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Synthesis of Perfectly Oriented $MAPb_{0,93}Cr_{0,07}Br_3$ Perovskite Crystals for Thin-Film Photovoltaic Applications

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ABSTRACT: Wide band gap methylammonium lead halide perovskites ($CH_3NH_3PbX_3$, X=halogen; CH_3NH_3: MA) are interesting materials for photovoltaic applications. They have recently gained substantial attention because of their high efficiency, low cost, superior optical properties. The most attractive and representative perovskites are methylammonium lead halides ($CH_3NH_3PbX_3$,) denoted as $MAPbX_3$, X = Br, Cl, I. usually the optical and structural properties of $CH_3NH_3PbBr_3$ can be adjusted by introducing other extrinsic ions such as chloride and bromide. In this work, instead of replacing the halogens I or Cl with bromine (Br) as usual, we preferred to act on the post-transition metal (Pb). To this end, we replaced lead with chromium (Cr) which is a transition metal and may have the same oxidation state (+2) as lead. $MAPb_{0.93}Cr_{0.07}Br_3$ thin films were deposited on ITO substrate by the spin coating process. X-ray diffraction analyses indicated the formation of a cubic perovskite with space group Pm3 m. The structural analysis reveals films with (110) and (220) as main peaks. Deposited films showed a strong absorbance in the UV–vis range. The band gap values were estimated from absorbance measurements. It was found between 1.60 and 1.80 eV. SEM analysis shows a morphology with good coverage and no apparent crystal orientation.

KEYWORDS: MABr; PbBr2; $(ClO4)_3Cr$, thin film perovskites, spin coating

I. INTRODUCTION

Perovskite materials of the form $MAPbX_3$ (A = Methylammonium =CH_3NH_3) ; X = halogen = I, Br or Cl) are attracting considerable interest owing to their potential for absorbing light in solar cells due to their broad spectral

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absorption, strong light harvesting, and long exciton diffusion length [1–6]. During the last recent years, perovskite materials have been one of the most widely investigated optoelectronic materials by researchers in many different areas [7]. Perovskite solar cells have yielded good device performance with the highest power conversion efficiencies that have risen from approximately η= 3% efficiencies [8] to almost 20.2% [8]. They are being widely used for many applications such light emitting diodes (LED) [10,11], the water splitting reaction and the degradation of organic dyes [12,13]. A variety of synthesis procedures have been employed to synthesize perovskite thin films, ranging from vacuum deposition [14], vapor-assisted solution processing [15], atomic layer deposition [16] and solution processing in one and two steps [17,18]. the corresponding processes are fast, simple, and low-cost. In this work, instead of introducing a halogen (I or Cl), we introduced a transition metal (Cr). The purpose of this article is to study the structural, morphological and optical properties of this perovskite.

II. EXPERIMENTAL PROCEDURE

II.1 PEROVSKITE PREPARATION

The precursor solutions were prepared by dissolving MABr, $PbBr_2$ and $(ClO_4)_3Cr$ powders at 45% wt Dimethylformamide (DMF) solution. The mixed solutions were stirred for 1 h to ensure the solution homogeneity. Thin film Perovskites were then produced by spin coating or dipping under speed of 3000 rpm for 30 s. Finally, the samples were annealed for 1 h at 80 ◦C and then kept in vacuum to avoid their degradation. Before the deposition, the ITO substrates were cleaned using soapy deionized water and were put in to the ultrasonic bath for 5 min. Then the substrates were thoroughly rinsed with deionized water and different solvents in the following order: acetone and 2-propanol previously warmed in the ultrasonic bath during 5 min each.

II.2 THIN FILM CHARACTERIZATION

The crystalline microstructures of the films on ITO substrates were determined using a RIGAKU Ultima IV in the Bragg-Brentano (θ-2θ) configuration employing CuKα radiation (λ = 1.54060 Å). The surface morphology of perovskite films was observed by an environmental scanning electron microscope FESEM (Quanta 200 – FEI) The absorption spectra of perovskite films were carried out at room temperature using spectrometer Ocean Optics HR4000 equipped with a Si-CCD detector and integrating sphere was used to collect specular and diffuse transmittance.

III. RESULTS AND DISCUSSION

Figure 1 shows the X-Ray diffraction patterns of $MAPbBr_3$ and $MAPb_{0,93}Cr_{0,07}Br_3$ deposited by spin coating onto ITO substrates. (200), (220), (116), (109), (400) and (330) peaks confirm the $MAPbBr_3$ phase matching well with (JCPDS#00-0105) reference. The samples have diffraction profiles corresponding to those expected for cubic Pm3m. The $MAPb_{0,93}Cr_{0,07}Br_3$ thin films have two main peaks along (110) and (220) directions which intensities increased considerably with the introduction of chromium ion. The absence of slight displacements of the peaks towards the upper angles is observed, contrary to what occurs in most cases. These shifts were usually due to the stresses of the crystal lattice caused by interstitial stations. No peaks belonging to impurities and secondary phase were also detected confirming the formation of single-phase crystals.

