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Triple-cation absorber layer for efficient and stable perovskite solar cell

5.1 Broad context

Issues related to the long-term stability and performance of the absorber layer are some of the major stumbling blocks for the commercialization of perovskite solar cells (PSCs). Unfortunately, pure perovskites $MAPbX_3$ and $FAPbX_3$ (X =Br or I) or mixed MA/FA and mixed halide compositions are sensitive to moisture and processing conditions. It often tends to form impurity phases such as PbI_2 and other polymorphs, which in turn act as nucleation sites for decomposition. The perovskite films are likely to degrade over time upon exposure to moisture, illumination and heat. The presence of small amounts of inorganics A cation such as Cs (caesium) improves thermal and structural stability, and restrict the formation of impurity phases. Benefiting to triple cation (TC) system $CsFAMAPbI_3$ as the absorber layer is utilized for PSCs. TC perovskite has restricted the formation of an undesired delta and PbI_2 impurities and thus improved phase, structural and thermal stability of perovskite layer [85]. Meanwhile, the TC based PSCs realized PCE close to 18.6% and maintained 65% of its efficiency after aging for 1000 h at 70° C kept in the vacuum oven.

5.2 Introduction

Pure hybrid perovskite PV absorber layers (such as $MAPbX_3$, $FAPbX_3$ and $CsPbX_3$ (X = Cl, Br or I)) have several drawbacks including structural, phase and thermal instability and cause degradation in the presence of moisture, air and heat [178].

Methyl ammonium lead iodide $MAPbI_3$, is the earliest and most studied formulations for PSCs. Goldschmidt's tolerance factor (t=0.91) suggests that at room temperature $MAPbI_3$ exists in the tetragonal phase (space group *I4cm*) with ionic radii of Pb^{2+}=0.132 nm, I^-=0.206 nm, and MA^+= 0.18 nm. The PbI_6 octahedra in $MAPbI_3$ are corner connected and the MA^+ cations are filled in the octahedral interstices [179,180]. $MAPbI_3$ shows a transition from tetragonal to cubic (or pseudo cubic) symmetry when heated above 55 °C [56]. $MAPbI_3$ have high sensitivity to environmental conditions due to the hydrophilic nature of organic MA cation. Due to its hydrophilic nature, contact with moisture and exposure to light induces trap-states, leading to degradation of cell performance [51].

Formamidinium lead iodide $FAPbI_3$ is characterized by a reversible phase transition between two polymorphs, a black or alpha (α phase) perovskite with trigonal symmetry (space group $P3m1$) forms at higher temperatures, ∼125−165 °C, while a yellow or delta (δ-phase) having a non-perovskite hexagonal symmetry ($P6_3mc$) exists at room temperature [57]. Black or alpha phase contains linear chains of $[PbI_6]$ octahedral with face-sharing, while the non-perovskite delta or yellow phase consists of a 3D network of corner-sharing octahedra [51]. Yellow or the delta phase is considered to have a large optical bandgap (E_g) and poorer charge-transport ability because of the linear chain-like $[PbI_6]$ octahedron structure, this unintentional phase transition in $FAPbI_3$ lowers the PV performance. Lately, inorganic cesium lead triiodide ($CsPbI_3$) perovskites have been explored significantly for its promising thermal stability. However, its large band gap (E_g) (~1.73 eV) makes them unsuitable for PV applications and it shows similar polymorphism, where α and δ-$CsPbI_3$ phases were reported and the photoactive α-$CsPbI_3$ is unstable in the ambient condition [58].

