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Optoelectronic and Photovoltaic Properties of the Air-Stable Organohalide Semiconductor $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$

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Abstract

Lead halide perovskite materials have shown excellent optoelectronic as well as photovoltaic properties. However, the presence of lead and the chemical instability relegate lead halide perovskites to research applications only. Here, we investigate an emerging lead-free and air stable compound $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ as a non-toxic potential alternative to lead halide perovskites. We have synthesized thin films, powders and millimeter-scale single crystals of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ and investigated their structural and optoelectronic properties. We demonstrate that the degree of crystallinity strongly affects the optoelectronic properties of the material, resulting in significantly different band gaps in polycrystalline thin films and single crystals. Surface photovoltage spectroscopy reveals outstanding photocharge generation in the visible (<700 nm), while transient absorption spectroscopy and space charge limited current measurements point to a long exciton lifetime and a high carrier mobility, respectively, similar to lead halide perovskites, pointing to the remarkable potential of this semiconductor. Photovoltaic devices fabricated using this material yield low power conversion efficiency (PCE) to date, but the PCE is expected to rise with improvements in thin film processing and device engineering.

1. Introduction

From the introduction of hybrid organic/inorganic halide perovskites as light harvesting materials in dye-sensitized solar cells¹, the research community has focused its attention towards the optimization of the devices by improving thin film fabrication processes^{2,3}, exploring alternate solar cell architectures^{4,5} and understanding the device and semiconductor physics of this remarkable new class of solution-processable semiconductor⁶⁻⁹. Most of the device-related work has therefore been based on lead halide perovskites such as $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbBr}_3$ ¹⁰⁻¹³ and non-stoichiometric compounds such as $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ ^{3,14,15}. However, all these compounds contain lead as a core element that is well known to be a toxic and persistent environmental pollutant that will limit or even prevent future large-scale market entry. Moreover,

the non-negligible stability problems of this class of materials remain unresolved¹⁶. Several attempts have been made to replace lead-based halide perovskite with tin based ones. Efficiencies up to 6% were reported based on $\text{CH}_3\text{NH}_3\text{SnI}_3$ and $\text{CH}_3\text{NH}_3\text{SnI}_{3-x}\text{Br}_x$ compounds, respectively^{17, 18}. Subsequently, solar cells based on fully inorganic compounds, $\text{CsSnI}_{3-x}\text{Br}_x$ and $\text{CsSnI}_{3-x}\text{F}_x$, were demonstrated with efficiencies approaching 2%^{19, 20}. Despite the suitable band gap (1.3 eV for $\text{CH}_3\text{NH}_3\text{SnI}_3$) and other optimal optoelectronic properties, such as a direct band gap resulting in high absorption coefficient, tin halide perovskites suffer from low carrier diffusion length, due to the presence Sn^{4+} ions in the place of Sn^{2+} .¹⁷ Furthermore, even in the presence of trace amounts of oxygen Sn^{2+} is completely converted into Sn^{4+} giving rise to a completely different material ($(\text{CH}_3\text{NH}_3)_2\text{SnI}_4$). These shortcomings limit the value and potential of tin halide perovskites for photovoltaic applications, making the search for an alternative material a matter of urgency.

Bismuth organo-halide compounds such as $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ have recently emerged as a possible candidate for photovoltaic and light harvesting applications. This material was first prepared and optically characterized by Kawai et al.^{21, 22} and structurally investigated through IR spectroscopy²³. Other compounds of the same family containing Sb and inorganic cations (Cs^+ , Rb^+) were also widely studied showing similar physical properties^{24, 25}. Only recently, $\text{Cs}_3\text{Sb}_2\text{I}_9$ deposited by thermal evaporation was investigated as a possible light harvesting material without yielding positive results, which the authors attributed to deep trap states promoting non-radiative recombination²⁶. Other studies dealing with this class of materials have also appeared²⁷⁻²⁹ but none of them have reported interesting power conversion efficiency or complete explanations as to why the semiconductors did not perform well.

We take the view that more in-depth optoelectronic and electronic characterization are needed to fully ascertain the potential of these semiconductors as light harvesting materials. In particular, the ability to synthesize and characterize both polycrystalline thin films and single crystals of this material should be of particular utility and value to understanding the inherent semiconductor properties and potential challenges in translating these into polycrystalline thin film based applications, such as photovoltaics. To investigate the role of crystalline order and defects, we have developed several solvent-based crystallization methods for thin films and single crystals of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$. These samples were subjected to a wide range of structural and spectroscopic investigations, including optical absorption spectroscopy, surface photovoltage spectroscopy (SPS), transient absorption spectroscopy (TAS), and ultraviolet photoelectron spectroscopy (UPS). Our results clearly reveal the immense role that defects play in mediating the optical, transport and optoelectronic properties of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ and demonstrate a clear potential for these materials to perform as well as lead halide perovskites.

2. Results and discussion

2.1 Solution-grown $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ films and single crystals

The raw material was prepared by reacting Bi_2O_3 with methylammonium iodide in concentrated hydroiodic acid at 120 °C for two hours²¹. It yielded a highly pure powder composed of thin hexagonal dark red crystals, see Fig. 1a. Thin films of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ were deposited by spin coating a solution of the compound prepared by dissolving the raw material produced by the

method described above or co-dissolving BiI_3 and $\text{CH}_3\text{NH}_3\text{I}$ with a 2:3 molar ratio in γ -butyrolactone (GBL) or GBL/dimethyl sulfoxide (DMSO) mixture 3:2 in volume. The co-dissolution of the salts is far more convenient providing a quantitative yield along with the simplicity of preparation and was finally chosen to prepare thin films for characterization and photovoltaic devices. The raw powder prepared with the first method was used only for optical and XRD characterization. Large $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ single crystals were grown by the antisolvent diffusion crystallization method already utilized to grow lead halide perovskite crystals of large size ($d \gg 1 \text{ mm}$)³⁰. It was possible to grow high quality single crystals having a hexagonal prism shape with sizes ranging from hundreds of micrometers to few millimeters as shown in Fig. 1b. Smallest sized crystals were used for single crystal XRD characterization while the largest ones, having very smooth surface were used for steady state and transient absorption measurements as well for PL. Large flat single crystals connected on the substrate (Fig. 1c) were grown by solvent annealing of large drops of the $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ solution in GBL/DMSO deposited on ITO or glass substrates for electrical and optical characterization.

