Synthesis, characterization of $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Cl}_n$ and $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Br}_n$ ($n=1, 2$) perovskites and use in dye-sensitized solar cells

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HIGHLIGHTS

- Air-stable $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{X}_n$ ($\text{X} = \text{Cl}, \text{Br}$; $n = 1, 2$) defect perovskites were synthesized.
- The halogen nature influences the photophysical properties of hybrid perovskite.
- $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{X}_n$ can work as hole transporters in dye-sensitized solar cells.

GRAPHICAL ABSTRACT

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ABSTRACT

New air-stable $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Cl}_n$ and $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Br}_n$ ($n = 1, 2$) defect perovskites were synthesized and their physicochemical properties were established. Rietveld analysis on the recorded XRD patterns revealed the presence of cubic structural modification with a 0D network of $[\text{SnI}_{6-n}\text{Cl}_n]$ and $[\text{SnI}_{6-n}\text{Br}_n]$ octahedra. The vibrational and electronic properties of the mixed-anion based trimethylsulfonium Tin (IV) perovskites investigated using Raman and UV-vis spectroscopy showed that upon substitution of Cl/Br for I, the electronic band gap slightly increased, while the lattice vibrations were also largely affected. Density functional theory (DFT) calculations permitted to determine the density of states (DOS) distribution and corresponding band energy structures, confirming the obtained increase of direct band gap values with halogen substitution. The lead-free Sn (IV)-based compounds were successfully incorporated as hole transporting materials (HTMs) in sensitized nanocrystalline solar cells (DSCs). For these devices, power conversion efficiencies as high as 5% were obtained, under 1 sun (A.M. 1.5G) illumination. Electrochemical impedance spectroscopic analysis indicated that the maximum device performance is associated with high charge recombination resistance and low electron transfer resistance at dye/perovskite and perovskite/Pt interfaces, respectively.

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1. Introduction

Hybrid perovskites are currently among the most promising materials for optoelectronic applications including solar cells and light emitted diodes (LEDs), due to their high efficiency, solution processing ability and low-cost production [1–3]. Recently, engineering approaches and optimization of the preparation procedures led to perovskite solar cells (PSCs) with power conversion efficiency (PCE) exceeding 23% [4, 10]. However, the practical application of these devices still remains under question, as serious environmental (toxicity) and technological issues (stability) are reported, mainly due to the presence of toxic lead (central metal) and highly hydrophilic organic cations (methyl ammonium-MA or formamidinium-FA) [11].

As a good alternative to lead perovskites, less toxic tin-based analogues were developed but the long-term performance of the corresponding devices is seriously affected by the progressive oxidation of Sn^{2+} to Sn^{4+} [12,13]. On the contrary, the Sn^{4+} -based molecular semiconductors Cs_2SnX_6 show enhanced stability and have been successfully employed as hole transporting materials (HTMs) in efficient dye-sensitized solar cells (DSSCs) [14–16]. These defect perovskites render DSSCs more attractive photovoltaics combining robustness, air-stability and low manufacturing costs [17–22]. In addition, some attempts were undertaken to replace the humidity sensitive FA and MA cations in the perovskite structure. Thus recently, the hydrophobic trimethylsulfonium $[(\text{CH}_3)_3\text{S}^+]$ organic cation was incorporated in $(\text{CH}_3)_3\text{SPbX}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) perovskites presenting enhanced chemical stability and very interesting structural and electronic properties [23–25]. Herein, we report in depth analysis of the trimethyl sulfonium tin (iv) mixed halide defect perovskites $[(\text{CH}_3)_3\text{S}]_2\text{SnI}_{6-n}\text{Cl}_n$ and $(\text{CH}_3)_3\text{S}_2\text{SnI}_{6-n}\text{Br}_n$ ($n = 1, 2$) and their use as HTMs in DSSCs, confirming efficient hole extraction across $(\text{CH}_3)_3\text{S}_2\text{SnX}_6$ to the Pt counter electrode in these devices.

2. Experimental section

2.1. Materials

All reagents including $(\text{CH}_3)_3\text{SBr}$ (TCI, 98%), Sn (Merck, granules), resublimed I_2 , dimethyl sulfide, methyl chloroformate (Sigma-Aldrich, > 99.9%) and solvents (acetonitrile, tert-butanol, ethanol, dichloromethane, chenodeoxycholic acid and dimethylformamide-DMF) were used as received without any further purification. For the construction of DSSCs, we used: TiO_2 paste (18-NRAO and WER4, Dyesol), TiCl_4 (Sigma-Aldrich), Z907 dye ((cis-bis(isothiocyanato) (2,2'-bipyridyl-4,4-dicarboxylato) (2'-bipyridyl-4,4'-dinonyl)-ruthenium(II), Dyesol), N719 dye (ditetrabutylammonium cis-bis(isothiocyanato)-bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II), Sigma-Aldrich), MK-2 dye (2-cyano-3-[5''-(9-ethyl-9H-carbazol-3-yl)-3',3'',3''',4-tetra-nhexyl-[2,2',5',2'',5'',2''']-quater-thiophen-5-yl]acrylic acid, Sigma-Aldrich), D35 dye ((E)-3-(5-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid, Dyenamo), Bis(trifluoromethane)sulfonimide lithium (Li-TFSI) (Acros) and *tert*-Butyl pyridine (TBP) (Sigma-Aldrich).

