Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

First principle study on hybrid organic-inorganic perovskite ASnBr₃ (A = Formamidinium, Dimethylammonium and Azetidinium)

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ARTICLE INFO

Keywords: Hybrid perovskites Density functional theory Photovoltaics Electronic structure GW approximation

ABSTRACT

The Organic-Inorganic halide perovskites of ABX₃ type (A: Organic cation, B: Metal cation, X: Halide anion) have exceptional electronic properties which attract broad interest. The widely studied Methylammonium Lead Iodide (MAPbI₃) is toxic and less stable. Hence there is a need to find potential alternative materials. We report in this study, the density functional theory calculations for the tin-based hybrid perovskite ASnBr₃ (where A is an organic molecule: Formamidinium, Dimethylammonium or Azetidinium). We considered 106 different combinations of the constituent element/molecules and shortlisted three potential structures based on the factors like material abundance, bandgap, toxicity and stability. The structures were systematically analysed for their structural and electronic properties based on Density Functional Theory (DFT) calculations using Generalized Gradient Approximation (GGA) functional and GW approximations. Wide tunable bandgap with the range of 2.09 to 4.9 eV and corresponding changes in the optical absorption properties obtained by substituting different organic cations. The tin-based organic-inorganic halide perovskite may find application in tandem solar cells, which may enhance the efficiency of solar energy conversion.

1. Introduction

The hybrid organic-inorganic perovskites are of great interest for photovoltaic applications. The ABX₃ perovskite constitutes of the monovalent ion 'A' (molecular organic cation such as Methylammonium - MA, Formamidinium - FA, Dimethylammonium -DiMA, Azetidinium - AZ), 'B' divalent ion (inorganic metal cation such as Lead, Tin), and 'X' - the halides. They provide exotic electronic properties such as long carrier lifetime, carrier mobility, and tunable optical bandgap. Besides, the same absorber material provides majority and minority charge carriers (Brenner et al., 2016). The mechanically stacked four-terminal perovskite-based tandem solar cell with FACs_{0.8}Pb_{0.2}(I_{0.7}Br_{0.3})₃ and (FASnI₃)_{0.6}(MAPbI₃)_{0.4} was reported (Zhao et al., 2018) to have the highest photovoltaic conversion efficiency of 23%. The high efficiency, together with the economic, low-temperature fabrication from liquid phase enables large scale production of these perovskite-based solar cells.

The perovskite solar cell faces significant problems such as instability and toxicity (Gidlow, 2004) due to the use of Lead, as in the case of widely studied Methylammonium Lead Iodide (MAPbI₃). For overcoming these disadvantages, constituent elements other than Lead are preferred. The replacement of lead with tin overcomes the toxicity. The instability is proposed to be decreased by substituting bromine instead of iodine, which has more electronegativity and forms stronger bonds with the metal atoms (Lindblad et al., 2015). The organic cation substitution and its effects on the properties are yet to be known. For the reasons mentioned above, the initial broad chemical search space of 106 different combinations of the perovskite structures was taken, and material abundance is calculated. The structural optimization is done for the short-listed materials based on material abundance and stability. The final contenders satisfying all the sorting filters are ASnBr₃ (A = Formamidinium, Dimethylammonium, Azetidinium, herewith FA, DiMA, AZ respectively).

The computation of the structural parameters of the $ASnBr_3$ is crucial as it significantly affects the properties. $ASnBr_3$ inorganic–organic halide-based perovskite systems form cubic, tetragonal, and orthorhombic structures. The $SnBr_6$ octahedra are formed by the Sn atom coordinating with six Br atoms. There is phase transformation with the function of temperature from orthorhombic to tetragonal and further to cubic structure (Feng and Xiao, 2014). As the temperature increases, the organic cation flips, rotates and undergoes very dynamic activity (Taylor et al., 2018). Experimental structural determination of the position of the organic cation is not feasible due to the dynamic oscillation. This dynamic oscillation results in material

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https://doi.org/10.1016/j.solener.2020.07.044

Received 24 September 2019; Received in revised form 1 June 2020; Accepted 13 July 2020 0038-092X/ © 2020 Published by Elsevier Ltd on behalf of International Solar Energy Society.





instability and variation in electronic properties during phase transition. Therefore, to find the structural parameters more accurately, DFT based simulation is performed.