In Fig. 1a-d we point out the apparent difference in the color of the single crystals grown by the two methods (consistently dark red) and the thin films, which have colors ranging from bright to reddish orange. The colour of the films was found to vary when different solvents were used. The colour is also affected by the addition of an anti-solvent (chlorobenzene) during the deposition and by the annealing procedure, providing important hints about the link between the processing approach, microstructure and optical properties of this material. In Fig. 1d and in Fig. S1 are shown $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ thin films deposited by spin-coating on ITO substrate with GBL and GBL/DMSO solvents by using the antisolvent assisted crystallization route (ASAC). Deposition by GBL yields dense bright orange films while GBL/DMSO mixture provides bright orange/reddish films. In both cases, films were obtained by a conventional annealing at 80 °C for 10 minutes on a hot plate in an inert atmosphere. Optical microscope images of these films are shown in Fig. S2a-b revealing that in both cases films are apparently very dense, and the substrate is covered homogeneously. Sub-micrometric analysis of the same samples by SEM (Fig. S3a-b) evidences the hexagonal structure of the material through the formation of hexagonal-shaped edges and tiles. In particular, films cast from GBL solutions result in flat nanometric particles having a size of 100-300 nm. Films cast from GBL/DMSO present a more networked and porous structure but with far larger grain size ($\geq 1 \mu\text{m}$). In both cases it is though evident that the film is not covering homogeneously the substrate, yet numerous pinholes are present.

When the annealing procedure is carried out in a closed container (Petri dish), skipping the anti-solvent addition during spin-coating, the resulting films, although less dense appear more reddish, thus much closer to the single crystal color, see Fig. S2c-d. With this procedure, the solvent is allowed to evaporate very slowly saturating the sample enclosure, thus continuously redissolving and recrystallizing the film providing superior crystallinity and a well-defined crystal orientation. This route was denominated saturated vapor crystallization (SVC). In Fig. S2c-d it can be recognized that with GBL/DMSO crystallites are substantially larger than the ones deposited by GBL alone confirming even, in this case, the presence of DMSO improves the crystallinity and promote the formation of large grains by slowing down the crystallization rate through the formation of labile complexes DMSO-metal^{2,31}. The formation of hexagonal flat single crystals is even more evident when large quantities of material are deposited on substrates through drop

casting and solvent annealed for long time. As can be seen in Fig 1c, in this way, 4-5 mm wide and up to 100 μm thick crystals are grown.

A very important aspect of this compound is the stability in the air that is notably high especially if compared to lead and tin halide perovskites. Exposure to air with a level of humidity ranging between 50-60 RHE for 30 days does not cause any color change and any deliquescence due to water absorption. This stability is attributable mainly to the oxidation state of bismuth (III) that is the most stable one for this element with a ground state electron configuration $[\text{Xe}].4f^{14}.5d^{10}.6s^2.6p^0$. Furthermore, as already reported for lead halide perovskite, the relativistic effects occurring in compounds with heavy elements induce a shift of the valence band edge of higher energy thus limiting the sensitivity to moisture³².

2.2 Single crystal X-Ray diffraction

The $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ compound belongs to a family of compounds which is described by the general formula $\text{A}_3\text{B}_2\text{X}_9$ (A = K, Rb, Cs, alkylammonium; B = Bi, Sb, W, Mo, Fe, V, Ti, Cr; X = Cl, Br, I). With the position A set for a methylammonium cation $(\text{CH}_3\text{NH}_3^+)$, the literature only refers to crystal structures that include halogen-antimonates or bismuthate as $[\text{B}_2\text{X}_9]^{3-}$ anion³³. Among the possible halogenates (Cl, Br, I), there are also some remarkable differences between the crystal structures. The chloride crystals $((\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{Cl}_9)$ crystallize at room temperature in orthorhombic symmetry (*Pmcn*) with a skeleton of one-dimensional double chain of BX_6 octahedra. The bromide crystals $((\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{Br}_9)$ crystallize in trigonal symmetry (*P-3m1*) with corrugated layers of BX_6 octahedra. The aforementioned crystal structures have been determined by single crystal X-Ray diffraction and firmly reported³⁴⁻³⁶. However, for the iodine crystals, only the space group (*P6₃/mmc*) has been unequivocally determined thanks to the consideration of Weissenberg photographs and their pyroelectric behavior. The structure of iodine based crystals was simply suggested by proposing an isomorphism with the known $\text{Cs}_3\text{Bi}_2\text{I}_9$ phases because the latter also crystallizes in hexagonal symmetry (*P6₃/mmc*)³⁷ albeit $\text{Cs}_3\text{Sb}_2\text{I}_9$ is also known to exhibit an additional trigonal phase (*P-3m1*) whose appearance depends on the synthesis conditions^{26, 38, 39}.

The successful growing in our laboratory of a $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ single crystal ($0.18 \times 0.12 \times 0.10$ mm) suitable for X-ray diffraction was an opportunity to progress in the structure resolution of such compounds. The symmetry of the experimental data set acquired at room temperature belongs to the Laue class 6/mmm. The refined unit cell parameters are $a = 8.5821(3)$ Å and $c = 21.7678(8)$ Å. Systematic absences were only noticed for $\{hhl\}$ reflections with $l = 2n+1$ suggesting one of the space group *P6₃mc* (186), *P-62c* (190), or *P6₃/mmc* (194). As reported, $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ crystals do not exhibit any pyroelectric effect at room temperature that indicates a centrosymmetric crystal structure³⁷. Therefore, the centrosymmetric space group (*P6₃/mmc*) was selected for the following structure refinement. Upon averaging the crystallographically equivalent reflections, the refinement was performed with 530 nonequivalent reflections with $I > 2\sigma(I)$. The final refined atomic coordinates with isotropic and anisotropic displacement parameters are grouped in Table 1.

