Effect of mixed iodine and bromine on optical properties in methylammonium lead chlorine (MAPbCl3) spin-coated on the zinc oxide film

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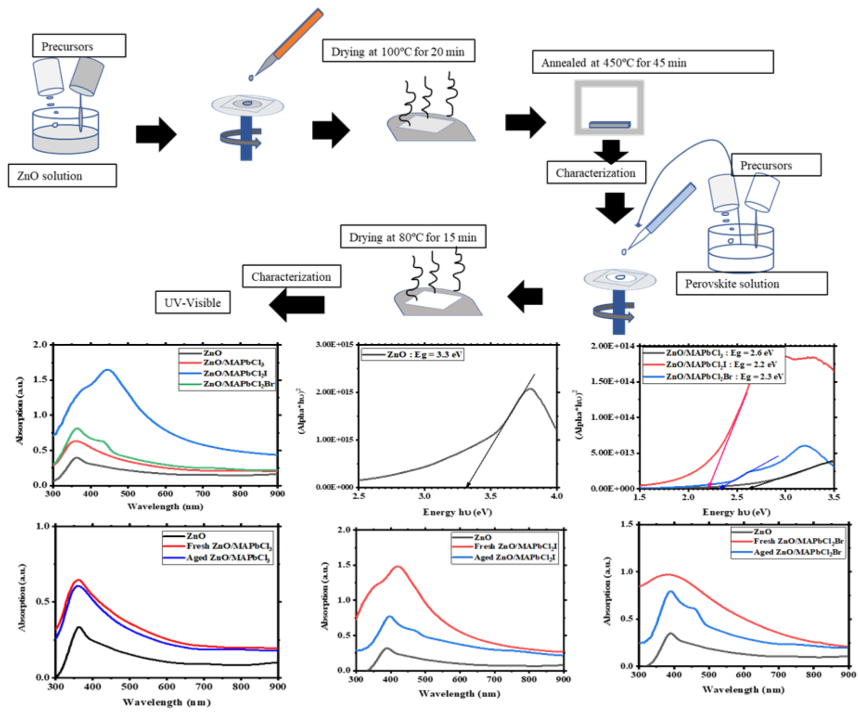
Abstract. The optical influence of mixing methylammonium lead chlorine ($MAPbCl_3$) with iodine and bromine was studied in this work. The spin coating method deposited three layers of perovskites ($MAPbCl_3$, $MAPbCl_2I$, and $MAPbCl_2Br$) on a layer of zinc oxide (ZnO). The zinc oxide solution was prepared by dissolving dehydrated zinc acetate [$Zn(CH_3COO)_2$, $2H_2O$]> 99.5% purity in ethanol to give a 0.5 M solution. The perovskite solutions were prepared using lead chloride ($PbCl_2$), methylammonium chloride (MACl), methylammonium iodide (MAI), and methylammonium bromide (MABr). The precursor containing iodine was dissolved in N, N-dimethylformamide (DMF) and the others in dimethyl sulphoxide (DMSO 99.9%). The films produced were characterized by UV-Visible. The analysis showed that the sample mixed with iodine has good properties. This sample absorbs the most and has a small band gap of 2 eV. The degradation study reveals that the unmixed sample ($MAPbCl_3$) is the most stable.

Keywords: Perovskite, ZnO, spin coating, optical property, absorption, band gap, stability.

Graphical abstract



1 Introduction

Photovoltaic cells have improved their efficiency in recent years thanks to perovskite. Therefore, it is a promising material in the field of photovoltaics that should be exploited to boost the world of photovoltaics [1]. The structure of the perovskite is of the form ABX_3 (A = Methyl ammonium ion (MA^+), formamidine ion (FA^+) or cesium (Cs); B = Lead ion (Pb^{2+}), tin ion (Sn^{2+}) and X = a halide ion (I^-, Br^- or Cl^-) [2,3]. The methylammonium lead halide ($MAPbX_3$) is an excellent material to boost the efficiency of solar cells due to its interesting properties. It has good absorption in the visible range, interesting optoelectronic properties, and better power conversion efficiency [4-6]. However, the properties of $MAPbX_3$ vary from halogen to halogen. Studies have shown that $MAPbI_3$ absorbs most in the visible and therefore has a smaller band gap. However, it is less stable. $MAPbBr_3$ also has good properties and is more stable than the former. The problem lies with $MAPbCl_3$. It is stable compared to $MAPbI_3$, but its optical properties are not interesting enough. Thus, this work aims to improve its properties by mixing it with iodine or bromine. The zinc oxide on which the perovskite has been deposited is a transparent n-type conducting material with a band gap of 3.3 eV [7,8]. high exciton binding energy of 60 meV, high carrier mobility, and good stability [9,10]. Therefore, solar cells use it as an electron transport layer [11,12]. Indeed, the electrons torn off in the perovskite layer by solar radiation are transported in the circuit through the ZnO layer. The diffusion of electrons between the perovskite surface and the ZnO surface creates surface defects [13]. The novelty of this work is to study the optical properties of the two layers together in heterojunction. The addition of iodine and bromine to MAPbCl3 can result in a tunable bandgap, allowing the absorption of a broader range of wavelengths. Iodine has a larger atomic size compared to bromine, which leads to a lower energy bandgap. By adjusting the ratio of iodine to bromine, the bandgap of the material can be modified, resulting in changes in the absorption and emission spectra.

