Partial replacement of Pb²⁺ in MAPbI_{2.6}Cl_{0.4} perovskite films and their photovoltaic performance

S. Derbali ^{a,b*}, K. Nouneh ^b, L.N. Leonat ^a, V. Stancu ^a, A. G. Tomulescu ^a, A. C. Galca^a, M. Ebn Touhami ^b, I. Pintilie ^a, M. Florea ^{a,*}

^a National Institute of Materials Physics, Atomistilor 405 A, 077125, Magurele, Ilfov, Romania, <u>Mihaela.florea@infim.ro</u>

^b Laboratory of Materials Physics and Subatomics LPMS, Faculty of Sciences, University Ibn Tofail Kenitra, 14000, Kenitra, Morocco, <u>sarah.derbali@infim.ro</u>

Abstract:

Replacing lead atoms in halide perovskite materials is of significant importance for the development of environmentally friendly perovskite solar cells. In this paper, we investigated the effect of doping the MAPbI_{2.6}Cl_{0.4} hybrid perovskite (MA-methyl ammonium) with non-toxic elements, such as alkaline earth metal ions (Mg²⁺) and transition metal ions (Zn²⁺). The structural, morphological, and optical properties of the prepared samples were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and UV-Vis. spectroscopy. Finally, the doped films were used as photoactive layers in solar devices in order to evaluate their photovoltaic performance. Zn proved to be more appropriate to replace partially Pb and films with higher quality were obtained. As a result, the MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} based solar cells have demonstrated a slight improvement of the photovoltaic performances, resulting in a uniform and narrower PCEs (power conversion efficiency) range, compared to pristine MAPbI_{2.6}Cl_{0.4} based devices.

Keywords

Hybrid perovskites, Zn^{2+} and Mg^{2+} doping, morphological characterizations, optoelectronic properties, solar cells.

1. Introduction

Perovskite materials have received extensive focus due to their impressive properties such as a suitable direct band gap, high absorption coefficient, small exciton binding energy, high carrier mobility, and a long carrier diffusion length ^{1–4}. The power conversion efficiency (PCE) of solar cells based on these materials has progressed from 3.8 % to more than 25 % ⁵. Despite the impressive progress of perovskite solar cells (PSCs), their large-scale development is hampered

by their low stability against some factors (humidity, heat, and continuous illumination), poor reproducibility, as well as their toxicity due to the presence of soluble lead salts and their potential impact on the environment 6,7 .

The instability problem has been improved by using different approaches such as compositional engineering of the A site, by adding inorganic cations, or by using larger organic cations in order to form the 2D perovskites, which have proven to be more stable ^{8–11}. The second challenge facing the PSCs is the presence of lead in the perovskite absorber material contributing largely to their exceptional photovoltaic properties. However, despite all the appealing characteristics, lead also contributes to the increased toxicity of the devices that hinders their commercial use for the moment. When it degrades, the hybrid perovskite decomposes back to its precursors such as PbI₂ which is very harmful to the human body and generally to the environment ^{12–14}. The decomposition reaction of MAPbI₃ (CH₃NH₃PbI₃) for example, is described as follows:

$$CH_3NH_3PbI_3 \longrightarrow CH_3NH_2 + HI + PbI_2$$
 Eq.1

This makes the perovskite-based solar panels very vulnerable to rain in case of an encapsulation failure-inducing a complete and irreversible degradation of the perovskite material, leaving behind PbI₂ in water with a concentration of 10^{-8} mol L⁻¹ that may contaminate the underground water resources ¹⁵. Replacing lead with nontoxic elements or elements with low toxicity, such as alkaline earth metals and transition metal ions, is an attractive strategy to reduce the amount of lead in solar cells; likewise, these metals are abundant in nature and have particularly interesting properties. It was claimed that lead-free perovskites possess high exciton binding energies that induce stable optical properties ¹⁶. The most obvious choice to replace lead is to use another element that has the same s² p² electronic structure such as Sn and Ge. However, the Sn and Ge are more stable in a *4*+ oxidation state, while Pb is most stable in a *2*+ oxidation state. As an example, it was reported that a partial and total substitution of Pb by Sn and Ge led to a PCE of 8.12 % using (FA_{0.75}MA_{0.25})SnI₃ absorber perovskite with an open circuit voltage of 0.61 V and PCE < 1 % with the absorbers types MAGeI₃ and CsGeI₃ ^{17,18}.