2. Methodology

2.1. Selection of materials

The initial list of ABX₃ combinations was made with 18 molecular cations, nine divalent metals and three halides occupying the A, B and X sites, respectively (see Tables A1 and A2). These combinations were screened by Markus et al. based on Goldschmidt Tolerance factor (TF), and Octahedral factor (μ) constitutes of 106 permutations (Becker et al., 2017). The ABX₃ structure can be formed, only if it satisfies the TF ranging within 0.9–1.12, and μ greater than 0.414. The formula for the TF, its derivative with respect to the radius of halide anion and the octahedral factor are given as follows.

$$TF = \frac{r_A + r_X}{\sqrt{2(r_B + r_X)}}$$
(1)

$$\frac{d(TF)}{dr_X} = \frac{r_B - r_A}{\sqrt{2(r_B + r_X)^2}}$$
(2)

$$\mu = \frac{r_{\rm B}}{r_{\rm X}} \tag{3}$$

TF is the ratio of various ionic radii, and the computed value gives a dimensionless number. It is an empirical formulation to check whether a structure can form with perovskite crystal structure or not. The TF is directly proportional to the radius of the A-site molecular cation and indirectly proportional to the B site metallic cation as shown in Eq. (1). The change in the TF with the change in the X site halogen is intricate because it appears on both the denominator and numerator. The differentiation of the TF with respect to the ionic radii of the halide atom gives us a clear trend by which the crystal structure is affected. When the ionic radii of B site are lower than that of A site, the substitution of a bigger halogen ion will decrease the TF. The trend reverses when the radius of B site is greater than that of the A site. The optimum range of TF for perovskite structures is within 0.9–1.13. When the TF crosses this range, the octahedra become distorted, and the phase changes from perovskite crystal structure to low dimensional face sharing octahedra.

The octahedral factor (μ) is the ratio of the ionic radii of the B-site and X-site elements, evaluates whether the octahedral hole of the X-site anion sub-lattice can accommodate the B-site cation. When μ is close to 0.414 (or $r_B = 0.414 r_X$), the six tightly packed rigid spheres of X-site atom form an octahedral hole, where B-site atom can occupy. According to the Pauling's first rule, when $\mu < 0.414$, the B-site cations and the six X-site anions will not be in proper contact, leading to instability due to lower coordination number. For μ slightly higher than 0.414, it forms a stable octahedral geometry due to all the six X-site anions in contact with B-site cation. When μ is even higher than 0.592, it allows seven X-site anions to be in contact with B-site cation, which increases the coordination number and hence changes the crystal structure.

The next stage of screening of the combinations is done based on the material abundance. The greater available raw materials reduce the cost of synthesis of the solar cells. This trend is in contrary to the silicon-based solar cells, where the silicon is abundant, but high-temperature processing causes high cost. For the perovskite solar cells due to the solution based low-temperature processing, the cost of the solar cell depends mostly on the initial precursors. The abundance of each element on the earth crust measured in parts per million (ppm) is taken from Ref (Kenneth Barbalace, 2019). For each combination of the ABX₃, the most abundance is calculated by taking the total abundance of each element substituted for the B-site and the X-site contribution divided by three, due to the number of atoms in the chemical formula. (Refer Table



Fig. 1. Schematic representation of the screening process for selection of ABX₃ compounds for detailed DFT analysis.

A3) The organic molecule occupying the A-site is not considered because, it is mainly composed of carbon, nitrogen and hydrogen which are highly abundant. The combination of different elements which has the weighted abundance greater than or equal to 2.30 is taken into consideration. The lanthanide rare earth elements such as Thulium, Dysprosium, Ytterbium, and Samarium are not taken for further analysis. This elimination reduces the list of 106 hybrid perovskite combinations to 44 combinations, as shown in Fig. 1.

The 44 combinations are taken for the next screening process in which the bandgap range of each combination is estimated. The Schottky-Queisser limit for optimal range of bandgap for the solar cell is 1.1–1.6 eV (Ganose et al., 2017). The combination with bandgap far away from the optimal range is avoided as it will not absorb significant portion of the photon energy in solar spectrum, resulting in low efficiency The Alkali earth metals such as Ca, Sr have low electronegativity and work function compared to Sn, Pb which results in a wide bandgap material (Chatterjee and Pal, 2018). They form ionic bonds with the halide ions. The Calcium based perovskites due to Ca²⁺ ion (4 s² orbital), which does not hybridize with the halide ions resulting in flat conduction band leads to low mobility. The Ca and Sr based perovskites have high bandgap and low mobility and are not suitable for solar cell application (Jacobsson et al., 2015) Hence, they are not considered for further analysis which reduces the list to 10 compounds.

