Efecto de la temperatura en la cristalización de películas de perovskita-ch_3n-h_3pbi_3-xcl_x
Effect of temperature on crystallization of perovskite films - $ch_3nh_3pbi_3$-xcl_x

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Resumen
En el presente documento, se analizó el efecto de la temperatura en la cristalización de películas delgadas de perovskita (CH3NH3PbI3-xClx) (las películas de perovskita se utilizan para producir células fotoeléctricas basadas que parecen ser dispositivos con menores costos de producción y mayor eficiencia que las células fotoeléctricas basadas en silicio). Para sintetizar las películas de perovskita, se sometió a cuatro muestras, con solución precursora, a un proceso de centrifugado durante 45 s a 2.000 rpm. Después, las muestras se trataron térmicamente a tres temperaturas. Asimismo, las muestras se caracterizaron mediante espectroscopia UV/Vis, espectroscopia de emisión y microscopia electrónica de fluorescencia, y se utilizó el software ImageJ para analizar el tamaño de los cristales. Se encontró que la muestra tratada a 80 oC presentó la mayor emisión de fluorescencia con 49539,09 CPS y la mejor distribución de tamaño de partícula. También se calculó la brecha energética (Eg), que resultó ser de 1,60 ± 0,01 eV (Una célula fotoeléctrica ideal tiene una energía de brecha de 1.4 eV para absorber la máxima cantidad posible de fotones de la radiación solar).
Palabras clave: Cristales de Perovskita; Cristalización; Células Fotoeléctricas.

Abstract
In the present manuscript, the effect of temperature on crystallisation of perovskite thin films (CH3NH3PbI3-xClx) was analysed (perovskite films are utilized to produce perovskite-based solar cells that appear to be devices with lower production costs and higher efficiency than silicon-based solar cells). To synthesise the perovskite films, four samples with precursor solution were spin coated for 45 s at 2000 rpm. After that, the samples were annealed at three different temperatures. Likewise, samples were characterised by UV/Vis Spectroscopy, Emission Spectroscopy, Fluorescence Microscopy, and ImageJ software were used to analyse crystal size. It was found that the sample annealed at 80 oC presented the highest fluorescence emission with 49539.09 CPS and the best particle size distribution. Band Gap Energy (Eg) was also calculated resulting in 1.60 ± 0.01 eV (An ideal solar cell has a band gap of 1.4 eV to absorb the maximum number of photons from the solar radiation).
Keywords: Perovskite Crystals; Crystallisation; Solar Cells.

1. INTRODUCTION

Perovskite-based solar cells (PBSC) appear to be an alternative to silicon-based devices due to their significantly better performance when it comes to cell stability and characteristics [1]. Likewise, PBSC have low production cost, high efficiency, and a simple production process. More specifically, perovskite crystals are a remarkable material that can be described by the formula ABX3. Where A and B are different-size cations and X is an anion. This material also contains an organic molecule, a heavy chemical element like Pb and a halogen atom [2]. However, the mixed halide perovskite CH3NH3PbI3-xClx (MAPbI3-xClx) can be synthesised by using an I- and a Cl- anions. It has been also proved that MAPbI3-xClx has an upgraded stability in air and a long-charged diffusion length compared to methylammonium lead iodide perovskites. However, chlorine presence in perovskite crystals is controversial. It has been discovered that nucleation dynamics can be affected by chlorine, yet undetectable in the final perovskite film. Nevertheless, the role of chlorine in perovskites is to perform as a surface passivator and as a dopant [3].

In 2009 Miyasaka et al. [4] developed a CH3NH3PbI3-based solar cell for the first time and a 3.8% of efficiency was reported. Due to this work, PBSC have been improved and nowadays numerous studies have reported more than 15% of power conversion. Several techniques have been applied to produce PBSC such as solution process (one step, two steps and vapour assisted), thermal evaporation [5] and annealing process. Nevertheless, one-step solution process has shown problems that can be influential for PBSC performance such as weak crystallisation of CH3NH3PbI3-xClx, non-uniformity and leakage [6].

Crystallisation is the main factor that determines the PBSC properties and performance. It has been studied and proved that improving the annealing fabrication process crystallinity of the perovskite films can be increased, therefore, electronic properties can be also upgraded [5].

In the present work, thin films of perovskite crystals were synthesised by spin-coating and annealing the samples at RT, 80, 100 and 125 oC to analyse the effect of temperature on crystallisation of perovskite layers. Furthermore, perovskite films were characterised by UV/Vis Spectroscopy, Emission Spectroscopy, Fluorescence Microscopy, and ImageJ Software was utilised to analyse the particle size of the crystals.

2. MATERIALS AND METHODS

Thin-films of iodide/chloride mixed-halide perovskite CH3NH3PbI3-xClx were synthesised at different temperatures and characterised by the following methodology described in this section.

