

# Synthesis and Characterization of Photosensible $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ Perovskite Crystalline Films<sup>1</sup>

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**Abstract**—Methylammonium lead-halide perovskites are very promising for applications as solar light-harvesting materials. This paper presents a study on the methylammonium iodide and iodide-chloride perovskite films prepared by spin coating from a liquid precursor. The powder diffraction spectroscopy has detected 10 lattice plane reflections common to a perovskite of a tetragonal crystal structure. The calculated cell parameters are  $a = 8.85 \text{ \AA}$  and  $c = 12.60 \text{ \AA}$ . The preparation conditions and their impact on the crystallization process and film morphology are discussed. A red shift of photoluminescence bands at low temperatures was evidenced. A photoelectrical study of perovskite films has revealed their high sensibility to illumination, especially in the visible spectrum, which gives a hint on their applications in photovoltaics.

**Keywords:** organic-inorganic perovskite, methylammonium lead halide, photo-sensibility

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## INTRODUCTION

Today, the energetic deficiency and global ecological crisis (greenhouse effect, environmental pollution) are the most critical issues for science and technology. The necessity to develop convertors of alternative sources of energy is one of the most important scientific tasks. These convertors must be of a high efficiency and stability, low cost, ambient-friendly, etc. [1].

Recently, hybrid perovskites have been found to be promising solar absorbers for applications in various solar cell structures. Methylammonium lead-halide perovskites exhibit many desirable properties such as a narrow-band-gap, long diffusion lengths, high excitonic lifetimes, and a high-gain photon-mode detection of visible light [2, 3].

The major mechanism of crystallization and morphology control of perovskite materials is not almost clear. The researchers strive to identify possibilities to improve efficiencies via the optimization of a charge carrier lifetime, the mobility and diffusion lengths [4]. An increase of the crystallite size is expected to be favorable for the improvement of the electronic parameters of material [5].

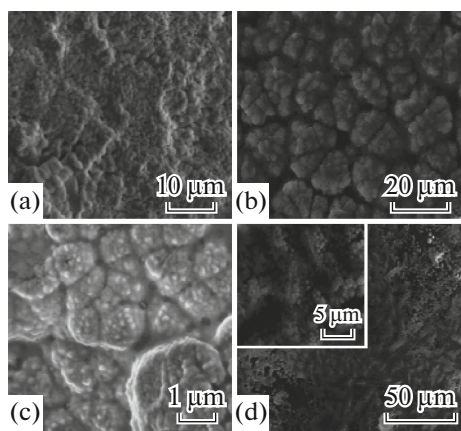
Methylammonium lead-halide perovskites can be grown by a plenty of methods, under various conditions. Usually, these methods are cheaper and more effective than those used for conventional inorganic semiconductors. The growth conditions, in their turn, display a heavy influence on the material characteristics.

In this work, we investigate the impact of the solvent type and organic salt concentration on the perovskite crystallization at a one-step deposition from a liquid precursor. The morphological, structural and photoelectrical properties of samples are investigated. Trap states are expected to be plentiful in a solution-processed crystal. According to [6], the traps have a low capture cross-section and, even if their density is not negligible, they play a minor role in the photovoltaic energy conversion and light amplification.

## EXPERIMENTAL

The perovskite films on the glass substrates have been prepared by spin coating. The glass substrates were cleaned in piranha solution and washed in deionized water. Dry substrates were fixed on the spin-coater and rotated at 2000 rpm, and then the liquid precursor was dropped on and rotated for 30 s. The

<sup>1</sup> The article is published in the original.

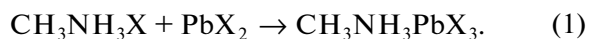


**Fig. 1.** SEM images of solution-processed perovskite films: (a)  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (1 : 1); (b)  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (2 : 1); (c)  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (3 : 1); (d)  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ . Solvent used is DMF.

perovskite crystallization happens after the solvent evaporation at spinning and thermal annealing. All samples were annealed at  $50^\circ\text{C}$  for 10 min. After that, the color change from yellow to brown was observed.

