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Suitability of K-doped $(CH(NH_2)_2)_x(CH_3NH_3)_{1-x}PbI_3$ Perovskite Absorber for Energy Harvesting

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Formamidinium lead iodide ($FAPbI_3$) based perovskite solar cells are more promising than methylammonium based counterparts due to their higher thermal stability. But $FAPbI_3$ film faces serious issue of photoactive phase instability at room temperature, hindering its usefulness as absorber in perovskite solar cells (PSCs). Recently, this problem has been well addressed through additive engineering. In this work, monovalent-cation engineering of $FAPbI_3$ perovskite via MA^+ (methylamine cation) and K^+ (potassium cation) mixing is performed. We present a detailed analysis of effect of cation doping on structural and optical properties of formamidine based perovskite material. The structural and optical characterizations show positive effect of cation mixing on phase stabilization, crystallization, and absorbance of perovskite thin films. The crystallite size is found to increase on doping with a maximum for $K_{0.05}(FA_{0.83}MA_{0.17})_{0.95}PbI_3$ sample. Also, the rise in absorbance in UV-Visible region of electromagnetic spectra is observed with doping.

Keywords: Perovskite absorber; Solar cells; Thermal stability; UV-Vis absorption

1 Introduction

Perovskite solar cell (PSC) technology is considered as photovoltaic technology for future and holds many promises upon its realization. The perovskite materials have gained much interest, being suitable as absorber layer material in the PSCs. Hybrid halide perovskite (HHP) materials are leading in terms of efficiency and ease of fabrication. The general perovskite structure is represented by a general formula ABX_3. Here, 'A' is mainly an organic or inorganic cation such as methylammonium (MA^+), formamidinium (FA^+), cesium (Cs^+), or their mixtures. 'B' is a divalent cation, such as lead (Pb^{2+}), and tin (Sn^{2+}) and 'X' is a halide anion, such as iodide (I^-), bromide (Br^-), and chloride (Cl^-).

Solar cell works in temperature range of 25-85 °C. The thermal stability of solar cell materials in this range is a must need to survive for a long time. $MAPbI_3$ material lacks in thermal stability due to weak bonding between organic part (CH_3NH_3) and inorganic part[1]. Replacing or partially substituting 'MA' part with stable organic and/or inorganic cations results in better thermal stability of the perovskite layer. The $FAPbI_3$ layer is more thermally stable than $MAPbI_3$, but it lacks moisture stability[2]. Also, $FAPbI_3$ has the problem of crystallization to yellow non-perovskite phase (δ-phase) at RT, which is not photoactive[3]. Researchers found that the substitution of a small amount of 'MA' at the A-site in $FAPbI_3$ material results in suppression of the yellow non-perovskite phase of $FAPbI_3$, and the material found to crystallize preferably into useful black perovskite phase[3]. The addition of cations such as Cs^+, K^+, and Rb^+ in the perovskite further enhances the material's stability and the solar device's performance[4]. K^+ addition has the advantage of hysteresis-less device with increased efficiency and stability[5–7]. In the present work, 'A'-cation engineering of 'FA' based material with 'MA' and 'K' substitution has been planned to perform. The effect of K-doping in $FA_{0.83}MA_{0.17}PbI_3$ thin films has also been aimed to check on its structural and optical properties.

2 Experimental methods

$FA_{0.83}MA_{0.17}PbI_3$ precursor solution was prepared by dissolving FAI (formamidinium iodide), MAI (methylamine iodide), and PbI_2 in DMF (dimethyl-

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formamide) such that $[(FAI)_{0.83} + (MAI)_{0.17}]$: PbI_2 retain 1:1 molar ratio and stirred for 24 hrs at room temperature. Similarly, $FAPbI_3$/$KPbI_3$ precursors were prepared by dissolving FAI-PbI_2/KI-PbI_2 salts in DMF in proper stochiometric ratio. All prepared solutions had a molarity of one molar. Potassium (K) doped precursor solutions, $K_x(FA0_{.83}MA_{0.17})_{1-x}PbI_3$ were prepared by mixing $KPbI_3$ and $FA_{0.83}MA_{0.17}PbI_3$ precursors in a volumetric ratio of 03:97, 05:95, and 10:90 for obtaining x = 0.03, 0.05, and 0.10, respectively. Cleaned glass substrates were used for thin film synthesis of various materials. Thin films of $FAPbI_3$, $FA_{0.83}MA_{0.17}PbI_3$, and $K_x(FA0_{.83}MA_{0.17})_{1-x}PbI_3$ (x = 0.03, 0.05, 0.10) were prepared by spinning their respective precursors on the glass substrates at spinning speed of 2000 rpm for 60 sec. Finally, the films were annealed at 150 °C for 5 minutes.