2.1. Perovskite crystals synthesis

Firstly, a precursor solution was prepared mixing methylammonium iodide with lead chloride dissolved in dimethylformamide (DMF) producing a mixed halide perovskite as is described by Equation (1):

$$3MAI + PbCl_2 \rightarrow MAPbI_{3-x}Cl_x$$

Where,

MA = CH3NH3

To synthesise the thin films of perovskite crystals, four samples were prepared. Firstly, 100 µL of precursor solution was pipetted on three peds. After

that, each sample was spin coated for 45 s at 2000 rpm by using a Laurell WS-650MZ-23NPPB centrifuge with the aim of remove exceeding solution and to create a uniform layer. Then, the samples were placed on three different hot plates at 80, 100, and 125 oC for 25 min to crystallise the precursor solution. Likewise, the fourth sample was prepared by pipetting 100 µL of the solution on a microscope slide and another slide was placed on top to create a semi-thin layer. This sample was crystallised at room temperature (RT = 19 oC) for 2 h [6].

2.2. Perovskite crystals characterisation

To characterise the perovskite crystals three techniques were utilised. Absorbance spectra were measured in the range of 300 – 800 nm by a Perkin Elmer Lambda 9 spectrometer. Similarly, Emission Spectroscopy was conducted on a FluoroMax–4 spectrometer in the range of 650 – 950 nm to measure the fluorescence emission spectra. Band Gap Energy (Eg) was calculated by using Equation (2) [7].

$$Eg = \frac{h\,C}{\lambda}$$

Where,

Eg = Band Gap Energy

h = Planck's constant (6.626 x 10-34 J s)

C = Speed of light (3.0 x 108 m s-1)

λ = Wavelength at maximum fluorescence emission (nm)

Finally, Fluorescence Microscopy was performed on an Olympus BX51 microscope to determine the effect of temperature on the size of crystals and ImageJ software was utilised to measure the crystal size.

3. RESULTS AND DISCUSSION

3.1. UV/Vis Spectroscopy

Figure 1 shows UV/vis absorption spectra of the perovskite layers at 80, 100 and 125 oC. Due to the annealing process, perovskite films changed its colour from light green/yellow to dark grey (Figure 2), consequently, their absorbance increased [5]. Additionally, it is clearly observed an onset of the absorption spectra at 374 nm approximately.

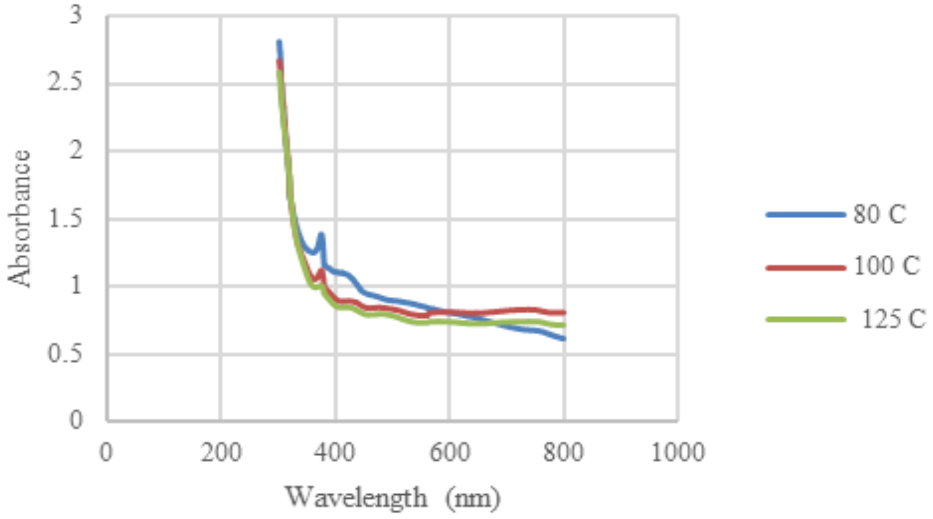

Figure 1. UV/Vis absorption spectra of perovskite films.

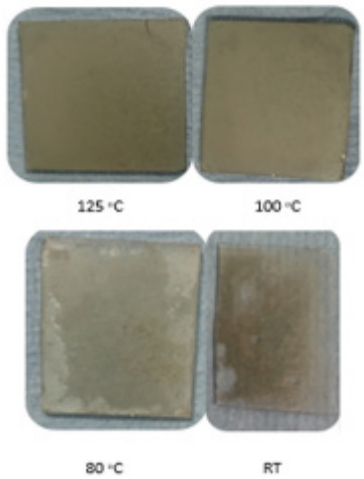

Figure 2. Perovskite films after annealing process.