The crystal structure is best described by perovskite-like fragments stacked along the *c*-axis (Figure 1). The fragments consist of hexagonal closed packed $(\text{CH}_3\text{NH}_3)_3\text{I}_3$ nets normal to the C_3 axis and Bi atoms located in the octahedral cavities formed by the I atoms. One-third of the I_6 -octahedra are empty so that two layers of the BiI_6 -octahedra belonging to each fragment are separated by a layer

of empty I_6 -octahedra, ultimately leading to a stacking sequence $(CH_3NH_3)I_3$ -Bi- $(CH_3NH_3)I_3$ - $(CH_3NH_3)I_3$ -Bi- $(CH_3NH_3)I_3$ along c -axis (Figure 2a). The BiI_6 octahedra of the adjacent fragments share one face and are related by a mirror plane normal to the C_3 axis (Figure 2b). In the latter isolated dimeric $[Bi_2I_9]^{3-}$ anions, the bismuth atoms are displaced from the center of the octahedra towards the directions opposite to the shared face. Three long $[Bi-I(2) = 3.247(3) \text{ \AA}]$ and three short $[Bi-I(1) = 2.957(3) \text{ \AA}]$ bond distances are formed while the terminal $I(1)$ atoms ($U_{iso} = 0.0764 \text{ \AA}^2$) are consistently more disordered than the bridging $I(2)$ atoms ($U_{iso} = 0.056 \text{ \AA}^2$). A common feature of all $(CH_3NH_3)_3Bi_2X_9$ ($B = Sb$ or Bi) phases is the isotropic disorder of the methylammonium cations because of their free overall rotation within the crystal^{33, 37}. For the particular case of $(CH_3NH_3)_3Bi_2I_9$, this behavior was investigated by 1H NMR and infrared spectroscopy as a function of temperature^{23, 40}. On cooling, phase transitions were noticed and suggested to be related to the gradual freezing of the $CH_3NH_3^+$ cations along c -axis. At room temperature, it practically means that the $CH_3NH_3^+$ cations are seen by X-Rays as spherical electronic densities because the timescale of X-ray scattering event is several orders smaller than the rotational motion. A first model using K^+ cations as dummy atoms (it has the same electron number as methylammonium) was used to simulate a spherical electronic density for the methylammonium positions⁴¹. The resulting statistical agreement factors were poor, and the latter model was discarded. The methylammonium cations were then positioned in two independent crystallographic positions similarly to the positions of Cs^+ cations in $Cs_3Bi_2I_9$ ($P6_3/mmc$)⁴² and their coordinates were refined with a C-N bond length fixed at $1.47 \text{ \AA}$ as a constraint. In both crystallographic sites, the axis of C-N bond is aligned with c -axis. Hence, the dynamic disorder of methylammonium is necessarily reflected through large atomic displacement parameters (table 1) as already observed for similar phases³³. The first position of $CH_3NH_3^+$ is described by the C(1)-N(1) atoms pair (both crystallographic positions 4f) which is located above and below each $[Bi_2I_9]^{3-}$ anions. The $CH_3NH_3^+$ orientation, with either the nitrogen or the carbon atom pointing towards the $[Bi_2I_9]^{3-}$ dimer, could not be differentiated as the statistical agreement factors for the two orientations were nearly equivalent. On the representation given Fig. 2b, the orientation was arbitrarily chosen with the carbon pointing towards the closest dimer. The second position is described by the C(2)-N(2) atoms pair (with respective crystallographic position 4e and 2b) which is located in the large cavity formed between three $[Bi_2I_9]^{3-}$ anions of the same plane. The presence of the mirror reflection plane ($x,y,1/4$) normal to the C_3 axis duplicates the methylammonium in two orientations along the c -axis. The occupancies for C(2) and N(2) crystallographic sites were refined respectively to 1/2 and 1, indicating an equiprobable orientation of the methylammonium in those cavities.

2.3 X-Ray diffraction of powder and films

The diffraction patterns of the powder and the films deposited by SVC and ASAC routes are shown in Fig. 3. The theoretical diffraction pattern calculated from our previous structure refinement is also displayed to help the reader in the assessment of the materials purity. The number and the positions of the reflections are matching the simulated powder pattern indicating that both powder and thin films were grown as a single phase of $(CH_3NH_3)_3Bi_2I_9$ without any detectable impurities (e.g. BiI_3) or amorphous materials (except for the scattering of silica glass). However, one can notice that for the pattern of thin-film grown by the SVC route the intensity of $\{00l\}$ and $\{11l\}$ reflections are overwhelming all the others, consistent with a high preferential orientation of the crystallites along $[00l]$ direction. The preferential orientation is maintained to a lesser extent for the

powder and thin film grown by ASAC route. This behavior can also be directly observed by microscopy (Fig. S2c and d), as the micrographs exhibit crystals lying on the substrate surface with *c*-axis normal to the surface. The Le Bail method was used to decompose the XRD patterns, and the results are shown in Table S1. The crystallite size of the powder and the films are relatively close (from 148 up to 205 nm). However, the hexagonal unit cell parameters seem to correlate with the crystallite size, with a slight decrease of both *a* and *c* cell parameters when the crystallite size decreases from 0.2 mm down to 148 nm.

2.4 Electronic properties and band structure

Steady-state optical absorption measurements revealed that the band-gap edge of the material is strongly affected by the material preparation. Polycrystalline films cast by spin coating show an absorption onset at 2.26 eV, a value much larger than the onset for the single crystal (1.96 eV). This trend was observed already for $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ ³⁰ and was explained in term of crystal disorder and lack of long-range structural coherence in nanostructured thin films^{30, 43}. Here, on the base of our experimental results we give a different explanation that evidenced a well-defined peak, which is clearly visible for thin films and almost absent in single crystal spectra. This feature is ascribable to electronic transitions in the Bi_2I_9 ⁻³ dimer/cluster^{21, 44}. A difference in the absorption spectrum, although not so evident, is also visible between the thin films crystallized by the two different routes ASAC and SVC. These results highlight the higher degree of crystallization achieved with the SVC method.

In Fig. 6a are reported the energy diagrams of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ measured by UV photoelectron spectroscopy (UPS) and photoelectron spectroscopy in air (PESA), along with the band gap estimated by Tauc plot shown in Fig. 6b. From UPS measurements, the work function of the compound was found to be 4.94 eV and its ionization potential 6.0 eV (Fig. 4). The film work function which corresponds to the difference between the Fermi level E_F and the vacuum level was determined from the spectra high binding energy cut-offs while the film ionization potential is obtained by adding the photoemission onset of the valence edge E_{VB} w.r.t. to the Fermi level E_F (1.12 eV). The energy of the valence band determined by PESA is 5.63 eV with respect to the vacuum level. This value was estimated from the onset of the square root of quantum yield vs. energy curve (Fig. S4). The difference between the valence band measured by UPS and PESA is 0.37 eV. This discrepancy is in line with what was observed for other semiconducting materials, organic and inorganic, that usually ranges from 0.3 eV to 0.5 eV. The simultaneous use of these techniques enhances the degree of confidence on the valence band values.