In addition, several studies highlighted the potential of the partial substitution of Pb by other metals, leading to the development of novel absorber materials with advanced morphological, optoelectronic, and photovoltaic properties ^{19–21,21–24,24–28}. For instance, bismuth-based perovskite (MA)₃Bi₂I₉ was studied and despite low values of efficiencies, up to 1.64 %, considered a record in 2017, showing excellent stability in air and high humidity ²⁹. The devices in which Pb was replaced with Ge, Bi, Sb, Sn, or Cu have reached efficiencies only up to 9%,

therefore there is still room to enhance their efficiencies and to improve their stability in air ¹⁶. Moreover, Frolova *et al.* reported a systematic study of the partial substitution of Pb²⁺ in MAPbI₃ by various elements including Cd²⁺, Fe²⁺, Ni²⁺, Co²⁺, Zn^{2+,} and Hg²⁺. The MAPb_{0.9}Hg_{0.1}I₃ based solar cells reached a PCE of 11.9% while the device based on MAPb_{0.9}Zn_{0.1}I₃ achieved a PCE of around ~2% ²⁰. However, according to the published works, Pb²⁺ remains the most suitable metal cation for the perovskite structure due to its electronic structure, leading to PSCs with the highest PCE. Therefore, in order to improve the performance of the PSCs, it is more appropriate to partially replace the Pb²⁺ with other elements than to perform a total replacement.

The main objective of this work is to investigate alternative metals to replace Pb and to study how partial replacement Pb^{2+} with Mg^{2+} or Zn^{2+} cations affects the optoelectronic properties of MAPbI_{2.6}Cl_{0.4} films. Therefore, the structural, optical, and morphological properties of the Mg and Zn doped hybrid perovskite films and their influence on the photovoltaic performances of the resulting solar cells were exhaustively investigated.

2. Materials and methods

2.1. Preparation of perovskite solar cells

2.5 x 1.5 cm² FTO-coated transparent substrates with a sheet resistance of 15 Ω /sq were chemical treated, cleaned first by cleaning agents and distilled water followed by ultrasonication in acetone and isopropanol, respectively, for 5 minutes each. Before spin coating, the FTO substrates received 10 minutes of plasma exposure and 0.7 mbar of O₂ in order to eliminate any organic contamination.

Preparation of compact and mesoporous TiO_2 layers: TiO_2 layers (c-TiO_2 and m-TiO_2) were deposited on FTO substrates by spray pyrolysis according to the protocol reported by Tomulescu *et al.*³⁰.

Preparation of perovskite layer: The precursor solutions of MAPb_{0.99}Zn_{0.01}I_{2.6}Cl_{0.4} and MAPb_{0.99}Mg_{0.01}I_{2.6}Cl_{0.4} were prepared by mixing methyl ammonium iodide (CH₃NH₃I), lead halides (0.8 M PbI₂ to 0. 2 M PbCl₂) and zinc chloride (ZnCl₂) or magnesium chloride (MgCl₂), respectively in a molar ratio of 1:1-x: x (x= 0 and 0.01, x is the mole fraction of doping in Pbsite) in a mixture of 600 mg of DMF and 78 mg of DMSO. The solutions are then stirred for one hour at room temperature. Before being used, the solutions are filtered through 0.2 μ m syringe filters to prevent particle leakage. Once filtered, the solutions are deposited by spin-coating at 2000 rpm for 25 s. After 9 s from the beginning of the centrifugation process, 100 μ L of diethyl ether (DEE) is injected as an anti-solvent. Finally, the formation of perovskite films is completed by annealing at 120 °C for 3 minutes on a hot plate. A similar preparation method was used for the precursor solution of $MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4}$ using different molar fractions of the Zn^{2+} host (x= 0, 0.025, 0.005, 0.0075, 0.01, and 0.03, x is the mole fraction of doping in Pb-site).

Preparation of Spiro-OMeTAD layer: 80 mg of spiro-OMeTAD was mixed with 1 ml of chlorobenzene, 28 μ l of 4-tert-butylpyridine and 18 μ l of bis(trifluoromethane) sulfonamide lithium salt in acetonitrile solution (520 mg/mL). Then 50 μ l of the prepared solution was deposited at 3000 rpm for 30 s by spin coating. Finally, Au electrodes were deposited by magnetron sputtering in the argon atmosphere through a shadow mask with an active area of 0.09 cm².

