PECULIARITIES OF THE FORMATION AND PROPERTIES OF ORGANIC-INORGANIC PEROVSKITE $CH_3NH_3PbI_3$

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Methylammonium lead iodide perovskite $CH_3NH_3PbI_3$ has attracted the attention of the scientific community due to the high efficiency of solar energy conversion. Recent developments in photovoltaic devices based on organic-inorganic perovskite materials have shown power conversion efficiency (PCE) of 25.2% (and to 28% in tandem architecture) [1, 2]. An important advantage of such elements is simpler and cheaper technology for manufacturing the solar cells based on organic-inorganic perovskites, as compared to silicon-based elements.

The films of organic-inorganic perovskites can be used in the development of various optical systems, as well as in the elements of solar energy conversion. Organic-inorganic perovskites can be easily synthesized by precipitation methods from solutions that are simple and reliable. These methods include one-step and two-step deposition, and it is possible to obtain high-quality organic-inorganic perovskite films using these methods [3].

The aim of this work was to investigate the influence of the ratio of initial reagents and solvent on the formation and properties of organic-inorganic perovskites films $CH_3NH_3PbI_3$

Organic-inorganic perovskite $CH_3NH_3PbI_3$ films were synthesized by a one-step method of deposition at different ratios of initial reagents (PbI_2 to CH_3NH_3I was taken in a ratio of 1:1, 1:2, 1:3) in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) solvent. To deposit films of perovskite $CH_3NH_3PbI_3$, solutions with different ratios of initial reagents were applied to the substrates by the spin-coating method.

It was found that the ratio of initial reagents (1:1, 1:2, 1:3) and solvent DMF, DMSO affect the peculiarities of the formation of organic-inorganic perovskite $CH_3NH_3PbI_3$. The formation of perovskite occurs due to the formation and decomposition of intermediate compounds. Depending on the ratio of starting reagents, different amounts of intermediate compounds are formed using DMF: 3 for a ratio of 1:1, and 4 and 2 for a ratio of 1:2, 1:3, respectively. When using DMSO, regardless of the ratio of reagents, 4 intermediate compounds are formed **(Figure 1).** Intermediate compounds formed by the use of DMF differ in structure and chemical composition from compounds formed by the use of DMSO. This indicates that the solvent is actively involved in the formation of perovskite.

The temperatures of formation of a single-phase film of organic-inorganic perovskite depend on the ratio of PbI_2:CH_3NH_3I and solvent. The single-phase perovskite films are formed at 115 °C, 170 °C, 175 °C for the ratio of starting reagents 1:1, 1:2, 1:3 in DMF solvent. When using the solvent DMSO single-phase films are formed at 190 °C, 205 °C at a ratio of 1:2, 1:3, respectively. At a ratio of 1:1, single-phase perovskite film is not formed.

For organic-inorganic perovskite $CH_3NH_3PbI_3$ films, the structural parameters were calculated by the full-profile Rietveld method using diffraction patterns. It was established that the diffractograms of organic-inorganic perovskites correspond to tetragonal symmetry (spatial group I4 / mcm, 140).

