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Air Stable, High Efficiency, Pt-Based Halide Perovskite Solar Cells with Long Carrier Lifetimes

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ABSTRACT

The search for Pb-free perovskite materials continues with limited success to find a suitable replacement for Pb with outstanding optoelectronic properties. Here we report Pb-free inorganic halide perovskite Cs_2PtI_6 with excellent absorption coefficient, long minority carrier lifetime and optical bandgap of 1.4 eV. Atmospheric precursor based solution processing results in high quality Cs_2PtI_6 with absorption coefficient of $4 \times 10^5 \text{ cm}^{-1}$ for photon energies $> 1.5 \text{ eV}$ and high minority carrier lifetimes of $> 2 \text{ } \mu\text{s}$ indicating low defect density in the material. Superstrate *n-i-p* solar cells processed with the structure F:SnO₂/CdS/ Cs_2PtI_6 /carbon/Cu show promising device efficiency of 13.88%. These planar devices processed under atmospheric conditions show low V_{oc} deficit ($< 0.3 \text{ V}$) without any hysteresis in forward and reverse scans indicating low trap densities. Pt offers an excellent model system for replacement of Pb due to high atomic number, oxidation resistance and stability. Cs_2PtI_6 is an atmospherically stable phase under AM1.5G and 65 °C upto 1000 hours.

Organic-inorganic hybrid halide perovskite solar cells (HPSCs) have attracted immense attention because of excellent optoelectronic properties and record power conversion efficiency (PCE) has reached 25.2% from 3.8% within a few years.^[1-6] Despite the very high efficiency already attained by HPSCs (ABX_3 ; A = MA, FA, Cs; B = Pb, Sn; X=I, Br, Cl) resulting from high absorption coefficient and electron-hole diffusion lengths; toxicity of Pb and stability of these materials are veritable issues. Replacing MA^+ and FA^+ with PEA^+ , BA^+ , Cs^+ has shown to enhance the stability of hybrid perovskite solar cells against thermal and moisture related degradation.^[7-11] The superior optoelectronic properties of Pb-based halide perovskites are attributed to the inactive Pb 6s orbitals, and can be replaced by Ge^{2+} , Sn^{2+} , Sb^{3+} , Bi^{3+} , Cu^{2+} with inactive s orbitals. Replacement of Pb^{2+} with Sn^{2+} and Ge^{2+} seems to be a logical solution for addressing the toxicity issues and results in excellent optoelectronic properties such as high absorption coefficient, high hole mobility resulting

in PCE of 9.6% for (GA,FA)SnI₃ [12] and 7.9% for mixed (FA,MA)GeSnI₃ [13] and 7.11% for CsSn_{0.5}Ge_{0.5}I₃. [14] However, a major challenge for Sn and Ge based Pb-free perovskites is poor power conversion efficiencies as divalent Sn²⁺ and Ge²⁺ tend to oxidize into 4+ oxidation state, generating excessive defects (Sn and Ge vacancies), and resultant short carrier diffusion lengths. The 2D structure Cs₂SnI₆ has received attention as a more stable alternative to CsSnI₃ based halide-perovskites for photovoltaic applications due to stable Sn⁴⁺ oxidation state and the strong covalency of Sn-I bonds in the [SnI₆]²⁻ octahedral. [15-25] Cs₂PdBr₆, Cs₂TiBr₆, Cs₂AgBiX₆, CsGe_{0.5}Sn_{0.5}I₃, AgBiI₄, (MA,Cs,Rb)₃Sb₂I₉ have been shown to be unsuitable for PV applications due to many reasons such as bandgap > 2 eV, low minority carrier diffusion lengths, deep level defects, resulting in high V_{oc} deficit and poor PCEs. [26-34]

In this work, we report for the first time Pt-based photoabsorber, Cs₂PtI₆ which has been synthesized by atmospheric solution processing from CsI and PtI₄ precursors in a solvent mixture of dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and γ -butyrolactone (GBL). Cs₂PtI₆ crystallizes with sharp Bragg peaks corresponding to *Fm* $\bar{3}$ *m* spacegroup with bandgap of 1.4 eV, hole mobility of ~ 62.6 cm²/V.s and minority carrier lifetime of > 2 μ s. Preliminary superstrate *n-i-p* devices fabricated using CdS electron transport layer (ETL) show best PCE of 13.88% with use of ethylene diamine (EDA) treatment for Cs₂PtI₆ based devices, one of the best efficiency and open-circuit voltages for Pb-free perovskites. The cost of Pt can be considered prohibitive for photovoltaic applications, however, Pt provides an excellent model system for replacement of Pb.