The optical properties of this class of compounds ($\text{A}_3\text{B}_2\text{X}_9$) have already been studied in several aspects^{21, 23, 24}, however these compounds have only very recently been investigated as potential light harvesting materials for photovoltaic applications²⁶⁻²⁹. Here we put in correlation the optoelectronic properties obtained by spectroscopic means with photocharges generation capabilities and eventually with the photovoltaic response of the compound. Given the color difference between the thin films, powder and single crystal (Fig. 1), a significant change of optical properties (mainly absorption) is expected. In Fig. 6a are shown the Kubelka-Munk functions $F(R)=(1-R)^2/2R$ of thin films (SVC, ASAC), powder and single crystal measured by diffuse reflectance spectroscopy. There is an evident difference between the shapes and onset values of $F(R)$ spectra of the material with three different morphologies. This difference of $F(R)$ is in evident

contrast with XRD results. Indeed, single crystal, powder and thin films deposited by both methods have the same crystalline structure, and they differ only in crystal orientation. Another peculiarity that leaps out is a quite narrow band centered at 495 nm that is present in all the spectra, although with different intensities. According to previous reports^{21, 22, 44}, the peak is originated from the $^1S_0 \rightarrow ^3P_1$ electronic transition in the cluster $\text{Bi}_2\text{I}_9^{-3}$ that, unlikely from group (IV) halide perovskites (e.g. $\text{CH}_3\text{NH}_3\text{PbI}_3$) where the PbI_4 octahedra are connected to each other by sharing vertexes, in $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$, $\text{Bi}_2\text{I}_9^{-3}$ clusters are isolated and not covalently bound to each other. Therefore, in this case, the electronic wavefunction is localized on $\text{Bi}_2\text{I}_9^{-3}$ clusters. The intensity of the peak is much more evident in the thin film while it is barely noticeable in the powder and even less in the single crystal spectra. Besides, for powder and single crystal it can be observed the apparition of a steep band-edge at lower energy typical of bulk semiconductors. This can be explained by the higher degree of crystallization and thus of order in the crystal that promotes the formation of an electronic band structure. This trend was not observed in ref.²¹ where even for single crystals the spectra were dominated by the intense $\text{Bi}_2\text{I}_9^{-3}$ band. This is probably due to a lower crystallinity of crystals grown in HI as we already observed from XRD analysis.

Having observed that crystal size and crystallinity impact the optical properties, we have carried out a study on the effect of crystallization on the thin films deposited by ASAC and SVC routes. Referring to optical microscope pictures shown in Fig. S2 and SEM pictures in Fig. S3, the intensity of the $\text{Bi}_2\text{I}_9^{-3}$ -related absorption peak appears to be inversely proportional to the crystallites size, in fact, films deposited from GBL solutions have more pronounced peak than thin films from GBL/DMSO solutions, due to a smaller grain size. This trend is confirmed for thin films deposited by the SVC route. For the film deposited from GBL/DMSO solution, there is a marked depletion of the peak and the apparition of a shoulder at ~640 nm that matches the absorption onset of the single crystal. This can be once more attributed to the increased crystals size and orientation. An opposite effect is observed when single crystals are crushed into fine powder and the color changes from deep red to orange blue-shifting the optical absorption. This is ascribable to the cleavage along the a,b crystallographic plane giving rise to smaller and more randomly oriented fine crystallites.

For the determination of the band-gap we used the Tauc plot obtained by tracing $(F(R)h\nu)^{1/\alpha}$ versus energy $h\nu$, where α is a coefficient that is equal to $1/2$ for direct and 2 for indirect band-gap transitions and $F(R)$ is the already defined Kubelka-Munk function that is proportional to the absorption coefficient $\epsilon(h\nu)$. For thin films cast from GBL/DMSO, the Tauc plot onset falls at 2.26 eV, a value comparable with a previous report²¹. Completely different are the Tauc plots of powder and single crystal revealing lower values of band-gap, 2.06 eV and 1.96 eV respectively. As mentioned above, the steep onset at lower energy testifies the formation of band structure in the highly crystalline form of the compound. Furthermore, for single crystal only, there is a second onset at 3.1 eV that can be associated with an indirect band-gap transition.

2.5 Optoelectronic properties

The photoluminescence emission band is centered at 637 nm, (Fig. 6b). As previously mentioned, the PL peak position does not vary between the single crystal, powder or thin-film. The peak is then rather broad and its intensity relatively low compared to the PL peak of a reference material such as $\text{CH}_3\text{NH}_3\text{PbI}_3$. Indeed, to have PL emission it is necessary to excite the material with a laser (473 nm) having an intensity of $100 \mu\text{W}/\text{cm}^2$. The fact that the position of the peak does not vary for the

thin film, powder or single crystal suggests that it arises from radiative recombination occurring in $\text{Bi}_2\text{I}_9^{3-}$ clusters. This is also supported by the experimental observation that the PL signal is generally more intense in thin films rather than in powder and single crystal. Indeed, it is likely that in single crystals or powder the close packing of the $\text{Bi}_2\text{I}_9^{3-}$ clusters may induce a stronger quenching with respect to the thin film.

Transient absorption measurements carried out on a single crystal and a thin film are shown in Fig. S5. The ground state bleach (GSB) recovery kinetics are monitored at 480 nm. Two time components were observed and fitted using a bi-exponential functional consisting of a fast surface component $\tau_1 = 17 \pm 1$ ns ($\tau_1 = 17 \pm 1$) and a slower bulk component $\tau_2 = 162 \pm 18$ ns ($\tau_2 = 364 \pm 43$ ns) for thin films (single crystals). These carrier lifetimes are comparable to recently reported values for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystals³⁰. For both single crystals and thin films, a longer lifetime was observed when probing the TA signal at 480 nm. However, contrarily to $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ cases, carrier lifetime is surprisingly longer in thin films with respect to the single crystal. This can be explained by the fact that probing at 480 nm; we mostly measure the lifetime of the electronic state of the $\text{Bi}_2\text{I}_9^{3-}$ cluster for which, as for PL, the lifetime is probably more quenched in the single crystal than in thin films due to a closer packing. In support of this, XRD results evidence a variation of the Bi-I bonds between the single crystal, powder and thin films demonstrating a different packing of the dimers within the crystal. This may explain also the small variation of the dimer-related peak in the F(R) spectra, since the Bi-I bond angle certainly affects the hybrid $^3\text{P}_1$ molecular orbital.