2.2. Material characterizations

XRD spectra were obtained using Bruker-AXS (D8 advance diffractometer) equipped with Cu-K α radiation source (λ = 0.1541 nm) and LynxEye 1D detector. Surface morphology was assessed by scanning electron microscopy (SEM) using a Zeiss GeminiSEM-500. The atomic force microscopy (AFM) images and roughness were collected by NT-MDT Aura Ntegra Prima system in noncontact mode. The absorbance spectra were recorded by Woollam spectroscopic ellipsometer in conventional spectroscopy mode. The photocurrent density vs. voltage curves was measured by AM 1.5 G simulated sunlight illuminations (100 mW/ cm², Model VeraSol-2 Class AAA LED, Oriel solar simulator).

3. Results and discussion

Since Mg^{2+} (72 pm) and Zn^{2+} (74 pm) have a smaller ion radius than Pb^{2+} (119 pm), the first step of this study was to calculate the tolerance factor, necessary to predict if these materials adopt a 3D structure (ABX₃) when Pb is replaced by Zn and Mg³¹. The tolerance factor values for doping with 1% of Mg^{2+} (MA(Pb_{0.99}Mg_{0.01})I_{2.6}Cl_{0.4}) or 1% of Zn^{2+} (MA(Pb_{0.99}Zn_{0.01})I_{2.6}Cl_{0.4}) are estimated by the Goldschmidt equation [Eq. 2] ³².

$$t = \frac{r_A + r_X}{\sqrt{2} (r_B + r_X)}$$
 Eq.2

Where r_A , r_B , and r_X are the ionic radii for A, B, and X ions, respectively. The ionic radii of the cations and anions used in this work are respectively: $r_{MA} = 2.17$ Å, $r_{Pb} = 1.19$ Å, $r_{Zn} = 0.74$ Å, $r_{Mg} = 0.72$ Å, $r_I = 2.20$ Å et $r_{Cl} = 1.81$ Å 32,33 .

The *t* values obtained for 1% Mg^{2+} or 1% Zn^{2+} indicate that both can replace Pb^{2+} while maintaining the 3D ABX₃ perovskite structure (see Table 1).

Fraction of doping	Perovskite type	Notation	Tolerance
in Pb-site (x)			factor (t)
x= 0	MAPbI _{2.6} Cl _{0.4}	MAPbI _{2.6} Cl _{0.4}	0.915
x= 0.01	MAPb _{0.99} Mg _{0.01} I _{2.6} Cl _{0.4}	Mg-1%	0.917
x= 0.01	MAPb _{0.99} Zn _{0.01} I _{2.6} Cl _{0.4}	Zn-1%	0.916

Table 1. Tolerance factors calculated for $MAPb_{0.99}Mg_{0.01}I_{2.6}Cl_{0.4}$ and $MAPb_{0.99}Zn_{0.01}I_{2.6}Cl_{0.4}$.

The structural properties of prepared MAPb_x(Mg_{1-x}/Zn_{1-x})I_{2.6}Cl_{0.4}, Mg-1% and Zn-1% perovskite films were explored by X-ray diffraction as shown in Fig. 1. The diffractograms of pristine MAPbI_{2.6}Cl_{0.4}, Mg-doped and Zn-doped perovskite films exhibit the main Bragg diffraction peaks of MAPbI₃ tetragonal perovskite in accordance with JCPDS card no. 00-068-0701. All the perovskite films contain additional phases which match a hexagonal PbI₂ phase and a MAPbCl₃ phase. However, for the Zn-1% sample the line at 12.6° assigned to PbI₂ is missing, indicating a completely integrated PbI₂ into perovskite. The presence of the MAPbCl₃ phase is not surprising considering the nature of the PbCl₂ precursor used.



Fig. 1. XRD patterns of pristine MAPbI_{2.6}Cl_{0.4} and MAPb_{0.99}(Mg_{0.01}/Zn_{0.01})I_{2.6}Cl_{0.4} perovskite films.

The surface morphology of the pristine MAPbI_{2.6}Cl_{0.4}, Mg-doped and Zn-doped perovskite films was examined by SEM. As shown in the SEM images (see Fig.2), the pristine MAPbI_{2.6}Cl_{0.4} film is crystallized in small grains of a cauliflower-like shape with several large pinholes and very clear grain boundaries. The Zn doping drives the formation of a compact film with a considerably reduced number of pinholes. However, Mg doping leads to the formation

of a needle-like structure with a rough surface, covered by large voids, detrimental for application in solar devices.