There are several deposition methods such as inkjet [12], spray, dip-coating, spin coating [14], chemical bath deposition (CBD) [15], etc. The spin coating technique has been used in this work because it is easy to use and less expensive. To achieve our objective, we will study in the first part the effect of incorporating iodine and bromine into $MAPbCl_3$ on optical properties. In the second part of the work, the study of the stability of the samples will be the subject of this part.

2 Film manufacture

2.1 Experimental procedure

The deposition was carried out in two main steps: the deposition of the zinc oxide layer on the Fluorine doped Tin oxide (FTO) glass substrates. After treatment, we deposited the perovskite on the ZnO layer. The zinc oxide solution was prepared and treated before deposition. To obtain this solution, dehydrated zinc acetate $[Zn(CH_3COO)_2, 2H_2O]$> 99.5% purity was dissolved in ethanol to obtain a 0.5 M solution. The resulting solution was heated at 60ºC for 3 hours. The resulting solution was deposited on the FTO by the spin-coating method. The substrate was spun at 3000 rpm for 30 seconds. The obtained samples were dried at 100ºC for about 15 minutes and annealed in an oven at 450ºC for 45 minutes. After performing the characterizations by UV-Visible, the samples were reused for perovskite deposition. Three perovskite solutions were prepared: $MAPbCl_3$, $MAPbCl_2I$, and $MAPbCl_2Br$. The preparation of one of the solutions requires precursors and a solvent. The $MAPbCl_3$ solution was prepared by dissolving methylammonium chloride (MACl) and lead chloride ($PbCl_2$) in dimethyl sulphoxide (DMSO 99.9%). $MAPbCl_2I$ was obtained by dissolving methylammonium iodide (MAI) and lead chloride ($PbCl_2$) in N, N-dimethylformamide (DMF). Finally, we used lead chloride ($PbCl_2$) and methylammonium bromide (MABr) dissolved in dimethyl sulphoxide (DMSO 99.9%). These different perovskite solutions were each deposited on a substrate coated with zinc oxide. The samples were dried and characterized. Fig. 1 below illustrates the different steps of the experimental process [16].

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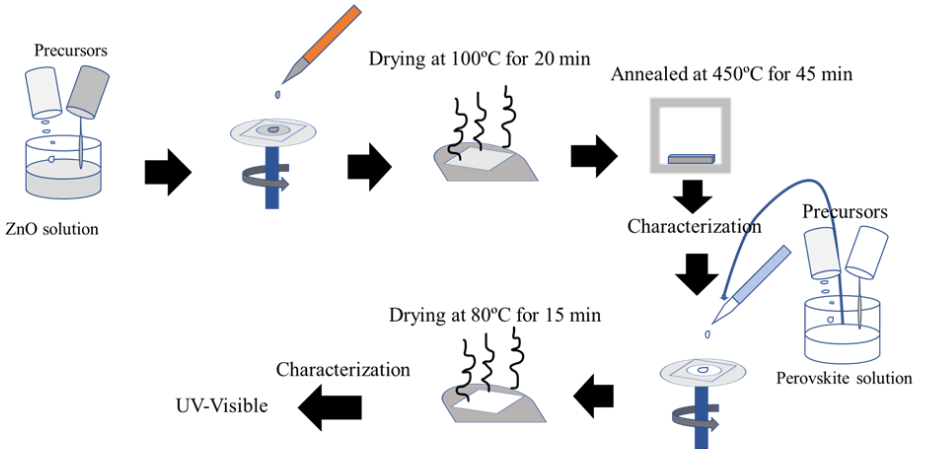

Fig. 1: Steps of the experimental process

2.2 Characterization technique

The SPECTROVIO C521O-C5220 was used to characterize by UV-Visible the samples produced in order to analyze their optical properties. The absorption and transmittance of the samples were measured. Results and discussions

3 Results and discussions

In this part, we present results and discussions of the UV-Visible characterization of samples. The absorption and band gap of the samples are shown in Figure 2 below. Fig. 2a shows the absorption. The results indicate that the layer coated only with zinc oxide absorbs the least. Among the heterojunction samples, the chlorine-based sample absorbs the least and the iodine-based sample absorbs the most. The difference in absorption between the iodine-based sample and the others is enormous. The presence of iodine increases the absorption of the sample considerably. Overall, the use of mixed iodine and bromine in MAPbCl3 can offer opportunities for tailoring the optical properties of the perovskite material. By adjusting the composition, the bandgap can be tuned, light harvesting can be improved, and the stability and defect formation can be controlled. These effects have implications for various optoelectronic applications, including solar cells and light-emitting devices, where optimizing the optical properties is crucial for achieving high performance.