2.6 Photovoltaic properties

The band gap found for $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ (1.96 eV) is a bit large compared to the optimal value requested for solar cell materials ($1.1 \text{ eV} < E_g < 1.6 \text{ eV}$), but it can still be of great interest especially as a replacement of hybrid lead halide perovskite and as a wide band gap absorber in tandem solar cell. Losses caused by lack of absorption in the near-IR can be compensated by a higher V_{OC} due to a larger band gap. Furthermore, it is worth to mention that large band gap light absorbers were already used successfully such as ruthenium complex N719 and similar ($E_g = 2.3 \text{ eV}$) in dye-sensitized solar cells⁴⁵ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ ($E_g = 2.3 \text{ eV}$) in halide perovskite/ TiO_2 architecture^{13, 32}. The material showed also optimal transport properties, similarly to what was already reported for halide perovskite materials^{25, 30}. Indeed, SCLC measurements on single crystals lying on conductive substrates gave value of mobility of the order of magnitude of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$. Photovoltaic devices based on the canonical architecture of lead halide perovskite solar cells, namely, $\text{FTO}/\text{TiO}_2/(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9/\text{spiro-MeOTAD}/\text{Au}$ have been thus fabricated showing efficiency of 0.11 %, a value in line with what was reported in report²⁹ and for similar materials²⁷. SPS measurements on incomplete devices with architecture $\text{FTO}/\text{TiO}_2/(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9/\text{spiro-MeOTAD}$ and EQE measurements on particular devices confirmed that the $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ has an effective role in light harvesting and photogeneration. The major cause of the low efficiency can be assigned to non-homogeneity of the film that causes high recombination and shunting problems. Furthermore, the elevate energy difference between valence bands of HTM and $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ may be responsible of hole transfer hindrance.

From the energy diagrams of Fig. 5a it can be seen that the conduction band of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ estimated by UPS and PESA is well aligned with the conduction band of TiO_2 (literature accepted

value). According to UPS measurements the difference of CBs is only of 0.26 eV. Still, according to UPS results, the valence band of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ lies 0.77 eV below HOMO level of spiro-MeOTAD (HTM) and a hole transfer between the two materials is thus possible. However, an HTM with a lower VB would allow a better charge transfer, as well as a higher V_{OC} , as result of a higher built-in voltage. In Fig. 5a, since the band-gap was estimated from optical measurements, it was also taken into account the variation of the band gap and consequently of the CB, between the thin film and the single crystal. This variation is depicted as an offset in orange color while the band-gap is represented by the red block. The difference in energy is subtle (0.2 eV) and it does not significantly affect the alignment with the CB of TiO_2 . It is worth to point out that for the thin films it would be more correct to talk about LUMO level rather than CB. This is because the band gap has been evaluated from the onset of the optical transition related to the isolated $\text{Bi}_2\text{I}_9^{-3}$ clusters that can be considered nothing but molecular species embedded in the whole lattice.

The experimental technique that better puts in evidence the light harvesting properties of this material is Surface Photovoltage Spectroscopy (SPS). SPS allows verifying directly whether a material is photoactive or not without making a complete device. The surface potential of thin films or incomplete devices without metallic contacts is measured by Kelvin probe under illumination with monochromatic light and in the dark. The surface photovoltage is thus the difference between the surface potential value under illumination and that in the dark. When illumination occurs, free carriers are photogenerated in the photoactive film and diffuse toward the built-in field in the space charge regions at the $\text{TiO}_2/(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ and $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9/\text{spiro-MeOTAD}$ interfaces in the incomplete device, but also at the free surface when measuring $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ only. Hence, through SPS, one actually measures the flattening of the bands occurring during illumination as compared to dark conditions, which is closely related to the open-circuit voltage of the complete device under the same illumination conditions. In Fig. 6b are shown SPS spectra of incomplete devices having the structure spiro-MeOTAD/ $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9/\text{TiO}_2/\text{ITO}$ obtained depositing $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ by ASAC and SVC routes respectively. The onset of the SPS spectrum of ASAC-deposited films shown in Fig. S6a-b occurs at 685 nm which is red-shifted respect to the F(R) edge of the normally deposited film (563 nm) thus more similar to the F(R) spectrum of the single crystal (643 nm) and matching the center position of the PL peak (Fig. 6a). Besides, the spectrum presents two bands; in particular the band at the lower wavelength (485 nm) seems to coincide with the cluster-related peak observed in the F(R) spectra. For the incomplete device based on film deposited by the SVC route (Fig S6c-d), the SPS spectrum has a rather different shape. It does not exhibit the shoulder at 485 nm, and it is more broadened toward higher wavelength. This is in perfect agreement with the F(R) spectra of SVC film which has a feeble cluster-related peak and shows a small shoulder in the same spectral region of the single crystal absorption onset. The absolute voltage measured for the ASAC semi-devices produced a much higher photovoltage than SVC ones. This might be due to a less homogeneous and dense coverage of TiO_2 in SVC compared to ASAC devices. To confirm the validity of this technique, SPS measurements on a reference $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film were also carried out. In Fig. S7, the SPS spectra of plain $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ films deposited on ITO are shown together for comparison. The onset of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is as expected red-shifted compared to the $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ due to a smaller band-gap but most importantly, the intensity of the absolute SPS signals are totally comparable, confirming a good photoresponse of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$, highlighted in particular by the high open-circuit voltage of devices based on this material.

The space charge limited conduction (SCLC) was used to estimate the mobilities (μ) of the charge carriers in the MAIB crystals. The conservative estimations and comparisons of the carrier mobility, carrier concentrations, trap densities and conductivity from the SCLC technique are shown in Fig. 7. All experimental details of SCLC measurements including the theory used are reported in the SI. The mobility of the material ($29.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) that is extracted from the child's regime, fitting data with the Mott-Gurney equation is relatively high for an hybrid organic/inorganic material and is comparable as order of magnitude to the $\text{CH}_3\text{NH}_3\text{PbI}_3$ ($38 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)³⁰. Also, the traps density estimated by fitting data in the TFL regime is rather low, even lower than in $\text{CH}_3\text{NH}_3\text{PbI}_3$. Furthermore, SCLC measurements in the ohmic regime allowed the estimation of conductivity and carrier density, obtaining reasonable values for this kind of material. It confirms the good potential of this material for photovoltaic applications.