Fig. 2. SEM images of pristine MAPbI_{2.6}Cl_{0.4} and MAPb_x(Mg_{1-x}/ Zn_{1-x})I_{2.6}Cl_{0.4} perovskite films.

The AFM analysis supports the results obtained by SEM (see Fig.S1). Pristine MAPbI_{2.6}Cl_{0.4} and Mg-1%- doped show a rough surface, as indicated by the high root mean square roughness (RMS) values calculated from the AFM images, while Zn-1%- doped reveals a smooth surface with an RMS of ~ 36 nm, compared to 227 nm of the Mg-doped sample, which is beneficial for more efficient extraction and transport of photo-generated charges in a solar device.

Based on these findings, the Zn^{2+} ions were chosen as appropriate doping ions for the fabrication of high-quality perovskite films. Therefore, in the following, we have explored the effect of Zn-doping with different concentrations, specifically 0.25%, 0.5%, 0.75%, and 3%.

Fraction of doping in	Perovskite type	Notation	Tolerance
Pb-site (x)			factor (t)
x= 0	MAPbI _{2.6} Cl _{0.4}	MAPbI _{2.6} Cl _{0.4}	0.915
$x = 2.5 \cdot 10^{-3}$	$MAPb_{0.9975}Zn_{0.0025}I_{2.6}Cl_{0.4}$	Zn-0.25%	0.916
$\mathbf{x}=5\cdot10^{-3}$	MAPb _{0.995} Zn _{0.005} I _{2.6} Cl _{0.4}	Zn-0.5%	0.916
$x = 7.5 \cdot 10^{-3}$	$MAPb_{0.9925}Zn_{0.0075}I_{2.6}Cl_{0.4}$	Zn-0.75%	0.916
x= 0.03	$MAPb_{0.97}Zn_{0.03}I_{2.6}Cl_{0.4}$	Zn-3%	0.919

Table 2. Tolerance factor calculated for $MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4}$.

Table 2 shows that the *t* values obtained for doping by 0%, 0.25 %, 0.5 %, 0.75 % and 3 % of Zn^{2+} are within the limits of the 3D perovskite domain (0.85 $\leq t \leq 1.11$) ³⁴, so all the studied compositions can adopt theoretically a 3D perovskite structure.

Fig. 3 shows the X-ray diffractograms for $MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4}$ perovskite films with different fractions of Zn^{2+} . All samples show the expected diffraction peaks associated with the (110), (020), (121), (022), (220), (130), (132), (040) and (330) planes of a MAPbI₃ tetragonal phase

(according to JCPDS-00-068-0701). In addition, the perovskite films reveal the presence of MAPbCl₃ phase as observed before (see Fig. 1).



Fig. 3. X-ray diffractograms of MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} perovskite films.

Furthermore, Table 3 shows the measured values of the full width at half maximum (FWHM) of the most intense reflection peak, 110, for all MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} perovskite films as well as the crystallite size determined using Scherrer's formula ³⁵. The narrowing FWHM of the 110 reflection for Zn-0.75% and Zn-1% perovskite films indicated enhanced crystallinity and increased crystallite size compared to the pristine MAPbI_{2.6}Cl_{0.4}. However, the differences in crystallite size are very small.

Table 3. FWHM values	provided	from the	main	reflection	peak	110
----------------------	----------	----------	------	------------	------	-----

Samples	FWHM (°)	Position of (110) peak (°)	Crystallite size (nm)
MAPbI _{2.6} Cl _{0.4}	0.2563	14.123	31.2
Zn-0.25%	0.2841	14.129	28.1
Zn-0.5%	0.2694	14.126	29.7
Zn-0.75%	0.2467	14.130	32.4

Zn-1%	0.2451	14.134	32.6
Zn-3%	0.2806	14.137	28.5

The surface morphology of MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} perovskite films was examined by SEM (see Fig.4). The films become more compact in the case of doping with a low concentration of Zn²⁺ (0.25% $\leq x \leq 1$ %), with a slight increase in grain size leading to a reduction in the density of the grain interfaces, which is beneficial for the reduction of recombination of generated charges. These results suggest that the Zn²⁺ ions influence nucleation and the resulting crystal growth process, which is in good correlation with the crystallite size obtained from X-ray diffraction. However, doping with 3% of Zn²⁺ leads to the formation of a large number of grain boundaries and pinholes, as evidenced in Fig. 4, leading to poor surface coverage. Consequently, the photovoltaic performance of the resulting solar cells may be negatively affected.