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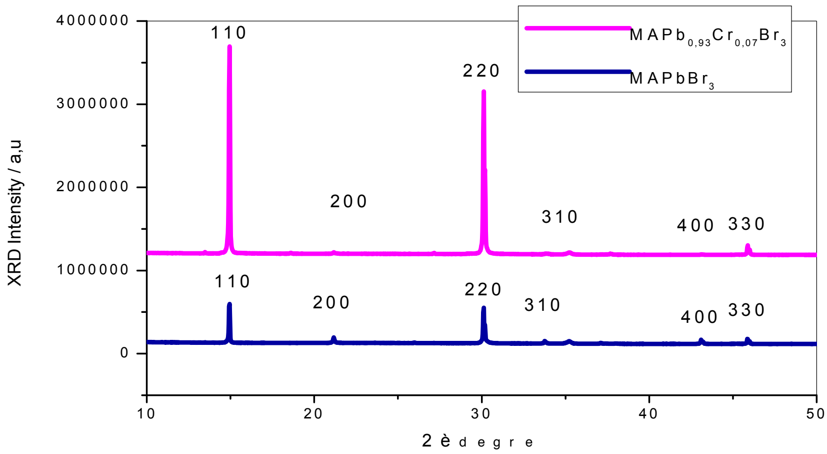

Fig 1: XRD patterns of $MAPbBr_3$ and $MAPb_{0,93}Cr_{0,07}Br_3$ deposited by spin coating Reference pattern JCPDS#00-0105 relates to a cubic Pm3m structure.

III.2 OPTICAL PROPERTIES

Variation of optical properties of $MAPb_{0.93}Cr_{0.07}Br_3$ and $MAPbBr_3$ perovskite films measured in the UV-visible absorption range was shown in Figure 2. The band deviation was estimated from the beginning of the absorption edge. The energy values of the band were estimated at 1.80 and 1.6 eV for $MAPb_{0.93}Cr_{0.07}Br_3$ and $MAPbBr_3$, respectively. The results revealed that the introduction of a very small fraction of slightly modifies the value of the band deviation. This modification of the energy of the space of the band is undoubtedly due to a structural distortion after the inclusion of Cr. The band gap values are very close to the accepted values and this makes the films suitable for optoelectronic devices.

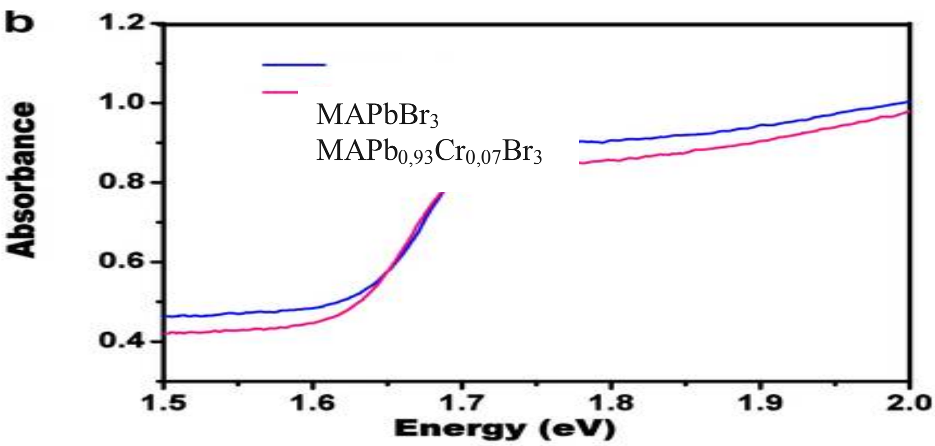

Fig 2: UV–vis absorption spectra of $MAPbBr_3$ and MA $MAPb_{0,93}Cr_{0,07}Br_3$.The energy values of the band were estimated at 1.80 and 1.6 eV for $MAPb_{0.93}Cr_{0.07}Br_3$and $MAPbBr_3$, respectively