2.2. Synthesis of the perovskites

Firstly, $(\text{CH}_3)_3\text{SnCl}$, $(\text{CH}_3)_3\text{SnI}$ and SnI_4 were synthesized according to our previous work [23,24]. Secondly, using the above precursors and solid-state chemistry protocols, $(\text{CH}_3)_3\text{S}_2\text{SnI}_{6-n}\text{Cl}_n$ and $(\text{CH}_3)_3\text{S}_2\text{SnI}_{6-n}\text{Br}_n$ ($n = 1, 2$) perovskite were also prepared. In particular, $(\text{CH}_3)_3\text{S}_2\text{SnI}_5\text{Cl}$ was prepared by reacting 626.6 mg SnI_4 with 112.5 mg $(\text{CH}_3)_3\text{SnCl}$ and 204 mg $(\text{CH}_3)_3\text{SnI}$ in 1:1:1 M ratio and $(\text{CH}_3)_3\text{S}_2\text{SnI}_4\text{Cl}_2$ by reacting 626.6 mg SnI_4 with 225 mg $(\text{CH}_3)_3\text{SnCl}$ in 1:2 M ratio. Regarding $(\text{CH}_3)_3\text{S}_2\text{SnI}_5\text{Br}$ it was prepared by reacting 626.6 mg SnI_4 with 157 mg $(\text{CH}_3)_3\text{SBr}$ and 204 mg $(\text{CH}_3)_3\text{SnI}$ in 1:1:1 M ratio while $(\text{CH}_3)_3\text{S}_2\text{SnI}_4\text{Br}_2$ was formed by reacting 626.6 mg SnI_4

with 314 mg $(\text{CH}_3)_3\text{SnI}$ in 1:2 M ratio. In all cases, equimolar precursor amounts were introduced in a silica tube sealed under vacuum (following grinding in a mortar and mixing) and heated in an oven at 110 °C for 2 days.

2.3. Electrodes and solar cells fabrication

The solar cells were prepared following a well-established procedure in our lab [23]. FTO conductive glass electrodes ($7 \Omega/\text{cm}^2$) were cleaned in ultrasounds (successively with Triton X100, deionized water and ethanol, for 15 min each step) and dried using N_2 flow. On the FTO electrodes, a 6 μm thick TiO_2 layer was deposited by doctor blade using the 18-NRAO paste, dried in air and then annealed for 60 min at 500 °C. This was followed by the deposition of a second TiO_2 scattering layer (also 6 μm thick), prepared using the WER4 paste with average particle size of 400 nm. The composite films were sequentially annealed [at 125 °C (5 min), 325 °C (15 min) and 525 °C (30 min)] and post-treated with a TiCl_4 aqueous solution (20 mmol L^{-1}) at 70 °C for 10 min. Then, the obtained composite titania electrodes were washed with deionized water and ethanol, dried and finally annealed at 500 °C for 30 min.

The TiO_2 electrodes were sensitized by immersion into dye solutions for approximately 72 h. For Z907, 0.3 mmol L^{-1} of dye and 0.3 mmol L^{-1} chenodeoxycholic acid in a 1:1 v/v mixture of acetonitrile: tert-butanol were used. In the case of N719 and D35 dyes, the electrodes were immersed into a 0.3 mmol L^{-1} and 0.2 mmol L^{-1} dye solution in ethanol, respectively. As for the MK-2 dye, the electrodes were immersed into a 0.3 mmol L^{-1} dye solution in a 1:1:1 v/v/v mixture of toluene: acetonitrile: tert-butanol.

For the perovskite solutions, 103.4, 98.7, 94.1, 94.3 and 85.2 mg of $(\text{CH}_3)_3\text{S}_2\text{SnI}_6$, $(\text{CH}_3)_3\text{S}_2\text{SnI}_5\text{Br}$, $(\text{CH}_3)_3\text{S}_2\text{SnI}_4\text{Br}_2$, $(\text{CH}_3)_3\text{S}_2\text{SnI}_4\text{Cl}$ and $(\text{CH}_3)_3\text{S}_2\text{SnI}_4\text{Cl}_2$ respectively, were dissolved in DMF (0.4 mL) under stirring at 50 °C (10 min). The perovskite solutions were filtered by PTFE 0.45 μm filter and then, 10.4 μL of TBP and 15 μL of Li-TFSI (from a stock solution of 520 mg Li-TFSI in 1 mL acetonitrile) were added as dopants to increase the conductivity of the $(\text{CH}_3)_3\text{S}_2\text{SnI}_{6-n}\text{Cl}_n$ and $(\text{CH}_3)_3\text{S}_2\text{SnI}_{6-n}\text{Br}_n$ HTMs. A drop of the perovskite solution was placed on top of the dye/ TiO_2 photoelectrode and left to dry at 50 °C. An extra drop of the perovskite solution was casted on the platinized (100 nm thick prepared by Pt sputtering on FTO glass) cathode electrode which was placed on top of the photoelectrode and the sandwich structure was dried again at 50 °C.

