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Rb as an alternative cation for templating inorganic lead-free perovskites for solution processed photovoltaics

P.C. Harikesh^{†§}, Hemant Kumar Mulmudi^{†*}, Biplab Ghosh^{†§}, Teck Wee Goh[#], Yin Ting Teng[§], Krishnamoorthy Thirumal[§], Mark Lockrey^{||}, Klaus Weber[‡], Teck Ming Koh[§], Shuzhou Li[⊥], Subodh Mhaisalkar^{§⊥}, Nripan Mathews^{§⊥*}

[†]Interdisciplinary Graduate School, Energy Research Institute at NTU, 639798 Singapore

[§]Energy Research Institute @NTU (ERI@N), Research Techno Plaza, X-Frontier Block, Level 5, 50 Nanyang Drive, 637553 Singapore

[‡]Centre for Sustainable Energy Systems, Research School of Engineering, The Australian National University, Canberra, ACT 2601, Australia.

[#]Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University (NTU), 21 Nanyang Link, 637371 Singapore.

^{||} Australian National Fabrication Facility, Department of Electronic Materials Engineering, Research School of Physics & Engineering, The Australian National University, Canberra, ACT 2601, Australia

[⊥]School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798 Singapore

ABSTRACT: Even though perovskite solar cells have reached 22% efficiency within a very short span, the presence of lead is a major bottleneck to its commercial application. Tin and Germanium based perovskites failed to be viable replacements due to the instability of their +2 oxidation states. Antimony could be a possible replacement, forming perovskites with structure $A_3M_2X_9$. However, solution processing of Cs, organic ammonium based Sb perovskites result in the formation of the dimer phase with poor charge transport properties. Here we demonstrate that Rb can template the formation of the desired layered phase irrespective of processing methodologies, enabling the demonstration of efficient lead-free perovskite solar cells.

Perovskite solar cells have evolved rapidly to attain more than 22 % efficiency¹ within a short span of four years. The reasons for such an unprecedented growth are manifold and include the defect tolerant properties of the material² leading to long carrier diffusion lengths³, a tunable band gap and solution processability, driving approaches to improve the performance of solar cells by changing the composition⁴⁻⁶ crystallization⁷⁻⁹ and device architecture¹⁰⁻¹². Despite these advantages, the presence of lead is a major bottleneck to its commercialization¹³⁻¹⁵. The major contenders for lead replacement are Tin¹⁶⁻²⁰ and Germanium^{21, 22} which belong to the same group as lead and hence are expected to show similar material properties. However Sn and Ge are lighter compared to lead and the inert pair effect, deemed to be the reason for the stability of Pb^{2+} ion²³, is weaker in them. Thus the +2 states of these elements are unstable and are easily oxidized to +4 states. The degradation into +4 ions and release of HI to the environment could also be dangerous¹⁵. On the other hand, recently reported copper based perovskites were limited by low voltages and currents²⁴. According to first-principle calculations, the reason for the phenomenal

performance of the lead based perovskites is linked to the outermost s electrons in the metal cation^{2, 25, 26}. These s electrons can hybridize with the halogen (anion) p orbitals to give anti-bonding character to the valence band maximum as well as reducing the ionization energy. Pb being heavy causes significant spin orbit coupling which pushes the conduction band maximum downwards. Hence the defects with high formation energies form only near or inside the band and do not form deep level traps. Thus it is rational to look for elements with similar electronic configuration as Pb^{2+} with outer s electrons as its replacement. The immediate possibilities are Bi and Sb which are in the nearest group as lead in the periodic table and have the ability to form +3 ions with similar electronic configuration as Pb^{2+} . This hypothesis is strengthened by recent reports on Bi based perovskites for solar cells²⁷⁻²⁹, double perovskites exhibiting long carrier lifetimes³⁰ and a report on $Cs_3Sb_2I_9$ ³¹ as photovoltaic material. Since Sb exists only in a stable +3 state, it constrains the ability to form a 3D corner sharing perovskite structure. Instead it forms $A_3Sb_2X_9$ compounds with a dimer structure (with fused bi-octahedron) or a layered structure

Figure 1. (a) Schematic showing the influence of A cation size on the structure of $A_3Sb_2I_9$. (b) The band structure and (c) the Density of states of $Rb_3Sb_2I_9$.