The Sn-Br based perovskite materials are considered for this study. The initial structural relaxation of the Sn-Br based perovskites with different molecular cation is done. The Hydrazinium (HY) and HydroxylAmmonium (HA) substitution structures displayed significant fluctuation in the total energy due to the smaller organic cation and the oscillatory movement outside the BX3 cage and H-Br molecule formations. So, they were unstable and are not considered further. The final three crystal structures for the DFT calculation considered are ASnBr₃ with the A-site substituted with Formamidinium (FA), Dimethylammonium (DiMA), Azetidinium (AZ).

2.2. Structural optimization calculation

The structural optimization is carried out for FASnBr₃, DiMASnBr₃, AZSnBr₃ using ABINIT code (Gonze et al., 2009) in order to find the ground state structure. The preprocessing and post-processing of the crystal structures are done using VESTA (Momma and Izumi, 2011). The Broyden-Fletcher-Goldfarb-Shannon minimization (BFGS) algorithm was used to optimize the atomic position in the unit cell. It uses

the gradient of the energy and the Hellman-Feynman forces (Feynman, 1939) of the atoms and stress in the unit cell to optimize the ion position iteratively. The lattice energy is converged to a minimum value by tuning various parameters in an iterative manner. The minimum convergence value for the energy difference between the two successive iterations is taken as $10 \times e^{-3}$ eV per unit cell. The perovskite structures were considered in orthorhombic and triclinic structures.

2.3. Inputs for computation

The present calculation is done using the DFT with the plane-wave basis using Optimized Norm-Conserving Vanderbilt Pseudopotentials (Hamann, 2013) (ONCVPSP) for the atoms in ABINIT code. The chosen ONCVPSP has excellent computational efficiency and accuracy. They use two projectors, fully non-local treatment of the valence electrons used for the ground state energy calculations. The non-locality is applied using the Legendre polynomial. The exchange and correlation effects of the electrons are treated using Generalized Gradient Approximation (Perdew et al., 1996) (GGA) implemented by Perdew, Burke and Ernzerhof (PBE). The GGA takes into account the gradient of the electron density for the calculation of electronic properties. The basis included for treating valence electrons are as follow: Sn with 4d, 5s, 5p states, Br with 4s, 4p states, C with 2s, 2p states, N with 2s, 2p states and H with 1s state. The lower-lying electrons below the mentioned orbital energy levels are treated as core electrons. The potentials and charge density were represented by spherical harmonics up to 1 = 6. The total energy convergence for the FASnBr₃ was tested concerning the energy cutoff, and it was found to stabilize after the cut-off value of 1088 eV. Hence this value is fixed for all the studied systems. Similarly, the sampling of the irreducible Brillouin zone is done with converged value of 8 \times 8 \times 8 kpt.

The GW calculation gives more accurate description of the excited states using the many body perturbation theory (Abrikosov et al., 2012; Fetter and Walecka, 2012) comprising the concept of quasi-particles and Green's functions formalism (Onida et al., 2002). The one-shot GW calculation is performed by utilizing the KS eigenvalues and Eigen functions obtained from the DFT-GGA as the initialization step. The next step is followed by the analysis of independent-particle susceptibility χ^0 and the matrix inversion is used to find the inverse dielectric matrix ε^{-1} for the calculation of the screened interaction. The screening calculation is done with the plasma-pole approximation. The screening calculation output is used for the generation of the exchange part of the self-energy operator. In the final step, the self-energy Σ is calculated and is used to find the GW quasiparticle energies. The one-shot GW approximation is done sampling the Brillouin zone with 220 eV energy cutoff and 60 numbers of bands. The GW correction for the DFT energy level for the arbitrary k-point is considered only at Gamma point for bandgap calculation.