Earlier reports suggest that the compositional engineering *i.e.* mixing of A cation (MA^+, FA^+, Cs^+), B cations (Sn^+, Pb^+) and X anions (I^-, Br^-, Cl^-) has been projected as an efficient way to tune the properties of perovskites and enhance the performance of PSCs. The mixing of the A cations is the most commonly employed method in compositional engineering [83,84]. The recent success of the MA/FA mixtures demonstrates that a small amount of MA is sufficient to induce a preferable crystallization into the photoactive phase of FA-based perovskite resulting in a greater stability when compared to the pure MA or FA-based compounds. As mentioned in Chapter 3, the incorporation of a smaller cations (MA^+) with a large dipole moment (MA^+ has ten times higher than that of (FA^+) exhibits stronger interaction with the PbI_6 octahedra, which stabilizes the 3D arrangement of α-$FAPbI_3$ with slight lattice shrinkage or changes in the optical properties [181,182]. However, even with addition of MA in FA, it is still challenging to avoid the yellow phase, it is often detrimental to achieve high efficiency of PSCs [55,183]. The presence of yellow phase impurities is unfavourable for the performance of the devices as it influence the crystal growth and morphology of the perovskite inhibiting efficient charge collection [184]. Recently, addition of inorganic cesium (Cs^+) with an ionic radius of 1.81 Å, which is considerably smaller than MA (2.70 Å) or FA (2.79 Å) and Cs^+ that has no dipole moment and partial substitution of FA^+ by Cs^+ leads to the contraction of the cuboctahedral volume, shifts the tolerance factor close to 1 forming a more stable α-phase, leading to better stability in the PSCs. Moreover, addition of small amount of Cs effectively suppress yellow phase or delta phase impurities resulting in pure, defect-free perovskite films [85,185].

Herein, triple cation perovskite system $CsFAMAPbI_3$ were utilized to avoid phase segregation and improve the structural and thermal stability. The improvements made are due to the control of trap state density without altering the morphology and the optical properties of films as well as the addition of more thermally stable cations in the perovskites. PSC based on TCs perovskite is fabricated on bigger substrate with an active area 0.06 cm^2, the thermal stability was explored for 1000 hours at 70°C in the vacuum oven.

5.3 Experimental

TiO_2 was deposited on FTO coated glass substrates by spray pyrolysis as mentioned in Chapter 2 [122]. The triple cation (Cs/FA/MA) perovskite solution ($Cs_{0.1}FA_{0.15}MA_{0.75}PbI_3$) was prepared by mixing 26 mg of cesium iodide (CsI, Sigma Aldrich, 99%) 26 mg of formamidinium iodide (FAI, Great cell solar), 119 mg of methylammonium iodide (MAI, Great cell solar), and 461 mg lead iodide (PbI_2, Sigma Aldrich, 99%) in mixture of DMSO and DMF (in 1:4 ratio). The solution prepared was spin coated using a three-step spin coating process: 500 rpm for 10 s, 1500 rpm for 15 s, and 3000 rpm for 30 s. during the last spin coating step, 100 μl CB (Sigma Aldrich 99.98%) was dripped as an antisolvent. The deposited perovskite film was then annealed at 100°C for 30 minutes on a hotplate [68]. Spiro-OMeTAD was used as HTL, 72.3 mg of Spiro-OMeTAD, 29 μL of TBP and 18 μL of Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile, 99.8%, Sigma-Aldrich) dissolved in 1mL of CB. The solution was spin coated at 4000 r.p.m for 30 seconds. and then finally gold electrode was deposited using thermal evaporation (detail in Chapter 2).

5.4 Result and discussion

Figure 5.1a-b shows the microstructure of triple cation ($CsFAMAPbI_3$) film on low and high magnification. **Figure 5.1a** shows the film is uniform, compact and absence of pinholes and cracks, although the grains and boundary separating the grains are hardly distinguished. It can be observed from the high magnified FESEM image (**Figure 5.1b)** that the perovskite film is uniformly covering without pinholes. The grains are large and compact with equiaxed morphology. The mean grain size is of the order of ≈600 nm. The uniform and complete coverage of the TiO_2 can be attributed to the greater wettability (measured contact angle ~37°) of perovskite solution, on TiO_2 substrate. A greater wettability favors a deposition of continuous precursor film which in turn favors the grain growth, while lower wettability hinders the grain growth and makes it more prone to discontinuities. Roughness of TiO_2 film also plays an important role in deciding the microstructure. A smooth film would allow lesser number of nuclei and favors large grained films, while on the other hand, a rough film would provide a greater number of nucleation sites resulting in small grained structure. Therefore, good wettability coupled with a smooth substrate surface favors the formation of desired large-grained compact films.