Figure 1 illustrates schematically the precursor based solution process used for deposition of Cs₂PtI₆ perovskite thin-films. The vacancy ordered perovskite Cs₂PtI₆ is synthesized using doctor blade process in atmospheric conditions resulting in cubic crystals of the *Fm* $\bar{3}$ *m* space group. Figure 2a shows X-ray diffraction (XRD) pattern for thin-films prepared on glass with PtI₄ based precursors in a solvent combination of DMF:DMSO with and without EDA. Cs₂PtI₆ phase can also be processed PtI₂ precursor in a solvent combination of DMF:GBL, however, the best quality films

result from CsI + PtI₄ precursors in DMF:DMSO. Films deposited using CsI + PtI₂ precursor in DMF:GBL results in ordered tetragonal and cubic Cs₂PtI₆ phase (ICDD 04-011-1068) as determined by splitting of (222), (400), (440), (622) peaks. The unit cell parameter is estimated as 8.3 Å in the *Fm* $\bar{3}$ *m* space group in good agreement with the structural data and the films exhibit a preferred orientation with enhanced {111} peak intensities. Due to the solutes used, it is expected that the DMF:GBL sample with PtI₂ based precursor has excess platinum in addition to Cs₂PtI₆ phase, which is confirmed by the high-intensity 39.7 degrees peak indicating preferred orientation along (511) for Cs₂PtI₆ or (111) Pt peaks. Pt can be expected as precipitates or interstitials, which may explain the lattice strain resulting in peak splitting. No preferred orientation is observed for PtI₄ based precursors in DMF:GBL, but these films showed poor adhesion and could not be used for characterization or device fabrication. With the use of DMF:DMSO solvent mixture with PtI₄ results in well-crystallized Cs₂PtI₆ structure as determined by the (111), (200), (220), (222), (400), (440), (622) peaks. No residual CsI or PtI₄ peaks are observed in XRD for Cs₂PtI₆, however, the peak doublets indicate lattice strain and can be fitted to the tetragonal and cubic standard patterns for Cs₂PtI₆. Composition of the thin-films determined by electron dispersive spectroscopy (EDS) and X-ray phototelectron spectroscopy (XPS) are in agreement with 15-19 at.% Cs, 9 at.% Pt, 45-58 at.% I, ~ 5 at.% Cl, and residual 25 at.% of O, C, K. ToF-SIMS data also confirms presence of Cl well intermixed with I as shown in inset of Figure 2b. EDS, XPS and ToF-SIMS data indicate presence of chlorine in films prepared with PtI₄ based precursors which is an impurity in PtI₄ solutes (99.95% metal basis). Figures 2c-e show top-down and cross-sectional scanning electron microscopy (SEM) micrographs for Cs₂PtI₆ films. For films deposited without EDA post-treatment a large density of pinholes is observed, but the use of EDA results in surface recrystallization. Further improvement in morphology and reduction of pinhole density will be needed to develop high quality polycrystalline films. Iodides of PPA (3-phenyl-2-propen-1-amine) additives have shown to assist the growth of uniform grains and passivation of grain boundaries. ^[35, 36]