(with corner sharing octahedron). It is also evident from density functional theory (DFT) calculations that the layered structure is superior compared to the dimer form in terms of having a direct band gap³¹, higher electron and hole mobilities and better tolerance to defects because of higher dielectric constants². However, the dimer form of $A_3Sb_2I_9$ has a preference over the layered form when formed via a solution process³¹. Further, the process to form the layered derivative of $Cs_3Sb_2I_9$ involves high temperature annealing in SbI_3 vapour which is difficult to reproduce due to processing constraints. In addition, it is known from DFT calculations that the compound could potentially form deep defects. However, the lack of solution processability prevents facile tuning of the chemical potentials to passivate such defects limiting the Open circuit voltage (V_{oc}) below 0.2V and current density below 0.2mA/cm². Hence developing a solution processable alternative which forms $A_3Sb_2I_9$ in the layered phase will open up avenues to improve the performance of devices by enabling defect passivation.

In this work, we show that Rb can be used as an alternative cation to template the formation of inorganic layered Antimony perovskites formed via solution pro-

cessing. Solar cells based on $Rb_3Sb_2I_9$ exhibited promising photocurrent densities higher than 2mA/cm² (considering a maximum possible theoretical photocurrent density of ~10mA/cm² for its 2.24eV bandgap) and an open circuit voltage of 0.55V. In addition, XPS and Cathodoluminescence measurements provide deeper insights into the defect characteristics of the material, indicating the need for optimised fabrication methodologies to attain better performance.

Results:

Investigating the effect of cation on stability of layered structure

It is known that the dimer form of $Cs_3Sb_2I_9$ has a preference over its layered derivative if formed via a solution process³¹. This violates Pauling's rules on crystal structures³² because the layered structure has corner sharing octahedra and should be preferred over the dimer form with face sharing octahedra in order to maximise the distance between two adjacent Sb atoms. The exact reason for this contradiction is unknown and has not been studied systematically. Some authors attribute it to the processing conditions claiming that the dimer form is pre-

ferred in presence of a polar solvent^{34, 33}. Previous reports suggest a link between the size of the A cation and the structure formed in case of ABX₃ compounds^{6, 34-36}. Our preliminary experiments on replacing Cesium (1.88Å, in XII coordination) in A₃Sb₂I₉ with Methylammonium, Formamidinium and their mixtures resulted in dimer phases (Figure S1). However, a smaller Rb (1.72Å, in XII coordination) at the A cation site formed a structurally different phase indicating that the size of A cation could affect the structure of A₃Sb₂I₉. In order to understand the effect of A cation substitution on the A₃Sb₂I₉ structure, we

Table 1. Formation Energy comparison of Dimer and Layered forms of A₃Sb₂I₉ with Cs and Rb cations

Compound	Formation Energy (eV)	
	Dimer	Layered
Cs ₃ Sb ₂ I ₉	-12.80	-12.70
Rb ₃ Sb ₂ I ₉	-12.40	-12.65