The X-ray diffraction (XRD) pattern confirm the formation of perovskite phase with tetragonal structure **Figure 5.1c** shows the major (110), (200), (211), (202), (220), (310), (312) and (224) reflections of the tetragonal perovskite structure are clearly observed at 14.05, 20.4, 24.9, 28.9, 32.5, 35.6, and 41.1°, respectively for the fresh samples [186]. Unlike, $FAMAPb(BrI)_3$ (Chapter 3) and $FAMAPbI_3$ (Chapter 4) perovskite absorber layer, the photo-inactive delta (δ) phase (hexagonal) and PbI_2 impurities at 11.06 and 12.40° were absent in the freshly prepared sample. This indicates that the addition of a small amount of Cs into the FA/MA mixed system restricts the phase segregation, improves the structural stability and suppresses the formation of yellow or delta phase [55,85,184]. The structural stability and suppression of the yellow phase can be rationalized by considering Goldschmidt's tolerance factor, which is larger than 1 for hexagonal δ-$FAPbI_3$. Compositional alloying of MA and Cs together in $FAPbI_3$ effectively reduces the tolerance factor close to 1 [187]. However, from the thermodynamic point of view, it is believed that the corresponding phase is more stable and thermodynamically favorable, which has lower formation energy. $FAPbI_3$ (Cs = 0%) has the lowest energy when it crystallizes in the form of a hexagonal structure; on the other hand, pure $CsPbI_3$ favors an orthorhombic structure. With the addition of Cs^+ in $FAPbI_3$, the formation energy of the hexagonal structure increases, while it decreases for the orthorhombic structure, which accurately describes the reason for the higher stability of the α-phase in mixed FA/Cs cation system. Another explanation for improved stability can also be specified by the concept of miscibility of $CsPbI_3$ and $FAPbI_3$ in the perovskite phase, it is shown that δ phases of $FAPbI_3$ and $CsPbI_3$ differ considerably in their atomistic structure and have different volume per stoichiometric unit: ($V\delta$-$FAPbI_3$ ≈ 256 $Å^3$ *vs.* $V\delta$-$CsPbI_3$ ≈ 222 $Å^3$) [188], while α and β perovskite $FAPbI_3$ phases are very similar to the perovskite phase of $CsPbI_3$, and have very close volume per stoichiometric unit ($V\alpha$-$FAPbI_3$ ≈ 256 $Å^3$ and $V\beta$-$FAPbI_3$ ≈249 $Å^3$ *vs.* $V\alpha$-$CsPbI_3$ ≈ 250 $Å^3$) [51]. This shows that the mixing of cations in the δ phase is not favorable, while it is highly favorable for α and β perovskite phases. Also, the energy contribution due to mixing in the δ phase is too huge to be compensated by the entropy of mixing, while in the α and β perovskite phases the addition of the energy and mixing entropy role leads to a decrease of the free energy, ensures the stabilization of the mixed 3D alpha perovskite phase over the δ phase.

When Cs and FA are mixed in solution, the perovskite phase forms directly, before the separated δ-phases can prevent mixing. Moreover, for mixed cation, the δ → α or β transition temperature is reduced by ≈200–300 K than for the pure $FAPbI_3$ which makes the perovskite phase stable at room temperature for the mixed Cs/FA system [189].

