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# Characterization of organic/inorganic perovskite material $CH_3NH_3PbI_3$ prepared by spray pyrolysis with moving nozzle method

Caractérisation du matériau pérovskite organique/inorganique $CH_3NH_3PbI_3$ préparé par la méthode de pulvérisation pyrolyse avec buse mobile

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ABSTRACT

Methylamine lead tri-iodide (MAPbI3 or $CH_3NH_3PbI_3$) is a promising organic/inorganic perovskite material in photovoltaic applications. It attracted researcher's attention for its good power conversion efficiency that stepped from 3.8 % in 2009 to up to 22 % in 2018. In this paper is reported a new low-cost method to fabricate CH3NH3PbI3 which is the spray pyrolysis with moving nozzle. Then it is reported different optical and electrical characteristics of the resulting perovskite. Results promote that a molarity of 2 moles and a processing temperature of 100°C can improve optical properties.

RÉSUMÉ

Le méthylamine plomb tri-iodure (MAPbI3 ou bien $CH_3NH_3PbI_3$) est un matériau pérovskite promoteur du type organique/inorganique qu'on utilise dans les applications photovoltaïques. L'évolution exponentielle de rendement des cellules solaire à base de ce matériau d'une valeur de 3,8 % en 2009 jusqu'à plus de 22 % en 2018 a attiré l'attention des chercheurs. Dans cet article, nous avons contribué par une nouvelle méthode de fabrication de couches minces de pérovskite $CH_3NH_3PbI_3$ à bas cout et ce en utilisant la méthode de "spray pyrolysis with moving nozzle". Les couches minces fabriquées ont montré des caractérisations optiques et électriques différentes. Les résultats obtenus montrent qu'une molarité de 2 moles et une température de traitement de 100° améliore les caractéristiques optiques du pérovskite $CH_3NH_3PbI_3$.

## 1 Introduction

Recently the hybrid perovskite $CH_3NH_3PbI_3$ organic-inorganic remains the most studied [1-3] from deferent point of views such as simulations and realisation processes. Simulation efforts have been investigated by[4] using GPVDM software and by [5,6] using Silvaco TCAD. However, realisation processes effects on material performances are widely studied such as temperature effects presented in [7]. Perovskite materials are important because of them applications in

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deferent knowledge fields such as low cost solar cell technology [8]. The solar absorption threshold of hybrid perovskite $CH_3NH_3PbI_3$ is compatible with solar radiation which makes it a good material for photovoltaic applications.

A number of techniques have been developed in manufacturing $CH_3NH_3PbI_3$ nanomaterials, which can be generally categorised as physical and chemical methods. The $CH_3NH_3PbI_3$ thin film deposition can be realized using several methods such as pulsed laser evaporation described in [9, 10], physical vapor deposition [11] and spray pyrolysis method [12, 13]. Chemical-based synthesis methods are generally adopted due to low production fees and high yield. Studies have shown that these substances are affected by several factors : the outside environmental conditions, concentration, including sedimentation temperature, annealing and used deposition method [14, 15].

Spray pyrolysis with moving nozzle (SPMN) is used to sustain the heat of substrate throughout the elaborating period. The aim of this work is to synthesize and study physical properties of $CH_3NH_3PbI_3$, to determine the effect of the molar ratio between the concentration of iodine and methylamine iodide and to investigate the effect of temperature.

## *2* Experimental details

### 2.1 Thin films preparation

We prepared the thin film using two ways :

In the first way, perovskite solution is prepared in the first step (see Figure 1.) with mixing 0.6 ml of Dimethylformamide (DMF) and $PbI_2$ with different molar ratios $[CH_3NH_3I]$ / $[PbI_2]$ according to Table 1.

**Table 1 - Constitution of the different perovskite solutions realized**

| Molar ratio [CH3NH3I]/[PbI2] | The weight of the reactants (g) | |
|---|---|---|
| | CH3NH3I | PbI2 |
| 0.5 | 0.05 | 0.286 |
| 1 | 0.098 | 0.286 |
| 2 | 0.196 | 0.286 |

Then preparation process follows steps presented in Figure 1. The value of temperature processing in step 4 is 100°C.