Fig. 2b and 2c show the band gaps of the samples. The band gap of zinc oxide found is 3.3 eV which corresponds to that found in the literature [17]. The band gaps of the heterojunction samples vary between 2 eV and 2.6 eV. The smallest band gap is that of the sample mixed with iodine and the largest is that of the unmixed sample ($ZnO/MAPbCl_3$). These properties are thus enhanced by mixing. With iodine, a significant improvement over bromine is obtained.

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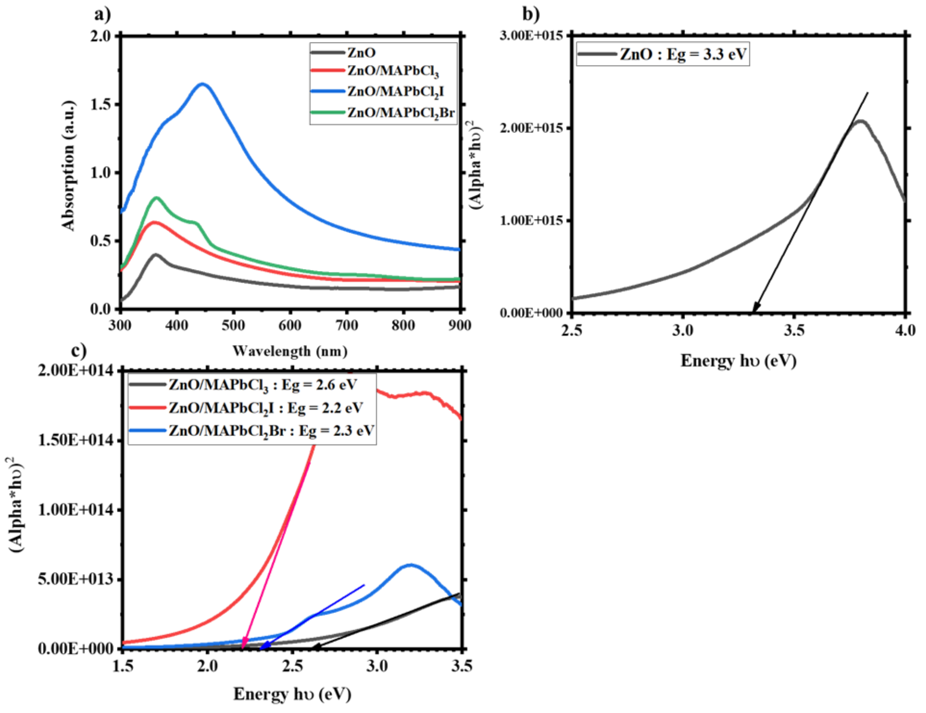

Fig. 2: Optical properties: a) absorption of ZnO , ZnO/$MAPbICl_2$, ZnO/$MAPbBrCl_2$, and ZnO/$MAPbCl_3$, samples, b) band gap of ZnO, c) band gap of ZnO/$MAPbICl_2$, ZnO/$MAPbBrCl_2$, ZnO/$MAPbCl_3$, samples heterojunction samples

We used the Tauc equation below to determine the band gaps [18,19].

$$(\alpha hv)^2 = \beta\,(hv - Eg) \tag{1}$$

In this equation, β is a constant and α is the absorption coefficient.

We constructed the function $(\alpha hv)^2$ as a function of the energy hv and determined the band gap by extrapolation. Table 1 below shows the different band gap values.

Table 1: Band gap of different samples

Samples	ZnO	$MAPbCl_3$	$MAPbCl_2I$	$MAPbCl_2Br$
Band gap (eV)	3.3	2.6	2	2.3
Wavelength (nm)	368	487	561	548

4 Degradation study

Perovskite is a very promising material in the field of photovoltaic energy. However, it is an unstable material when exposed to humidity and air [20]. This part of the work is therefore dedicated to the stability analysis of perovskite samples. The mechanism of degradation of the three films produced is according to the following equation [21]:

$$\mathbf{MAPbCl_2X \rightarrow MAX + PbCl_2}$$

Where X = Cl, I. Br.

