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RESEARCH ARTICLE

SURFACE MORPHOLOGY AND OPTICAL PROPERTIES OF MA-DOPED FAPbBr3 THIN FILMS FOR PHOTOVOLTAIC APPLICATIONS

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Abstract

In general, the optical and structural properties of perovskites can be improved by doping in order to use them for various applications. In this work, we have developed by the method of spin coating in one step thin layers of $FA_{1-x}MAxPbBr_3$, x gradually taking the values0.2; 0.4; 0.6; 0.8 and 0.1. An analysis of the structural and optical properties was made after their characterization. The results obtained indicate thatthe thin films produced exhibit low dislocation densities and good lattice strain values. All have a main peak of maximum intensity located at the 2Ө angle of 26.84° for the crystallographic plane (111) and their grain size decreases with the increase in the percentage of methylammonium (MA) from 501 nm to 452 nm. From the morphological point of view, we have well-covered, dense and crack-free surfaces. We also obtained an improvement in the band gap which gradually decreases during doping from 2.68eV for 2% MA to 2.40 eV for 10% MA. At the end of our study, it should be noted that MA-doped $FAPbBr_3$ thin films are of goodquality and can be used in the photovoltaic field.

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Introduction:-

In recent years, the production and consumption of energy have increased considerably. The energy demand of developing countries is growing exponentially and the excesses of the industrial revolution are being felt. The massive increase in the concentration of carbon dioxide in the atmosphere and the climatic consequences that this induces threaten humanity. Recent reports byscientists from COP21 have shown that the goal of zero greenhouse gas emissions is a necessary condition for mitigating global warming. This objective can only be achieved by using energy sources with a low carbon footprint and, preferably, environmentally friendlyA questioning of our behavior relating to energy production is therefore necessary. The search for new solutions to the challenges of climate change and sustainable development then led scientists to explore renewable energies in general and photovoltaics in particular. Photovoltaics has already proven itself as a renewable energy source. The idea that the Sun can meet the needs of humanity is relevant because the Earth receives in an hour as much solar energy as our civilization consumes in a year [1].However, to prevail, the photovoltaic sector must more than ever face productivity and price challenges. The silicon sector has developed well over time and is now able to supply society with a large quantity of reliable and high-efficiency solar panels. However, some point to the relatively high carbon footprint of silicon

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solar cells due to their energy-intensive manufacturing process, as well as the difficulty of recycling them [2]. These drawbacks have led scientists to develop solar cells based on cadmium telluride (CdTe) or Cu(In, Ga)Se chalcogenides. Their low-temperature processes significantly reduce energy consumption during module manufacturing, thereby reducing CO_2 emissions.Always in search of more efficient and inexpensive cells, the efforts of scientists have been directed in recent years towards the development of high performance materials composed of abundant elements such as graphite, copper thiocyanate CuSCN or copper oxide. fluor-doped tin FTO which make it possible to dispense with expensive metals. These materials are already used in opto-electronic devices and have shown their efficiency [3, 4].Halogenated hybrid perovskites fall within this research context. They are versatile semiconductors that combine high performance, low cost and low temperature processability for various applications such as photovoltaics or light emission. They are very popular due to their benefits [5-10]. Several methods are used to synthesize perovskite thin films. They range from vacuum deposition [11], vapor assisted solution processing [12], atomic layer deposition [13], one and two step solution processing [14,15] to spin coating [16]. . These deposition methods are rapid, simple and inexpensive. However, although they have many advantages, they still have challenges to overcome, the main one being their structural instability. Perovskites have the formula ABX_3 (where A = MA, FA, Cs; B = Pb, In, Sn and X = Br, Cl and I) and this structure is evolutionary. Several comparative studies are carried out on perovskites. For example in the literature, it is said that the band gap of $MAPbBr_3$ is significantly higher than that of MAPIs.[17].Similarly, methylamonium perovskites ($MAPbX_3$) are more stable than formamidinium perovskites ($FAPbX_3$) but the latter have a smaller band gap than $MAPbX_3$. Doping is generally done at the level of the halogens and the structural and optical properties are studied. In this work, ourdoping will be done at the level of the organic cation. Lead formamidinium tribromide $FAPbBr_3$is doped with methylammonium MA ($FA_{1-x}MA_xPbBr_3$) and an investigation is carried out on their structural and optical properties of the resulting thin film.