resort to a DFT analysis to compare the formation energies of the dimer and layered forms of A₃Sb₂I₉ with A = Cs and Rb. The details of the DFT calculations are available in the methods section. The formation energy of dimer and layered form of Cs₃Sb₂I₉ differed by only 0.1eV (as shown in Table 1), consistent with the experimental observation that both forms can exist depending on synthesis conditions. In case of the bigger Cesium (1.88Å), the space for accommodating the cation in between the corner sharing octahedra is limited. However, a face sharing bi-octahedron creates enough space for a larger cation at the expense of a lower Sb-Sb distances as discussed in reports on similar structures^{37, 38}, thus making the dimer form preferable in case of Cs. However, the higher difference (0.25eV) in formation energy for the Rb based systems indicates an increased preference for the layered phase. This can be linked to the smaller ionic radius of Rb (1.72 Å) as shown schematically in Figure 1a. To study the viability of layered Rb₃Sb₂I₉ as an absorber for solar cells, the band structure of Rb₃Sb₂I₉ was calculated using the Perdew–Burke–Ernzerhof (PBE) functional. This showed a direct bandgap of ~1.98 eV at the Γ point (Figure 1b). However, the possibility of indirect transitions cannot be neglected completely (Figure S7b). The partial density of states (PDOS) plots depicted in Figure 1c revealed that the VBM is mainly derived from I *p* states with a small contribution from Sb lone-pair *s* states at the top of the valence band. On the other hand, the conduction band was found to be a mixture of I *p* and Sb *p* states. The nature of the density of states of the compound is very similar to methyl ammonium lead iodide. The material is also expected to have very high absorption coefficients due to the possible *p*-to-*p* transitions.

Crystal structure of Rb₃Sb₂I₉ and thermal stability

Rb₃Sb₂I₉ powder was synthesized as detailed in the methods section. The crystal structure was determined starting from Rb₃Bi₂I₉³⁹ by replacing Bismuth atoms with Antimony. The final structure has a *P1c1* space group with *a* = 14.60Å, *b* = 8.19 Å, *c* = 25.17 Å and *beta* = 125.05° (Table S1, Figure S2). Figure 1a shows the structure of Rb₃Sb₂I₉ and its comparison with the reported Cs₃Sb₂I₉ dimer⁴⁰. The

latter has fused (Sb₂I₉)³⁻ bi-octahedra clusters surrounded by Cs atoms while Rb₃Sb₂I₉ has distorted corner sharing octahedra. The fused bi-octahedra in Cs₃Sb₂I₉ provide enough space to accommodate the Cs atoms hence stabilising the dimer form.

Rb₃Sb₂I₉ was thermally stable up to 250 °C as inferred from the TGA and DSC data given in Figure S3. It exhibited two-step decomposition with the first step starting at around 250°C associated with around 60% weight loss (loss of SbI₃). Even though a stability up to 250°C is high enough for processing the material, there is a possibility that SbI₃ can sublime from hot spots in the film at even lower temperatures when in thin films³¹. Thus the temperature of processing was kept at 120°C for the thin film studies discussed later in the text. The DSC also showed no signs of phase change in between - 40°C to 200°C which is high enough range to operate a solar cell.

Thin film formation and characterization

In order to form the thin films, stoichiometric ratios of the precursors were dissolved in DMF and spin coated after filtering as discussed in detail in the methods section. The films were annealed at 120°C for 10 minutes for all the characterizations. XRD shows that the films formed were found to be single phase without traces of unreacted precursors as given in Figure 2b. However a detailed examination using XPS revealed that the I/Sb and the I/Rb ratios were lower than the expected ratios as tabulated in Table 2 pointing to iodine deficiencies in the

Table 2. Ratios of Sb and Rb in comparison with Iodine extracted from XPS

	I/Sb	I/Rb
Expected	4.5	3
Rb ₃ Sb ₂ I ₉ pristine	4.1	2.8
Rb ₃ Sb ₂ I ₉ - SbI ₃ treated	4.33	3.0