2.4. Apparatus

To perform X-ray powder diffraction (XRPD) analysis, a Siemens D-500 diffractometer was used operating in Bragg-Brentano geometry with $\text{Cu-K}\alpha_1$ ($\lambda = 1.5406 \text{ \AA}$) and $\text{Cu-K}\alpha_2$ ($\lambda = 1.5444 \text{ \AA}$) radiation. Data were collected over the angular range $5^\circ \leq 2\theta \leq 80^\circ$ counting for 3 s at each step of 0.02° in detector position and were refined by Rietveld analysis using the JANA2006 package. A dispersive Renishaw in-Via Reflex spectrometer was employed (with 250 mm focal length and a high sensitivity, deep depletion CCD detector) to record the micro-Raman spectra in the $30 - 3200 \text{ cm}^{-1}$ frequency range. A near-infrared solid-state laser (785 nm) beam was focused on the sample's surface using a $\times 50$ long focal distance objective lens of a microscope (Leica DMLM) providing a power density of approximately $1 \text{ mW } \mu\text{m}^{-2}$. To investigate the dependence of the vibrational properties on the temperature (over the range $-193^\circ\text{C} - 110^\circ\text{C}$), perovskite samples (powder) were loaded into a THMS600PS Linkam heating-cooling optical stage under Ar atmosphere. Diffuse reflectance (R) spectra of the perovskite materials (in the form of 1 mm thick pellets) were recorded on a Hitachi U-3010 UV-Vis spectrophotometer equipped with an integrating sphere and the obtained data were transformed in Kubelka-Munk $F(R)$ units as: $F(R) = (1-R)^2/2R$. The solar cell performance was determined using a Xenon 300 W source solar simulator in combination with AM 1.5G optical

Fig. 1. a) XRPD patterns of $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Br}_n$ and $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Cl}_n$. b) Crystal structures of the compounds based on Rietveld refinement.

Fig. 2. Raman spectra of $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Br}_n$ (a); and $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Cl}_n$ (b) perovskite, where $(n = 1, 2)$.

filters (1 sun). Current density-voltage (J - V) characteristics were obtained with an Autolab potentiostat (PGSTAT-302N) at a scan rate of 100 mV s^{-1} and the illuminated (active) area was set to 0.152 cm^2 by using a mask in front of the cell.

2.5. Computational methodology

All first principles calculations were performed to obtain electronic partial density of states (PDOS) and energy band structure, using the plane wave pseudopotential method of quantum density functional theory (DFT) in the gas phase (CASTEP package) [25]. The electron-ion interaction was simulated with the GGA/PBE exchange-correlation [26–28]. The cut-off energy was set at 450 eV for all compounds and equilibrium geometry optimization was carried out using BFGS algorithm to get well relaxed structures.

3. Results and discussion

3.1. Structural analysis

For all samples, the XRPD patterns did not show peaks of unreacted precursors or other impurities (Fig. 1a). The new perovskites $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Cl}_n$ and $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Br}_n$ ($n = 1, 2$) obtained from solid-state synthesis present high crystallinity and have OD cubic symmetry (space group $Pa\bar{3}$, No. 205), in agreement with our previous work on $((\text{CH}_3)_3\text{S})_2\text{SnX}_6$ ($X = \text{Cl}, \text{Br}, \text{I}$) [23]. A small gradual shift of the characteristic peaks around 11.3° , 13.1° , 26.4° and 27.2° is observed towards higher 2θ values with increasing Cl or Br content. The partially substitution of iodide (ionic radius, $\text{I}^- = 220 \text{ p.m.}$) by smaller size chloride (ionic radius, $\text{Cl}^- = 181 \text{ p.m.}$) or bromide (ionic radius, $\text{Br}^- = 196 \text{ p.m.}$) [29], is accompanied with the octahedral deformation. Their distortion and shrinkage is confirmed by the observed shift of XRD peaks to higher angles, as shown in Fig. S1. Structural analysis was

Fig. 3. a) Diffuse reflectance spectra (in Kubelka-Munk units) for $((CH_3)_3S)_2SnI_{6-n}Cl_n$ and $((CH_3)_3S)_2SnI_{6-n}Br_n$. b) Band structures of the $((CH_3)_3S)_2SnI_5Br$ compound.

Fig. 4. a) EDX spectra of $((CH_3)_3S)_2SnI_{6-n}Cl_n$ and $((CH_3)_3S)_2SnI_{6-n}Br_n$. b) EDXS mapping of $((CH_3)_3S)_2SnI_4Cl_2$ and corresponding SEM picture.

performed for $((CH_3)_3S)_2SnI_{6-n}Cl_n$ and $((CH_3)_3S)_2SnI_{6-n}Br_n$ ($n = 1, 2$) with the Rietveld method using initially the structural model of $((CH_3)_3S)_2SnI_6$, without further refinement of the trimethyl sulfonium group. For the 0D crystal structure refinement, the following Wyckoff sites were used: Sn atoms on 4b (0.5,0.5,0.5), S atoms on 8c (x, x, x), C atoms on 24d (x, y, z) and split position of mixed halide on 24d (x, y, z). In the last case the halide sites are mixed-occupied by I and Cl/Br atoms in a 0.167:0.833 ratio for I_5Cl and I_5Br and a 0.333: 0.667 ratio for I_4Cl_2 and I_4Br_2 . Moreover, the default values for C–H bond lengths have been added for the three non-equivalent crystallographic H atoms at 24d (x, y, z) without any more refinement and thermal displacement values were refined isotropically for all non - hydrogen atoms. Thus, the obtained refined crystal structure is shown in Fig. 1b, and the atomic parameters are listed in Table S1.