Materials and Methods:-

The productsTo obtain better quality films, the substrate must be properly treated.For this purpose it was bathed in several solutions such as ELLMANEX, ethanol, acetone and isopropanol for 15 minutes each time. For the preparation of the perovskite solution, we dissolved methylamonium bromide (FABr), lead dibromide (PbBr2) in dimethylformamide (DMF) and formamidinium bromide(MABr) from 2% to 10% by weight of MABr in steps of 2. The different FA1-xMAxPbBr3 solutions are then deposited on the rotating substrate by the one-step spin-coating method. The substrates arerotated at 4000 rpm for 50 seconds. Ether was used as an anti-solvent. The samples were annealed at 80°C for 20 minutes on a hote plate.

Characterization is a very important step in the experimental study of the active layers of the photovoltaic solar cell as well as of the cell itself. In the present work several analyzes were made. The crystalline microstructures of the films were determined using a RIGAKU Ultima IV in the Bragg-Brentano (θ-2θ) configuration using CuKα radiation (λ = 1.54060 Å)The range of 2ϴ diffraction angles was set between 10° and 60°. The surface morphology of perovskite thin films wasobserved by a scanning electron microscope (SEM). Finally, UV-Visible spectroscopy was used to determine the optical properties of elaborate thin layers.

Results and Discussion:-

The determination of the structural characteristics of the processed films is very important. To obtain these parameters, we send incident radiation onto the sample. A part of the radiation that is reflected by the sample is collected by the detector of the analysis apparatus according to Bragg's law: $2d\sin(\Theta) = n\lambda$**[18].**In addition, X-ray diffraction provides structural parameters such ascrystallographic orientation, effective lattice strain (ε) which can be calculated using the Scherrer .equation from the XRD parttern data **[19].**

$$\varepsilon = \frac{\beta * \cos(\Theta)}{4 * \sin(\Theta)} \quad - \frac{K\lambda}{D * 4\sin(\theta)} \qquad (1)$$

Where β is the maximum width at half maximum (FWHM), K=0.95 (Scherrer constant), λ is thewavelength of light incident on the material, D is the crystal size and θ is the Bragg angle. Thedislocation density of the lattice is evaluated using equation 2.

$$\delta = \frac{1}{D^2}\,(2)$$

The data from this analysis are represented by XRD diagrams (peaks) according to the intensity on the ordinate and the diffraction angle 2ϴ on the abscissa. These peaks, which are the response of the electron cloud and thus of the arrangement of the atoms in the crystal, correspond to the crystallographic planes.In this study, we have several peaks whose intensity varies with the percentage of methylamonium (MA) incorporated**(Figure 1).** All samples have a main peak with the highest intensity located at the 2ϴ angle of 26.84° for the (111) crystallographic plane. Peaks of lower intensity are also observed at the 2ϴ angles of 15°, 34.11° and 38.12° corresponding to the (001), (012) and (112) planes respectively. The good resolution and non-duplication shows that we have single-phase thin films. The intensities of the different peaks being similar, we can say that thecrystal structure of the thin films is not related to the MA percentages we used for the doping of $FA_{1-x}MAxPbBr_{3.}$

Figure 1: XRD patterns of lead formamidinium tribromide (FAPbBr3) thin films doped with Methylammonium(MA)

Table 1 shows some characteristics of the crystal microstructure of lead-formamidinium tribromide ($FAPbBr_3$) thin films doped with methylammonium (MA). Summarized are grain size values, dislocation density values and lattice strain values. In this table, it can be seen that the size of the grains decreases with the increase in the percentage of methylammonium (MA). This is explained bythe fact that the ionic radius of formamidinium (2.79 Å) is only slightly greater than that of methylammonium (2.70 Å). However, this decrease is not very large. It should also be noted that all the thin layers produced have low dislocation densities and good lattice strain values. The doping of lead-formamidinium tribromide ($FAPbBr_3$) with methylammonium (MA) therefore has noconsiderable effect on their crystallinity. It can be deduced from all the foregoing that all the thin layers prepared have excellent structural quality.