sample. Furthermore, the elemental scan of Sb 3d shown in Figure 2(c) reveals the presence of two doublets with Sb 3d^{5/2} binding energy positions at 531.0 eV and 531.8 eV separated by 0.8 ± 0.05eV. This suggests the existence of two different chemical states of antimony, the expected 3+ and possibly the oxidized 5+ oxidation state respectively⁴¹. Considering the fact that the films are phase pure from XRD, the stoichiometrically lower ratio of Iodine may be due to the presence of iodine vacancies at the sample surface. In light of previous theoretical calculations on layered Cs₃Sb₂I₉ with a similar structure³¹, these iodine vacancies are expected to create deep traps in the band gap. However, changing the chemical potentials of the reacting precursors by introducing excess of precursors is a possible strategy to passivate such vacancies by altering their formation energies^{16, 31, 42}. Thus a possible route would be to add an excess of SbI₃ to the initial mixture. However, due to the limited solubility of RbI and SbI₃ in DMF, any excess of SbI₃ tends to be precipitated and removed during the filtering process before spin coating, thus severely limiting the ability to tune the composition of the reaction mixture. To address this

Figure 2. (a) The procedure adopted to form $\text{Rb}_3\text{Sb}_2\text{I}_9$ films, (b) the comparison of XRD of untreated and SbI_3 treated films and (c) the XPS comparison of both films showing the $\text{Sb} 3d^{3/2}$ and $\text{Sb} 3d^{5/2}$ peaks (d) The absorption coefficient and cathodoluminescence (at accelerating voltage of 5KV and beam current of 0.2nA) of SbI_3 treated $\text{Rb}_3\text{Sb}_2\text{I}_9$ and (e) the variation of Cathodoluminescence with fixed accelerating voltage (5KV) and varying excitation power (in log scale). I_b is the beam current and I_{CL} is the CL intensity.

problem, we adopted a novel strategy to provide this excess of SbI_3 by dissolving it in toluene and dripping it while spin coating as depicted in Figure 2a. XPS measurements (Table 2 and Figure 2c) show that the films treated with excess of SbI_3 exhibited near ideal stoichiometry with a single +3 oxidation state of Sb with $\text{Sb} 3d^{5/2}$ binding energy position at 530.7 eV. Furthermore, XRD reveal that the untreated films were highly oriented along the (002), (004) and (006) planes which are parallel to the layers of corner sharing octahedra. Such a preferential orientation can hinder the charge transport across the films as the effective masses are higher in direction per-

pendicular to the layers as reported in similar materials³¹. However, the films which were spin coated using the modified procedure, did not exhibit such preferred orientation probably because of faster crystallization of the perovskite. In addition to all these advantages, the coverage of the perovskite films deposited using the SbI_3 treatment was better compared to the pristine films (Figure S5). The untreated films formed only islands of the perovskite on TiO_2 , exposing significant amount of TiO_2 . Increasing the annealing temperature and durations above 120°C and 10 minutes did not improve the film crystallinity (Figure S6). However, annealing for less than 10

minutes resulted in residual DMF in the sample evident from the higher amounts of C and O impurities (Table S2).

Optical and electronic characterization

The $\text{Rb}_3\text{Sb}_2\text{I}_9$ films were red in colour in contrast to the orange coloured films obtained in case of the $\text{Cs}_3\text{Sb}_2\text{I}_9$ dimer possibly arising from the direct nature of the band gap. Furthermore, the SbI_3 treated films were more reflective and smoother looking compared to the untreated films. To gain more insight into these observations, we carried out UV-Visible absorption spectroscopy. The absorption coefficient of the $\text{Rb}_3\text{Sb}_2\text{I}_9$, calculated from transmittance and total reflectance values⁴³, was found to be higher than $1 \times 10^5 \text{ cm}^{-1}$ at 2.5 eV which is comparable to the values for methyl ammonium lead iodide³ indicating that very thin layers of the material would suffice to provide adequate absorption (Figure 2d). Such high values are expected based on the p-to-p direct transitions evident from the calculations discussed previously. The Tauc plot fitting (Figure S7a) of $\text{Rb}_3\text{Sb}_2\text{I}_9$ assuming direct and indirect band gaps yielded a values of 2.24 eV and 2.1 eV respectively. In semiconductors, the absorption coefficient at energies just below the band edge decreases exponentially with decreasing energy, with the absorption tail defined as the Urbach tail. The slope of this exponential tail (called Urbach Energy) represents structural disorders, impurities, deep traps, phonon effects and excitons⁴⁴⁻⁴⁷. A higher Urbach energy represents pronounced effect of these phenomena. The extracted Urbach energies of $\text{Rb}_3\text{Sb}_2\text{I}_9$ were in the range 85-90 meV for the SbI_3 treated samples for 3 different annealing temperatures considered (Figure S8a). This value is very high compared to the conventional photovoltaic materials including Methyl ammonium lead iodide (which exhibits an Urbach Energy of around 15 meV only⁴⁸) indicating significant effect of the above mentioned phenomena. In addition, the Urbach energies of the pristine films were even higher (105 to 115 meV) compared to treated samples indicating that defects are more dominant in pristine films.