Fig. 4. SEM images of MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} perovskite films.

These findings can be explained by the strong interaction of Zn^{2+} with the halide anions (such as Γ) and its high coordination with the free electron pair of the organic nitrogen group (methyl ammonium, $CH_3NH_3^+$) which leads to the growth of the perovskite lattice in larger grains. Therefore, the films with an appropriate proportion of Zn^{2+} ($x \le 1$) show larger grain sizes than the pristine MAPbI_{2.6}Cl_{0.4}. Even so, doping with a high concentration of Zn leads to the formation of increasingly larger grains so that inherent pinholes appear between the grains, thus affecting the film surface coverage and charge transport. This proportion corresponds to 3% of Zn^{2+} in our case.

On the other hand, the presence of needle-like grains indicates the presence of an additional phase characteristic to unreacted PbI₂, which is consistent with the XRD results (see Fig. 3).



Fig. 5. AFM Images of MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} perovskite films in a 20 x 20 μ m² scan area.

The perovskite films examined also by AFM seem to be compact (Fig.5). The RMS of the different samples was calculated from the AFM images. It can be noted from Table 4 that pristine MAPbI_{2.6}Cl_{0.4}, Zn-0.5%, and Zn-3% perovskite films show large RMS values indicating rough surfaces, while Zn-0.75% and Zn-1% films show smaller RMS values indicating a smoother surface in good agreement with data obtained from SEM.

Table 4. RMS values of MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} perovskite films.

Samples	RMS
MAPbI _{2.6} Cl _{0.4}	94 nm
Zn-0.25%	79 nm
Zn-0.5%	94 nm
Zn-0.75%	39 nm
Zn-1%	36 nm
Zn-3%	98 nm

The optical absorption spectra of the prepared perovskite films are presented in Fig. 6. The perovskite films show high absorption as Zn^{2+} proportion increases (up to x =3%). Considering

the same amount of deposited material, the absorbance enhancement is related to the quality of the perovskite films through grain size, pinholes reduction and good coverage of the film, resulting in increased light absorption. Thereafter, the absorbance decreases for Zn-3% film due to the presence of the cracks and a large number of pinholes on the film surface (see Fig.4). Our results are consistent with Zhu et al.'s work, who stated that replacing Pb²⁺ with 1 % Zn²⁺ allows absorbance improvement, while it decreases when the proportion of Zn²⁺ exceeds 1 % ³⁶.



Fig. 6. Vis-NIR absorbance spectra of MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} perovskite films.

The band gap of the prepared MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} perovskite films were determined from the absorption spectra using the Tauc relation (see Fig. 7) 37 .



Fig. 7. Optical band gap of MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} perovskite films determined from linear fits of Tauc plots.

The obtained band gap values are 1.58 eV, 1.588 eV, 1.589 eV and 1.592 eV for the MAPbI_{2.4}Cl_{0.6}, Zn-0.5%, Zn-0.75%, and Zn-3% films, respectively. According to the literature, the band gap of ABX₃ perovskite material increases as the electronegativity of the B cation decreases [15]. In this case, Zn^{2+} has a lower electronegativity of 1.65, than Pb²⁺ which has 2.33, leading to stronger Zn-I bonds than the Pb-I bonds. Therefore, the strong Zn-I bonding induces a small but definitive increase in band gap of MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} perovskite films. In contrast, the Zn-0.25% and Zn-1% films exhibit lower band gap than the pristine MAPbI_{2.4}Cl_{0.6}, reflecting an anomalous behavior, which might occur due to the reflection of the rough surface of the perovskite, leading to some errors in the UV-Vis measurements.



Fig. 8. (a) Schematic illustration of n-i-p mesoscopic configuration of PSCs, (b) J-V curve under forward and reverse scans of the champion MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} solar cells.

