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Study of the Optical and Structural Properties of Perovskite Thin Films Prepared by Two Sequential Deposition Techniques at Room Temperature

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Abstract:
Perovskite thin films are widely used in optoelectronic applications because of their special properties, such as low cost, the tunable bandgap and the lifetime of the thin film. Several manufacturing techniques have been used to prepare perovskite thin films, like dip coating, spin coating, evaporation technique, etc. Solar cells efficiency prepared with perovskite thin films reached to 22.1% in 2016. This research work is about studying the perovskite thin-film characteristics, using first the method of spin-coating technique for the PbI_2 thin film preparation on a glass substrate and then preparing perovskite thin film by dip-coating technique, the whole process was conducted at room temperature. Characteristics features of perovskite thin films were investigated using UV-VIS spectroscopy, X-ray diffraction (XRD), furrier transmission infrared (FTIR) spectrum, diffused reflection spectrum (DRS), field emission scanning electron microscope (FESEM), and EDS. The results manifested the perovskite thin film with optical band gap (1.6-1.8 eV), low absorbance compared with other studies because of the solvent type used, and a dense thin film with low homogeneity.
Keywords: *perovskite thin films, dip-coating technique, band gap value, morphology.*

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I. INTRODUCTION

There is an urgent need to use renewable energy sources after the natural energy sources become harmful to the environments. Solar cells are the best solution for that issue[1], photovoltaics is the best way to generate the electricity because it can directly convert the sunlight to electricity[2]. Solar cell technology has different types based on the materials, makingon, and the method of preparing

these materials. It could be classified into two specific types, crystalline, and thin films based technology [3]. The properties of the crystalline silicon-based solar cells give the crystalline techniquea greater interest among the other technologies, such properties arestability, and high power conversion efficiency (PCE); on the other hand, its manufacturing high cost of the large scale makes this technique limited to manufacture only in a small scale. Solar cells based on thin films, like copper-indium-gallium-selenide (CIGS) and CdTe,are considered as a low-cost manufacture technique but that has an important disadvantage, which is the material abundance. Dye-sensitized solar cells (DSSC), organic solar cells and quantum dot solar cellshave good properties, such as the low cost and easy to manufacture, but by comparing their performance with thetraditional inorganic counterparts, they are still not good enough [4]. The new technology, which could be considered a promising technique in the industry, is the perovskite solar cells.

Perovskite is classified under the thin film based technology of photovoltaics with high performance [5]. ABX_3 is the formula of the crystal structure of perovskite (A, B are cations and X is an anion), CaTiO3 is the first compound of perovskite which was discovered in 1839 by Gustav Rose. After that, many material compounds of organic oxides have been discovered which have the same structure of perovskite, such as SrTiO3,PbTiO3,BaTiO3,BiFeO3, etc.Ferroelectric (for ceramic condensers), pyroelectric, dielectric,piezoelectric, etc. are the best applications for perovskite metal oxides [6]. Perovskite material takes these interests because of its optical and structural properties [7-8], the high absorption coefficient[9], the bandgap of its direction (1.4-3.0 eV)[10-11], an ambipolar charge transport [12-13], and the long charge carrier diffusion length[14].

Many ways were used to manufacture the hybrid lead halide perovskite material, such as vacuum evaporation and simple solution process, and by changing the chemical composition, the morphological, optical and electronic properties can be tuned[15-16].

The present study aims toprepare the perovskite thin films by spin coating the lead iodide thin film on a glass substrate and then dipping the lead iodide thin film samples in MAI solution to transform the lead iodide thin film into perovskite thin film. Also, the optical and structural properties for both PbI_2thin films and $MAPbI_3$ thin films will be studied.