3. Results and discussion

3.1. Geometric structure

The crystal structure for FASnBr₃ (shown in Fig. 2) is optimized as described above and the structural parameters are tabulated in Table 1. The FASnBr₃ structure due to the simultaneous effects of the loosely hinged Sn-Br-Sn bond and the dynamic effects of the A-site molecular cation creates a rich landscape of different phases with crystal structures ranging from triclinic, monoclinic, orthorhombic, and tetragonal to cubic. Also, these structures transform as a function of the temperature. The orthorhombic perovskite structure is the low-temperature phase. For the Sn-Br based perovskite system, the orthorhombic phase changes to the tetragonal phase, with the phase transition temperature of 12 °C (Scaife et al., 1974). In the low-temperature phases (triclinic, monoclinic, orthorhombic), when the molecular cations are positioned with their C-N bonds perpendicular to the c-axis of the unit cell, they fit

inside the Sn-Br cage, making the structure energetically more stable. However, as the temperature increases, the kinetic energy of the molecular cation overcomes the hydrogen bond and undergoes dynamic reorientation. According to experimental study there is a 90° flipping in the picosecond time range (Taylor et al., 2018) resulting in tetragonal and cubic phase. The hydrogen bond corresponds to the two H on either side of the NH₂ group, symmetric to the central CH group of the Fomamidinium molecular cation. In the orthorhombic FASnBr₃, Br forms four hydrogen bonds of length less than 2.8 Å.

When FA (size of 2.77 Å) is substituted with DiMA (2.96 Å) and AZ (2.84 Å) in the A-site, the lattice parameters and hence the volume expand to accommodate these bigger organic molecular cations. Also, there is a distortion or rotation of the BX_6 octahedra which can be observed as the deviation in the B-X-B bond angles (Meloni et al., 2016; Stoumpos and Kanatzidis, 2015) from the standard 180°. Deviation in these bond angles from 180° are listed in Table 2, and it is found that AZ undergoes maximum distortion of 163° along the equatorial plane. The combined effect of all the changes in the bond length and angles with the hydrogen bond dictates the decreasing stability and the increasing bandgap of FA, DiMA and AZ compounds. When more hydrogen atoms from the A-site cation bond with X-atom, the stability increases (Geng et al., 2014). The long-range interaction of the molecular cation also determines the crystal structure. The calculated lattice parameters of the FA structure is overestimated when compared with the experimental value. This overestimation is due to the neglect of van der Waals interaction between the organic molecule, Formamidinium, and the Sn-Br atom. This long-range interaction affects the structure with relatively shorter bonds between the atoms, which is reflected in the experimental lattice parameters (Kumawat et al., 2016).

For the case of FA, the Br atom is at equidistance from the Sn atoms along the c-axis. On the other hand in DiMA and AZ, the Br atoms are displaced from the middle of the axis, resulting in two different Sn-Br bond lengths (see Table 2). The displacement of the Sn atoms is due to the Sn²⁺ lone pair dynamic stereo-chemical activity (Fabini et al., 2016). The FA, DiMA and AZ show the maximum difference in the Sn-Br bond length (Δ) of 0.2 Å, 1.23 Å, and 1.21 Å, respectively, in the equatorial direction.

The initial position of the molecular cation affects the result of structural optimization. Hence, we constructed different models with the molecular cations at different positions such as perpendicular to the c-axis, diagonal to the B-X cage in the c-a plane, diagonal to the B-X cube in the c-a and c-b plane at 45° angle. The molecular cations of the three structures are initially set perpendicular to the c-axis for the structural relaxation. As they undergo structural optimization, they reorient themselves to take up minimum energy positions, where the force and stress are also minimized. The FA molecular cation fits inside the B-X cage perpendicular to the c-axis. The orientation of the DiMA and AZ molecular cations inside the B-X cage is not perpendicular to the c-axis. The reorientation is due to a more energetically stable position counteracting the hydrostatic pressure from the B-X cage due to the lattice expansion. The DiMA cation is slightly rotated parallel to the aaxis, and the AZ cation is rotated both about a-axis and b-axis. The DiMA cation due to the CH₃ has steric hindrance to the rotation. The AZ cation has a hinged rotation with two hydrogen atoms as the center, from the NH2 group forming a long-range hydrogen bond, with the nearby bromine anion in the range less than 2.8 Å.

3.2. Electronic properties

The three structures substituted with FA, DiMA and AZ, have the VBM and CBM occurring at the same momentum vector point (R kpt), resulting in direct bandgap nature. The corresponding band gap values are given in Table 1. The GW based calculated bandgap for the FASnBr₃ is 2.09 eV, which is close to the experimental bandgap value of 2.4 eV (Pisanu et al., 2018). Similarly, the GW approximation based calculated bandgap for the DiMASnBr₃ and AZSnBr₃ is 2.6, and 4.9 eV,



Fig. 2. Crystal structures of (a) FASnBr₃, (b) DiMASnBr₃ and (c) AZSnBr₃.