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III.3 SCANNING ELECTRON MICROSCOPY (SEM) ANALYSES

Scanning electron microscopy (SEM) was used to study the surface morphology of films $MAPb_{0.93}Cr_{0.07}Br_3$ and $MAPbBr_3$ (Figure 3 and Figure 4). Figure 3 shows that the chromium-free perovskite film has a homogeneous texture and that the crystal particles are aggregated into larger crystals. The SEM analysis shows a morphology with good coverage and no apparent crystal orientation. The bottoms are well covered, homogeneous, dense, continuous and compact without cracks or voids. The grains are small. Figure 4 shows the texture of the perovskite film with chromium. We find that the presence of chromium has widened the grains. The big grains size is explaining by agglomeration of small grains to form one more big. The incorporation of chromium therefore affects the morphology of the film. The deposited films seem to be a bit rough. Their structure is less uniform with well-defined grain boundaries. We also note a variation in the size of the grains. Dispersed grains are present on the surface of all films. These particles are highly probable colloidal particles formed and adsorbed on the substrate during the growth of the films.

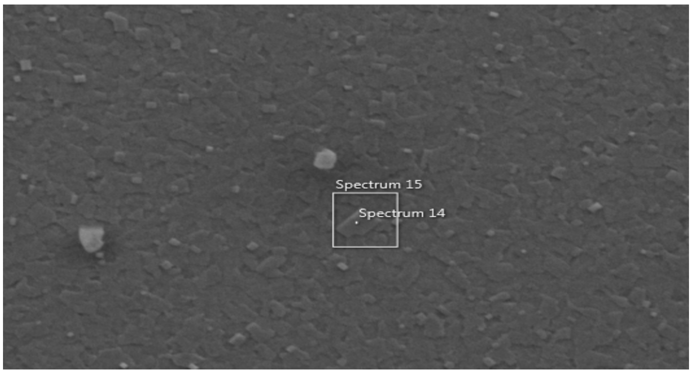

Fig 3: Top view SEM image of MAPb Br_3 deposited on ITO substrate using the spin coating processthe precursor solutions were prepared by dissolving MAB rand $PbBr_2$ powders at 45% wt Dimethylformamide (DMF) solution

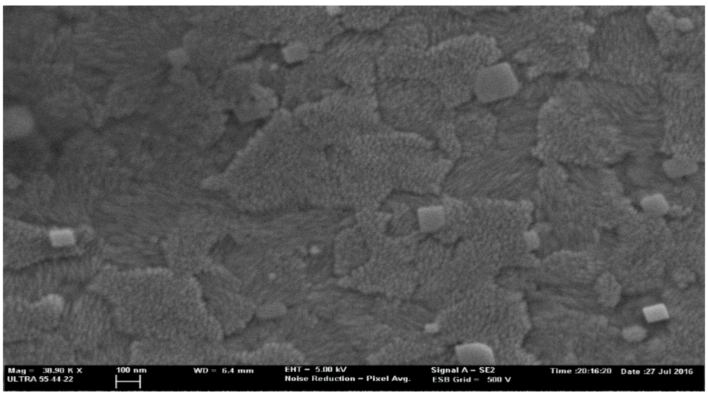

Fig 4: Top view SEM image of $MAPb_{0,93}Cr_{0,07}Br_3$ deposited on ITO substrate using the spin coating process.The precursor solutions were prepared by dissolving MABr, $PbBr_2$ and $(ClO_4)_3Cr$ powders at 45% wt Dimethylformamide (DMF) solution

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III.4 ELEMENTAL ANALYSIS

Energy Dispersive Spectroscopy (EDS) is a quantitative and qualitative tool to measure atomic concentration of elements present in sample after elaboration. The quantitative elemental analyses of all films were done by energy dispersive X-ray spectroscopy. The EDS spectra reveal that all the films deposited using the spin coating process contain the Pb,Br and Cr as expected. The other peaks that are not expected to be in the deposited films may be resulted from the substrates. The representative EDS spectra of samples deposited from solution with The precursor solutions are shown in Fig 5 and fig 6. On the EDS spectra of $MAPbBr_3$ deposited on an ITO substrate using the centrifugal coating method, the presence of lead (Pb) and bromine (Br) is observed (Fig 5). Figure 6 shows the EDS spectrum of $MAPb_{0.93}Cr_{0.07}Br_3$ deposited on an ITO substrate using the same centrifugal coating method. Here we see chrome in addition to lead and bromine. Our intention to substitute some of the lead with chromium is confirmed. The atomic percentages of the elements Pb, Br and Cr are given in Tables 1 and 2. Table 1 gives the atomic percentages of Pb and Br of the compound $MaPbBr_3$. In this table, it can be seen that the experimental results are close to the theoretical results. This same observation is made for the atomic percentages of Pb, Br and Cr in the $MAPb_{0.93}Cr_{0.07}Br_3$ compound (Table 2).In conclusion, it is found that the compounds MaPbBr3 and $MAPb_{0.93}Cr_{0.07}Br_3$ are fairly stoichiometric.