Figure 3a shows the absorption coefficient vs. wavelength plots and steady-state photoluminescence (PL) emission spectrum for films prepared using PtI_4 based precursors in DMF:DMSO solvent mixtures with and without EDA. UV-Vis-NIR spectroscopy and Tauc plot analysis shows direct bandgap of 1.36-1.4 eV and possible indirect optical bandgap of 1.3 eV. The films also show high absorption coefficient at bandedge and high minority carrier lifetime as measured by TRPL. Bandgap of these films was also confirmed by photoluminescence measurements which show emission peak at 878 nm for Cs_2PtI_6 films which slightly smaller than predicted with density functional theory (DFT) results for Cs_2PtI_6 reported by Cai et al.^[37] of 1.463 eV and 1.472 eV for cubic and tetragonal phases calculated using hybrid HSE06 functionals. The intensity of the PL peak for Cs_2PtI_6 suggests direct nature of the bandgap as also predicted by DFT calculations. Figure 3b shows the minority carrier diffusion lifetime as determined by TRPL of 2.832 μs and 2.693 μs for Cs_2PtI_6 films with and without EDA. The improvement in the carrier lifetime resulted in devices with improved fill-factor (FF), also evident by high carrier collection in quantum efficiency curves. The absorption coefficient of Cs_2PtI_6 is repeatably measured as $4 \times 10^5 \text{ cm}^{-1}$ at photon energy $> 1.5 \text{ eV}$ which is higher compared to MAPbI_3 films.^[5] UV-Vis-NIR spectroscopy measurements conducted on liquid precursors indicates PtI_4 based precursors in DMF:DMSO shows adduct formation with Lewis base DMSO but upon annealing Pt^{4+} results in formation of Cs_2PtI_6 . In order to further confirm the structure of Cs_2PtI_6 , Raman spectroscopy measurements were conducted using 532 nm laser on Cs_2PtI_6 films deposited on glass. We observe sharp Raman peaks at 154 cm^{-1} , 175 cm^{-1} , 313 cm^{-1} , 343 cm^{-1} , and 474 cm^{-1} as shown in Figure 3c.^[38-41] The highest frequency longitudinal optical (LO) phonon mode expected for these ABX_3 and A_2BX_6 perovskite structures is at 375 cm^{-1} , and peaks below this can be assigned to symmetric and asymmetric bending and stretching of Pt-I bond and 474 cm^{-1} translational optical (TO) mode associated with vibrations in PtI_6 octahedra.^[41] The high minority carrier lifetime and high absorption coefficient for Cs_2PtI_6 are very encouraging and present a potentially stable Pb-free perovskite material with tunable bandgap for photovoltaic and other optoelectronic applications.

The calculated band structure of Cs_2PtI_6 shows that the material can exhibit both indirect and direct bandgaps with valence band derived primarily from I p states, and conduction bands derived from hybridized Pt d and I p states. These calculations suggest that the conduction band minimum (CBM) is slightly shifted in k -space with respect to valence band maximum (VBM), making the fundamental bandgap indirect. However, the experimentally observed high absorption coefficient indicates Cs_2PtI_6 behaves as a direct-bandgap semiconductor, where absorption and emission of photons occur via allowed transitions, but at the same time recombination rate is much slower, similar to MAPbI_3 solar cells. In MAPbI_3 , this behavior has been attributed to the dipole moment of the organic cations in tetragonal and cubic crystal phases or due to spin-orbit-coupling (SOC) effects in Pb. With the absence of organic cation in Cs_2PtI_6 , SOC in Pt is a likely cause of indirect bandgap, although there is no clear evidence of split of conduction band due to Rashba splitting from our preliminary DFT calculations. Further experiments with temperature dependent TRPL and a rigorous analysis of absorption spectra may be needed to determine if the photo-excited carriers undergo a phonon-assisted recombination pathway.

To get more insight into the high absorption coefficient of Cs_2PtI_6 compared to MAPbI_3 , atomistic calculations were conducted using the ASE and GPAW codes and using the GLLBSC exchange correlation functional that has demonstrated very good results, comparable to many body and hybrid functionals methods, for the calculations of the electronic properties. Figure 4b shows the band structure and projected density of states for Cs_2PtI_6 , calculated by means of Density Functional Theory (DFT). It has a direct band gap of 0.85 eV calculated for the structure at the experimental lattice parameters. This value underestimates the experimental band gap and the values reported by Cai et al. ^[37] that were calculated with the hybrid functional HSE06, although, for structures with slightly overestimated lattice parameters. The Projected Density of States (PDOS) shows that the valence band is mainly composed of I- p states, and the conduction band of Pt- d states hybridized with I- p orbitals. Comparing PDOS of Cs_2PtI_6 and MAPbI_3 (Figure 4a), we