Table 1	
Structural relaxation calculated Lattice parameter and band gap.	

Compound	Volume (Å ³)	Lattice parameters (Å)						Calc Band gap (eV)			Expt Band Gap (eV)
		a	b	с	α	β	γ	SR	SOC	GW	
FASnBr ₃ DiMASnBr ₃ AZSnBr ₃	221.95 (219.74ª) 259.29 267.11	6.156 (6.034ª) 6.363 6.478	5.891 6.593 6.590	6.121 6.188 6.271	90.00 ⁰ 92.40 ⁰ 88.82 ⁰	90.00 ⁰ 89.01 ⁰ 92.51 ⁰	90.00 ⁰ 88.760 92.71 ⁰	0.86 2.18 2.28	0.63 2.03 2.16	2.09 2.60 4.90	(2.40 ^ª) _ _

^a Experimental values, (Pisanu et al., 2018).

Table 2

Calculated bond length, angle and the hydrogen bond number.

Compound	Sn-Br bond le	ength (Å	Å)	Sn-Br-Sn bond angle (deg)			
	Equatorial	Δ	Apical	Equatorial	Apical		
FASnBr ₃ DiMASnBr ₃ AZSnBr ₃	2.882–3.079 2.695–3.925 2.688–3.902	0.2 1.2,3 1.2.1	3.068 2.682–3.543 2.706–3.568	177–180 169–172 163–178	171 167 176		

respectively. In order to check the effect of spin–orbit coupling (SOC) on the electronic structure, we have performed a complete self-consistent calculation by including (SOC). Since the tin-bromide systems are typically lighter than the lead-iodine system, the effect of SOC on the former is also smaller than the later, with the variation of 0.2 eV in the band-gap values. A closer look into the electronic structure elucidates lowering of conduction band minimum and a slight broadening of these bands. The site and orbital-projected DOS reveal that these bands are resulting due to the Sn-p orbitals. So the influence of SOC is more significant on Sn than other constituents of the compounds.

The SOC effects decrease the band gap and increases the curvature of the bands resulting in the lighter effective masses for the holes and the electrons. The lowering of the effective mass is seen for the FA and DiMA substituted structures. For the AZ substituted structure, there is a slight increase in the average electron and hole effective mass with SOC effects changing the Sn-Br bond length. The average effective mass for the FAPbI₃ system is found to be 0.30 and 0.39 for hole and electron, respectively.

The electronic structure of the FA structure exhibits total bands of 25 within the energy range of -8 to 8 eV. The bands are grouped into the energy levels, in the valence band region (i) -8 to -6 eV consisting of 3 bands with peaks of Sn 4 s at -7.04 eV, CH, NH group p-orbital contribution at -6.53 eV. For (ii) -4.5 to -4 eV have 3 bands. For (iii) -3 to 0 eV contains 7 bands with peaks of Sn 4p, 5 s at -3.84, -1.24 eV, respectively. The Br 4p orbital contributes to the peaks at -3.39 and -1.79 eV, N 2p orbital peaks at -3.17 eV. In the conduction band region, for (iv) 0.9 to 4 eV presents two bands with Sn 5p state peaks at 1.89 and 3.71 eV and (v) 4 to 8 eV, there are ten bands with highly disperse and relatively low electron density antibonding contribution from all the sites.

The electronic structure of DiMA has total bands of 26 within the energy range of -8 to 8 eV. The valence bands are grouped into the energy levels, (i) -7 to -6.2 eV with 3 bands, (ii) -4.9 to -4.4 eV contains 3 bands, (iii) -3.6 to 0 eV with 10 bands. The nitrogen amine group 2p orbital contribution has a small peak at -0.66 eV, closer to the VBM. The Br p-orbital peak is shifted to 1.56 eV, compared to the Br contribution in FA structure.

The electronic structure of AZ contains total bands of 28 within the energy range of -8 to 8 eV. The valence bands are grouped into the energy levels, (i) -7 to -5.7 eV, consisting of 3 bands, with deep stabilized bands of Sn 4 s at 6.64 eV, C-N at -6.51 eV (ii) -5.3 to -4.3 eV, has 2 bands, (iii) -3.5 to 0 eV has 10 bands, with the Br porbital peak is shifted to 2.21 eV, compared to the Br contribution in FA structure. The distributed band of C is due to the chain of three carbon atoms at -3.92 eV and -2.14 eV.