In the second way perovskite solution is prepared according to the Figure 1., in which we used deferent processing temperatures in the thermal processing (see Figure 1 step 4) namely 70°C, 80°C, 90°C, 100°C, 120°C, 130°C and 150°C. The molar ratio use in this second way is 1.5.

### 2.2 Thin films characterization

The band gap energy has been obtained from the optical transmittance spectrum using (UV–VIS spectrophotometer Shimadzu, Model 1800) operating in the wavelength 300-900nm range.

## *3* Results and discussion.

### 3.1 Optical properties: the band gap

Figure 2 shows the variation of the transmittance as a function of the wavelength for three layers developed with three molar ratios : 0.5, 1 and 2 (see Table 1), the transmittance measurements have been made in the wavelength range of 250-850 nm. In the region between 600 and 850 nm, the transmittance of deposited films is in the order of 43%, 34%, and 26% respectively. Low permeability values can be attributed to the dispersion of light from crystal defects, Tauc's relation is used :

$$\alpha h\nu = A\left(h\nu - Eg\right)^n \tag{1}$$

Where $E_g$, $v$, $h$ and α and are the band gap energy, the photon frequency, the Planck constant and the absorption parameter respectively. The parameter $n$ is taken to be equal to 1/2 based on consideration that perovskite has a direct gap and $\boldsymbol{A}$ is a constant.

Plots of $(\alpha hv)^2$ vs $hv$ are obtained from optical absorption data and presented in Figure 3 for the first way prepared layers and in Figure 4 for the second way prepared layers.