To further explore the optoelectronic properties, Cathodoluminescence spectroscopy was utilised. The CL intensity of the SbI_3 treated sample was found to be approximately twice as bright as the untreated sample (Figure S9) possibly due to a higher density of non-radiative recombination centres in the untreated sample. The spectrum can be deconvoluted to 3 different peaks centred at 1.98 eV, 1.63 eV and 1.41 eV. To further understand the origin of these peaks, the variation of the intensities of the peaks with excitation power was plotted (Figure 2e) and the saturation rate of the emissions found. From the power resolved measurements it was found that the 1.98 eV emission (close to the absorption edge) has a near linear dependence on excitation power ($I_{\text{CL}} \propto I_b^{0.82}$) indicating that it could be from band-to-band transition as reported in case of other perovskites⁴⁹. The slight shift of the emission from the band gap could be due to excitonic effects as observed in other layered materials^{50, 51}. The 1.41 eV and 1.63 eV peaks saturated faster with increasing excitation powers ($I_{\text{CL}} \propto I_b^{0.61}$ and $I_{\text{CL}} \propto I_b^{0.71}$ respectively) indicating that these peaks may be associated with

some recombination centre with a long relaxation time such as deep level defects, as observed in other materials⁵². The CL spectrum of the $\text{Cs}_3\text{Sb}_2\text{I}_9$ dimer (Figure S10) is very broad with the defect peaks dominating the Near Band Edge (NBE) emission.

Hall measurements suggested p type conductivity for $\text{Rb}_3\text{Sb}_2\text{I}_9$. However, the measurement gave variable values for the mobility and carrier densities at different magnetic fields (Table S4). This p type behaviour may be caused by defects close to the valence band. Figure S11 shows the valence band spectra and the work function of $\text{Rb}_3\text{Sb}_2\text{I}_9$ as obtained from UPS measurements. The schematic band diagram (inset of Figure 3b) is obtained using the energy of the Valence band and the band gap calculated from the Tauc plot. The ionisation potential of 5.66 eV obtained from Photoelectron Spectroscopy in Air (PESA) measurement (Figure S11) is relatively close to the value of 5.54 ± 0.04 eV obtained from UPS measurements.

Photovoltaic characterization

The optical and electronic characterization aided us to choose the right device configuration for the material: TiO_2 as electron transport layer, Poly-TPD as hole transport layer and Gold as counter electrode for fabricating the solar cells. The devices were fabricated using the thin films formed by SbI_3 treatment with the SEM cross section as depicted in Figure 3a. The thickness of TiO_2 was kept around 400 nm to ensure sufficient absorption of above bandgap energy photons. Several devices were fabricated and the statistical analysis is shown in Table S5 with the best device exhibiting a voltage of 0.55 V and a short circuit current density of 2.12 mA/cm² (Figure 3b). The untreated devices showed lower Voc and Current Density compared to the SbI_3 treated samples (Table S6). The external quantum efficiency (EQE) (Figure 3c) plot is in agreement with the absorbance spectrum with the onset of current from around 600 nm and the device exhibited a maximum of around 30 % EQE in its absorption range. The internal quantum efficiency (IQE) was calculated using the total reflectance and transmittance ($\text{IQE} = \text{EQE}/(1-R-T)$) of the device and exhibited values <32%. This shows that only <32% of the absorbed photons are converted to carriers and collected at electrodes. The device efficiencies were also severely limited by the open circuit voltages of <0.6 V considering the high band gap. This low Voc and the low IQE is possibly caused by recombination occurring at the defect levels suggested by the CL measurements. In order to get more insight into the recombination behaviour of the material, the variation of Voc with natural logarithm of light intensity was studied as shown in Figure 3d. In case of a bimolecular recombination requiring an electron and a hole, the slope of this plot must give a value of $k_b T/q$ ^{16, 53}. The slope obtained from our analysis yielded a value of 1.95 $k_b T/q$. This indicates that Shockley-Read-Hall like recombination through defect levels is dominant over bimolecular recombination. Furthermore, the variation of short circuit current with light intensity was also studied. Previous studies claim a power law dependence of Jsc with Intensity according to relation,