The prepared MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} films were employed for the fabrication of solar devices in the following mesoporous architecture FTO/c-TiO₂/m-TiO₂/MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4}/Spiro-OMeTAD/Au, (Fig.8a). The J-V curves for the champion MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} solar cells are depicted in Fig.8b, and the average values of the photovoltaic parameters for all the prepared devices are summarized in Table 5. The photovoltaic characteristics of each device are presented in the supplementary data in detail (Table S1-S6). Table 5 shows that the solar cells containing 1% of Zn²⁺ exhibit the best performances, PCE of 6.82 %, with a J_{SC} of 11.7 mA/cm², V_{OC} of 0.905 V, FF of 65%, R_S of 16 Ω /cm² of and R_{sh} of 2641 Ω /cm². Moreover, the higher R_{sh} of the devices with 1% of Zn²⁺ is most likely caused by the low interfacial ohmic losses and current leakage, which usually arises from the presence of defects in the material.

On the other hand, the cells containing 0.25% of Zn^{2+} achieved a PCE of 6.69 %, which is comparable to that of the standard devices with MAPbI_{2.6}Cl_{0.4}. However, 0.25% based devices show higher J_{SC} and V_{OC} compared to the pristine MAPbI_{2.6}Cl_{0.4} devices, which is attributed to efficient charge extraction and reduced carrier accumulation at the interfaces in 0.25 % Zn²⁺ based devices. The obtained results prove that the performances of PSCs are strongly linked to the active layer quality. Thus, the smooth and compact films containing Zn²⁺ led to some enhancement in the photovoltaic performances of the resulting solar cells.

Zn fraction (%)	Voc (V)	Jsc (mA/cm ²)	FF (%)	Rs (Ω cm²)	Rsh (Ω cm²)	PCE (%)
0	0.909	11.1	67	16	1626	6.69
0.25	0.941	11.7	61	18	1113	6.69
0.5	0.915	11.0	65	17	1856	6.45
0.75	0.899	9.9	66	16	1756	5.85
1	0.905	11.7	65	16	2641	6.82
3	0.869	6.2	50	30	1803	2.75

Table 5. Average values of photovoltaic parameters for all the prepared $MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4}$ solar devices.



Fig. 9. Statistical distribution of photovoltaic parameters for samples MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} based solar cells.

In addition, for $MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4}$ based solar cells, PCEs distribution is more uniform and narrower compared to pristine $MAPbI_{2.6}Cl_{0.4}$ based devices, especially the cells containing 1% of Zn^{2+} (see Fig. 9d). The narrower PCE distribution of $MAPb_{0.99}Zn_{0.01}I_{2.6}Cl_{0.4}$ based PSCs strongly indicates better reproducibility compared to the $MAPbI_{2.6}Cl_{0.4}$ PSCs, which is mainly due to the formation of uniform hybrid halide films having high quality and limited defects. In

contrast, the PCE distribution of MAPb_{0.997}Zn_{0.003}I_{2.6}Cl_{0.4} based PSCs is broad, owing to the incomplete coverage, pinholes, and large grain size of the absorber Zn-3% perovskite film. Although the achieved PCE for MAPb_{1-x}Zn_xI_{2.6}Cl_{0.4} based solar devices is still low, these results are promising to develop strategies for further improvement of the performance of these cells with moderately reduced toxicity since the Zn-doped perovskite films demonstrated interesting morphological and optical properties.

4. Conclusion

Addressing the toxicity of hybrid perovskite material is one of the key challenges to deploying their usage in commercial applications. Here we have studied the B-site doping in MAPbI_{2.6}Cl_{0.4} perovskite with Mg and Zn to reduce the Pb content while maintaining good morphological and optoelectronic properties of the active layer. Zn proved to be the most appropriate B-site doping component. In fact, Zn doping in MAPbI_{2.6}Cl_{0.4} was successfully achieved without altering the crystal structure. At low concentrations of Zn doping, higher quality perovskite films were obtained with a dense surface, larger grains, and fewer pinholes. Furthermore, Zn-doping has resulted in an enhancement of the absorbance for 0.25%, 0.5%, 0.75%, and 1% of Zn^{2+} , which is attributed mainly to the improved quality of the perovskite films. The band gap of these films was found to lay between 1.571 eV and 1.592 eV, which fall within the suitable band gaps for PSCs application. Thus, the PSCs based on Zn-doped perovskite films have shown a slight improvement of photovoltaic performances compared to the standard devices. The MAPb_{0.99}Zn_{0.01}I_{2.6}Cl_{0.4} mesoporous solar cells achieved the best performances with a PCE_{average} of 6.82 %. Overall, Zn doping demonstrates encouraging results for further optimization of Zndoped MAPbI_{2.6}Cl_{0.4} films properties and opens the possibility of using toxicity- reduced perovskites for application in PSCs devices.