In Fig. 6b is shown a typical EQE spectrum of the photovoltaic device based on $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$. Contrarily to what was expected, EQE and SPS spectra are very different in spectral response. EQE spectrum shows that the device is producing photocurrent only at a low wavelength, and a large part of the spectrum is missing, say above 500 nm. The depletion of EQE can be explained in terms of high recombination of photogenerated charges in the $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ film due to its inhomogeneity and discontinuity between crystallites (Fig. 3). Indeed, while in the SPS the light is shone on top of the material and only the surface photovoltage is probed without any current flow (open-circuit), for EQE the light is shone through the FTO/ TiO_2 and the photogenerated charges can be effectively separated at the interface with TiO_2 (short-circuit). Since the low-wavelength range of the radiation is absorbed almost entirely in the first nanometers of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ layer near the TiO_2 interface, photogenerated charges can be effectively separated near this interface. However, radiation with progressively higher wavelength will be absorbed deeper and deeper in the film and, due to the poor morphology, will recombine before reaching the TiO_2 interface, resulting in a very low photocurrent as well as EQE signal in this range. This could be already inferred from the low fill factor of the J/V characteristic that is the signature of high carrier recombination. In Fig. 8 it is shown the current density vs. voltage characteristic (J/V) of photovoltaic devices based on $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ as a light absorber having Au/spiro-MeOTAD/ $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ / TiO_2 /ITO architecture. For the majority of the devices tested we found an efficiency of 0.11 % with a fill factor of 32 %. The observed short circuit current density J_{SC} and open circuit voltage V_{OC} in average were 492 mA/cm^2 and 722 mV respectively.

3. Conclusions

In conclusion, we have successfully synthesized $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ in a single crystals, powder, and thin film through different techniques of growth and deposition. The raw material was produced starting from bismuth oxide and directly mixing the iodides while thin-films were deposited out of solutions of the salts or from the raw material itself in polar solvents by spin coating. The compound showed an exquisite stability toward air and humidity that is the major drawback for lead and tin halide perovskites. Highly crystalline standalone and on-substrate single crystals were prepared by the antisolvent diffusion and by the solvent annealing methods respectively and utilized to determine the crystalline structure and to study some fundamental physical properties of the material. The crystalline structure was obtained by single crystal and X-ray powder diffraction and

structure refinement analysis. Optical absorption measurements revealed that the crystal size and orientation strongly affect the light absorption properties so that the band gap can range from 1.96 eV (single crystal) to 2.26 eV (thin film). Furthermore, it was found that the polycrystalline thin film absorption is mainly characterized by the cluster band while the single crystal exhibits an absorption band typical of semiconductors. Transient absorption spectroscopy performed on single crystal, and thin film revealed long-lived electron/hole pairs in the visible spectral range that is ascribable to the optical transition in $\text{Bi}_2\text{I}_9^{-3}$ -clusters. Likewise, PL evidences the peculiar electronic transition in $\text{Bi}_2\text{I}_9^{-3}$ -clusters. To improve the crystallinity and to have a preferential crystals orientation, thin films of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ were cast by two different routes and with two different solvents. In particular, SVC method resulted in highly oriented single crystals film. By surface photovoltage spectroscopy, it was demonstrated that thin films of the material exhibit a significant photocharge generation properties similar to the well-assessed $\text{CH}_3\text{NH}_3\text{PbI}_3$ that was used as a reference. Photovoltaic devices were ultimately fabricated showing a good photoresponse in the UV-VIS range although the efficiency turned out to be still low. This can be attributed mainly to a poor morphology of the film that gives rise to relevant recombination.

4. Methods

4.1 Synthesis of raw $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$

Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) was prepared adding to 14 ml (0.136 mol) of a methylamine solution (40 % wt in H_2O , Sigma Aldrich), 15 ml (0.113 mol) of hydroiodic acid (57 % wt in H_2O , stabilized 99.95 %, Sigma Aldrich). The salt was recovered by drying the solution in a rotary evaporator and then recrystallized three times in anhydrous ethanol. $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ crystals were synthesized by reacting for 3 hours at 120 °C 0.932 g (0.002 mol) of Bi_2O_3 (99.99%, Alfa Aesar) with 0.3179 g (0.002 mol) of $\text{CH}_3\text{NH}_3\text{I}$ previously synthesized, dissolved in 13.2 ml of hydroiodic acid further stabilized with 2 ml of hypophosphorous acid (50 % w/w aqueous solution, Alfa Aesar). During the slow cooling down of the reaction mixture, already at 90-80 °C there is the formation of hexagonal dark red crystallites in part floating on the mother liquor. They were separated by vacuum filtration and then washed quickly with absolute ethanol and by diethyl ether. Finally, the reddish crystals were then dried overnight under vacuum and can be used as raw material.

4.2 Growth of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ single crystal

0.75 mol of Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) and 0.33 mol of bismuth triiodide (BiI_3) (STREM Chemicals 99.999% Puratrem) (3:2 molar ratio) were dissolved in 1 ml of γ -butyrolactone ($\geq 99\%$ Sigma Aldrich) stirring the solution overnight at 60 °C. When the salts were completely dissolved, the vial containing was placed in a sealed bottle containing 6 ml of anhydrous dichloromethane (DCM) ($\geq 99.8\%$ extra dry Acros Organics) avoiding any contact between the solution and the anti-solvent (DCM). After 1 day, DCM diffused almost completely into the $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ solution causing a decreasing of solubility and thus the growth of hexagonal single crystals. Single crystals were separated from the mother solution and rinsed several times with anhydrous DCM.

4.3 Deposition of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ thin film

(CH₃NH₃)₃Bi₂I₉ films on glass, mesoporous TiO₂ or on ITO substrates were deposited by spin coating technique. The solutions were prepared by dissolving 0.75 mol of CH₃NH₃I and 0.33 mol of BiI₃ in 1 ml of GBL and/or in 1 ml of GBL/DMSO 7:3 v/v mixture. Two distinct spin-coating/annealing procedures were used; a) antisolvent-assisted crystallization route (ASAC) where 100 μ l of the as prepared (CH₃NH₃)₃Bi₂I₉ solution was spun for 10 s at 500 rpm then accelerated to 4000 rpm and after 10 s, 80 μ l of chlorobenzene (99.8 % anhydrous, Sigma-Aldrich) were swiftly added on the rotating sample to promote the crystallization and to keep the sample under spinning still for one minute. The sample is then annealed at 70 °C for 10 minutes to allow all the solvents to evaporate. Bright orange films were obtained by this method. b) Saturated vapor crystallization route (SVC) where a (CH₃NH₃)₃Bi₂I₉ solution was deposited with the same procedure as in a) but without the addition of chlorobenzene. The film was then annealed in a closed Petri dish at 60°C overnight to allow a very slow solvent evaporation. The slow evaporation rate and the stable equilibrium between the solvent and the film for a long time promote a better crystallization. A red-orange film with microcrystalline structure was obtained.