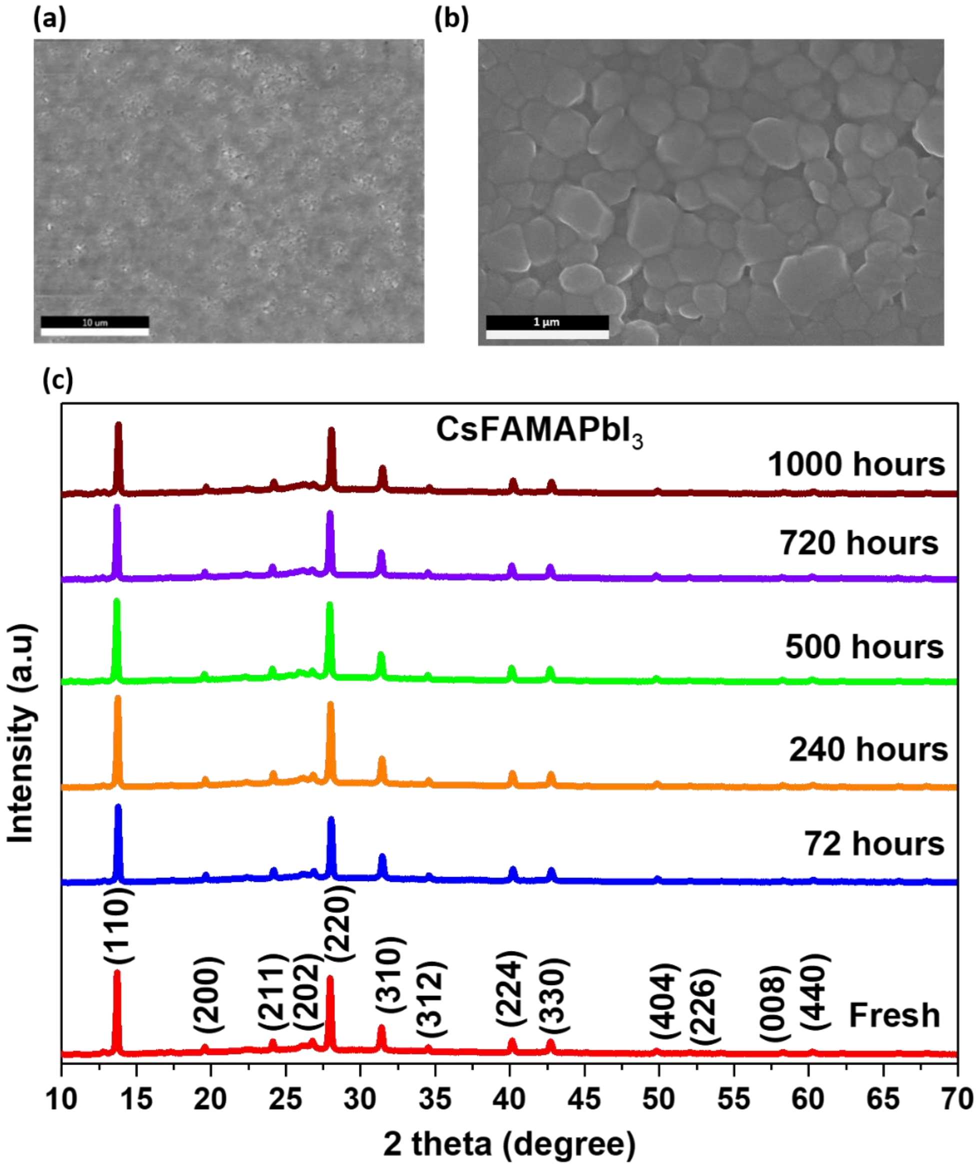

Figure 5.1 a) and b) SEM images of $CsFAMAPbI_3$ perovskite film on TiO_2, c) XRD showing the thermal stability of triple cation for 1000 hours.

Later, the samples were kept in a vacuum oven at 70°C and taken out at regular intervals for the XRD characterization to monitor the thermal stability for the next 1000 hours. After 1000 hours, there is no significant change in the intensity of major peaks, and also there is the absence of peak shifts, while there is no sign of delta and PbI_2 peak which confirms the structural as well the thermal stability of triple cation system (**Figure 5.1c**). The enhanced thermal and structural stability is attributed to the addition of Cs, an inorganic cation, which has superior thermal stability and is stable at temperatures above 300°C [58]. Also, the incorporation of Cs ions in FA-sites led to a contraction of cuboctahedral volume and thereby enhanced (FA–I) interaction, which was mainly responsible for the improved stability of $CsFAMAPbI_3$ [190].

UV-vis spectroscopy was utilized to characterize the optical absorption and to estimate the band gap of the deposited films. **Figure 5.2a** shows the absorbance while the inset shows the Tauc plot of perovskite films. The absorbance curve shows a sharp absorption edge nearly at 790 nm, indicating that $FAMACsPbI_3$ films strongly absorb almost entirely in the visible range while only partially absorbing in the near IR regime up to 790 nm. Considering the perovskite as a direct band gap material, the band gap of the absorber film is plotted in Tauc plot (inset of **Figure 5.2a**) and was calculated using **Equation 2.1** (Chapter 2). The calculated band gap was 1.57 eV which matched well with the previous reports [191]. The band gap (E_g) of $CsFAMAPbI_3$ is slightly wider when compared to the band gap of $FAMAPb(BrI)_3$ (E_g=1.53 eV) and $FAMAPbI_3$ (E_g=1.45eV) perovskite absorber layer described in Chapter 3 and 4, respectively. The increase in the band gap of triple cation is related to the stronger Pb–I interaction, which is also revealed by a reduction in lattice parameter [190]. In addition to crystalline structures, morphological defects or traps in perovskite films would also influence optical properties. Therefore, the steady-state photoluminescence (PL) spectra of triple cation perovskite layer coated on glass/TiO_2 substrate were characterized to study the photophysical properties of mixed cation. PL peak from the freshly prepared sample was observed at 780 nm (as shown in **Figure 5.2 b),** which matches well with the band gap of the $CsFAMAPbI_3$ (E_g=1.57eV) film indicating the band-to-band transition. The PL intensity of mixed cation perovskite film is intense suggesting lesser recombination and efficient charge transfer. To check the thermal stability of the triple cation perovskite absorber layer, coated films were kept in a vacuum oven at 70°C. The PL peak intensity of 720 hours old films was reduced significantly, at the same time, a slight blue shift in the PL peak was also observed. The PL peak shift (observed at 775 nm) indicates a slight change in the band gap while the drop in the intensity could be due to the decomposition or change in crystal structure to the lower symmetry [30,182]. Another reason for the decrease in intensity corresponds to an increase in non-radiative recombination, which can be caused by the degradation of the sample. It has also been observed that under illumination of perovskite film by laser creates trap states in the film [192].