II. EXPERIMENTAL WORK AND CHARACTERISTICS

The experimental work started with cleaning the glass substrate with ethanol and DI water. The PbI_2 solution was preparedby mixing the lead iodide powder with DMF solution as a solvent (0.2M of PbI_2, both are Sigma Aldrich, 99.9% purity for PbI_2 and 99.8% purityfor DMF). Deposition the lead iodide thin film on the glass substrate was done by spin coating technique with different speeds,at constant time, and annealing the final thin film.In order to study the optical and structural properties of PbI_2 thin films, the PbI_2 thin film was first

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dipped into MAI solution (0.42M in 2-propanol, Sigma Aldrich, 99.9%purity) for 30 min in a gloved box filled with N_2 gas,then rinsed with 2-propanol and dried in N_2 gas; after drying, annealing to 70°C for 30 min was done.

The optical and structural properties of the prepared films were studied using these devices;the optical properties were determined using Metertech SP8001 UV-VIS spectrophotometer. The structural properties were analyzed by Shimadzu XRD Model 6000. The FTIR measurements were conducted by BRUKER ALPHA (platinum-ART) with wavelength ranging from 500-3500cm^{-1}. By using Avalight-DH-S-BAL2048 analyses, the diffused reflectance wasmeasured, and the FESEM spectrograph was taken by MIRA 3 Tescan.Energy Dispersive Spectroscopy (EDS) for PbI2 thin film was taken byARYA Electron Optic (Maxtek AP1.3).

III. RESULTS AND DISCUSSION

The study of the optical properties of the thin films was started with absorbance; the absorbance spectrum of perovskite thin films depicts that the absorption becomes strong in the visible and near-infrared region, fig(1), with absorbance onset near 800nm [16]; the obserbanceof this thin film is much lower than absorbance spectrum from these prepared with mixed solvent and DMSO solvent[18].

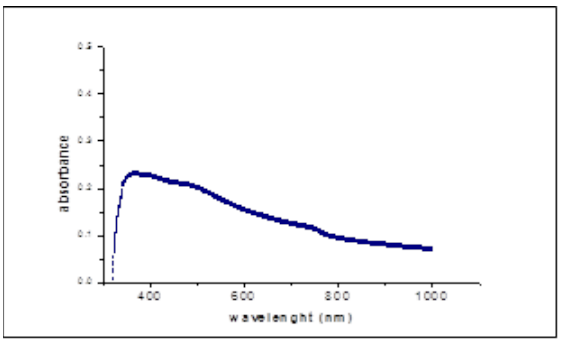

Figure (1): Absorbance spectrum of perovskite thin films prepared by dip-coating technique for 30 min.

Before the specific wavelength absorbed from the material, one can calculate the amount of the wavelength,which is penetrated, by calculating the absorption coefficient (α), where the absorption coefficient can be calculated by the following equation:

$$\alpha = \frac{2.303 \times A}{\tau} \quad (1)$$

Where: A is the absorbance, and t is the thickness of the thin film.

From figure (2), the absorption coefficient of perovskite thin films was low, that means the thin films absorbed the light poorly. The plot between α and hυgives a brief description of what kind of transition happened between the valence band and the conductive band [16].

$$\alpha = \frac{4\pi k}{\lambda} = \frac{\ln\left(\frac{1}{T}\right)}{t} \quad (2)$$

Where: t is the thickness, and T is the transmittance.

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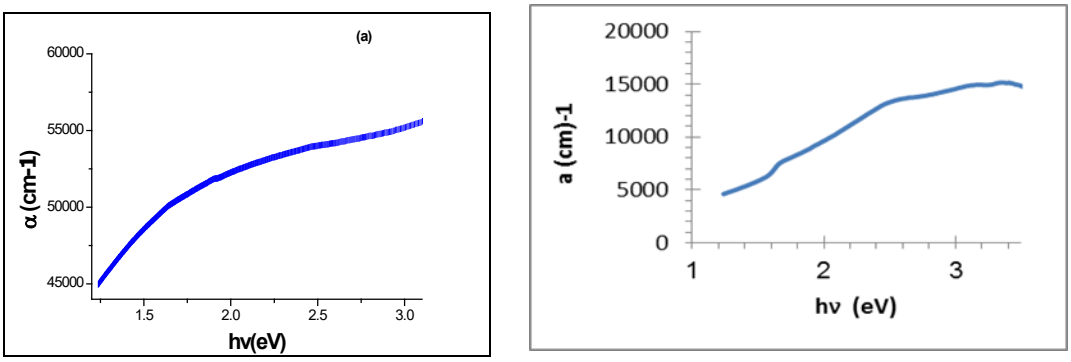

