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Збірник містить тези доповідей І Міжнародної наукової конференції, у яких викладені результати наукових досліджень у галузях хімії, хімічної технології, матеріалознавства, екологічної безпеки і охорони навколишнього середовища, технології хімічної освіти, фармації.

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SYNTHESIS AND PROPERTIES OF ORGANIC-INORGANIC PEROVSKITE $CH_3NH_3PbI_3$ USING DMSO SOLVENT ANG DIFFERENT RATIO OF INITIAL REAGENTS

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One of the promising candidates for the manufacture of solar cells are organic-inorganic perovskites ABX_3, where A is mainly methyl ammonium (CH_3NH_3), B is Pb, Sn, and X is Cl, Br, I. These materials are characterized by direct interband optical transitions, so they have a high absorption coefficient in the visible spectral range, large diffusion length of charge carriers [1] high mobility of charge carriers [2]. Due to these characteristics of perovskites, the photoelectric elements based on them show a significant increase in the efficiency of conversion of solar energy into electrical energy, as evidenced by the fact that in 10 years it has grown from 3% [3] to 25.2% [4].

The most common methods for fabricating the organic-inorganic perovskites film are the so-called one-step solution application processes: all soluble components are dissolved in an organic solvent such as N-dimethylformamide (DMF), γ-butyrolactone (GBL) or dimethyl sulfoxide (DMSO), and deposited on the substrate.

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

Lead iodide (PbI_2) and methylammonium iodide (CH_3NH_3I) were used as initial reagents. For the deposition of $CH_3NH_3PbI_3$ films, the initial reagents PbI_2 and CH_3NH_3I with ratios of 1:1; 1:2; 1:3 were dissolved in DMSO and stirred at 70 °C for 1 hour. The crystalline $CH_3NH_3PbI_3$ films were formed in a dry box. The previously prepared clear solution was deposited to the purified glass substrate by spin-coating with speed 1200 rpm for 30 seconds. Thermal treatment of films was carried out on a preheated hot plate at temperatures from 20 to 205 °C for 15 minutes.

Scanning electron microscopy was used to study the morphology of perovskite films. The ratio of initial reagents PbI_2 and CH_3NH_3I (1:1, 1:2 and 1:3) affects the morphology of the synthesized films (**figure 1**).

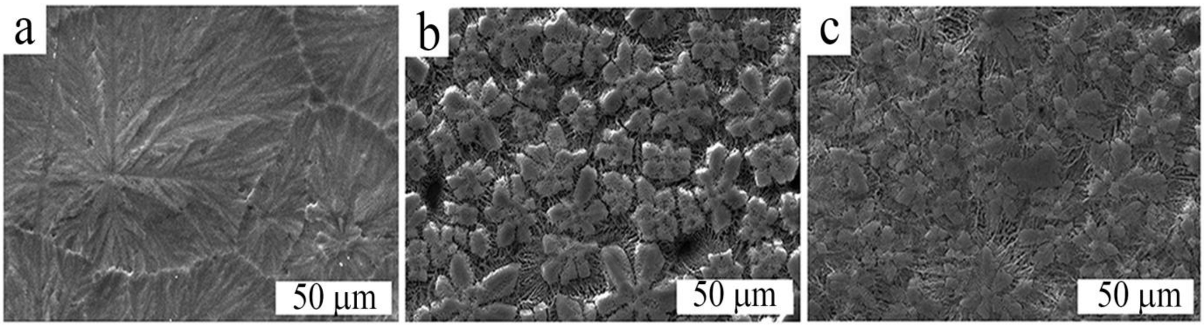

Figure 1. The surface of the perovskite films $CH_3NH_3PbI_3$, obtained at different ratios of the initial reagents PbI_2 and CH_3NH_3I: 1:1 - (a); 1:2 - (b); 1:3 - (c).

It was established that in the synthesis of films with the ratio PbI_2:CH_3NH_3I = 1:1 the particles grow in the form of leaves with a particle size of 60 μm, at a ratio of 1:2 and 1:3 the particles grow from the center of crystallization in 6 and 5 directions, respectively. As the ratio of starting reagents increases, the particle sizes decrease from 60 µm (1:1) to 20 µm and 15 µm for (1:2) and (1:3), respectively. It is known that the change in the ratio of initial reagents can significantly affect the formation of $CH_3NH_3PbI_3$ precursors and, accordingly, the further growth of perovskite crystals and their form [**Ошибка! Закладка не определена.**].