note that the former is mostly formed by Pt-*d* and I-*p* states at the band gap edges, while the latter Pb-*p* and I-*p* states. The strength of the *d-p* transition of Cs₂PtI₆ compared with the *p-p* transition of MAPbI₃ might be the reason why the absorption coefficients of the former is higher than the ones of the latter. The calculated absorption spectra for these materials confirm these findings, although it starts later, the absorption of for Cs₂PtI₆ is steeper, as shown in Figure 4c.

To assess the photovoltaic properties of Cs₂PtI₆, we fabricated planar superstrate *n-i-p* devices with the structure glass/F:SnO₂/CdS/Cs₂PtI₆/carbon/Cu. As XPS analysis showed some surface oxides, an EDA treatment was used on some devices before the application of the carbon paste. Figure 5a shows the current density vs. voltage (J-V) characteristics in dark and under AM1.5 simulated solar spectrum at 1000 W/m² at 25 ± 2 °C. Cs₂PtI₆ show high open circuit voltage (V_{oc}) 1.07 V and 1.2 V with and without EDA, and a short-circuit current density (J_{sc}) of ~ 20 mA/cm² corresponding to a maximum EQE of 65%. These devices show low V_{oc} deficit which agrees well with low radiative recombination also determined by the high minority carrier diffusion length. With the use of EDA an improvement in FF is observed indicating passivation of grains and pinholes. A decrease in V_{oc} of about 100 mV is also observed with the use of EDA, which is within the standard deviation of the data. The EQE spectrum shows integrated current density (Int. J_{sc}) of 17.9 mA/cm² and 18.8 mA/cm² for devices with and without EDA. These integrated J_{sc} values are smaller than J_{sc} estimated by JV measurements indicating voltage dependent current collection due to photoconductivity of ETL. EQE curves show band edge at 840- 860 nm agreeing well with UV-Vis determined absorption edge and PL bandgap. The low FF for the devices can be attributed to the high series resistance estimated as ~ 14 ohm cm² for champion device and light-dark JV curve crossover in forward bias. Further reduction of pinhole to improve film quality and reduction in perovskite layer thickness should result in improvement of the fill-factor (FF). As shown in Figure 3, the EDA treatment slightly improved the carrier lifetime which can also contribute to the improvement in device FF due to improved carrier collection. It should be noted however, the

difference in carrier lifetime may be due to sample-to-sample variation and other factors such as reduced parasitic resistance can also contribute to improved FF. Better quality and stable electron transport layer (wider bandgap than CdS) may be needed to improve J_{sc} by allowing transmission of more blue photons. The overall EQE improvement can also be expected by improvement of film quality in particular reduction of deep trap states, film thickness and interface recombination. Better quality electron and hole transport materials, reduction in perovskite thickness and improved film quality, can improve PCE further for Cs_2PtI_6 devices. Note that no hysteresis in forward and reverse scans was observed in these devices. Device performance data from 10 different devices of each type is shown in Figure 5c. The best device efficiencies for Pb-free materials are reported for $CsGe_{0.5}Sn_{0.5}I_3$ and $(PEA,FA)SnI_3$ as close to 10%, therefore, these Pt based materials clearly offer potentially stable and Pb-free alternatives to existing $(FA,MA,Cs)Pb(I,Br)_3$ devices.

Halide perovskites are known for low formation and decomposition energies, therefore we tested the thermal stability of Cs_2PtI_6 phase prepared by solution process using differential scanning calorimetry. Figure 6a shows the DSC data collected on Cs_2PtI_6 pellets with decomposition between 525 °C - 575 °C, significantly higher than 130 °C for $MAPbI_3$.^[36] Cs_2PtI_6 films were also exposed to AM1.5 G at 65 °C for 1000 hours with UV-Vis and XRD measurements to determine the bandgap and structure thereafter. Figures 6b and 6c shows no change in the absorbance data or the Cs_2PtI_6 diffraction peaks. Devices tested under AM1.5 G at 65 °C for 500 hours shows a decrease in V_{oc} and FF due to device shunting as shown in Figure 6d. The shunts are expected to develop due to pinholes in the Cs_2PtI_6 films and can be improved with film quality. These device improvements and detailed device stability analysis will be discussed elsewhere.