Figure (2): Absorption coefficient for perovskite thin films with different thicknesses (a is 325.1 nm) and (b is 244.5 nm)

The bandgap calculated from the UV-VIS spectrum is about 1.8eV for 325nm sample thickness and 1.65eV for 244.5nm sample thickness, fig(3), [19-20]. The bandgap can be calculated by the formula below:

$$(\alpha h\nu)^n = A(E - Eg) \quad (3)$$

Where:Eg is the optical band gap for n=2 which is the allowed direct transition, h□is the photon energy in eV, α is the absorption coefficient, and A is constant. The results elucidated that the energy gap is shifted to the right with increasing the thickness of the thin films.

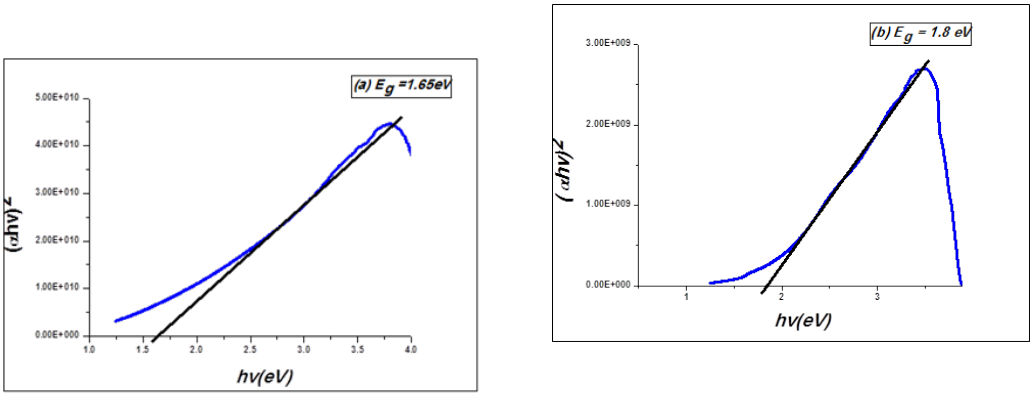

Figure (3): energy bandgap of Perovskite thin films with different thickness (a-244.5nm, b-325.1nm)

The extinction coefficient (k), fig(4),gives an indication about how much the substrate absorbed the light and it can be calculated by this formula:

$$K = \frac{\ln\left(\frac{1}{T}\right)\lambda}{4\pi t} \quad (4)$$

Where: T is the transmittance, t is the thickness, and λ is the wavelength.

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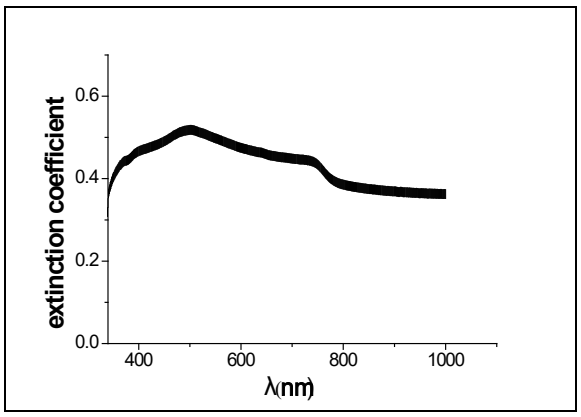

Figure (4): The extinction coefficient of perovskite thin films prepared by dip-coating technique for 30 min.