The lattice parameters of $((CH_3)_3S)_2SnI_{6-n}Br_n$ decreased from 13.46

to 13.37 and 13.29 Å for $n = 1$ and 2, respectively. Accordingly, the lattice parameters of $((CH_3)_3S)_2SnI_{6-n}Cl_n$ decreased from 13.46 to 13.33 and 13.21 Å for $n = 1$ and 2 respectively.

3.2. Electronic and vibrational properties

Fig. 2 shows the micro-Raman spectra of $((CH_3)_3S)_2SnI_{6-n}Cl_n$ and $((CH_3)_3S)_2SnI_{6-n}Br_n$ ($n = 1, 2$) perovskite materials. Two different types of Raman active modes are observed, external vibrations in the $[SnI_{6-n}Cl_n$ or $I_{6-n}Br_n]$ octahedra, appearing at frequencies between 30 and 200 cm^{-1} as well as internal vibrations of the organic trimethyl sulfonium $(CH_3)_3S$ molecule, at wavenumbers above 200 cm^{-1} . In addition, for the pure iodide perovskite, three Raman vibrational modes of the SnI_6 octahedra are observed: the non degenerate $\nu(A_{1g})$ due to the Sn–I symmetric stretching, doubly degenerate $\nu(E_g)$ due to the Sn–I

Fig. 5. a, b) Density of state $((CH_3)_3S)_2SnI_5Br$ and $((CH_3)_3S)_2SnI_5Cl$ compounds, respectively. c, d) Partial density of state of Sn and mixed halogen in $((CH_3)_3S)_2SnI_5Br$ and $((CH_3)_3S)_2SnI_5Cl$ compounds.

Fig. 6. a) Photovoltaic performance of $((CH_3)_3S)_2SnI_{6-n}Cl_n$ and $((CH_3)_3S)_2SnI_{6-n}Br_n$ compounds on Z 907 dye. b) I-V curve of $((CH_3)_3S)_2SnI_6$ based on different type of transition metal complex (Z907, N719) and organic (MK2, D35) dyes.

asymmetric stretching vibration, and triply degenerate $\delta(F_{2g})$ as the halogen-Sn-I asymmetric bending deformation [25], which were approximately located at 119, 91 and 78 cm^{-1} , respectively. Amongst them, the $\nu(A_{1g})$ is by far the most intense. In mixed halide materials $((CH_3)_3S)_2SnI_{6-n}Cl_n$ and $((CH_3)_3S)_2SnI_{6-n}Br_n$ halide ions (I, Br/Cl)

occupy the octahedron corners randomly like in $MAPbI_{3-x}Br_x$ [30,31]. For this reason, several new high energy $\nu(A_{1g})$ bands are observed in the Raman spectra, at 134, 146, 164 cm^{-1} for $((CH_3)_3S)_2SnI_{6-n}Cl_n$ and 126, 133 and 149 cm^{-1} for $((CH_3)_3S)_2SnI_{6-n}Br_n$. The new bands are attributed to randomly occupied octahedral corners by I and Cl/Br ions,

Table 1

Photovoltaic parameters of cells employing the entitled perovskite compounds and different dye sensitizers.

Dye	Compound	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	PCE %
D35	((CH ₃) ₃ S) ₂ SnI ₆	4.34	0.49	0.53	1.12
MK2	((CH ₃) ₃ S) ₂ SnI ₆	10.50	0.4	0.42	1.77
N719	((CH ₃) ₃ S) ₂ SnI ₆	9.54	0.49	0.57	2.68
Z 907	((CH ₃) ₃ S) ₂ SnI ₆	20.05	0.48	0.53	5.07
	((CH ₃) ₃ S) ₂ SnI ₅ Br	14.03	0.51	0.56	4.02
	((CH ₃) ₃ S) ₂ SnI ₄ Br ₂	6.36	0.49	0.53	1.64
	((CH ₃) ₃ S) ₂ SnI ₅ Cl	12.06	0.55	0.60	4.00
	((CH ₃) ₃ S) ₂ SnI ₄ Cl ₂	8.66	0.59	0.58	2.95

according to their halide compositions. Moreover, we fitted the most intense $\nu(A_{1g})$ phonon band with a Gaussian curve (Fig. 2), for all investigated perovskite, which indicates a red frequency shift of this band was observed from 119 to 126 and 134 cm⁻¹ upon iodide substitution with Br or Cl, correspondingly. This is in agreement with the model of harmonic oscillator [15,24], taking into account the differences in the atomic mass of the Sn–Cl and Sn–Br halides. Furthermore, the relative intensities of the newly formed high energy $\nu(A_{1g})$ bands considerably change for the di-substituted ((CH₃)₃S)₂SnI₄Br₂ and ((CH₃)₃S)₂SnI₄Cl₂ compounds, reflecting the uniform distribution of substituting anions in the atomic level. Recorded frequencies of all these vibrational bands are in good agreement with the Cs₂SnX₆ (X = Cl, Br, I) analogues [15].