The XRD analysis of prepared samples was performed with Bruker D8 Advance apparatus. UV-Visible absorption data was obtained using Shimadzu UV-3600 Plus spectrometer.

3 Results and Discussion

In this work, samples $FAPbI_3$, $FA_{0.83}MA_{0.17}PbI_3$, and $K_x(FA0_{.83}MA_{0.17})_{1-x}PbI_3$ (x = 0.03, 0.05, 0.10) are abbreviated as FA, FAMA, K(3%), K(5%), and K(10%), respectively. The XRD plot of Fig. 1 shows that FA sample contains extra peaks at 2θ angle of 12.17°, 26.61°, and 33.22° which corresponds to δ-$FAPbI_3$ phase [3]. These peaks are not present in FAMA and K-dopped samples, which shows that MA and MA-K mixing results in successful suppression of non-perovskite δ-phase in $FAPbI_3$. All samples show peaks at angle ~ 14.3° (characteristic peak of α-$FAPbI_3$) and ~ 13° (characteristic peak of PbI_2)[3, 5]. However, the relative intensity of PbI_2 peaks in K-doped samples is higher, which can be attributed to more residual PbI_2 left in K-doped samples. It is observed that small PbI_2 residue could be useful for passivating defects inside perovskite and reducing non-radiative recombination[8]. But too excess of PbI_2 residue can induce series resistance and serious hysteresis that are detrimental for device performance[9]. The comparison of relative intensity of PbI_2 and perovskite α-phase peaks of K-doped samples at 13° and 14.3°, respectively, shows that highest PbI_2 residual is left in K(10%) followed by K(3%) and the K(5%) is with least residual PbI_2.

It is also observed that most of peaks of K(3%) sample are shifted toward lower angles as compared to that in FAMA, while peaks of K(5%) and K(10%) samples are observed to be shifted toward higher angles as shown in Fig. 2 for 14.3° peak. Shifting of peaks toward lower angles could be assigned to the expansion of unit cell in K(3%) sample. However, if K^+ substitutes the 'A'- site cation, it cannot expand the unit cell due to smaller ionic radius of K^+ ion (138 pm) as compared to FA^+ (253 pm) and MA^+ (217 pm) ions. So, K^+ may either has been gone to interstitials or two K^+ ions may have been substituted the A-site cation to expand the unit cell[6].

When doping concentration is increased further to 5% and above, lattice contraction is observed. On addition of smaller ion, shifting of peaks toward higher angle can be the sign of substitution of host ion by dopant ion. Hence, in K(5%) and K(10%) samples, there could be the substitution of K^+ at 'A'-site into the FAMA matrix.

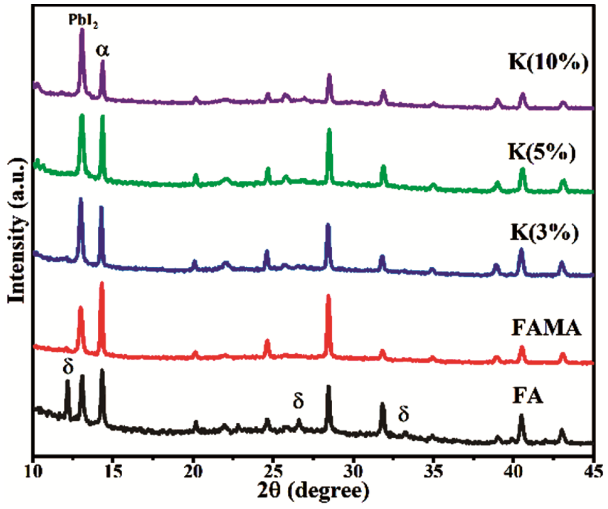

Fig. 1— XRD plot of pristine and MA-and/or K-doped $FAPbI_3$ perovskite films.