The deposited PbI_2 thin films on a glass substrate havea hexagonal structure with patterns (002), (003), (004) for the peaks at 2θ=25.66°, 38.81°, and52.53, respectively; after dipping the lead iodide thin film in MAI solution for a period of time to transform it to perovskite thin films.By taking the XRD measurements of these thin films, it was found that the thin film has a strong peak on (110) at (13,27°); the PbI_2 thin-film starts with a peak on (002) at (25.66°); this peak doesn't appear in the perovskite pattern which gives an indication that all the lead iodides transform into perovskite, as illustrated in figure(5).

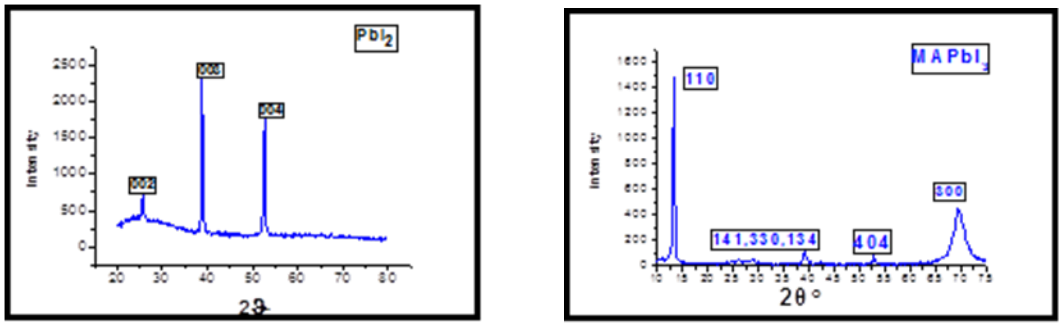

Figure (5): XRD pattern for PbI_2 thin film prepared by spin coating technique and for perovskite thin film prepared by dip-coating technique

In figure (6), the diffused reflection spectrum gives a close value for the energy gap (1.82eV) to the value calculated from the UV-VIS spectrum. The Kubelka-Munk function was usedto calculate the absorption coefficient α from this equation

$$\mathbf{F(R) = \alpha = \frac{(1-R)^2}{2R}} \quad (5)$$

Where: R is the reflected light percentage.

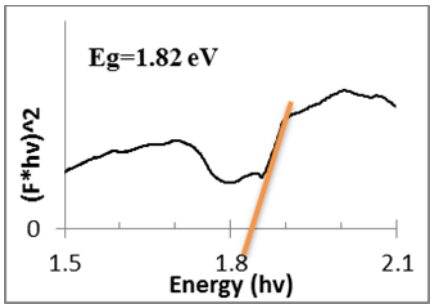

Figure (6): The diffused reflection with energy gap for perovskite thin films

The intermediate phase of the FTIR spectroscopy ranges from (500)to (3500) cm^{-1}; figure (7) illustrates that from (3300)

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to (3500) cm^{-1},the symmetric and asymmetric vibration were found; from (1400) to (1700) cm^{-1},the symmetric bending was found; and from (1100) to (1200) cm^{-1},therewere stretching modes between C–N. These resulted peaks agree with the other previous works[20-21].