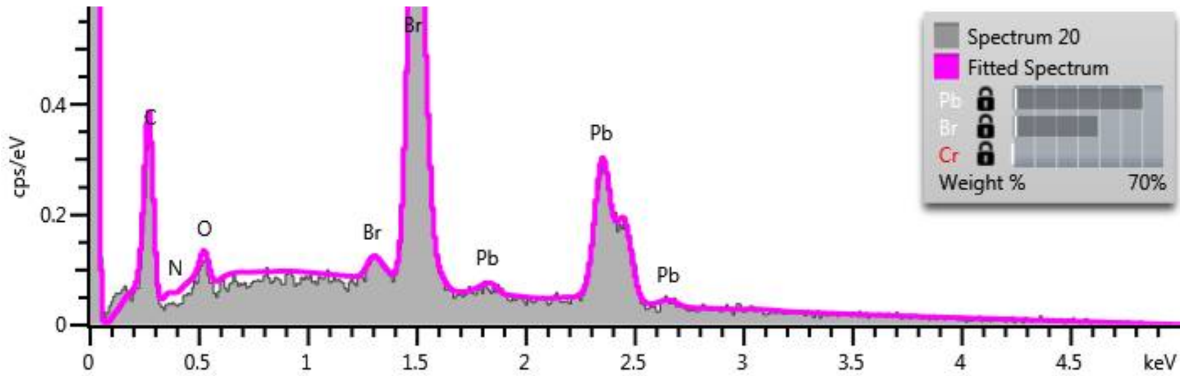

Fig 5. EDS spectra of $MAPbBr_3$ deposited on ITO substrate using the spin coating process. the presence of lead (Pb) and bromine (Br) is observed

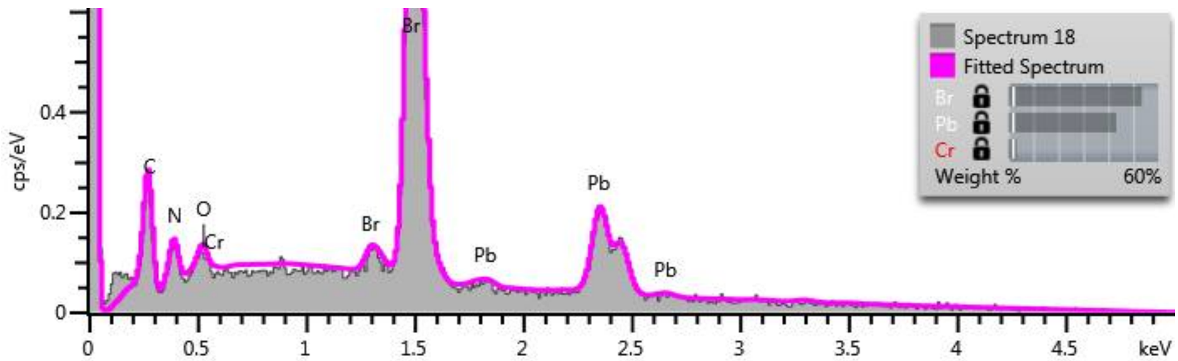

Fig 6. EDS spectra of $MAPb_{0,93}Cr_{0,07}Br_3$ deposited on ITO substrate using the spin coating process. the presence of lead (Pb) , bromine (Br) and chromium (Cr)is observed

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Table1: Composition of MAPbBr3 / ITO glass substrate obtained EDS

Element	Atomic %(theoretical)	Atomic %(experimental)
Br	75	74.60
Pb	25	25.40
Cr	00	00

Table2: Composition of $MAPb_{0,93}Cr_{0,07}Br_3$ / ITO glass substrate obtained EDS

Element	Atomic %(theoretical)	Atomic %(experimental)
Br	75	73.97
Pb	23.25	23.40
Cr	1.75	2.63

IV. CONCLUSION

In this work, perovskite $MAPb_{0.93}Cr_{0.07}Br_3$ was prepared by the centrifugal coating method (MABr), lead bromide (II) ($PbBr_2$) and $(ClO_4)_3Cr$. According to SEM, the surface morphologies of the films were free from defects. The incorporation of chromium affects the morphology of the film. The deposited films seem to be a bit rough. The presence Sof chromium has widened the grains. The EDS spectra revealed that all of them contained Pb, Br and Cr as expected. $MAPb_{0.93}Cr_{0.07}Br_3$ films are also stoichiometric. All deposited films showed a high absorbance in the UV-vis range. The band deviation values were estimated from the absorbance measurements. It was found between 1.60 and 1.80 eV. The band deviation values are very close to the accepted values. This makes the films suitable for optoelectronic devices.

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