$$J_{sc} \propto I^\alpha$$

Figure 3. (a) The SEM cross section of the device, (b) the IV curve under forward and reverse scans of the best device with the Energy levels of $\text{Rb}_3\text{Sb}_2\text{I}_9$ shown in inset (c) and the corresponding IPCE spectrum with the integrated current density. (d) The variation of V_{oc} with natural logarithm of light intensity with the variation of J_{sc} with light intensity plotted in the inset.

where an $\alpha \sim 1$ is regarded as a system with weak bimolecular recombination⁵³. $\alpha < 1$ is generally associated with space charge effects, variation in mobility between carriers or energy barriers in the device. From the Figure 3d, the fitting gave $\alpha = 1$ excluding the possibility of the abovementioned effects. Thus the only possibility for the reduced V_{oc} is the recombination through defect levels in the material itself. Another possible factor limiting the performance could be the anisotropic charge transport arising from the layered nature of the material²⁴. Unoriented grains could impede the charge transport, increasing carrier losses. The solar cells from $\text{Cs}_3\text{Sb}_2\text{I}_9$ gave much lower current densities $\sim 0.3 \text{ mA/cm}^2$ (Figure S14) probably due to more pronounced effect of defects as evident from the CL spectra.

Discussion

The ability to form $\text{A}_3\text{Sb}_2\text{I}_9$ structures with the presence of valence shell s electrons and similar electron density of states and p-p transitions as lead halide perovskites make antimony a potential candidate for lead replacement. However, the photovoltaic properties are found to be highly dependent on the phase of $\text{A}_3\text{Sb}_2\text{I}_9$ - Dimer or layered. Here we adopted a simple solution processable

methodology to develop the desirable layered antimony perovskite with the structure $\text{A}_3\text{Sb}_2\text{I}_9$. The study demonstrates that a smaller cation like Rubidium can effectively stabilise the structure in its layered form. These findings may also be extended to lead based perovskites to stabilise other reported unstable structures and to unlock a less explored genome of inorganic perovskites. The findings from cathodoluminescence and XPS prove the need for carefully tuned fabrication methodologies in antimony based and other lead free materials to obtain materials very close to stoichiometry as these may not be as tolerant to defects as lead. The charge transport anisotropy due to the layered nature of the material could also be a limiting factor, which may be overcome by aligning the inorganic layers along the charge transport direction (perpendicular to the plane of Gold and FTO layer). In addition to the approach followed, exploring alternative device architectures could also be a strategy to improve the performances. Better hole transporting materials may be studied as opposed to the undoped Poly-TPD used in the present work. In addition to this, the band diagram indicates the possibility of utilising an alternative electron transporting layer (ETL) like SrTiO_3 with a higher conduction band edge compared to TiO_2 to improve the V_{oc}

assuming that the voltage in these materials may not be purely defined by the material itself.