Moreover, temperature dependence Raman experiments were performed in order to study the lattice vibrational modes and phase transitions over wide range (–190 to 100 °C of temperature). The results for the ((CH₃)₃S)₂SnI₆ compound, presented in Fig. S2, show that a phase transition at lower symmetry occurs below –50 °C. This phase transition most likely incorporates tilting of the inorganic octahedra, as already reported for MAPbI₃ perovskite and other defect perovskite compounds (Cs₂SnI₆) [15].

To determine the optoelectronic properties of the ((CH₃)₃S)₂SnI_{6-n}Cl_n and ((CH₃)₃S)₂SnI_{6-n}Br_n (n = 1, 2) perovskites, Fig. 3a shows the corresponding diffuse reflectance spectra. The bandgap energies gradually increased from 1.43 to 1.50 eV upon partial iodide substitution. Accordingly, E_g values equal to 1.43, 1.46, 1.47 and 1.49 eV are estimated for [I₅Br], [I₅Cl], [I₄Br₂] and [I₄Cl₂] inorganic frameworks, respectively, thus confirming their close dependence on the chemical composition of the perovskite and especially on the nature of the anionic (halogen) species.

The experimental results are in good agreement with the preformed

DFT calculations. As example, the corresponding band diagram along the crystal symmetry directions in the first Brillouin zone are presented in Fig. 3b for ((CH₃)₃S)₂SnI₅Br. The coordinates of the special points of the Brillouin zone are G (0, 0, 0), X (0.5, 0, 0), R (0.5, 0.5, 0.5), M (0.5, 0.5, 0), in terms of the reciprocal lattice unit vectors, give a direct band gap value of about 1.55 eV. Relatively higher E_g values were obtained for the ((CH₃)₃S)₂SnI_{6-n}Cl_n and ((CH₃)₃S)₂SnI_{6-n}Br_n compounds (Fig. S3 given in supplementary information). The calculated bandgap values gradually increase with increasing bromide or chloride substitution (Table S2) and refer to direct band gaps between the valence and conduction bands at the G symmetry point for all samples.

3.3. Morphology and chemical composition

The morphology of the bulk materials of ((CH₃)₃S)₂SnI_{6-n}Cl_n and ((CH₃)₃S)₂SnI_{6-n}Br_n was investigated using Scanning Electron Microscopy (SEM) and their chemical composition was determined by Energy-dispersive X-ray spectroscopy (EDXS). SEM micrographs of mixed halide compounds are very similar to those recorded for ((CH₃)₃S)₂SnI₆ [23] exhibiting angular grain shapes. EDXS data were obtained from three different spots for each compound and the mean values of elemental content match well the nominal (theoretical) chemical composition of the samples (Table S3). The characteristic EDXS spectra are shown in Fig. 4a and the EDXS maps for ((CH₃)₃S)₂SnI₄Cl₂ (Fig. 4b) show large areas with good lateral uniformity which verifies the uniform distribution of different atoms on the bulk materials.

3.4. First principles DFT calculations

The DFT calculations (Figs. 5 and S3) of the cubic structures of ((CH₃)₃S)₂SnI_{6-n}Cl_n and ((CH₃)₃S)₂SnI_{6-n}Br_n (n = 1, 2) were carried out on the optimized geometry of cell structures refined from XRD data. The XRD results were used in order to make an in-depth analysis of their structural, electronic, and energetic properties.

Partial density of state (PDOS) diagrams reported in Fig. 5c and d, shows that the main contribution to the top valance band comes from the 5p state of mixed halogen I₅Br with little participation of the 5s state. In contrast, the main contribution to the top valance band of ((CH₃)₃S)₂SnI₅Cl is the 5p state of mixed halogen I₅Cl, which predicts stronger covalent bond with Sn atoms than subtitled bromide. On the other hand, the main contribution to the conduction band arises from anti-bonding 5p states of the halogen atoms and 5s states of Sn atoms. The strong hybridization of halogen (5p)–Tin(5s) bonds leads to mostly covalent interaction and permits the transfer of electrons from halogens

Fig. 7. a) Nyquist plot for ((CH₃)₃S)₂SnI_{6-n}Cl_n and ((CH₃)₃S)₂SnI_{6-n}Br_n compounds on Z907 sensitizer dye (The equivalent electrical circuit employed to simulate the EIS data is shown in the inset). B) Nyquist plot for ((CH₃)₃S)₂SnI₆ based on Z907, N719, MK2, and D35.

to tin atoms, thus improving the stability of compounds.

3.5. Solar cells

$((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Cl}_n$ and $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Br}_n$ perovskites were employed in electrolyte-free DSSCs of the type: **FTO/TiO₂-dye//Mixed halide perovskite//Pt/FTO**. The mesoporous nanocrystalline TiO₂ electrodes were sensitized by different molecular antennas including both metal-organic (Z907, N719) and organic (MK2, D35) dyes. The *J*-*V* curves of the DSSCs incorporating $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Cl}_n$ or $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Br}_n$ as HTMs are shown in Fig. 6a. It should be noted that in all cases the perovskites were doped with Li-TFSI and TBP additives in order to increase their hole carrier concentration and improve the corresponding DSSCs photovoltaic characteristics as previously reported [32,33].