In summary, we have reproducibly created high quality thin-films of Pb-free perovskite Cs_2PtI_6 via atmospheric solution process with experimentally determined bandgap of ~ 1.4 eV. Cs_2PtI_6 crystallizes in a cubic crystal structure with the space group $Fm\bar{3}m$, with a lattice parameter of about 8.3 Å with high {111} peak intensities. SEM analysis shows well-formed micron-sized

crystallites with improved film density with the use of ethylene diamine treatment. These atmospherically processed films contains low oxygen levels (mostly surface CsO_x) and Cl impurity from PtI_4 precursors as determined by EDS, ToFSIMS and XPS. Cs_2PtI_6 shows enhanced stability and excellent optical absorption, hole mobility and minority carrier lifetimes. Generally, the Pb-free perovskites have substituted Pb^{2+} with homovalent Sn^{2+} in AMX_3 structures, resulting in a stability issue due to conversion to Sn^{4+} . The layered perovskite variant A_2BX_6 structures are an interesting alternative with improved stability due to the strong covalency of the $[\text{BX}_6]^{2-}$ clusters. However, no Pb-free perovskite material has yet shown a combination of high optical absorption and minority carrier diffusion lengths $> 1 \mu\text{m}$ like MAPbI_3 . For the first time we have demonstrated a Pb-free halide perovskite material, Cs_2PtI_6 , with high absorption coefficient compared to MAPbI_3 and minority carrier lifetime $> 2 \mu\text{s}$. The high absorption coefficient in Cs_2PtI_6 results from the stronger d - p transitions as compared to the p - p transitions in MAPbI_3 . The combination of high absorption coefficient and high minority carrier diffusion lifetime in Cs_2PtI_6 suggests presence of direct-indirect transition behavior similar to MAPbI_3 , perhaps due to high Z of Pt. Superstrate n - i - p devices with FTO/CdS/ Cs_2PtI_6 /carbon/Cu have been reported for the first time, with maximum PCE of 13.88% and low V_{oc} deficit. Further improvement in device efficiency is envisioned with the improvement of Cs_2PtI_6 film quality and better selection of ETL and HTL materials. It is noted that cost of Pt-based precursors is higher compared to Pb-based precursors,^[42] however, Pt offers a model system for Pb-free perovskite materials and may offer a pathway to ultra-thin wide bandgap top cells for tandem solar cells. The key advantages of Cs_2PtI_6 over MAPbI_3 include high stability, absorption coefficient, minority carrier lifetimes and tunable bandgap for applications beyond photovoltaics such as water splitting, photocatalytic CO_2 reduction, and other optoelectronic devices.