The FA bands are more disperse and the electrons are more delocalized when compared to the DiMA and AZ. This difference is because

Table	3
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Effective mass of the charge carriers obtained using SR and SOC approximations (shown in brackets).

	Effective hole ma	ass, m _h *			Effective electron mass, me*				
Structure	Γ-R	R-Y	Y-S	S -Γ	Γ-R	R-Y	Y-S	S -Γ	
FA DiMA AZ	0.25 (0.23) 0.68 (0.65) 0.81 (0.78)	0.32 (0.28) 0.62 (0.58) 0.70 (0.73)	0.43 (0.41) 1.06 (0.95) 0.99 (1.22)	0.30 (0.29) 1.03 (0.97) 1.11 (1.04)	0.43 (0.36) 0.82 (0.75) 0.83 (0.90)	0.40 (0.37) 0.85 (0.72) 0.88 (0.84)	0.61 (0.51) 0.94 (0.77) 0.73 (0.66)	0.35 (0.33) 0.51 (0.54) 0.68 (0.75)	



Fig. 3. SR-DFT and with SOC calculated (a),(c),(e) electronic band structure and respective (b),(e),(f) PDOS of the three compounds (a),(b) $FASnBr_3$, (c),(d) $DiMASnBr_3$ and (e),(f) $AZSnBr_3$.



Fig. 4. ε_2 optical plots of (a) FA, (b) DiMA, (c) AZ, (d) averaged ε_2 in all three directions *a,b,c*.

of the minor deviation in the Br atom offset from the center of Sn-Br-Sn, lower bond length and more orbital overlap between the bromine and tin. While for DiMA and AZ, due to lattice stretching, the reduced orbital overlap between the Sn-Br severely localizes the electron and results in low dispersion of the bands. The charge carrier effective mass and mobility depend upon the dispersion of the VBM and CBM. FA due to its highly dispersed bands shows a lower effective mass of holes and electrons compared to the other two structures, as seen from the effective mass Table 3. The effective mass is increasing as we go along the FA, DiMA and AZ in the bandgap region k-path of Γ –R and R-Y. The bandgap of MAPbI₃ (1.6 eV) is closer to the optimum bandgap 1.4 eV for maximum solar energy absorption, than the tin-based perovskites FASnBr₃, DiMASnBr₃ and AZSnBr₃. Owing to the heavier Pb, the effect of SOC in the lead-Iodine system is in the range of 1 eV compared to the SR-DFT calculation (Mosconi et al., 2016). However, the SOC does not change the band-gap significantly in the case of tin-bromide systems because the constituents are lighter compared to the lead-bromide systems (Im et al., 2015; Katan et al., 2015). The difference in the bandgap value due to the SOC effect is approximately in the range of 0.2 eV.

The MAPbI₃ system has average effective mass of 0.33 and 0.23 for hole and electron, respectivelyMosconi et al. (2015) whereas the FAPbI₃ system has average effective mass for 0.30 and 0.39 for hole and electron, respectively. The average effective mass of holes for the tin is relatively lower than that of the lead which shows enhancement in the hole conductivity for FA substituted tin based perovskites.

The substitution of a bigger sized molecular cation such as DiMA and AZ, when compared to FA, results in lattice stretching and B-X bond distortion. The calculated tolerance factor (TF) for the structures FA, DiMA and AZ, are 1.075, 1.091, and 1.119, respectively. This result in the red-shift of the lowest-lying conduction band and less disperse

contribution of the tin 5p states due to the opening of the bandgap. The peaks of the C and N p-orbitals shift due to the varying bond formation energy due to the difference in their molecular cation structure and composition.

For the AZ structure, the less orbital overlap with the relatively higher Sn-Br-Sn bond angle and very high Br atom offset is the cause of high bandgap at the range of 4.9 eV calculated with GW. In general, the VBM is made of Sn 5s, Br 4p states and the CBM is made of Sn 5p states. The concentration of the charge carriers in the VBM and CBM is due to the funnel effect. The funnel effect increases the efficiency of the photovoltaic device due to the lower charge carrier entropy (Osterloh, 2014). From the TDOS shown in Fig. 3, we can observe the funnel effects at the VBM region produced by the shallow density of states. This funnel effect is more pronounced in order for FA > AZ > DiMA. It gives various advantages such as small carrier effective masses, high open-circuit voltage (V_{oc}) and less entropy loss (Grånäs et al., 2016). The significant contribution to the funnel effect is due to the Br 4p states. The VB region with the funnel holds maximum concentration of the charge carriers to be effective in absorbing the incident photons.