Acknowledgement

S.D. acknowledges the Romanian Ministry of Foreign Affairs and Agence Universitaire de la Francophonie for the Eugen Ionescu research scholarship no.15/2019. LL acknowledges the Romanian Ministry of Research and Innovation and UEFISCDI for financial support through Project PN-III-P2-2.1-PED-2019-1411. The research leading to these results has received funding from the EEA Grants 2014–2021, under Project contract no. 36/2021 (project code: EEA-RO-NO-2018-0106). and Core Program PN23080303.

References

- 1 J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park and N.-G. Park, *Nanoscale*, 2011, **3**, 4088–4093.
- 2 T. C. Sum and N. Mathews, *Energy Environ. Sci.*, 2014, 7, 2518–2534.
- 3 Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao and J. Huang, *Science*, 2015, **347**, 967–970.
- 4 Z. Zhang, M. Wang, L. Ren and K. Jin, *Sci Rep*, 2017, 7, 1918.
- 5 Best Research-Cell Efficiency Chart, https://www.nrel.gov/pv/cell-efficiency.html, (accessed May 21, 2021).
- 6 A. B. Djurišić, F. Z. Liu, H. W. Tam, M. K. Wong, A. Ng, C. Surya, W. Chen and Z. B. He, *Progress in Quantum Electronics*, 2017, **53**, 1–37.
- M. V. Khenkin, E. A. Katz, A. Abate, G. Bardizza, J. J. Berry, C. Brabec, F. Brunetti, V. Bulović, Q. Burlingame, A. Di Carlo, R. Cheacharoen, Y.-B. Cheng, A. Colsmann, S. Cros, K. Domanski, M. Dusza, C. J. Fell, S. R. Forrest, Y. Galagan, D. Di Girolamo, M. Grätzel, A. Hagfeldt, E. von Hauff, H. Hoppe, J. Kettle, H. Köbler, M. S. Leite, S. (Frank) Liu, Y.-L. Loo, J. M. Luther, C.-Q. Ma, M. Madsen, M. Manceau, M. Matheron, M. McGehee, R. Meitzner, M. K. Nazeeruddin, A. F. Nogueira, Ç. Odabaşı, A. Osherov, N.-G. Park, M. O. Reese, F. De Rossi, M. Saliba, U. S. Schubert, H. J. Snaith, S. D. Stranks, W. Tress, P. A. Troshin, V. Turkovic, S. Veenstra, I. Visoly-Fisher, A. Walsh, T. Watson, H. Xie, R. Yıldırım, S. M. Zakeeruddin, K. Zhu and M. Lira-Cantu, *Nat Energy*, 2020, 5, 35–49.
- 8 W. Chi and S. K. Banerjee, Chem. Mater., 2021, 33, 1540–1570.
- 9 S. Derbali, K. Nouneh, M. Florea, L. N. Leonat, V. Stancu, A. G. Tomulescu, A. C. Galca, M. Secu, L. Pintilie and M. E. Touhami, *Journal of Alloys and Compounds*, 2021, 858, 158335.
- 10A. Gabriel Tomulescu, L. Nicoleta Leonat, F. Neaţu, V. Stancu, V. Toma, S. Derbali, Ștefan Neaţu, A. Mihai Rostas, C. Beşleagă, R. Pătru, I. Pintilie and M. Florea, *Solar Energy Materials and Solar Cells*, 2021, 227, 111096.
- 11 T. Zhu, Y. Yang, K. Gu, C. Liu, J. Zheng and X. Gong, *ACS Appl. Mater. Interfaces*, 2020, **12**, 51744–51755.
- 12S. Kundu and T. L. Kelly, *EcoMat*, 2020, 2, e12025.
- 13E. J. Juarez-Perez, L. K. Ono, M. Maeda, Y. Jiang, Z. Hawash and Y. Qi, *J. Mater. Chem. A*, 2018, **6**, 9604–9612.
- 14L. Ma, D. Guo, M. Li, C. Wang, Z. Zhou, X. Zhao, F. Zhang, Z. Ao and Z. Nie, *Chem. Mater.*, 2019, **31**, 8515–8522.
- 15D. Fabini, J. Phys. Chem. Lett., 2015, 6, 3546-3548.
- 16R. Kour, S. Arya, S. Verma, J. Gupta, P. Bandhoria, V. Bharti, R. Datt and V. Gupta, *Global Challenges*, 2019, **3**, 1900050.
- 17Z. Zhao, F. Gu, Y. Li, W. Sun, S. Ye, H. Rao, Z. Liu, Z. Bian and C. Huang, *Advanced Science*, 2017, **4**, 1700204.
- 18T. Krishnamoorthy, H. Ding, C. Yan, W. L. Leong, T. Baikie, Z. Zhang, M. Sherburne, S. Li, M. Asta, N. Mathews and S. G. Mhaisalkar, *J. Mater. Chem. A*, 2015, **3**, 23829–23832.
- 19 Y. Zhou, J. Chen, O. M. Bakr and H.-T. Sun, Chem. Mater., 2018, 30, 6589-6613.
- 20L. A. Frolova, D. V. Anokhin, K. L. Gerasimov, N. N. Dremova and P. A. Troshin, J. *Phys. Chem. Lett.*, 2016, **7**, 4353–4357.
- 21 D. Hong, P. Zhao, Y. Du, C. Zhao, Y. Xia, Z. Wei, Z. Jin and Y. Tian, *iScience*, 2020, 23, 101415.
- 22J. Lu, S.-C. Chen and Q. Zheng, Sci. China Chem., 2019, 62, 1044–1050.