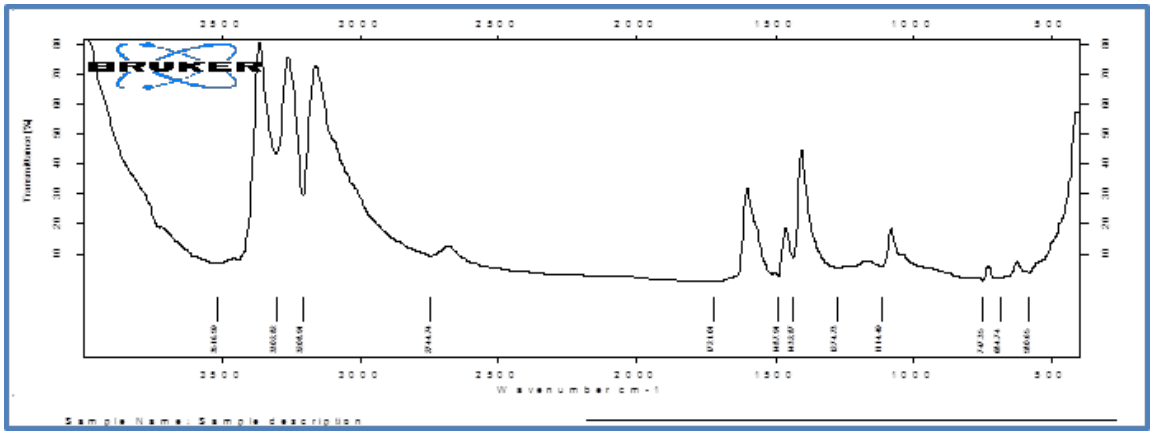

Figure (7): FTIR spectrum of perovskite thin films prepared by a spin coating technique

The EDS measurements give a description ofhow the PbI_2 thin-film converts completely to perovskite.Figure (8) evinces a sharp peak for Pb and another one for iodide; that gives an indication about the homogeneity and uniformity of the perovskite thin-film [21].

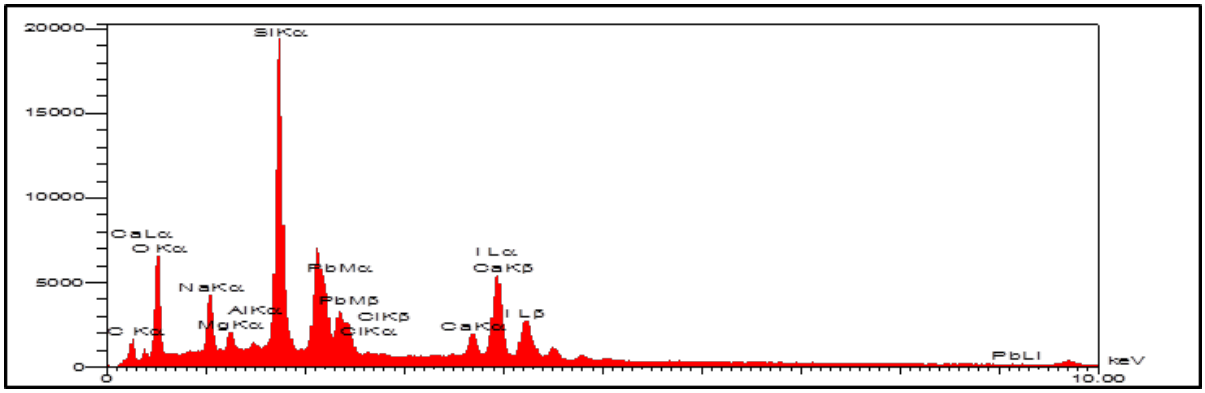

Figure (8): EDS spectral pattern for perovskite thin film prepared by dip-coating technique.

The FESEM image gives a clear indication about the surface morphology of the thin film layers; the images view that the surface roughness uniformed with grains having rod shapes and holes. This surface nature could belong to the fast crystallization rate of the DMF which causes smooth coverage uniform thin films just, as shown in figures(9) and (10).

The FESEM analysis of perovskite thin films can prove the tetragonal phase of the perovskite, which appears earlier with the XRD measurements.