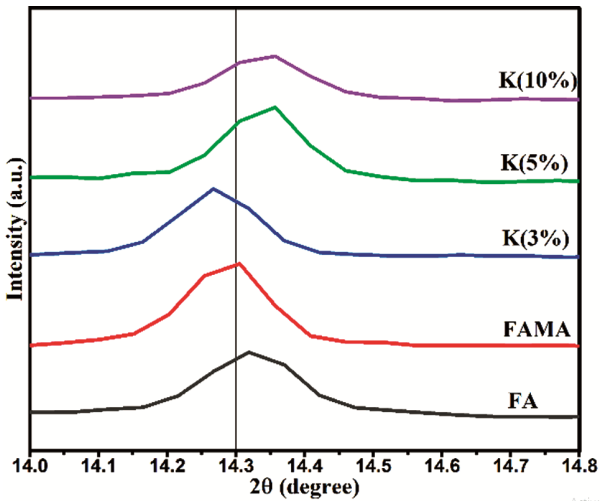

Fig. 2 — Enlarged XRD spectrum between 14-14.8°.

Table 1— Crystallite size and strain of FA, FAMA, K(3%), K(5%), K(10%) polycrystalline films using Williamson-Hall method.

Sample name	Crystallite size (nm)	Strain ($\times 10^{-3}$)	Band gap (eV)
FA	66.02	1.21	1.48
FAMA	91.82	1.71	1.52
K(3%)	130.80	2.22	1.52
K(5%)	134.61	2.46	1.51
K(10%)	129.58	2.52	1.52

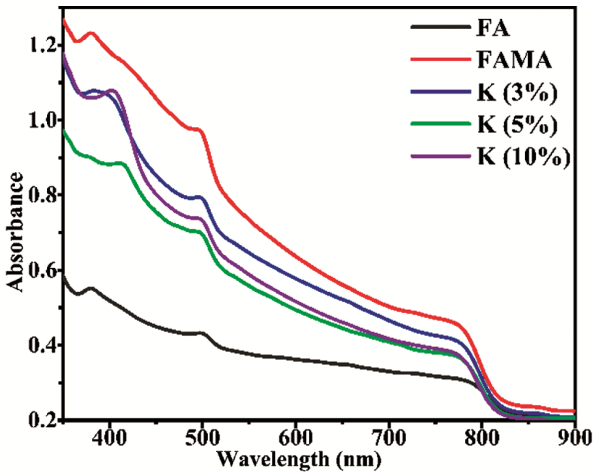

Fig. 3 — Absorbance plot of perovskite thin films.

Crystallite size is also calculated using W-H method. Values of crystallite size and strain are tabulated in Table 1. Average crystallite size of $FAPbI_3$ crystallites is found to be 66 nm, which is increased by ~ 39 % when FA is substituted by 17 % MA. Further, K-doping in this composition results in further enhancement of crystallite size. Maximum crystallite size of 134.61 nm is observed in K(5%) sample. Also, positive strain is seen in all the samples, which increases from FA to FAMA to K-doped samples due to distortion in structure.

The FA sample shows minimum absorbance in UV-Vis wavelength range out of five compositions (Fig. 3). FAMA shows maximum absorbance followed by K(3%), K(10%), and K(5%). One of the reasons of larger absorbance of FAMA can be its larger film thickness than other samples. The larger film thickness is evident from XRD results also (Fig. 1), as negligible peak of glass substrate (a broad hump in 2θ range $20<2\theta< 35°$, clearly visible in FA plot) is observed in FAMA sample due to film thickness greater than the penetration depth of X-rays.

Also, peaks at ~ 405 nm start appearing for K-doped samples, these peaks can be ascribed to K_2PbI_4 (Ref. 5) which is a potassium rich phase present in the material. This peak is observed to become more sharper as K-concentration increases, which can be interpreted as the increase in K_2PbI_4 content. The shoulder peaks at ~ 500 nm can be assigned to unreacted PbI_2 present in all samples[10,11], as evident from XRD results also. Tauc plot analysis shows band gap of 1.48 eV for FA sample and the other samples *i.e.* FAMA and its K-doped compositions show band gap of 1.516 ± 0.002 eV (given in Table 1). Here, it is observed that band gap does not get much affected with K-doping.

4 Conclusion

From XRD results, it is found that the MA and K doping into $FAPbI_3$ results in successful suppression of non-photoactive δ-phase of $FAPbI_3$ which make it useful for photovoltaic application. Some amount of PbI_2 residue is observed in all samples. Crystallite size is found to increase with K-doping and maximum crystallite size of 134.61 nm is obtained for K(5%) sample. The optical characterizations show that K-doping hardly affects the band gap of FAMA material. FAMA and K-doped FAMA samples show higher absorbance in UV-visible region of spectra as compared to that in $FAPbI_3$ film.

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