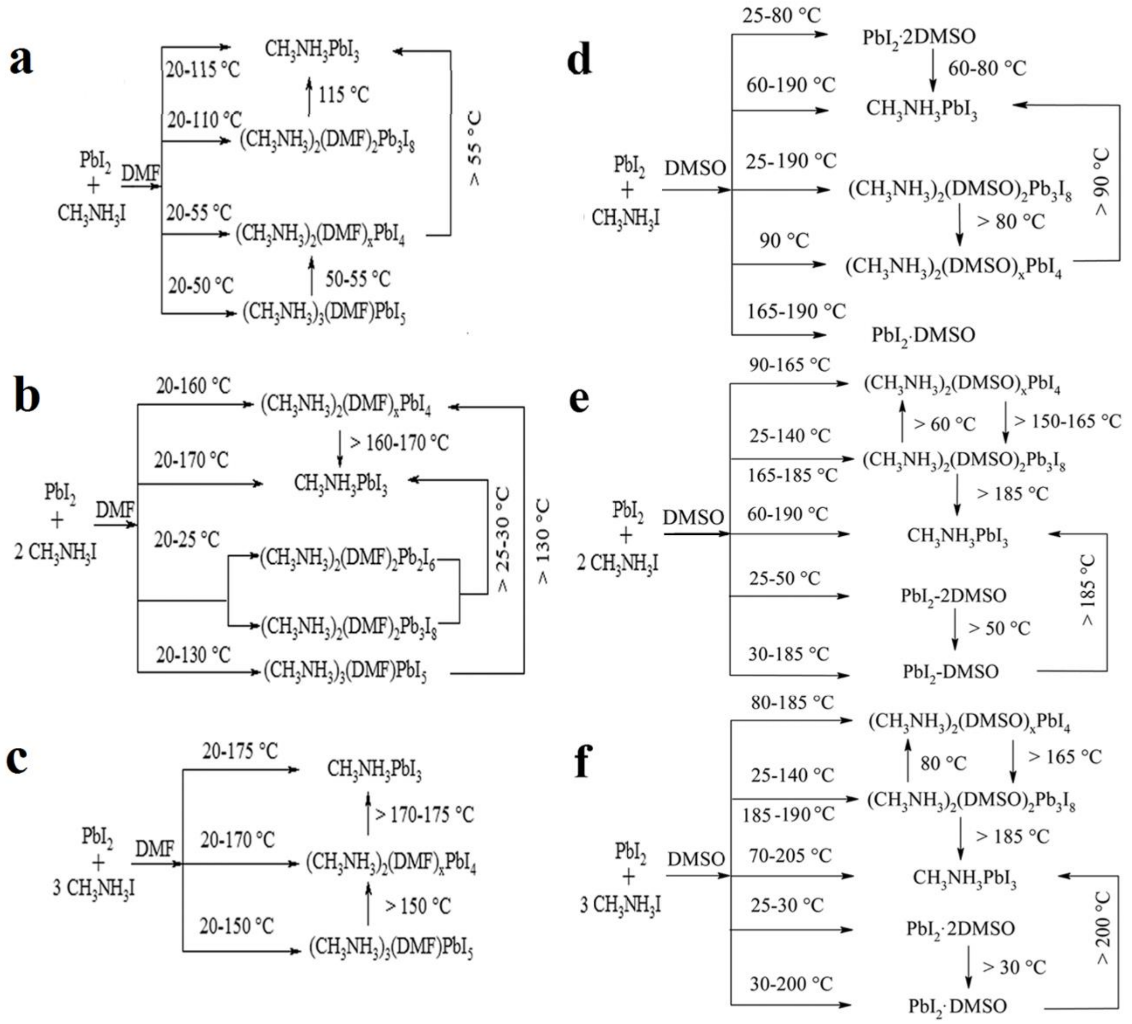

Fig. 1. The scheme of the formation of perovskite and intermediate compounds at the ratio PbI_2:CH_3NH_3I – 1:1 (a, d), 1:2 (b, e), 1:3 (c, f) and using DMF (a, b, c) and DMSO (d, e, f).

It was shown that depending on the solvent and the ratio of initial reagents, there are slight changes in the unit cell volume of perovskite $CH_3NH_3PbI_3$ **(Table. 1).** Since the experimental values of the unit cell volume of perovskite are slightly higher than the theoretical value of $V_{unit\ cell}$ = 990 Å^3 [4] regardless of the same ratio of starting reagents, then these changes can be explained by the including of the solvent in the perovskite structure. The determination of solvent content in structure of perovskite (x) was performed according to formula (1):

$$x = \frac{\frac{V_{perovskite}}{Z_1} - \frac{V_{(PbI_2)}}{Z_2} - \frac{V_{(CH_3NH_3I)}}{Z_3}}{V_{solvent} - V_{(CH_3NH_3^+)}}, \qquad (1)$$

where Z_1, Z_2, Z_3 – formula unit for perovskite, PbI_2, CH_3NH_3I, respectively, $V_{perovskite}$, $V(PbI_2)$, $V(CH_3NH_3I)$ – the unit cell volume of perovskite, PbI_2, CH_3NH_3I, respectively. $V_{solvent}$ – the volume of the solvent molecule, $V(CH_3NH_3^+)$ – the volume of methylammonium cation $CH_3NH_3^+$.

It was found that at the same ratios of initial reagents, the DMF solvent enters the structure of perovskite in greater quantities than DMSO. The inclusion of the solvent in the structure of perovskite affects not only the structural parameters but also the electrophysical characteristics, in particular, the bandgap *Eg* **(Table. 1).**

The electrophysical characteristics of organic-inorganic perovskite films were investigated using the method of surface photovoltage spectroscopy and transmission measurements. It was shown that the bandgap of perovskites varies depending on the ratio of initial reagents and solvent used in the synthesis. It was found that the bandgap for perovskites obtained in DMSO is less than for films obtained using DMF.

Table 1. The structural and electrophysical characteristics of the organic-inorganic perovskites $CH_3NH_3PbI_3$ synthesized at different ratios of reagents PbI_2 and CH_3NH_3I in DMF, DMSO solvent.

Parameters	**DMF**			**DMSO**		
	1:1	**1:2**	**1:3**	**1:1**	**1:2**	**1:3**
Deposition temperature	**115 °C**	**170 °C**	**175 °C**	**150 °C**	**190 °C**	**205 °C**
$\mathbf{V_{perovskite}}$, **Å**^{3}	**994.5(3)**	**998.6(5)**	**997.5(4)**	**991.3(1)**	**994.7(4)**	**994.5(2)**
$\boldsymbol{E_g}$**, eV**	**1.59**	**1.62**	**1.57**	**1.57**	**1.53**	**1.54**
x, %	**5.8**	**7**	**6.7**	**5.5**	**6.6**	**6.5**

In summary, peculiarities of formation and properties of organic-inorganic perovskite films $CH_3NH_3PbI_3$ depending on the ratio of starting reagents and solvent DMF, DMSO were studied. As the ratio of PbI_2:CH_3NH_3I increases, the temperature of formation of a single-phase $CH_3NH_3PbI_3$ perovskite film increases. It was found that for perovskite films obtained at different ratios of PbI_2:CH_3NH_3I in DMF, DMSO there are slight changes in the structural (unit cell volume) and electrophysical (bandgap) characteristics. These changes are related to the solvent that is included in the crystalline structure of perovskite. It was shown that DMF is included in the structure of perovskite in greater quantities than DMSO.

References:

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