EXPERIMENTAL AND THEORY SECTION

Cs_2PtI_6 films were fabricated through precursor-based solution processing (Figure 1) in atmospheric conditions. 0.25 - 0.4 M solution of Cesium Iodide and Platinum (IV) Iodide (Alfa-Aesar CAS: 7790-46-7) solutes with a molar ratio of 1:1 was prepared in DMF and DMSO (Sigma-Aldrich CAS 68-12-2 and 67-68-5) and 50-50 volumetric mixtures thereof. The precursor solution was mixed at 80 °C for 2.5 hours, drop casted and spread using a doctor blade technique onto pre-heated glass substrate at 70 °C. The substrates were then annealed in a vacuum oven at -15 in Hg and 100 °C for one hour. An ethylene diamine (EDA) spray treatment was applied on some films followed by a 100 °C anneal in vacuum for 30 min. Film samples were stored in a nitrogen filled glovebox after annealing before further device processing. X-ray diffraction measurements were carried out on a Bruker diffractometer under ambient conditions using $\text{CuK}\alpha$ radiation. Vesta was used to create crystal structure and PDF-4 was used for X-ray diffraction data analysis and phase identification. Optical transmittance and reflectance measurements were performed using Shimadzu UV-2600 spectrophotometer followed by a Tauc analysis to determine optical bandgap of the thin-film samples on glass. Devices with area of 0.25 cm² were processed on F:SnO₂ (FTO) and chemical bath deposited (CBD) cadmium sulfide (CdS) followed by perovskite absorber deposition, annealing at 100 °C for one hour. Carbon paste ElectroDAG 440B from Acheson followed by annealing at 100 °C for one hour. In some films ethylene diamine (EDA; 1, 2- Diaminoethane; Sigma Aldrich CAS Number 107-15-3) was sprayed and annealed before application of carbon paste. The front contact was formed by indium paste and the back contact was formed by Cu tape attached to the carbon paste. For CdS deposition, a mixture of 22 ml of 0.015 M CdSO_4 , 28 ml of NH_4OH in 150 ml of deionized water was heated to a temperature of 65 °C, Tec10 glass was submerged for 1 minute and 22 ml of 0.75 M Thiourea was added and additionally stirred for 12 mins, with an expected CdS thickness of 80-100 nm. The sample was then dried with N_2 flow and annealed in ambient on a hot plate at 120 °C for 5 mins to get rid of residual H_2O . Current-voltage characteristics were measured using an ABET solar simulator calibrated to 1 sun and a Keithley 2400 sourcemeter with a 10 mV step size. The external quantum efficiency (EQE) spectra were

obtained using QE XL+ tool from PV Measurements Inc. consisting of a xenon lamp, a monochromator, a lock-in amplifier, and calibrated Si and Ge photodetectors. For quantum efficiency, the integrated quantum efficiency (IQE) or integrated J_{sc} was solved via

$$IQE = \int_{\lambda_{start}}^{1200\text{ nm}} \frac{q\lambda}{hc} \left(\frac{QE}{100} \right) E_{0,AM1.5}(\lambda) d\lambda \quad (1)$$

with E_0 , AM1.5 as the AM1.5G spectral irradiance, QE as the quantum efficiency, and q as the elementary unit charge.

Raman spectra were measured using WiTec Laser Confocal/Raman Microscope with 532 nm laser. Lateral and depth distribution of the films were measured by TOF-SIMS profiling, and 3D imaging using an ION-TOF ToF-SIMS V instrument. Dual-beam depth profiling was completed with a $150 \times 150 \mu\text{m}^2$ primary-beam area, and a $500 \times 500 \mu\text{m}^2$ sputter-beam raster. A 30 keV Bi^{1+} beam was used as an analysis beam, which was scanned on the center of the sputtered crater. A 1 keV O^{2+} beam or a 2 keV Cs^+ beam was used as a sputter beam with beam current of 255 nA and 157 nA, respectively. Photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements were conducted at Molecular Foundry using a setup built around a Nikon Eclipse Ti-U microscope with 0.3NA objective. For one photon excitation a 405 nm nanosecond pulsed laser system (Thorlabs NPL41B, 6ns pulse width, 1MHz repetition rate) has been used and PL was filtered with 540nm and 532nm long-pass filters.

Density Functional Theory (DFT) calculations were performed to clarify the electronic properties of Cs_2PtI_6 in comparison with MAPbI_3 . All calculations were performed using the GPAW code [43,44] and the Atomic Simulation Environment (ASE). [17] In order to obtain reliable results, we have calculated the electronic properties using the GLLB-SC functional [45] with a density of 5 k-point/Å and the spin-orbit coupling correction. This functional includes an estimation of the derivative discontinuity and has shown good accuracy with respect to more sophisticated methods and

experimental values.^[46-48] Details about the methodology used to calculate the absorption spectrum can be found here.^[49, 50]

KEYWORDS

Cs₂PtI₆; halide perovskite solar cells; Air stable; Pb-free; stability.