From the *J*-*V* plots (Fig. 6) the values of short-circuit photocurrent density (*J*_{sc}), open-circuit voltage (*V*_{oc}), fill factor (*FF*) and power conversion efficiency (PCE) were deduced. PCE is defined as the ratio of the maximum electrical power produced by the cell (*JV*)_{max} over the incident light power (*P*), following equation (1):

$$\text{PCE \%} = \frac{(\text{JV})_{\text{max}}}{P} \times 100 \quad (1)$$

For the calculation of the fill factor values we used equation (2):

$$\text{FF} = \frac{(\text{JV})_{\text{max}}}{J_{\text{sc}} V_{\text{oc}}} \quad (2)$$

Table 1 summarizes the photovoltaic parameters. Among the different types of cells, those combining the Z907 sensitizer (transition metal complex) with the perovskite (HTMs) based on pure iodide and monosubstituted Bromide/chloride, achieved the highest performance, 5.07% and ~4%, correspondingly, Fig. 6a. The highest value of the photocurrent density (20.05 mA/cm²) was recorded for the pure iodide-based perovskite. This value was reduced to 14.03 and 12.06 mA/cm² for monosubstituted bromide and chloride respectively. In contrast, the fill factor (*FF*) increased with increasing the electronegativity of the substituted halogen taking values of (0.53, I), (0.56, Br) and (0.60, Cl), respectively. It is well known that doping the perovskite with a small amount of Cl or Br results in a decrease of recombination rate and increase of charge carriers lifetime [34,35]. Also, quite high efficiency of 2.7% was observed for the N719 sensitizer (Fig. 6b) than those obtained with organic of MK2 and D35 dyes (1.77% and 1.12%, respectively).

In fact, electrochemical impedance spectroscopic analysis performed (Fig. 7) confirms that the mono substituted halogen (chloride or bromide) perovskites in cells based on Z907 sensitizer present higher recombination resistance (*R*_{rec}) than the pure iodide-based reference (Table S4). This implies suppressed recombination rates and can justify the slight increase in the observed *V*_{oc} values. In contrast, the recombination resistance of cells employing perovskites with di-substituted halogens regained low values, similar to those of the pure iodide-based perovskite. This complies with the decrease of *V*_{oc} for $((\text{CH}_3)_3\text{S})_2\text{SnI}_4\text{Br}_2$, however it cannot justify the *V*_{oc} increase for $((\text{CH}_3)_3\text{S})_2\text{SnI}_4\text{Cl}_2$, which is rather due to down-shift in the valence band energy level of this particular perovskite.

Despite the suppressed recombination kinetics for the mono-substituted halogen perovskite in Z907-based solar cells, the charge transfer resistance at the perovskite/platinum interface (*R*_{Pt/per}) increased in all cases. Thus, a *R*_{Pt/per} value of 0.65 Ohm cm² was attained for pure iodide perovskite and increased to 2.13, 3.44 and 4.14 Ohm cm² for monosubstituted bromide and chloride and disubstituted chloride perovskites, respectively. This tendency comprises well with decrease of the short-circuit photocurrent for all cells with mixed halides. Moreover, Fig. 7b presents comparative impedance spectra for cells with $((\text{CH}_3)_3\text{S})_2\text{SnI}_6$ based on different, Z907, N719, MK2, and D35 dyes. Table S4 summarizes the corresponding EIS fitting parameters. The cells based on the organic dye present higher charger transfer and lower recombination resistance which shows off the reasons behind their

relatively low photovoltaic efficiency. The poor photovoltaic behavior of the cells with organic dyes could be attributed to the fact that the TiO₂ layer (thickness, structure) was optimized for the organometallic dyes but not for the organic dyes [16].

4. Conclusions

Lead-free, air-stable, low toxic $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Cl}_n$ and $((\text{CH}_3)_3\text{S})_2\text{SnI}_{6-n}\text{Br}_n$ (*n* = 1, 2) defect perovskites have high potential for solar cell applications. The photophysical characterization and DFT computational calculation confirm that the lattice vibrations modes and electronic bandgaps are between 1.38 and 1.5 eV and depend largely on the effect of mixing I and Cl/Br atoms. We successfully utilized the novel perovskite compounds as HTMs in electrolyte-free dye-sensitized solar cells, based on mesoporous titania electrodes sensitized by a number of transition metal complexes (Z907, N719) and organic (MK2, D35) dyes. A power conversion efficiency (PCE) of 4% under the standard illumination conditions of 100 mW/cm² (A.M. 1.5G) were achieved for the $((\text{CH}_3)_3\text{S})_2\text{SnI}_5\text{Br}$ and $((\text{CH}_3)_3\text{S})_2\text{SnI}_5\text{Cl}$ layer sandwiched between sensitizer metal-organic Z907 and Pt interface. Electrochemical impedance results confirm low hole extraction resistance of mono substituted halogen at the perovskite-Pt electrode. Overall, our results promote trimethyl sulfonium tin-based perovskites as chemically stable hole-transport material in lead free solar cells.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matchemphys.2019.122310>.