Table 1:- Grain size, dislocation density and XRD lattice deformation of FA1-xMAxPbBr3 thin films.

Samples	**Grain size (nm)**	**Dislocation density δ (nm $^{-1}$)**	**Latticestrain (ε)**
2% MA	501	3,98.10^{-6}	0.176
4% MA	461	4,70.10^{-6}	0.192
6% MA	474	4,45.10^{-6}	0.187
8% MA	480	4,34.10^{-6}	0.185
10% MA	452	4,89.10^{-6}	0.196

Scanning electron microscopy (SEM) was used to study the surface morphology of $FA_{1-x}MA_xPbBr_3$ thin films. **Figure 2** shows the micrographs of $FA_{1-x}MA_xPbBr_3$thin films that were elaborated with a percent of at 4% and 8 % of AM. this technique makes it possible to see the grain size of the crystals on the surface of the sample. the images show well covered, dense surfaces without cracks. However, the layers have a few clusters showing spaces like holes. The best surface is that of the 8% MA layer which is well covered with good grains. From these surface images, we can conclude that the surface image improves with the percentage of methylammonium (MA). However, all the elaborate layershave good surfaces which allow them to be used for photovoltaic applications.

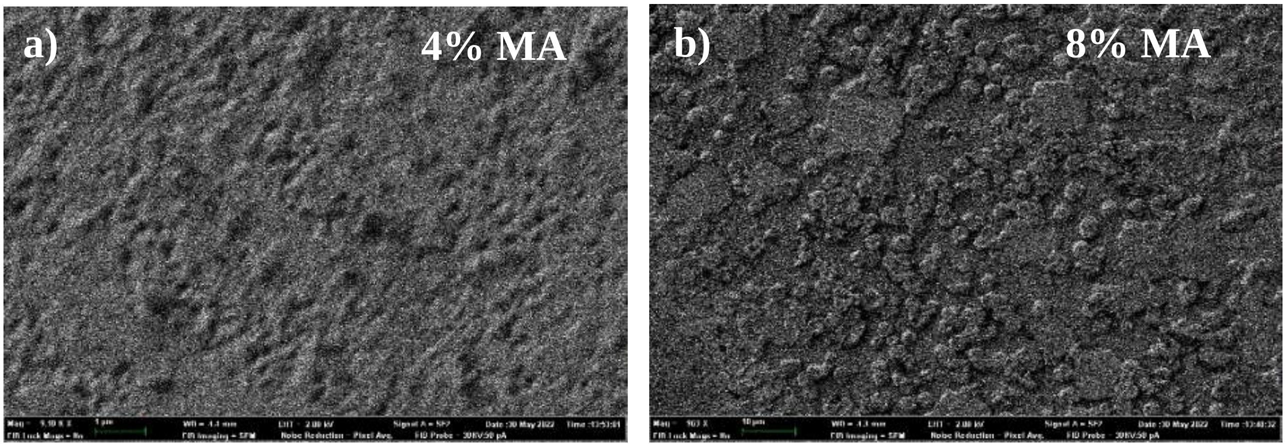

Figure 2:- Surface images of the different thin films a) 4%MA; b) 8%MA;

Photovoltaic solar cells are designed and manufactured to capture the maximum amount of solar radiation and convert it into electricity. It is therefore obvious to carry out UV-visible analysis to determine the optical properties.

Figure 3a shows the absorption diagrams of the different thin films. The highest absorbance is that of the 10% AM layer between 300nm and about 600nm, while over the whole visible absorption spectrum (300nm - 900nm) the 4% and 8% AM layers have the lowest absorption coefficients. Between 600nm and 900nm the 2% AM layer has the highest light absorption coefficient. From about 700nm the absorptions are almost equal to the difference of the 2% AM layer.Although it is important that a thin film absorbs more light, it is even more importantthat these light rays generate many excitons (electron-hole pairs) to account for the efficiency of the film.