Time-resolved PL (TRPL) was measured onto the glass/TiO_2 substrate to examine the recombination dynamics of the photo-excited states in triple cation films. PL decay curve (**Figure 5.2c**) for fresh and 720 hours old samples is fitted to a bi-exponential equation ($Y=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)$) [128]. The shorter decay time (τ_1~2.25 ns) manifests the filling of the trap states, while the longer decay time (τ_2~8 ns) is attributed to the radiative recombination of photo-generated carriers. The average lifetime ($\tau_{avg} \approx$5ns), calculated using **Equation 2.3** (given in Chapter 2), of the fresh sample and, similarly, the 720 hours old sample was fitted bi-exponentially. It has been noticed that there is a slight change in both shorter decay time (τ_1~1.5 ns) as well as in longer decay time (τ_2~9 ns), which brings change in average lifetime time close to $\tau_{avg} \approx$7 ns. This suggests the presence of defects in the film affects the photophysical properties and the charge extraction ability of ETL and also shows the recombination of photo-generated carriers, shown in the PL curve after 720 hours of storage **(Figure 5.2c).** Comparing both numbers, we can conclude that after storing the sample for 720 hours, there is a reduction in PL intensity that can be because of the presence of defects also increases the recombination and affects the charge extraction ability of ETL. It can be summarized from the XRD and PL curve that, both structural stability and photophysical properties of triple cation film behave differently. XRD shows that the films were structurally intact, while there is a significant drop in PL intensity which is due to an increase in non-radiative recombination the creation of trap states in the film and not because of the structural instability in the film. Thus, it shows that the thermal and structural stability of the triple cation $FAMACsPbI_3$ absorber layer.

Finally, PSCs were fabricated utilizing a triple cation absorber layer based on the planar n-i-p architecture comprising of $FTO/c\text{-}TiO_2/(CsFAMAPbI_3)$/spiro-OMeTAD/Au on 2.5cm x 2.5cm substrate (details in Chapter 2). The corresponding J-V Characteristics are shown in **Figure 5.2d**. The maximum PCE of 18.60% (V_{oc} = 1.09 V, J_{sc} = 27.28 mA cm^{-2} and FF = 62.18%) was achieved in the freshly prepared device. The device was kept for 1000 hours inside a vacuum oven at 70° C to check the thermal stability. PCE close to 12.2% (V_{oc} = 0.945V, J_{sc} = 22.50 mA cm^{-2} and FF = 57.30%) was obtained in stored PSC after 1000 hours. This indicated that the absorber layer was still intact and a cell still could be fabricated using the stored absorber layer. For comparison, the J-V curves of both cells are plotted in **Figure 5.2d**. As can be seen, the performance of triple cation perovskite degrades by 35% of the initial efficiency after 1000 hours. J_{sc} decreases by 20% of the initial value after 1000 hours, which could be due to lower light absorption caused by α-to-δ phase transition in the perovskite absorber. The degradation of FF may also be attributed to the increased amount of δ-phase which causes recombination as can be inferred from the PL results [187,190]. Triple cation ($CsFAMAPbI_3$) based PSCs retain 65% of their initial PCE after being stored at 70 °C for1000 h.