4.4 Structural Characterization

Single crystal XRD patterns were acquired by an Agilent CrysAlis PRO diffractometer operating at room temperature with Mo K α monochromated radiation (λ = 0.71073 Å). The computational cell refinement data reduction and absorption correction were processed using Agilent CrysAlis PRO software (See SI for details). Crystal data, data collection parameters, and structure refinement details are given in Table S1. The structures were solved by direct methods from SHELXT⁴⁶ and refined by full matrix least-squares techniques from SHELXL⁴⁶. Small size single crystal (~10 of μ m) utilized for this measurements was grown by the antisolvent diffusion route described in the method section and mounted onto the diffractometer loop. Powder and thin film XRD patterns were collected on a Bruker D8 Advanced A25 diffractometer in the Bragg–Brentano geometry equipped with a Cu tube (Cu–K α ; λ = 0.15418 nm) operating at 40 kV and 40 mA using a linear position sensitive detector (opening 2.9°). The diffractometer was configured with a 0.1° diverging slit, 2.9° anti-scattering slit, 2.5° Soller slits, and a nickel filter to attenuate the contributions from Cu–K β fluorescence. Data sets were acquired in continuous scanning mode over the 2 θ range of 10–80°. A step size of 0.012° was applied with a counting time of 1s per step for the films and 6 s per step for the powder. Even after an extensive grinding of the microcrystals and a careful loading of the sample holder to minimize the textural effect, the XRD pattern of the powder exhibited an enhanced intensities of the {00l} and {11l} reflections. Attempts to refine the structure with the Rietveld method including a March-Dollase function^{47, 48} did not provide satisfactory agreement due to the persistent preferred orientation along the {00l} direction. Hence, Le Bail method with the fundamental parameters approach⁴⁹ implemented in the software TOPAS V4.2 (Bruker-AXS) was used to analyze the XRD patterns for the powder and the films of (CH₃NH₃)₃Bi₂I₉⁵⁰. The refinements were performed with the P6₃/mmc space group as previously determined by single crystal X-Ray diffraction. The profile parameters included the scale factor, a sample displacement parameter, and a three-term polynomial for the background. The fundamental parameters approach analytically calculates the instrumental broadening in the peak profile. The particle size was calculated from the Lorentzian contribution of this profile.

4.5 Optoelectronic Characterization

Thin film and single crystal diffuse reflectance spectroscopy measurements (DRS) were performed using a Varian Cary 6000i UV-vis near-IR spectrometer equipped with diffuse reflectance accessory Labsphere DRS 1800. Thin films deposited by spin coating on a glass substrate and a 3 mm wide hexagonal single crystal were mounted on a glass slide support placed in the center of the integrating sphere. Transient absorption spectroscopy measurements on the thin film and single crystal were carried out by an EOS Sub-Nanosecond Transient Absorption Spectrometer (Ultrafast Systems, LLC) utilizing two-channel probe-reference detection method. The excitation pulse at 350 nm was generated using spectrally tunable Optical Parametric Amplifier (Light Conversion Ltd) pumped by a Ti: sapphire femtosecond regenerative amplifier operating at 800 nm and producing 35 fs pulses with a repetition rate of 1 kHz (Spectra-Physics). The white light probe pulse was generated by a supercontinuum source. The pump and probe beams were overlapped spatially and temporally on the sample, and a broadband UV-VIS detector was used to collect the reflected probe light from the sample to record the time-resolved excitation-induced difference spectra (Fig. S5). The samples were the same used for steady-state diffuse reflectance measurements, but, in this case, the single crystal was glued on a tiny PMMA support to avoid any light scattering not arising from the single crystal itself. Photoluminescence spectroscopy measurements were performed by a nano-/micro-Raman and PL setup NT-MDT Ntegra spectrometer using a low resolution grating with 150/500 grooves to cover the entire emission wavelength range. The chosen exciting laser source was a Cobolt Blues solid state laser emitting at 473 nm. Due to the low power of the excitation light, monochromatized Xe lamp, it was not possible to get any PL from a normal spectrofluorometer. Surface photovoltage spectroscopy (SPS) measurements were performed using a KP Technology Kelvin Probe setup equipped with a SPS40 module for SPS measurements. The signal was acquired illuminating the sample from 300 nm to 1000 nm by monochromatized light modulated by an optical chopper rotating at 22 Hz and recovering the photovoltage signal by a lock-in amplifier triggered by the KP signal.

4.6 Electronic Characterization

UPS experiments were carried out using an Omicron ultrahigh-vacuum (UHV) analysis chamber (base pressure 1×10^{-10} mbar). Samples were prepared depositing $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ on a gold substrate by spin coating an approximately 30 nm thick film. The thin film was transferred to the chamber with minimal air exposure from a nitrogen glove box. A hemispherical electron energy analyzer (Omicron SPHERA) at 3.0 eV pass energy and an ultraviolet He (I) attenuated lamp with photon energy of 21.22 eV were used to record the spectra. The analyzer resolution (105 meV) was determined by measuring the width of the Fermi edge of a sputtered cleaned polycrystalline gold foil. The film work function was calculated by subtracting the sum of the total width (16.28 eV) of the photoelectron spectrum of the photon energy. A negative bias of 5V was applied to the substrate before the UPS measurement.

Measurements of photoelectron spectroscopy in air (PESA) were performed by a Riken Keiki AC-2 PESA Spectrometer equipped with a deuterium lamp with an energy range between 3.40 eV to 6.20 eV. The sample was prepared by spin-coating a film of the material (~500 nm) on an ITO conductive substrate. Best results were obtained using a light intensity between 5 nW-10 nW.

Electronic mobility measurements were performed by the mean of SCLC on flat $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ single crystals deposited on patterned ITO. Device fabrication involved the growth of large flat single crystals on ITO substrate by the SVC method drop-casting the $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ solution in GBL/DMSO on the substrate. The thickness of each crystal was measured by a Bruker optical profilometer. As-grown crystals were thermally evaporated with Au pads (100 nm) by an Angstrom thermal evaporator at a 0.5 Å/s deposition rate. The I/V curves of the device were acquired by a Keithley 2400 Source Meter contacting the top of the crystal and the underlying ITO by silver paint and wires. The device in the configuration ITO/ $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ /Au was used for the current-voltage characteristics carried out in the dark at 300 K.

4.7 Photovoltaic Characterization

Current-voltage characteristics were recorded by applying an external potential bias to the cell and recording the generated photocurrent with a digital source meter (Keithley 2400 Source Meter). The cells were illuminated with an AM1.5 solar simulator (ABET Technology) equipped with a 150 W xenon lamp. Before each measurement, the light intensity was calibrated with a silicon reference cell. The scans were performed from 0 V to 1.1 V using both forward and reverse bias. EQE measurements were performed using EQE/IQE equipment (PV technology). All the characterizations were carried out in a nitrogen filled glovebox.