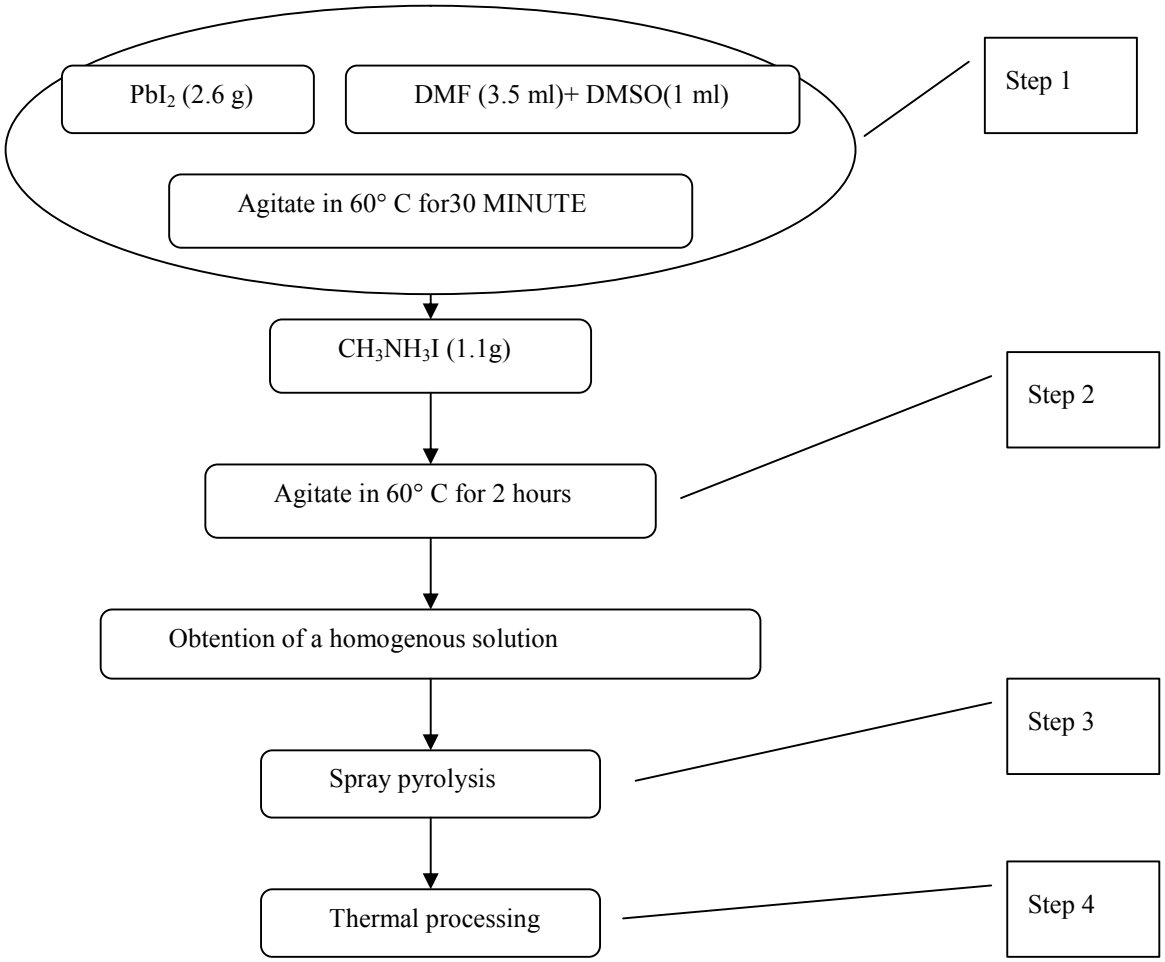


Fig. 1 – Perovskite deposition method.

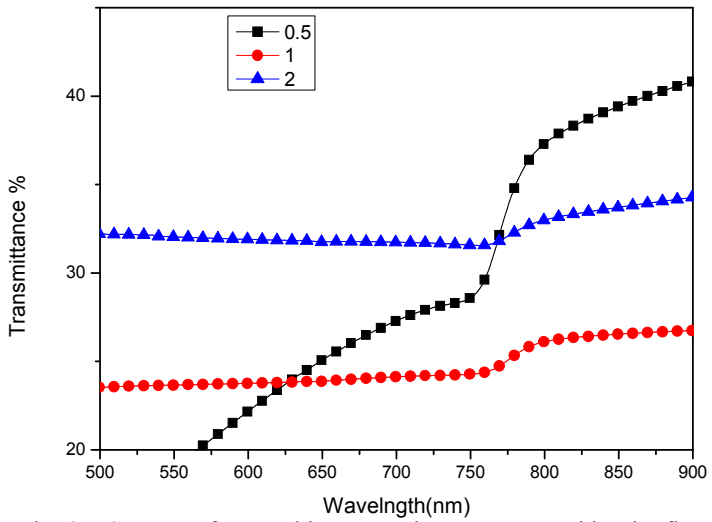


Fig. 2 – Spectra of perovskite transmittance prepared by the first way.