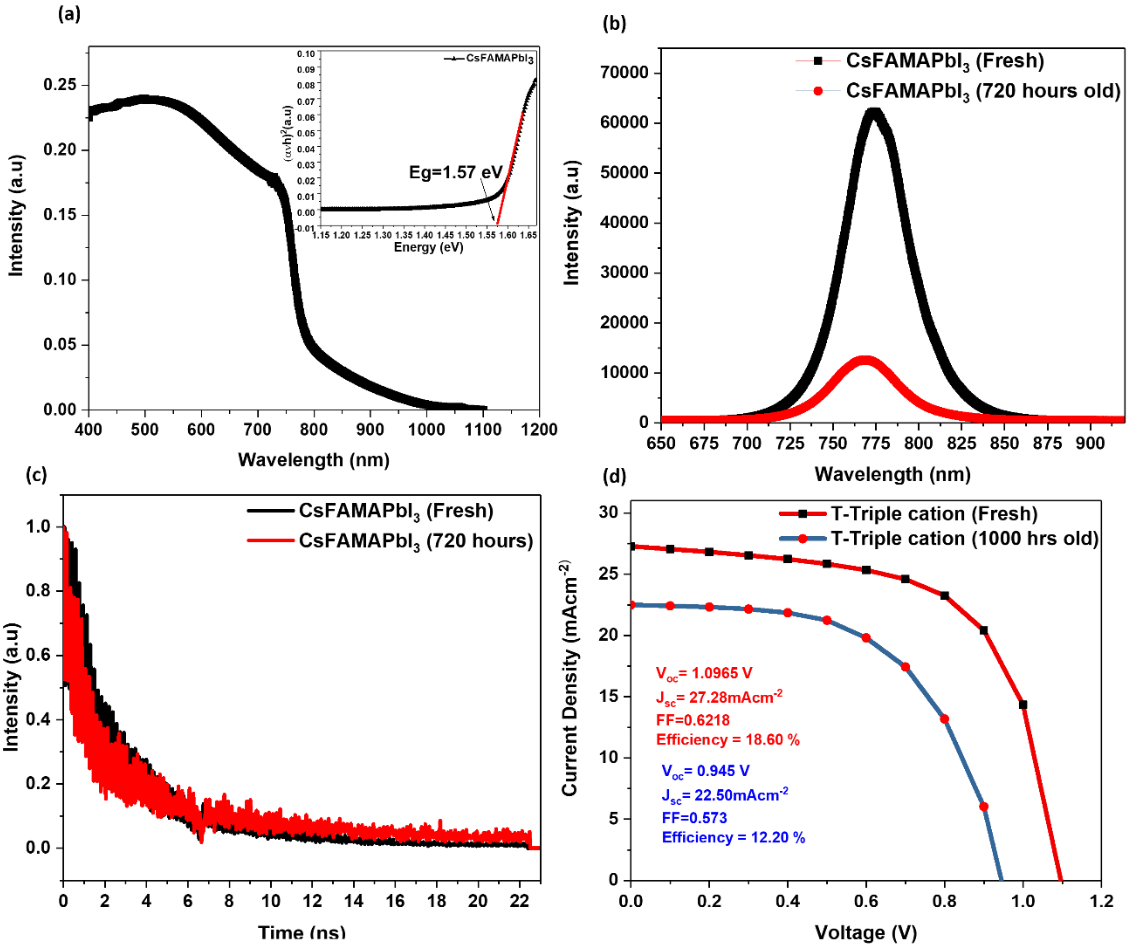

Figure 5.2 a) Absorbance and Tauc plot (inset) of TC perovskite, b) PL measurement of TC fresh (black) and 720 days old (red), c) life-time measurement of TC fresh (black) and 720 days old (red), d) J-V curve of TC fresh (red) and 1000 hours old (blue).

5.5 Conclusion

Mixing of three cations (FA, MA, and Cs) at A site of $APbI_3$ perovskite absorber layer is studied for improving stability and overall performance of PSC. The XRD shows the structural, phase and thermal stability of triple cation system for 1000 hours when stored at 70 °C. Addition of small amount of inorganic Cs cation along with FA/MA restricts the phase segregation, provides the thermal stability and suppress the photo-inactive delta or yellow phase. PL results of the triple cation shows that there is only minor instability in perovskite film, when kept in heat exposure for 720 hours. TRPL data also confirm the structural as well thermal stability of mixed cation perovskite layer by following the same trend for fresh and 720 hours old sample. Lastly, the PSC based on triple cation system shows the PCE of 18.60% and retains 65% of their initial PCE after 1000 hours. Overall, this work reveals that triple cation system is a viable approach for improving stability, to enhance device longevity through structural and thermal stability which contributes toward the rise in overall stability of PSCs.