4.8 Device Fabrication

FTO substrates (Dyesol TEC7 Glass Plate) were patterned using laser etching. Successively the substrates were ultrasonicated for 1 hour in water containing 2% of Hellmanex III detergent, then rinsed with DI water and sonicated in sequence for half an hour with acetone and then isopropanol respectively. Finally, they were rinsed with DI water and dried with dry nitrogen. Previous the deposition they were further cleaned from organic residuum by UV/ozone cleaner for 10 minutes.

A solution of 730 μl titanium isopropoxide (98% Acros Organics,) in 10 ml of anhydrous ethanol acidified by 73 μl of HCl (99.999% metal basis, Sigma-Aldrich) was spin-coated on the FTO substrates at 2000 rpm for 30 s, dried at 125 °C for 10 minutes and then annealed in an oven for 1 hour at 500 °C. The films were further treated then with a 120 mM aqueous solution of TiCl_4 (99.999% metal basis, Sigma-Aldrich) for 20 minutes at 70 °C, rinsed by DI water and annealed once again at 500 °C for 30 min. $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ film was deposited in agreement to what was described above. Successively, a doped spiro-MeOTAD (98%, Borun Chemicals Inc.) film was cast on it by spin-coating at 2200 rpm a 80 mM spiro-MeOTAD solution in chlorobenzene added with 17.6 μl of lithium bis(trifluoromethanesulfonyl)amide (Sigma-Aldrich) 520 mg/ml stock solution in acetonitrile, 28.8 μl 4-tertbutyl pyridine (96%, Sigma-Aldrich) and 29 μl of tris(2-(1H-pyrazol-1-yl)pyridine)cobalt(III)bis(trifluoromethylsulphonyl)imide (FK102 Co(III) TFSI salt, Dyesol) 300 mg/ml stock solution in acetonitrile. On top of the HTL, it was thermally evaporated a 100 nm thick layer of gold. The shading mask for gold and the underlying patterned FTO define a device area of 0.075 cm^2 . Incomplete devices were fabricated with the same procedures but without depositing the primary metal contact.

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Author contributions statement

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analysis by Samy Ould-Chikh and Xiaohe Miao, transient absorption measurements by Erkki Alarousu, Mobility measurements by Murali Banavoth, UPS and XPS measurements by Guy Olivier Ngongang Ndjawa and Aram Amassian, SEM imaging by Jeremy Barbe.

Figure 1: **a)** Small single crystals powder grown from Bi_2O_3 and $\text{CH}_3\text{NH}_3\text{I}$ in concentrated HI. **b)** Large single crystals grown by slow antisolvent diffusion method **c)** Large 70 μm thick single crystal grown on ITO substrate by the SVC method. **d)** $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ thin films deposited by the antisolvent assisted crystallization method (ASAC) using GBL/DMSO and GBL as solvents and chlorobenzene as antisolvent.

Figure 2: **a)** A representation of the layered structure of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$, characterized by isolated $[\text{Bi}_2\text{I}_9]^{3-}$ anions and two crystallographic inequivalent CH_3NH_3^+ cations. **b)** The structural motif forming the layer structure of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$. Note that half-filled spheres used for C(2) - N(2) denote an half occupancy and C(1) and N(1) positions can be switched. Unit cell of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ obtained from single crystal diffraction pattern.

Figure 3: Diffraction patterns of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ thin films, powder and simulated powder from single crystal XRD measurements.

Figure 4: UPS spectra showing the valence region of ~30 nm $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ thin film on gold foil and the secondary-electron cutoff (inset) used to determine the work function of the sample. The x axis shows the binding energy relative to the gold substrate Fermi level (E_F). The work function was found to be 4.94 eV. The valence band maximum appears at 1.12 eV below the Fermi level corresponding to an ionization potential of 6.0 eV.

Figure 5: **a)** Electronic levels of (CH₃NH₃)₃Bi₂I₉ measured by UPS and PESA. Conduction bands of TiO₂ is literature accepted value while spiro-MeOTAD was measured by PESA. **b)** Tauc plots of (CH₃NH₃)₃Bi₂I₉ single crystal, powder and thin film deposited from GBL/DMSO solution by ASAC and SVC methods. From the onset of the plots they were estimated band-gaps single crystal, powder and thin film.

Figure 6: a) Diffuse reflectance reported as Kubelka-Munk function $F(R)$ and PL spectra of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ thin film deposited on glass substrate. The blue arrow indicates the shoulder where the SVC film starts to have a single crystal-like absorption. The star at ~ 900 nm indicates a weak peak probably due to defects states. The PL spectrum was acquired from a single crystallite using a 473 nm laser as excitation source. The center peak position is not affected by the crystallite orientation (hexagonal crystals) while the peak intensity is, due to the surface orientation and roughness. b) Surface Photovoltage Spectroscopy of $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ incomplete devices and External Quantum Efficiency spectrum of FTO/ TiO_2 / $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ /spiro-MeOTAD/Au device.

Figure 7: Current to voltage curve of the ITO/ $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ /Au device reported in double logarithmic scale.

Figure 8: J/V characteristic of a typical FTO/TiO₂/(CH₃NH₃)₃Bi₂I₉/spiro-MeOTAD/Au device.

Atom	Site	x	y	z	SOF	U _{iso}
Bi	4f	1/3	2/3	0.3449(1)	1	0.0409(7)
I(1)	12k	0.6673(5)	0.8336(2)	0.4187(1)	1	0.076(1)
I(2)	6h	-0.0036(6)	0.4982(3)	1/4	1	0.0578(9)
N(1)	4f	1/3	2/3	0.606(9)	1	0.226(3)
C(1)	4f	1/3	2/3	0.539(9)	1	0.368(3)
N(2)	2b	0	0	1/4	1	0.263(1)
C(2)	4e	0	0	0.1825(5)	0.5	0.253(3)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Bi	2U ₁₂	2U ₁₂	0.037(1)	0	0	0.0214(4)
I(1)	0.071(2)	2U ₁₂	0.072(1)	2U ₁₃	0	0.045
I(2)	0.054(1)	2U ₁₂	0.057(1)	0	0	0.0302(6)
N(1)	2U ₁₂	2U ₁₂	0.226(4)	0	0	0.113(1)
C(1)	2U ₁₂	2U ₁₂	0.368(4)	0	0	0.184(1)
N(2)	2U ₁₂	2U ₁₂	0.263(2)	0	0	0.1314(7)
C(2)	2U ₁₂	2U ₁₂	0.253(4)	0	0	0.127(1)

Table 1: Atomic coordinates, occupancies with isotropic and anisotropic displacement parameters (Å²)