The  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite precursor solution was prepared by dissolving  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{PbI}_2$  in the following molar ratios: sample 1—1 : 1, sample 2—2 : 1, sample 3—3 : 1 in *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and gamma-hydroxybutyric acid lactone (GBL). Also a precursor with molar ratios of organic to inorganic of 3 : 1, with mixed halides of  $\text{PbI}_2$  95% and  $\text{PbCl}_2$  5% was prepared, which should result in  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  with  $x = 0.15$  [7–9].

Methylammonium lead-halide perovskite was formed via the following reaction:



The reaction occurs in the presence of a polar solvent (DMF, DMSO or GBL) that results in a complex formation. Both methylammonium halide (MAX) and lead halide react with the formation of a perovskite attached to the solvent molecule [10]. A perovskite-solvent bond breaks at heating and crystallization occurs. Under an excess of  $\text{CH}_3\text{NH}_3\text{I}$  (MAI) a better dissolution of lead halides was observed. This

proves the bond formation between MAI and  $\text{PbI}_2$  in a precursor. At the same time, the color of the precursor changes from lemon yellow for the  $\text{PbI}_2$  solution to honey yellow for the maximal concentrations of MAI in the perovskite precursor.

Figure 1 illustrates SEM images of perovskite films for  $\text{CH}_3\text{NH}_3\text{PbI}_3$  with organic/inorganic ratios of (a) 1 : 1; (b) 2 : 1; (c) 3 : 1 and (d)  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ . Morphology study confirms that for all types of precursor the desired perovskite crystalline films are formed. In case of an equimolar precursor, a highly uniform and continuous film is obtained. When the molar concentration of organic is raised, the film exhibits a heterogeneous morphology with agglomerates of crystallites. The crystallite sizes decrease from 2  $\mu\text{m}$  for an equimolar precursor to 30–60 nm for triple ratio of MAI.

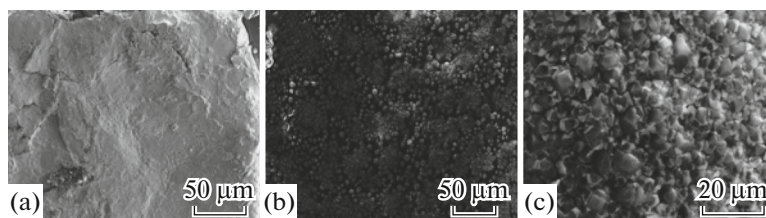
Morphologies of the iodide-chloride perovskite and pure iodide prepared under the same conditions are similar by the crystallite dimensions and their arrangement on the surface. Presumably, more differences may appear via increasing the Cl concentration [11].

It was found experimentally that the best solubility of perovskites occurs in GBL, lower in DMF and the worst in DMSO. Furthermore, the films obtained from a DMSO precursor are non-uniform and sporadic. Films with good coverage are obtained using DMF and GBL solvents. In Fig. 2 the influence of the solvent on the sample morphology is clearly observed.

The most of solvents like methanol, ethanol, THF, DMSO, DMF, etc. can coordinate to the metal and thus change the coordination environment. In addition, they can remain in the crystal package and stabilize it by hydrogen bonding interactions [12].

The formation of bigger crystallites of 2–5  $\mu\text{m}$  is inherent to GBL precursors, while DMF precursors allow a growth of crystallites under 200 nm under the same conditions.

This is possible due to a difference between boiling temperatures of solvents. GBL boils at  $204^\circ\text{C}$  and DMF at  $153^\circ\text{C}$ , that is, GBL precursor will evaporate slower. As was mentioned before, crystallization of lead halide perovskites occurs at the solvent evaporation, hence, a slow evaporation of GBL offers more time for the growth of crystallites and their dimensions thus increase.



**Fig. 2.** SEM images of (3 : 1) perovskite films obtained using: (a) DMF; (b) DMSO; (c) GBL solvents.