The study of the degradation of the three samples ($ZnO/MAPbCl_3$, $ZnO/MAPbCl_2I$, and ZnO/MAPbClBr) was carried out on UV-Visible. The characterizations of the samples were done two weeks after the deposition. The ZnO sample in the UV-Visible analyses allows a better understanding of the evolution of the heterojunction properties. ZnO is a stable material [22].

Fig. 3 below shows the absorption of fresh and degraded samples. These results show that the absorption of the sample mixed with iodine decreases strongly compared to the other samples. We note a slight decrease in the absorption of the unmixed sample ($ZnO/MAPbCl_3$). These results indicate that the stability of $ZnO/MAPbCl_3$ in terms of absorption decreases with mixing. This stability decreases strongly with the presence of iodine.

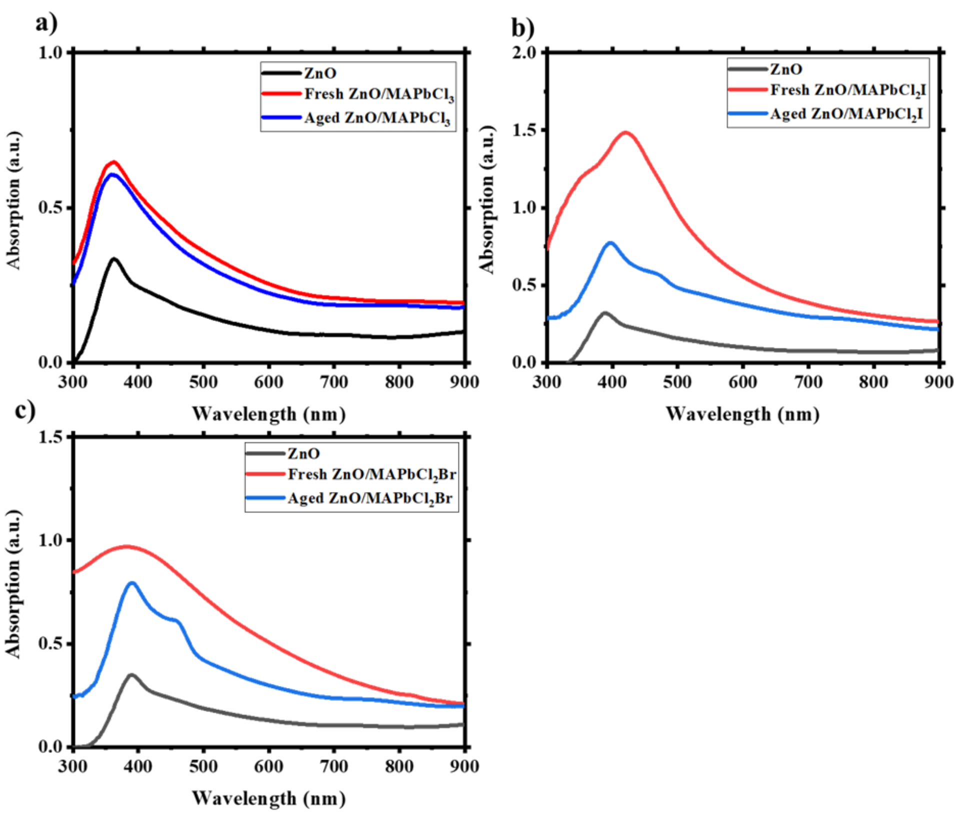

Fig 3: Absorption analysis two weeks after of samples: a) $MAPbCl_3$, b) $MAPbCl_2I$, c) $MAPbCl_2Br$

The absorption in all three cases is maximal between 350 nm and 500 nm. The degraded samples always absorb in the UV-Visible range. Of the three samples, the sample mixed with bromine shows an average degradation compared to the other two. The presence of bromine in the lead-based methylammonium chloride reduces its stability. This stability study shows that mixing lead-based methylammonium chloride with bromine and iodine decreases its stability. Zinc oxide is a stable material. Fig. 3 and Fig. 2a show that its absorption is not changed. Hence its stability [23,24].

5 Conclusion

In this work, we studied the effect of mixing iodine and bromine in $MAPbCl_3$ deposited on a ZnO layer to improve the properties of $MAPbCl_3$. The study involved UV-Visible analyses. This analysis showed that the sample mixed with iodine has good properties. This sample absorbs the most and has a small band gap of 2 eV. For this analysis, the unmixed sample ($ZnO/MAPbCl_3$) is the sample with the worse properties. The properties of the $ZnO/MAPbCl_3$ sample are therefore improved by mixing. However, the degradation study reveals that it is the most stable. Mixing with iodine or bromine decreases its stability.

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