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Figure 1. Schematic of atmospheric solution processing of Cs₂PtI₆ (E_g ~ 1.4 eV) from precursors based on CsI and PtI₄ prepared in solvent mixtures of DMF:DMSO by doctor blade or spin coating process. The use of ethylene diamine (EDA) treatment results in recrystallization of Cs₂PtI₆ resulting in formation of polycrystalline films with lesser density of pinholes.

Figure 2. a) X-ray diffraction data for Cs₂PtI₆ films on glass with y-axis as XRD intensity in CPS or counts per second. The intensity has been offset on Y-axis to about to clearly represent the data. b) Depth dependent ToF-SIMS concentration profiles and insets of 3-d renderings for Cl, I, Pt and Cs for thin-films prepared using PtI₄ based precursors in solvent mixture DMF:DMSO. Data presented as intensity of the elements on y-axis and sputter time through film thickness on x-axis. c-e) Top-down and cross-sectional SEM images for thin-films prepared with PtI₄ based precursors in solvent mixtures of DMF:DMSO identified as Cs₂PtI₆, image (d) is after EDA treatment. Average film thickness of 10-15 μm has been obtained by doctor-blade process.

Figure 3. (a) UV-Vis absorption coefficient and PL emission spectra, (b) TRPL decay curves to determine minority carrier lifetime and (c) Raman spectra for Cs_2Ptl_6 perovskite thin-films deposited on glass.

Figure 4. (a, b) Band structures and Projected Density of States (PDOS) for Cs_2PtI_6 (left) and MAPbI_3 in the cubic symmetry (right). Compared with MAPbI_3 , Cs_2PtI_6 has a smaller band gap, a conduction band formed by an hybridization of Pt-d and I-p state, and it does not show a split of the conduction band due to the Rashba splitting. Spin Orbit Coupling (SOC) corrections are also different as for MAPbI_3 it counts for roughly 1 eV, while for Cs_2PtI_6 only for around 0.15 eV. The work function for Cs_2PtI_6 with termination (111), which is the most common surface for these materials as shown from XRD and SEM can be obtained from the “potential versus vacuum” and it is equal to 4.8 V. (c) Absorption spectra for Cs_2PtI_6 and cubic MAPbI_3 . The absorption strength at the first excitation is larger for Cs_2PtI_6 than cubic MAPbI_3 . The arrows indicate the band gap for the two materials.

Figure 5. (a) Device stack for thin-film superstrate *n-i-p* devices fabricated in this study F:SnO₂ (FTO)/CdS/ Cs_2PtI_6 /Carbon/Cu and estimated band alignments (b) Dark and light current density – voltage (JV) curves with table showing device power conversion efficiency (PCE), open circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill-factor (FF) for best Cs_2PtI_6 devices prepared with and without EDA treatment. (c) PCE, V_{oc} , J_{sc} , FF distribution for 10 best devices of each type fabricated (c) External quantum efficiency (EQE) and Integrated J_{sc} (mA/cm²) for Cs_2PtI_6 devices prepared with and without EDA treatment.

Figure 6. (a) Differential scanning calorimetry thermal profiles for Cs_2Ptl_6 pellets prepared from the powder using the thin-film process described experimentation section (b) UV-Vis absorbance vs. photon wavelength and (c) XRD diffraction pattern for Cs_2Ptl_6 thin-films on glass before and after accelerated stress test (AST) at 65 $^{\circ}\text{C}$ and AM1.5G solar spectrum in air for 1000 hours. The intensity of 1000 hrs data has been offset to clearly represent the data. (d) Dark and light current density – voltage (JV) curves with table showing device power conversion efficiency (PCE), open circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill-factor (FF) for a representative Cs_2Ptl_6 device before and after 500 hours of AST at 65 $^{\circ}\text{C}$ and AM1.5G solar spectrum in air.

Cs₂PtI₆ with bandgap of 1.4 eV is shown to be promising Pb-free material for perovskite solar cells. These thin-films show a carrier lifetime of $> 2 \text{ ns}$, absorption coefficient of $4 \times 10^5 \text{ cm}^{-1}$, and superior thermal and atmospheric stability. A superstrate planar n-i-p device with an efficiency of 13.88% and low Voc deficit is demonstrated by solution processing.