Methods

1. Calculations using DFT

The electronic structure calculations are realized through VASP with the standard frozen-core projected augmented-wave method (PAW) with 300 eV as the cut-off energy for basis set. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) functionals was used for exchange correlation^{54–59}. The crystal structures of Dimer and layered forms of $\text{Cs}_3\text{Sb}_2\text{I}_9$ were obtained from previous literature⁶⁰. The hypothetical crystal structure of the $\text{Rb}_3\text{Sb}_2\text{I}_9$ dimer was modelled by replacing the Cs with Rb in $\text{Cs}_3\text{Sb}_2\text{I}_9$ (dimer) and the layered form of $\text{Rb}_3\text{Sb}_2\text{I}_9$ was modelled using by replacing Bi with Sb in the reported layered $\text{Rb}_3\text{Bi}_2\text{I}_9$ structure³⁹. The atomic positions were relaxed until force/atom is less than 0.05 eV. All structural relaxations were performed with Gaussian smearing of 0.01 eV. Rb, Sb and I atoms are described by $4p^65s^1$, $5s^25p^3$, $5s^25p^5$ valence electrons respectively. A $3\times4\times1$ Gamma K-point grid are applied for Brillouin zone integration.

2. $\text{Rb}_3\text{Sb}_2\text{I}_9$ synthesis and refinement of crystal structure

Powder samples of $\text{Rb}_3\text{Sb}_2\text{I}_9$ were obtained by heating the stoichiometric ratio of precursors in DMF (0.2M, 2ml) in a Petri dish at 120°C for 2 hours to completely remove the solvent. The powder XRD patterns were obtained on Bruker D8 Advance diffractometer in Bragg-Brentano configuration with Cu K α X-Rays of wavelength 1.54187 Å at 40kV and 40mA. The step size was kept at 0.02° with a step time of 2 s for all the powder samples. The thin films were characterised at a higher step size of 0.04° and stepping time of 0.5s. The intensity of the strongest reflection was more than 10000 for the sample used for refinement of crystal structure. The experimental fitting was carried out using TOPAS V4.1 in a range of 10 to 80° 2 θ . The crystal structure was refined starting from $\text{Rb}_3\text{Bi}_2\text{I}_9$ ³⁹ by replacing the Bi atoms with Sb and visualised using VESTA⁶¹. The final fit converged with a GOF of 1.85, R_{wp} of 3.93% and R_{exp} of 2.13%.

3. TGA and DSC

Thermogravimetric analysis was performed in a temperature range from 27°C to 800°C on TGA Q500 V6.7 (TA instruments). The ramp was fixed at 10°C/minute and the whole measurement was performed under nitrogen atmosphere. Differential scanning calorimetry was performed on Q10 V9.9 Build 303 calorimeter (TA instruments) at the same rate of 10°C/minute in nitrogen environment. The temperature range was from -80°C to the decomposition temperature of the respective perovskites.

4. Thin film formation

RbI and SbI₃ were dissolved in 3:2 molar ratios to form 0.2 M, 1ml solution in Dimethylformamide. The solution was heated at 75°C for 2 hours and the filtered after cooling to room temperature using a PTFE filter. The final solution (Solution1) was clear and dark red in colour and was heated again at 75°C before further processing. Substrates were cleaned by diluted detergent, deionized water and ethanol by sonication for 10 minutes in each. The substrates were dried under Nitrogen gas and treated in ozone plasma for 30 minutes. The spin coating was done in a procedure similar to the solvent Engineering process reported for perovskite solar cell preparation. The solution for treatment was prepared by dissolving 10mg of SbI₃ in toluene. The films were formed by spin coating solution 1 at 4000 rpm for 30s with the SbI₃ solution dripped after 3 s of the start of spin coating. The films were further cleaned by spin coating toluene solution at 4000rpm for 30s to remove any excess SbI₃. The films were annealed at 120°C for 10 minutes unless specified otherwise.

