

## مطالعه استحاله ساختاری پروسکایت های ترکیب هالوژنی

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چکیده - مواد پروسکایتی به واسطه خواص اپتوالکترونیکی خارق العاده ای که دارند، در طی سال های اخیر مورد توجه بسیاری قرار گرفته اند. علی رغم پیشرفت های فراوان در زمینه ساخت سلول های خورشیدی پروسکایتی با بازده بالا، همچنان ابهامات فراوانی در مورد نحوه عملکرد آنها وجود دارد. یکی از مهمترین مشکلات سلول های خورشیدی پروسکایتی پایداری طولانی مدت این مواد است. در این پژوهش نحوه تشکیل پروسکایت با استفاده از دو پیش ماده یدید سرب و متیل آمونیوم کلرید بررسی شده است. یدید سرب با استفاده از روش لایه نشانی دورانی رایج در روش های چند مرحله ای لایه نشانی شده است. در مرحله بعدی این پیش ماده در معرض ماده متیل آمونیوم کلرید در زمان های مختلف قرار گرفته است. نتایج به دست آمده با روش های مشخصه یابی الگوی پراش اشعه ایکس و همچنین طیف جذب نوری، نشان دهنده تغییر مواد تشکیل شده در زمان های متفاوت است.

کلید واژه - پروسکایت، سلول خورشیدی، استحاله ساختاری، روش چند مرحله ای

## Study of Structural Phase Transformation in Halide Perovskites

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Abstract- Perovskite materials have gained a lot of attention because of their extraordinary optoelectronics properties. Solar cells based on these materials have reached power conversion efficiency of above 20% in a short period of time. However, there has still work to do about their stability and durability. In this work we demonstrate the effect of  $CH_3NH_3Cl$  on  $PbI_2$  to produce a perovskite layer.  $PbI_2$ , the first precursor, was deposited using common spin coating method mentioned in the literature. The deposited layer was exposed to  $CH_3NH_3Cl$  solution. XRD and UV-Visible characterizations were done. The devices fabricated using this layers have shown power conversion efficiency of 5.4%.

Keywords: Solar cells, Perovskites, Sequential deposition, Phase transformation

## Study of Structural Phase Transformation in Halide Pervoskites

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### 1 Introduction

Metal Halide perovskites due to their excellent optoelectronics properties have emerged as a potential absorber layer for thin film solar cells[1]–[3]. Their high carrier mobility and high optical absorption are the main reasons of their excellent photovoltaic properties[4], [5]. Solar cells fabricated using perovskite materials have reached the efficiencies above 20% recently[6]. Moreover the main advantages of these materials over other photovoltaic technologies are their low cost and facile deposition methods[5], [7]. But still, they lack a long durability and also presence of lead in their structure has caused environmental concerns[5], [8].

Methyl ammonium lead triiodide ( $\text{MAPbI}_3$ ) is the main perovskite material that is used as light absorber for solar cells[5], [9]. Mixed halide perovskites are also used to tune the bandgap and durability of fabricated devices and [10]–[12]. Bromine as another halide has been added to the structure of perovskite[10]. Increased bandgap in comparison to  $\text{MAPbI}_3$  is the first consequence of adding bromine in the perovskite structure[10]. Another effect of bromine is increasing the stability of perovskite structure. It has been shown by Noh and et al that perovskites with a certain amount of bromine in their structure are more resistant to humidity and other environmental effects[10].

But chlorine as another halide has a different behaviour in perovskite structure. The first solar cell using perovskite as light absorber in the work

of Snaith and co-workers, used  $\text{MAPbI}_{3-x}\text{Cl}_x$  [11]. Later studies on  $\text{MAPbI}_{3-x}\text{Cl}_x$  have showed a diffusion length longer than  $1\mu\text{m}$ [4]. Yang and co-workers showed that chlorine is escaping the structure during the formation on perovskite layer and it only helps to enlarge the grain boundaries [13].

In this work, we have used methyl ammonium chloride ( $\text{MACl}$ ) to convert  $\text{PbI}_2$  to perovskite layer. Perovskite layers showed a two phase structure at short times of dipping but for the long times a single phase structure of mixed halide perovskite is fabricated. The best cell fabricated using this method showed a power conversion efficiency (PCE) of 5.4%

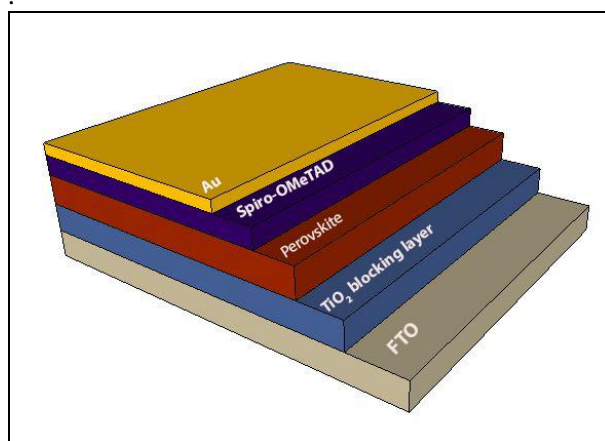


Figure 1: Fabricated device structure

### 2 Experimental Details

#### 2.1 Preparing compact layer

FTO-coated glass substrates were patterned by Zn powder and 2M HCl solution etching. The

patterned FTO substrates were cleaned by soap-deionized water solution, followed by ultrasonication at 50°C deionized water, ethanol, and isopropanol, and then subject to an O<sub>3</sub>/ultraviolet treatment for 20 min to room temperature. First a ltc-TiO<sub>2</sub> deposited on FTO and after treated with 200mM TiCl<sub>4</sub> at 70° C for 20 minutes[14].