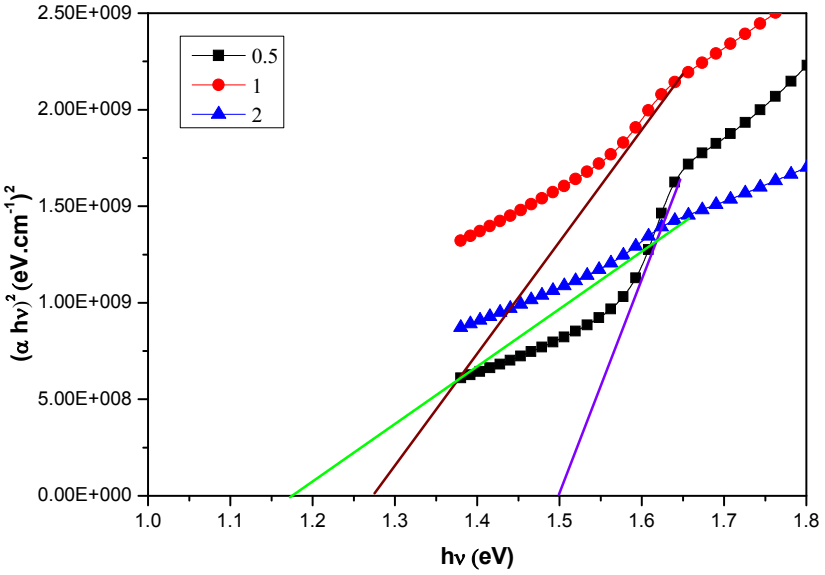


Fig. 3 – Curves presenting the variation of $(\alpha h\nu)^2$ in function of $h\nu$ and direct band gap deduction for deferent concentrations (first way).

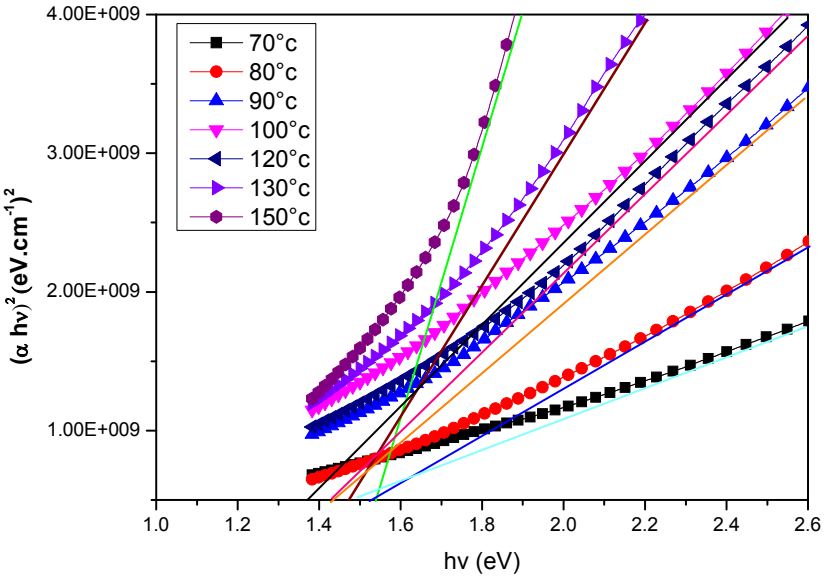


Fig. 4 – Band gap ($E_g$) for as sprayed perovskite and annealed thin films using deferent processing temperatures (second way).

Photodynamic data was used to engender pieces of $(\alpha hv)^2$ vs $hv$, as presented in Figure 3 and Figure 4. Band gap values resulting for deferent molarity and deferent values of temperature processing are presented in Table 2 and Figure 6 respectively. It is noticed that the obtained band gap values are around 1.5 eV which means that it is a good absorber for visible light.

### 3.2 Optical properties: Energy of Auerbach

Auerbach energy $E_u$ is a principal optical characteristic of thin film layers, it is calculated using equation (2) :

$$\ln(\alpha) = \ln(\alpha_0) + \frac{h\nu}{E_u} \tag{2}$$

From the curve drawing of the variation of $\ln(\alpha)$ in function of $(h\nu)$ presented in Figure 5 (for the first way prepared layers), we can obtain the reverse Auerbuch energy using the value obtained in the straight line intersection with the abscise line.

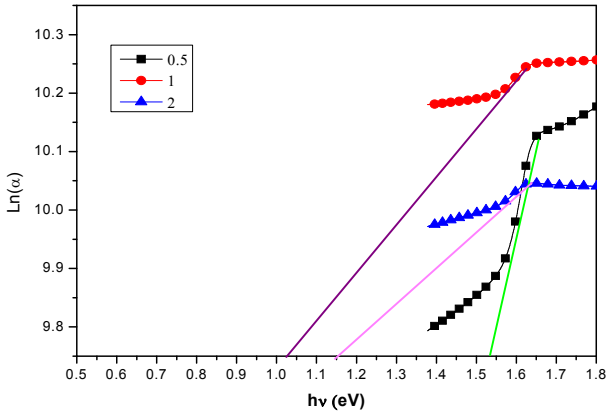


Fig. 5 – Curve presenting $\ln(\alpha)$ in function of $(h\nu)$ and deduction of Auerbach energy values deferent concentrations.