3.3. Optical properties

The optical response of ASnBr₃ (A = FA, DiMA, AZ) compounds using GGA approximation for the applied field of the electromagnetic radiation is shown in Fig. 4. The complex dielectric function $\varepsilon(\omega,q)$ gives the light-matter interaction. It is used to calculate the optical properties. The dielectric function dependent on frequency (ω) of the photon corresponds to the energy transfer, and wave vector (q) corresponds to the electron-photon momentum transfer. The wave vector momentum is negligible compared to the electron momentum in the



Fig. 5. (a) Reflectivity, (b) absorption coefficient and (c) refractive index of the three compounds.

optical range. The dielectric function consists of real and imaginary parts as shown by the following relation.

 $\varepsilon(\omega) = \varepsilon_1(\omega) + i. \varepsilon_2(\omega)$ (4)

The dielectric loss function plot for a, b, and c axis of the unit cell is

shown in Fig. 4. The FA structure shows optical anisotropy due to the shift in the peaks of the b-axis compared to those along with a and caxis. This optical anisotropy is due to the molecular cation orientation with its shorter lattice length (5.89 Å) along the b-axis. The Sn-Br planes formed by the c-a axis, where the excited electron hops relatively easily through the shorter Sn-Br bonds parallel to the b-axis than through the other two axes. This same trend can be seen for the dominant peak of the AZ, where the c-axis has the shortest lattice length (6.27 Å). In the DiMA structure, the b-axis has minor peaks due to the most extended lattice length (6.59 Å). The energy levels of all the significant peaks correspond to the transition between the Br 4p to Sn 5p bands. Fig. 4d shows dielectric component ε_2 calculated from $(\epsilon_a$ + ϵ_b + $\epsilon_c)/3$ for all the three structures. The rapid flipping about 90° and reorientation of the molecular cation in the diagonal direction to the unit vectors averages the structure to cubic structure. The average response shows that FA has wide range of optical absorption compared to the DiMA and AZ.

The comparison of the computational result with the experimental result can be made by analyzing the following optical properties such as reflectivity, absorption coefficient and refractive index. The reflectivity (R) is calculated using the Fresnel equation from the complex dielectric constant. The absorption coefficient $I(\omega)$, refractive index n is calculated by the below equations and shown in Fig. 5.

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2$$
(4)

$$I(\omega) = 2\omega \left[\frac{abs(\varepsilon(\omega)) - \varepsilon_1(\omega)}{2} \right]^{1/2}$$
(5)

$$n = \left[\frac{abs(\varepsilon(\omega)) + \varepsilon_{l}(\omega)}{2}\right]^{1/2}$$
(6)

The reflectivity, absorption coefficient and refractive index (Fig. 5) show a prominent peak in the range of 2–4 eV for FA, and in the range of 5–6 eV for DiMA and AZ. The reflectivity of the FA goes to maximum value at 3.5 eV. The absorption coefficient of the DiMA and AZ is greater than FA in the range of 5–7 eV. The FA shows broad absorption range than DiMA and AZ.

4. Conclusion

In summary, we have screened a vast combination of different elements in the perovskite structure and shortlisted 3 out of 106 compounds based on the elemental abundance, bandgap and structural stability. The shortlisted compounds are taken for the ab-inito study, with the replacement of Pb, by non-toxic Sn, in addition to various organic cation substitution like Formamidinium, Dimethylammonium and Azetidinium. The results for the equilibrium lattice shows the interplay of the molecular cation size on the electronic band structure, PDOS and optical properties are shown for the respective equilibrium lattices. The substitution of organic cations provides broad bandgap tuning capability from 2.09 to 4.9 eV. The results also show the trend, as the increase in the tolerance factor corresponds to the increase in the bandgap and the effective mass of the charge carriers. The computationally demanding GW calculation closely predicts the experimental bandgap. The PDOS result shows that the funnel effects from the shallow DOS, are mainly contributed by the Br atom. The results provide insights and stimulate further research in the progress of the next generation environmental-friendly materials for solar cells application.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.solener.2020.07.044.

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