- 23 S. Derbali, K. Nouneh, M. Florea, F. Neatu, S. Neatu, L. N. Leonat, M. Secu, A. G. Tomulescu, V. Stancu, L. Pintilie, M. E. Touhami and A. C. Galca, *Phys. Scr.*, 2020, 95, 044003.
- 24 V. Stancu, L. N. Leonat, A. G. Tomulescu, S. Derbali, L. Pintilie, C. Besleaga, A. C. Galca, F. Neaţu, Ștefan Neaţu, M. Florea and I. Pintilie, *Phys. Scr.*, 2020, **95**, 075707.
- 25 A. Swarnkar, W. J. Mir and A. Nag, ACS Energy Lett., 2018, 3, 286–289.
- 26X. Deng, B. Luo, Z. Zhang, Y. Yao, C. Zhao, M. Shi and E. Tian, *Physica B: Condensed Matter*, 2021, **603**, 412703.
- 27 R. Chen, D. Hou, C. Lu, J. Zhang, P. Liu, H. Tian, Z. Zeng, Q. Xiong, Z. Hu, Y. Zhu and L. Han, *Sustainable Energy Fuels*, 2018, **2**, 1093–1100.
- 28X. Ge, X. Qu, L. He, Y. Sun, X. Guan, Z. Pang, C. Wang, L. Yang, F. Wang and F. Rosei, *J. Mater. Chem. A*, 2019, **7**, 27225–27235.
- 29Z. Zhang, X. Li, X. Xia, Z. Wang, Z. Huang, B. Lei and Y. Gao, *J. Phys. Chem. Lett.*, 2017, **8**, 4300–4307.
- 30 A. G. Tomulescu, V. Stancu, C. Beşleagă, M. Enculescu, G. A. Nemneş, M. Florea, V. Dumitru, L. Pintilie, I. Pintilie and L. Leonat, *Energy Technology*, 2020, **8**, 1900922.
- 31 In Ionic Compounds, John Wiley & Sons, Ltd, 2006, pp. 171–171.
- 32W. Travis, E. N. K. Glover, H. Bronstein, D. O. Scanlon and R. G. Palgrave, *Chem. Sci.*, 2016, **7**, 4548–4556.
- 33G. P. Nagabhushana, R. Shivaramaiah and A. Navrotsky, PNAS, 2016, 113, 7717–7721.
- 34C. Li, X. Lu, W. Ding, L. Feng, Y. Gao and Z. Guo, Acta Cryst B, 2008, 64, 702–707.
- 35 P. Scherrer, Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klasse, 1918, **1918**, 98–100.
- 36X.-Y. Zhu, M.-W. Chen, B. Wang, N. Liu, M.-Q. Ran, H. Yang and Y.-P. Yang, *Opt. Express, OE*, 2018, **26**, A984–A995.
- 37 P. R. Jubu, F. K. Yam, V. M. Igba and K. P. Beh, *Journal of Solid State Chemistry*, 2020, **290**, 121576.