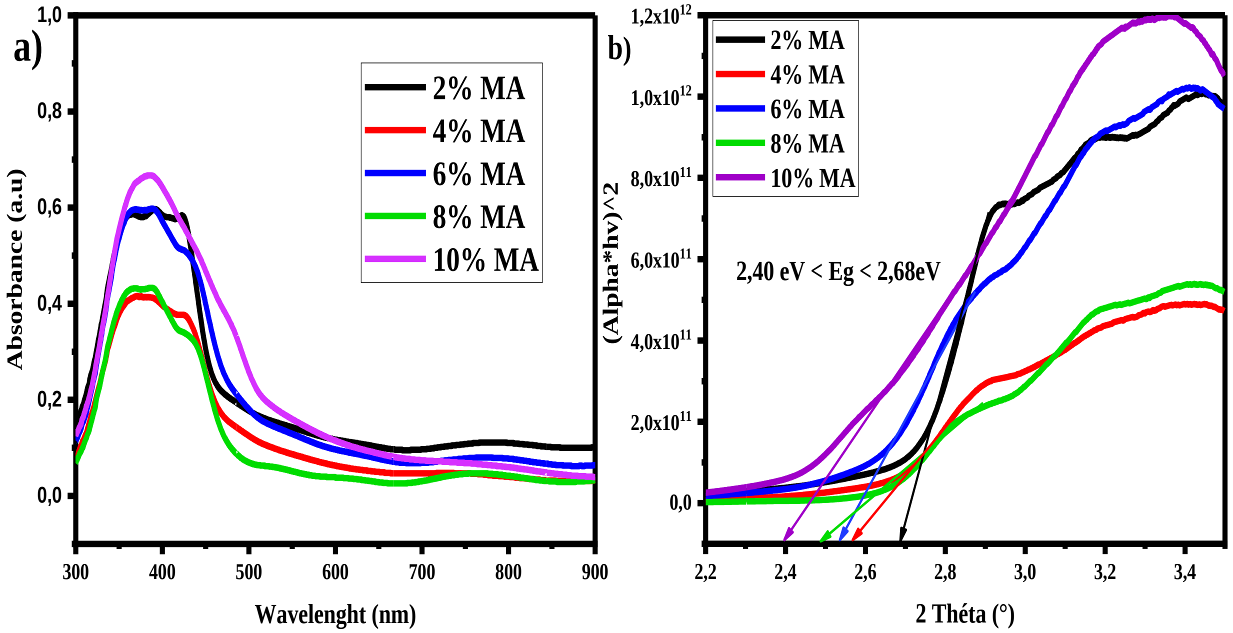

Figure 3:- Absorption diagram of thin film 3a) and band gap 3b

Using the curves in Figure 3b, we determined the values of the band gap of the different thin layers and recorded them in **Table 2.** The smaller the band gap, the better the layer since the captured photons will more easily generate electron-hole pairs. The band gap varies between 2.40 eV and 2.68 eV**(Figure 3b)**. It can be seen that the band gap decreases with the percentage of AM **(Table 2).** The smallestband gap is for the 10% AM layer and the largest for the 2% AM layer. When the absorption and band gap are combined, the best layer from an optical point of viewis the 10% AM layer.

Table 2:- Calculation of the band gap of the different percentages of MA methylammonium.

Bandgap calculated from UV visible		
Samples	**Wavelength (nm)**	**Eg (eV)**
2% MA	**461**	**2,68**
4% MA	**479**	**2,56**
6% MA	**505**	**2,53**
8% MA	**597**	**2,49**
10% MA	**632**	**2,40**

Conclusion:-

$FA_{1-x}MA_xPbBr_3$thin films were prepared by the one-step spin-coating method.Structural results showed a single preferred crystallographic orientation along the (111) plane. The thin layers produced show low dislocation densities and good lattice strain values. The doping of lead-formamidinium tribromide ($FAPbBr_3$) with methylammonium (MA) therefore has no significant effect on their crystallinity.From the morphological point of view, there is generally a good surface morphology with good grains which is favorable to good light absorption. We obtained also an improvement of the forbidden band which gradually decreases during the doping from 2.68eV for 2% of MA to 2.40 eV for 10% of MA.At the end of our study, it shouldbe noted that MA-doped $FAPbBr_3$ thin films are of good quality and can be used in the photovoltaic field.

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