3.2. Emission spectroscopy

Figure 3 displays fluorescence emission spectra of the perovskite films at RT, 80, 100 and 125 oC. The sample that was annealed at 80 oC reported the highest fluorescence emission with 49539.09 CPS at 771 nm. Thus, for this study, it can be concluded that 80 oC is the optimum temperature to synthesise perovskite crystals (CH3NH3PbI3-xClx).

Likewise, Eg was calculated by using the wavelength at the highest fluorescence emission for each annealing temperature. The Eg value resulting 1.60 eV ± 0.01 as is shown in Table 1 and it is corroborated with previous studies (An ideal solar cell has a band gap of 1.4 eV to absorb the maximum number of photons from the solar radiation) [8, 9].

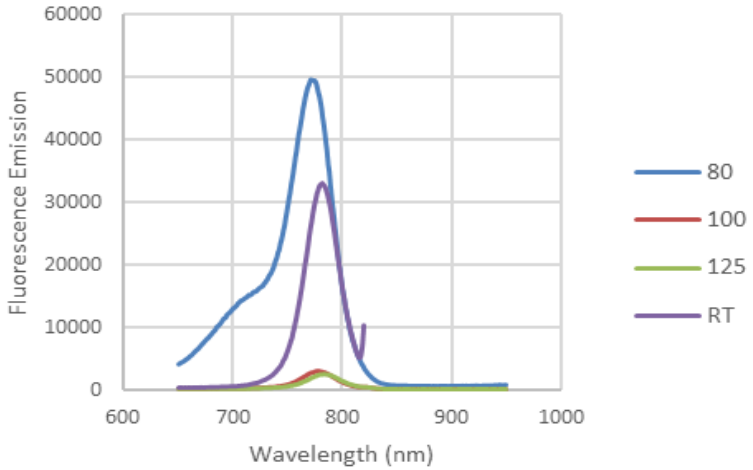

Figure 3. Fluorescence Emission espectra of perovskite films

Temperature (ºC)	**Wavelength (nm)**	**Eg (eV)**
RT	782	1.59
80	771	1.61
100	777	1.60
125	783	1.59
	Average	1.60
	Standard deviation	0.01

Table 1. Band gap energy (Eg) for each sample

3.3. Fluoresence Microscopy

To evaluate the crystal size, 20 measures of each sample were taken randomly by using ImageJ software and results are displayed in Table 2. More specifically, the most consistent values were shown by 80 oC sample. Standard deviation for this set of data was the smallest (0.72 µm) which means that maximum (3.52 µm) and minimum (0.79 µm) values of crystal size were not significantly separated from the average (1.48 µm), thus, it can be concluded that this data presented uniformity and 80 oC is the optimum temperature for perovskite crystallization (CH3NH3PbI3-xClx). In addition, images taken from Fluorescence Microscopy are shown in Figure 4. In this figure, it is clearly observed that 80 oC sample is the one with the best crystal distribution. This is crucial, since it has been proved that improving the crystallization process of the perovskite films can also upgrade their electronic properties [5]

	Temperature (ºC)			
Cristal Size (µm)	*RT*	*80*	*100*	*125*
Min	4.46	0.79	4.15	6.90
Max	15.45	3.52	14.28	17.99
Average	9.38	1.48	9.16	10.76
Standard Deviation	3.30	0.72	2.58	3.22

Table 2. Crystal size statics at each annealing temperature

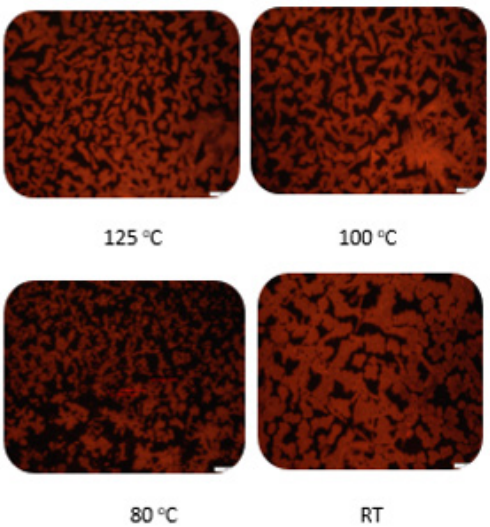

Figure 4. Images of the Fluorescence Microscopy at each annealing Temperature

4. CONCLUSIONS

Perovskite crystal thin films were synthesised by applying the aforementioned methodology. More specifically, the best sample, which was annealed at 80 oC, presented the highest fluorescence emission with 49539.09 CPS at 771 nm and the best uniformity for crystal size with 1.48 ± 0.79 μm. Eg was also calculated resulting in 1.60 ± 0.01 eV. Likewise, for future work, it is recommended to analyse annealing time and humidity as variables because they can affect the crystallisation process. Finally, Scanning Electron Microscopy and X-ray diffractometry could also be carried out to characterise the crystals.

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