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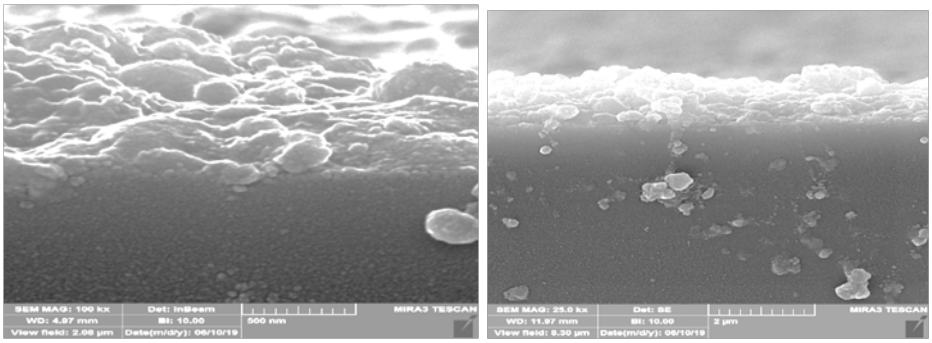

Figure (9): Cross-section for perovskite thin films with different magnifications

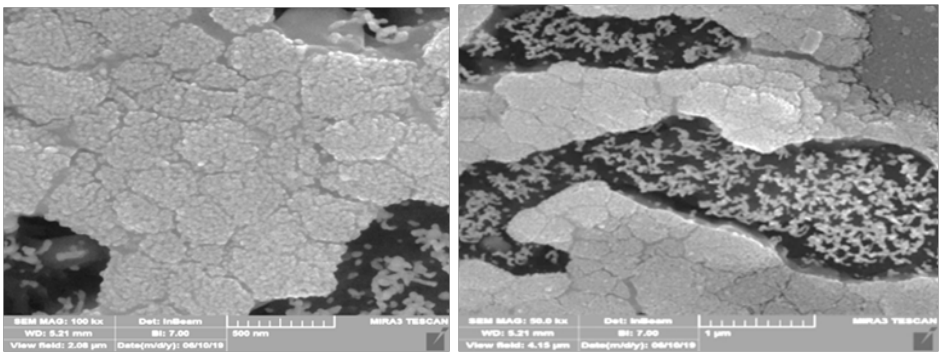

Figure (10): FESEM images for perovskite thin films prepared with the dip-coating technique with different magnifications

Figure (11) demonstrates the Raman shifting for perovskite thin-film;it was found that the ratio of symmetric to asymmetric stretching is bigger than of the PbI_2since the charged complex hasa more symmetric charge distribution, which is occurred because of introducing the extra stoichiometric amount of iodide anions. Also, it is due to the decreasing of the force constant of Pb-I bond; the symmetric mode has a slight shift to the lower energy end in the complex coordination of iodide-saturated. Because of the DMF lower coordination to the lead ion, it only shows a slight change of the donor mode(C= O) [22].

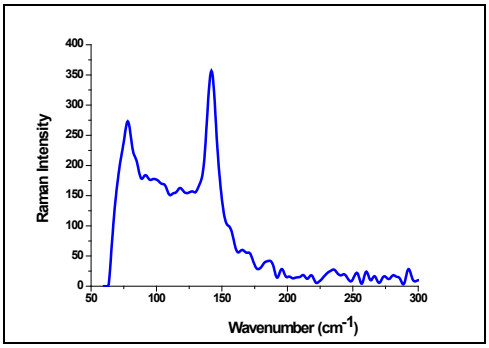

Figure (11): Raman shift of perovskite thin film prepared by dip-coating technique

IV. CONCLUSION

In summary, two-step sequential depositions for perovskite thin filmswere used. Firstly,the spin coating methodwas employed to prepare the lead iodide thin film with a specific time and speed

duration.Secondly,the dip-coating technique was utilized to convert the lead iodide thin film to perovskite. The characteristics of perovskite were discussed depending on the measurements carried outon the samples. From UV-VIS,it was foundthat the obserbancewas low,and the bandgap was about 1.6-1.8eV for different thicknesses which it was closer to the bandgap value calculated from the diffused reflection spectroscopy. The XRD pattern manifestedthat the perovskite has a tetragonal type structure with a complete transform of PbI_2 to $MAPbI_3$. The FESEM analysis supports the results of the XRD pattern of the tetragonal structure of perovskite and the smooth coverage, the density of the thin film and the inhomogeneity of it.

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