## 2.2 Deposition of perovskite layer

PbI<sub>2</sub> layer was deposited by spin coating of 1.25M solution of PbI<sub>2</sub> in *N,N*-dimethylformamide (DMF). The layers are dipped into a MACl precursor with a concentration of 10mg/mL for different times. It is followed by a thermal annealing of 100° C on a hotplate for 10 minutes.

## 2.3 Deposition of Spiro-OMeTAD/Au

Spiro-OMeTAD-based hole transporting layer was deposited using preparation method mentioned in previous works [9]. Au as a back contact was deposited by thermal evaporation. The fabricated layer is 100nm thick.

## 3 Results and Discussion

Fabricating perovskite layer with the sequential steps method is a well-known and common method to produce a uniform and low pin-hole layer[3]. In this regard, we used MACl for the second precursor to convert the first precursor to perovskite.

Fabricated perovskite layer in the first time due to the figure 2 has shown a two phase structure. We can see in the XRD results that there are two peaks for perovskite layer. One in 14.1 for the MAPbI<sub>3</sub> and one in 15.6 for the mixed perovskite layer. But as we increase the dipping time the peak relating to MAPbI<sub>3</sub> is disappearing. Moreover, the main peak in the 12.6 is related to remained PbI<sub>2</sub> layer. But as shown in figure 2(black curve), by increasing the time of dipping all the PbI<sub>2</sub> is converted to perovskite. XRD results also indicate a high crystalline mixed perovskite layer.

One of the main characteristics for absorber layers in solar cells are their absorption spectrum. MAPbI<sub>3</sub> absorbs light from 1.55 eV photon energy and higher[15]. Fabricated perovskite layers have shown two absorption onset, indicating their two phase structure.

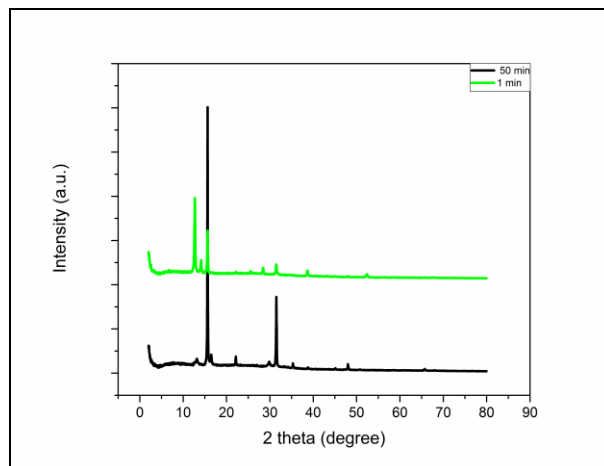


Figure 2: XRD measurement for fabricated layers

Figure 3 shows the absorption spectrum of the deposited layers.

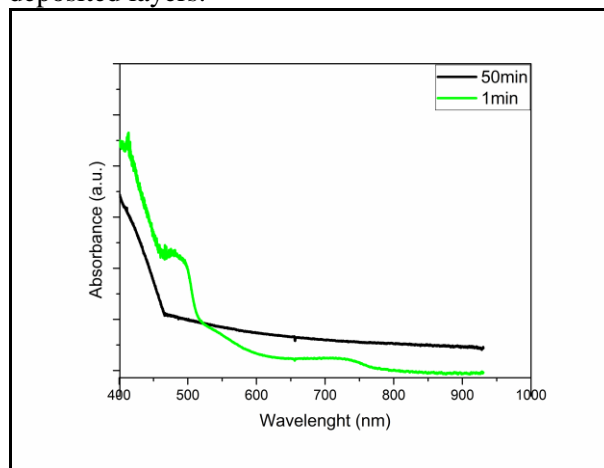


Figure 3: UV-Visible spectrum for fabricated layers

Fabricated devices using the two phase perovskite layers with the normal device architecture, has reached a PCE of 5.4% and open circuit voltage of 1.02 volts.

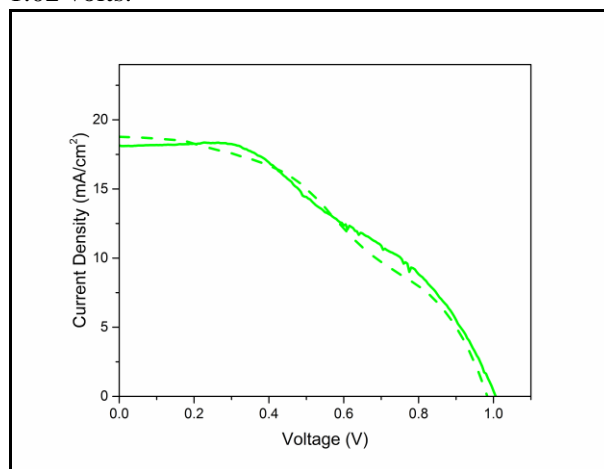


Figure 4: J-V measurements of fabricated devices (dashed line shows the reverse scan)

## 4 Conclusion

A sequential method with a new second precursor was studied. For short periods of dipping in second precursor a two phase perovskite structure was fabricated. As we increased the time of dipping the MAPbI<sub>3</sub> disappeared.

Devices fabricated using the two phase perovskite layer has shown a PCE of 5.4% and open circuit voltage of 1.02 volts.

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