References

- [1] S. Il Seok, M. Grätzel, N.-G. Park, Methodologies toward highly efficient perovskite solar cells, *Small* 14 (2018), 1704177.
- [2] D.A. Egger, A.M. Rappe, L. Kronik, Hybrid organic-inorganic perovskites on the move, *Acc. Chem. Res.* 49 (2016) 573–581.
- [3] P. Gao, M. Graetzel, M.K. Nazeeruddin, Organohalide lead perovskites for photovoltaic applications, *Energy Environ. Sci.* 7 (2014) 2448–2463.
- [4] M. Saliba, J.P. Correa-Baena, C.M. Wolff, M. Stollerfoht, N. Phung, S. Albrecht, D. Neher, A. Abate, How to make over 20% efficient perovskite solar cells in regular (n-i-p) and inverted (p-i-n) architectures, *Chem. Mater.* 30 (2018) 4193–4201.
- [5] J.-P. Correa-Baena, A. Abate, M. Saliba, W. Tress, T. Jesper Jacobsson, M. Grätzel, A. Hagfeldt, The rapid evolution of highly efficient perovskite solar cells, *Energy Environ. Sci.* 10 (2017) 710–727.
- [6] M.A. Green, A. Ho-Baillie, Perovskite solar cells: the birth of a new era in photovoltaics, *ACS Energy Lett.* 2 (2017) 822–830.
- [7] S.D. Stranks, P.K. Nayak, W. Zhang, T. Stergiopoulos, H.J. Snaith, Formation of thin films of organic-inorganic perovskites for high-efficiency solar cells, *Angew. Chem. Int. Ed.* 54 (2015) 3240–3248.
- [8] H.S. Jung, N.G. Park, Perovskite solar cells: from materials to devices, *Small* 11 (2015) 10–25.
- [9] M. Grätzel, The light and shade of perovskite solar cells, *Nat. Mater.* 13 (2014) 838–842.
- [10] M.M.S. Sanad, A.M. Elseman, M.M. Elsenety, M.M. Rashad, B.A. Elsayed, Facile synthesis of sulfide-based chalcogenide as hole-transporting materials for cost-effective efficient perovskite solar cells, *J. Mater. Sci. Mater. Electron.* 30 (2019) 6868–6875.
- [11] G. Niu, X. Guo, L. Wang, Review of recent progress in chemical stability of perovskite solar cells, *J. Mater. Chem. A* 3 (2015) 8970–8980.
- [12] I. Chung, J.H. Song, J. Im, J. Androulakis, C.D. Malliakas, H. Li, A.J. Freeman, J. T. Kenney, M.G. Kanatzidis, CsSnI₃: semiconductor or metal? High electrical

