[40] S. Nagane, D. Ghosh, R. L. Hoye, B. Zhao, S. Ahmad, A. B. Walker, M. S. Islam, S. Ogale, and A. Sadhanala, Lead-free perovskite semiconductors based on germanium–tin solid solutions: structural and optoelectronic properties, The Journal of Physical Chemistry C 122, 5940 (2018).

[41] F. Brivio, K. T. Butler, A. Walsh, and M. Van Schilfgaarde, Relativistic quasiparticle self-consistent electronic structure of hybrid halide perovskite photovoltaic absorbers, Physical Review B 89, 155204 (2014).

[42] F. Tran and P. Blaha, Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential, Physical review letters 102, 226401 (2009).

[43] H. Dixit, N. Tandon, S. Cottenier, R. Saniz, D. Lamoen, B. Partoens, V. Van Speybroeck, and M. Waroquier, Electronic structure and band gap of zinc spinel oxides beyond lda: ZnAl$_2$O$_4$, ZnGa$_2$O$_4$ and ZnIn$_2$O$_4$, New Journal of Physics 13, 063002 (2011).

[44] B. Traoré, G. Bouder, W. Lafargue-Dit-Hauret, X. Rocquefelte, C. Katan, F. Tran, and M. Kepenekian, Efficient and accurate calculation of band gaps of halide perovskites with the tran-blaha modified becke-johnson potential, Physical Review B 99, 035139 (2019).

[45] F. D. Murnaghan, Finite deformations of an elastic solid, American Journal of Mathematics 59, 235 (1937).

[46] F. Hao, C. C. Stoumpos, R. P. Chang, and M. G. Kanatzidis, Anomalous band gap behavior in mixed Sn and Pb perovskites enables broadening of absorption spectrum in solar cells, Journal of the American Chemical Society 136, 8094 (2014).