The ratio of starting reagents also affects the formation of organic-inorganic perovskite and intermediate compounds. It was found that depending on the ratio of starting reagents (1:1, 1:2, and 1:3) and heat treatment temperature, the formation of organic-inorganic perovskite $CH_3NH_3PbI_3$ occurs according to similar schemes: through the formation of 4 intermediate compounds. In addition to $CH_3NH_3PbI_3$ perovskite, other intermediates may be present in the films: $(CH_3NH_3)_2(DMSO)_xPbI_4$, $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, $PbI_2·2DMSO$, $PbI_2·DMSO$**.** XRD has shown the presence of certain intermediate compounds in the synthesized film depends on the ratio of the initial reagents and the processing temperature of the film (**Table 1**).

Table 1. Temperature interval of existence of intermediate compounds and organic-inorganic perovskite $CH_3NH_3PbI_3$ at different ratios of initial reagents.

Compound	Temperature interval of existence		
	1:1	1:2	1:3
$(CH_3NH_3)_2(DMSO)_2Pb_3I_8$	25-190 °C	25-140 °C 165-185 °C	25-140 °C 185-190 °C
$(CH_3NH_3)_2(DMSO)_xPbI_4$	90-95 °C	90-165 °C	80-185 °C
$PbI_2·2DMSO$	25-80 °C	25-50 °C	25-30 °C
$PbI_2·DMSO$	165-190 °C	30-185 °C	30-200 °C
$CH_3NH_3PbI_3$	60-190 °C	60-190 °C	70-205 °C

It was found that at temperatures below 60 °C for films obtained at a ratio of 1:1, 1:2 the formation of organic-inorganic perovskite is not observed. While for films obtained at a ratio of 1:3 the formation of organic-inorganic perovskite is not observed at temperatures below 70 °C (**Table 1.**). At a ratio of 1:1, single-phase perovskite film is not formed, which is consistent with the literature [6].

The unit cell parameters of the $CH_3NH_3PbI_3$ film have been determined by the full-profile Rietveld method using X-ray diffraction patterns. Calculations of the structural parameters indicate that diffractograms of organic-inorganic perovskites corresponds to the tetragonal symmetry (space group I4/mcm, 140). The unit cell parameters of the films of organic-inorganic perovskites are shown in Table 2. It should be noted that the unit cell volume is smaller for the film deposited at ratio of the initial reagents of 1:1. This fact is probably could be explained by increase in the content of the organic component in the perovskite crystal structure with increasing ratio of the initial reagents.

Table 2. The structural parameters of the organic-inorganic perovskites $CH_3NH_3PbI_3$ at different ratios of starting reagents PbI_2 and CH_3NH_3I (1:1, 1:2 and 1:3), prepared in DMSO as a solvent

	1:1	1:2	1:3
Unit cell parameters			
a, Å	8.883(6)	8.893(9)	8.887(6)
c, Å	12.56(1)	12.57(4)	12.58(1)
V, $Å^3$	991.3(1)	994.7(4)	994.5(2)
Deposition temperature	150 °C	190 °C	205 °C

In summary, the change in the ratio of the initial reagents PbI_2 and CH_3NH_3I in the DMSO solvent can affect the morphology and properties of $CH_3NH_3PbI_3$ films. It was shown that films obtained from DMSO solutions with different ratios of initial reagents(1:1, 1:2, 1:3). are characterized by different morphology. The formation of organic-inorganic perovskite occurs according to similar schemes: through the formation of 4 intermediate compounds In addition to $CH_3NH_3PbI_3$ perovskite, other intermediates may be present in the films: $(CH_3NH_3)_2(DMSO)_xPbI_4$, $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, $PbI_2 \cdot 2DMSO$, $PbI_2 \cdot DMSO$. It was found that at a ratio of 1:1 and 1:2 at temperatures of T< 60 °C and at a ratio of 1:3 at T< 70 °C organic-inorganic perovskite is not formed.

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