5. XPS, UPS and PESA measurements

The XPS and UPS measurements were performed using Omicron EA-125 hemispherical electron analyser under UHV conditions ($<1\times10^{-9}$ torr) with a 1486.6 eV monochromated Al K α source for XPS, and monochromatic HeI 21.2 eV line source for UPS. XPS wide scans were measured in CAE mode using 50.0 eV pass energy, while elemental scans with 20.0 eV pass energy. All XPS elemental peaks were fitted with Gaussian-Lorentzian profile over Shirley background. UPS spectra were collected under -10 V bias, CAE mode with 2.00 eV pass energy.

6. Cathodoluminescence and UV-Vis absorption measurements

The measurements were performed on FEI Verios scanning electron microscope (SEM) equipped with a Gatan MonoCL4 Elite cathodoluminescence (CL) system. Samples were prepared in the similar procedure as described in thin film formation (methods section). To avoid any background luminescence signal from TiO₂/FTO, Samples were prepared on silicon substrate. Power resolved CL spectroscopy was performed by exposing a fixed area of sample (30 μm^2) with a constant accelerating voltage at 5kV and varying the beam current from 0.1–3.2nA.

The absorption, reflectance and transmittance spectra were obtained using a UV-vis spectrometer (SHIMADZU UV-3600 UV-vis-NIR Spectrophotometer) with an integrating sphere (ISR-3100). For measuring the Internal Quantum Efficiency, the Total Reflectance and Transmittance measurements were carried out on the whole device with the light entering through the FTO side and getting reflected back by the gold electrode to the absorber for secondary absorption (Figure s15).

7. Hall measurements

Hall effect measurements were performed on a Lake Shore 7700A Series Hall effect/electronic transport measurement system (HMS) The samples were prepared on

1cmx1cm microscopic glass slides, similar to procedure described in the thin film formation (methods section). The measurements were made in van der Pauw configuration. Linear IV curve measurements were done before performing the variable field measurements. The DC excitation current was varied from -5nA to 5nA with a dwell time of 2sec. Hall and resistivity measurements were performed with field reversal and linear sweep from 0.5-4.5 kG (field step 1 kG). Hall mobility was calculated using zero-field resistivity value.

8. Solar cell fabrication and characterization

The FTO substrates were cleaned as discussed above and the blocking layer of TiO₂ was deposited by spray pyrolysis of 600µl Titanium diisopropoxide bis (acetylacetonate) solution (75% in ethanol) and 400 µl Acetylacetone diluted with 9 ml ethanol. The substrates were then treated with 100mM TiCl₄ solution for 30 minutes at 70°C and annealed at 500°C for 30 minutes. TiO₂ paste (30NRD-Dyesol) was diluted with ethanol in the ratio 1: 3.5 and spin coated at 5000rpm for 30 seconds followed by annealing at 500°C for 30 minutes. The films were again treated with 20mM TiCl₄ solution at 70°C followed by 500°C annealing before depositing the perovskite films. The perovskite films were deposited as discussed previously. 10mg of poly-TPD dissolved in 1ml toluene and heated at 80°C was spin coated at 4000rpm for 30s to form the hole transporting layer. Finally, 100nm gold electrodes were thermally evaporated using shadow masking to define an active area of 0.2cm².

Photovoltaic characterisation was carried out using a AM 1.5G solar simulator equipped with a 450W xenon lamp (model 8u72, Oriel). Its power output was adjusted to match AM 1.5G sunlight (100mW/cm²) by using a reference Si photodiode. I-V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2612A digital source meter. The voltage scan was done at 160mV/s from -0.1 to 0.7V with 121 intermediate points. All devices were measured by masking the active area with a black tape mask of 0.2cm² area. Incident-photon-to-current conversion efficiency (IPCE) was measured using a PVE300 (Bentham), with a dual Xenon/ quartz halogen light source, measured in DC mode, with no bias light.

ASSOCIATED CONTENT

Supporting Information. Details of structural refinement and detailed characterizations including XPS, TGA, DSC and CL are available in supplementary information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Nripan@ntu.edu.sg

*Hemant.Mulmudi@anu.edu.au

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