Synthesis of CH$_3$NH$_3$PbI$_3$ hybrid perovskite crystals for optoelectronic devices

S Dyussembekova* 1,2, V Kinev2, A Smirnova2 and P Gladyshev2

1The Institute of Nuclear Physics, 1 Ibragimova St., 050032, Almaty, Republic of Kazakhstan

2Dubna State University, Dubna, Russia

E-mail: saule.dyussembekova@mail.ru

Abstract. This article is deals with the synthesis of hybrid organic-inorganic perovskite crystals. We present a brief review of the literature devoted to the synthesis of perovskite crystals. We have analyzed methods for the synthesis of perovskite crystals to select optimal conditions. Bulk perovskite crystals of CH$_3$NH$_3$PbI$_3$ were synthesized. The resulting crystals were analyzed by X-ray phase analysis, which confirms the formation of tetragonal perovskite crystals and can be used to obtain thin films.

1. Introduction

Perovskite materials, due to the high mobility of electric charge carriers and the short lifetime of electron-hole pairs, can be used to create high-performance devices such as thin-film solar cells, LEDs, photosensors, lasers, and field transistors [1,2]. Currently, thin-film solar cells based on hybrid perovskites have achieved an efficiency of 25.5% [3]. Hybrid organic-inorganic perovskites with the general formula ABX$_3$ (A=CH$_3$NH$_3$+, HC(NH$_2$)$_2$+; B=Pb, Sn; X=I, Br, Cl) with a metal cation substituted for an organic ammonium base have the greatest application in photovoltaics and represent a revolutionary class of photosensitive materials that are widely used in new generations of solar panels [4-6].

Among the most promising methods of forming thin film perovskite semiconductors, we emphasize the vacuum method of Flash-evaporation [7]. Flash-evaporation is a method based on the fact that film deposition is performed by continuous vacuum evaporation of small portions of a multicomponent compound. Since the particles have different sizes and get into the heat exchanger at each moment in random order, therefore, there are particles that have different sublimation temperatures and are at different stages of evaporation of the constituent components. The simultaneous presence of such particles in the heat exchanger provides, on average, the same fluxes of evaporated substances, and consequently, the stoichiometric composition of the deposited film is obtained with high accuracy. This method is also called the discrete evaporation method [7,8]. The Flash – evaporation method allows the deposition of hybrid perovskite films even from their powders. Therefore, to form high-quality films it is necessary to produce perovskite crystals with a given composition and stoichiometry.

2. Perovskite crystals synthesis methods

The method of crystal growth is chosen based on the chemical and physical characteristics of the crystallized substance. The crystal growth mechanism determines the properties of the final material, so understanding this process is decisive for predicting and controlling the properties of the resulting material. We considered the method of crystal growth from solution.

2.1. Inverse temperature crystallization method

The method of volumetric crystal growth of perovskite material CH$_3$NH$_3$PbI$_3$, is presented in paper [9]. The choice of a suitable solution medium is a determining factor for high-quality crystal growth. In the case of hybrid perovskites, the most widely used solvents are gamma-butyrolactone (GBL), N,N-dimethylformamide (DMFA) and dimethylsulfoxide (DMSO). The solubility of PbX$_2$ and MAX (MA=CH$_3$NH$_3$+, X=Cl, Br, I), in these solvents or their mixtures varies differently; MAPbBr$_3$ is known to crystallize better from N,N-dimethylformamide, while MAPbI$_3$ crystallizes better from gamma-
butyrolactone.

2.2. Antisolvent vapor-assisted crystallization (AVC)

One of the crystal growing methods is the antisolvent vapor-assisted crystallization (AVC) method. In this method, an antisolvent slowly diffuses into the precursor solution, which leads to the growth of volumetric MAPbX3-type crystals. This method of crystal growth uses solvents with high solubility and moderate coordination in MAX and PbX2, such as N, N-dimethylformamide (DMFA) or gamma-butyrolactone (GBL) and an antisolvent in which both perovskite precursors are totally insoluble, dichloromethane (DHM) [10,11].

2.3. Cooling HX-based precursor solutions method

The temperature reduction method is suitable for the growth of perovskite crystals because the solubility of organohalide perovskites in the appropriate acid-halide solvents changes significantly with temperature [12]. High-quality large macrocrystals can be obtained by immersing the seed in a solvent. In this case, the growth of seed will occur with decreasing temperature. Decreasing solution temperature causes saturation of dissolved perovskite precursors containing an inorganic metal salt and an organic halide salt.

2.4. The method of crystal growth with top seed in solution

The volumetric macrocrystal MAPbI3 is obtained by growing in solution with a top seed. The seed crystal is fixed on a silicon substrate at the top of the solution. Volumetric MAPbI3 macrocrystals measuring 10 mm in length and 3.3 mm in height were obtained by dissolving small seed crystals in the lower part of the solution, since the temperature difference between the lower and upper parts of the flask contributed to oversaturation of the solution [12,13]. The method of temperature reduction is simple, convenient and applicable for growing high-quality perovskite crystals.

3. MAPbI3 crystals synthesis

In order to obtain crystals of MAPbI3 we use modified temperature reduction method described in [13]. 7.4 g of lead (II) acetate trihydrate (Pb(CH₃COO)*3H₂O) was dissolved in 25 ml of hydrogen iodide acid (HI) (57 wt. %) in a 250 ml flask, which was then placed in a heated oil bath at 100 °C. A solution consisting of 5 mL of HI and 1.7 mL of methylamine (CH₃NH₂) was then added to the flask. The temperature of the resulting solution was then lowered to 75˚C and allowed to stand for 24 hours to precipitate small crystals. The resulting small crystals were washed with isopropyl alcohol and dried in vacuum. The obtained crystals were used as a seed for the growth of larger crystals. The solution described above was prepared in which the seed crystals were placed. This mixture was allowed to stand in an oil bath at 75 °C for 48 hours. The obtained crystals had a size of 2*2*3 mm.

![Figure 1. Image of CH₃NH₃PbI₃ crystals](image_url)

4. Results

The growth of volumetric MAPbI3 crystals was carried out by reducing the temperature of the solution containing CH₃NH₃ and Pb(CH₃COO)₂·3H₂O dissolved in HI. As a result, volumetric crystals of perovskite composition MAPbI₃, linear size of 2 mm were obtained. For crystal structure identification of the obtained crystals the XRD analysis was carried out (Figure 2). The analysis was carried out on the device Malvern PANalytical Empyrean ser.2, Cu K-α radiation, PSD Detestor Pixel 3D. The maximum operating range (depending on the accessories) was 111°<2θ<168°, minimum scanning step: 0.0001°, angle setting reproducibility: < 0.0002°.
There are intense reflexes at 2θ=13.94°, 14.16°, 28.54° and 31.99° with interplanar distances of 6.34 Å, 6.25 Å, 3.12 Å and 2.79 Å in the directions of planes (002), (110), (220) and (130) on the diffractogram of the sample. When comparing with the literature data [14], no significant differences in the diffractograms are observed. On this basis, we can conclude that we obtained hybrid perovskite crystals with a tetragonal structure, space group I4/mcm.

5. Conclusion

In this paper, we reviewed synthesis methods of hybrid organic-inorganic perovskite crystals and some advantages of perovskite thin films formation by Flash-evaporation method. Perovskite crystals were synthesized by the modified reduced temperature method. XRD analysis of the obtained crystals confirmed the formation of perovskite crystals with a tetragonal structure. Obtained perovskite crystals will be used to produce thin films by Flash-evaporation method.

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