- conductivity and strong near-infrared photoluminescence from a single material. High hole mobility and phase-transitions, *J. Am. Chem. Soc.* 134 (2012) 8579–8587.
- [13] F. Hao, C.C. Stoumpos, D.H. Cao, R.P.H. Chang, M.G. Kanatzidis, Lead-free solid-state organic-inorganic halide perovskite solar cells, *Nat. Photonics* 8 (2014) 489–494.
- [14] B. Lee, C.C. Stoumpos, N. Zhou, F. Hao, C. Malliakas, C.Y. Yeh, T.J. Marks, M. G. Kanatzidis, R.P.H. Chang, Air-stable molecular semiconducting iodosalts for solar cell applications: Cs_2SnI_6 as a hole conductor, *J. Am. Chem. Soc.* 136 (2014) 15379–15385.
- [15] A. Kaltzoglou, M. Antoniadou, A.G. Kontos, C.C. Stoumpos, D. Perganti, E. Siranidi, V. Raptis, K. Trohidou, V. Psycharis, M.G. Kanatzidis, P. Falaras, Optical-vibrational properties of the Cs_2SnX_6 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) defect perovskites and hole-transport efficiency in dye-sensitized solar cells, *J. Phys. Chem. C* 120 (2016) 11777–11785.
- [16] A. Kaltzoglou, M. Antoniadou, D. Perganti, E. Siranidi, V. Raptis, K. Trohidou, V. Psycharis, A.G. Kontos, P. Falaras, Mixed-halide $\text{Cs}_2\text{SnI}_3\text{Br}_3$ perovskite as low resistance hole-transporting material in dye-sensitized solar cells, *Electrochim. Acta* 184 (2015) 466–474.
- [17] D. Perganti, M. Giannouri, A.G. Kontos, P. Falaras, Cost-efficient platinum-free DSCs using colloidal graphite counter electrodes combined with D35 organic dye and cobalt $^{(II/III)}$ redox couple, *Electrochim. Acta* 232 (2017) 517–527.
- [18] N. Balis, A.A. Zaky, D. Perganti, A. Kaltzoglou, L. Sygellou, F. Katsaros, T. Stergiopoulos, A.G. Kontos, P. Falaras, Dye sensitization of titania compact layer for efficient and stable perovskite solar cells, *ACS Appl. Energy Mater.* 1 (2018) 6161–6171.
- [19] T. Stergiopoulos, M. Konstantakou, P. Falaras, Dye solar cells combining a TiO_2 surface-blocking organic sensitizer and solvent-free ionic liquid-based redox electrolyte, *RSC Adv.* 3 (2013) 15014–15021.
- [20] M. Konstantakou, T. Stergiopoulos, V. Likodimos, G.C. Vougioukalakis, L. Sygellou, A.G. Kontos, A. Tserepi, P. Falaras, Influence of fluorine plasma treatment of TiO_2 films on the behavior of dye solar cells employing the $\text{Co}^{(II/III)}$ redox couple, *J. Phys. Chem. C* 118 (2014) 16760–16775.
- [21] G. Konti, G.C. Vougioukalakis, M. Bidikoudi, A.G. Kontos, C. Methenitis, P. Falaras, A $\text{Ru}^{(II)}$ molecular antenna bearing a novel bipyridine–acrylonitrile ligand: synthesis and application in dye solar cells, *Polyhedron* 82 (2014) 12–18.
- [22] A.N. Kabanakis, M. Bidikoudi, M.M. Elsenety, G.C. Vougioukalakis, P. Falaras, Synthesis of novel semi-squaraine derivatives and application in efficient dye-sensitized solar cells, *Dyes Pigments* 165 (2019) 308–318.
- [23] M.M. Elsenety, A. Kaltzoglou, M. Antoniadou, I. Koutselas, A.G. Kontos, P. Falaras, Synthesis, characterization and use of highly stable trimethyl sulfonium tin $^{(IV)}$ halide defect perovskites in dye sensitized solar cells, *Polyhedron* 150 (2018) 83–91.
- [24] A. Kaltzoglou, M.M. Elsenety, I. Koutselas, A.G. Kontos, K. Papadopoulos, V. Psycharis, C.P. Raptopoulou, D. Perganti, T. Stergiopoulos, P. Falaras, Synthesis, characterization and optoelectronic properties of chemically stable $(\text{CH}_3)_3\text{SPbI}_{3-x}\text{Br}_x$ and $(\text{CH}_3)_3\text{SPbI}_{3-x}\text{Cl}_x$ ($x = 0, 1, 2, 3$) perovskites, *Polyhedron* 140 (2018) 67–73.
- [25] M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M. C. Payne, First-principles simulation: ideas, illustrations and the CASTEP code, *J. Phys. Condens. Matter* 14 (2002) 2717–2744.
- [26] D. Vanderbilt, Soft self-consistent pseudopotentials in a generalized eigenvalue formalism, *Phys. Rev. B* 41 (1990) 7892–7895, <https://doi.org/10.1103/PhysRevB.41.7892>.
- [27] S.J. Clark, M.D. Segall, C.J. Pickard, P.J. Hasnip, M.L.J. Probert, K. Refson, M. C. Payne, First principles methods using CASTEP, *Z. Krist.* 220 (2005) 567–570.
- [28] N. Hernández-Haro, J. Ortega-Castro, Y.B. Martynov, R.G. Nazmitdinov, A. Frontera, DFT prediction of band gap in organic-inorganic metal halide perovskites: an exchange-correlation functional benchmark study, *Chem. Phys.* 516 (2019) 225–231.
- [29] B. Saparov, D.B. Mitzi, Organic-inorganic perovskites: structural versatility for functional materials design, *Chem. Rev.* 116 (2016) 4558–4596.
- [30] M. Ledinský, P. Löper, B. Niesen, J. Holovský, S.-J. Moon, J.-H. Yum, S. De Wolf, A. Fejfar, C. Ballif, Raman spectroscopy of organic-inorganic halide perovskites, *J. Phys. Chem. Lett.* 6 (2015) 401–406.
- [31] A. Kaltzoglou, C.C. Stoumpos, A.G. Kontos, G.K. Manolis, K. Papadopoulos, K. G. Papadokostaki, V. Psycharis, C.C. Tang, Y.K. Jung, A. Walsh, M.G. Kanatzidis, P. Falaras, Trimethylsulfonium lead triiodide: an air-stable hybrid halide perovskite, *Inorg. Chem.* 56 (2017) 6302–6309.
- [32] J. Krüger, R. Plass, L. Cevey, M. Picirelli, M. Grätzel, U. Bach, High efficiency solid-state photovoltaic device due to inhibition of interface charge recombination, *Appl. Phys. Lett.* 79 (2001) 2085–2087.
- [33] G. Boschloo, L. Häggman, A. Hagfeldt, Quantification of the effect of 4-tert-butylpyridine addition to I^-/T^{3+} redox electrolytes in dye-sensitized nanostructured TiO_2 solar cells, *J. Phys. Chem. B* 110 (2006) 13144–13150.
- [34] D. Kiermasch, P. Rieder, K. Tvingstedt, A. Baumann, V. Dyakonov, D. Kiermasch, Improved charge carrier lifetime in planar perovskite solar cells by bromine doping, *Sci. Rep.* 6 (2016) 39333.
- [35] C. Wehrenfennig, M. Liu, H.J. Snaith, M.B. Johnston, L.M. Herz, Charge-carrier dynamics in vapour-deposited films of the organolead halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, *Energy Environ. Sci.* 7 (2014) 2269–2275.