Corresponding Auerbach energies for deferent concentrations concluded from Figure 5 are presented in Table 2. It is remarked that Auerbach energy decreases with concentration increased. In addition, we note that the molar ratio [CH3NH3I] / [PbI2] has a significant effect on the value of the energy separator, and thus we obtain many applications through these properties.

**Table 2. Auerbach energy and Bandgap of deposited samples (first way).**

| **Molar ratio [CH3NH3I]/[PbI2]** | **Optical gap $E_g$(eV)** | **Auerbach energy $E_u$(meV)** |
|---|---|---|
| 0.5 | 1.50 | 970 |
| 1 | 1.54 | 869 |
| 2 | 1.46 | 653 |

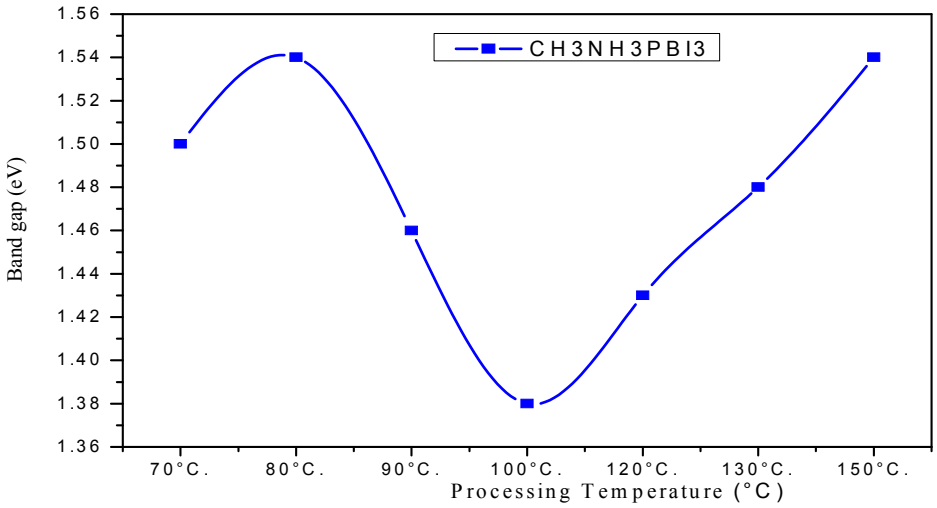


Fig. 6 – Variations of the band gap energy in terms of processing Temperature.

**Table 3. Auerbach energy of deposited samples (second way).**

| Annealing time | Auerbach energy (meV) |
|---|---|
| 70°C | 296 |
| 80°C | 654 |
| 90°C | 617 |
| 100°C | 806 |
| 120°C | 641 |
| 130°C | 666 |
| 150°C | 757 |

From Figure 6, we observe that the value of the separator increases from 70 to 80°C from 1.5 to 1.54 eV and then decreases to 1.38 eV at 120°C and then increases to 1.54 eV at 150 °C. The reason for the increase in the first stage is the lack of crystalline defects. As for the second phase, the ratio of crystalline defects to crystallization is considered, or the third stage, we notice an increase in the value of the energy separator to 1.54 eV, which indicates that there is a relative deformation on the crystal.

## 4 Conclusions

It is found that the prepared layers using both ways have a band gap values between 1.38 and 1.45 eV which forms a good visible light absorber. Meanwhile, using the spray pyrolysis with moving nozzle deposition method we can conclude from the first way processing that the better molarity concentration that gives lower energy of Auerbach and hence a lower crystalline defects is 2 Moles. Whereas, Concerning the temperature processing (second way processing), it is discovered that the temperature processing of 100°C gives butter crystalline structure that corresponds to lower Auerbach energy.

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