Solid State Sciences

Synthesis of organic-inorganic perovskite CH3NH3PbI3 using DMSO solvent

--Manuscript Draft--

Manuscript Number:	SSSCIE-D-20-00262
Article Type:	Full Length Article
Keywords:	organic-inorganic perovskite
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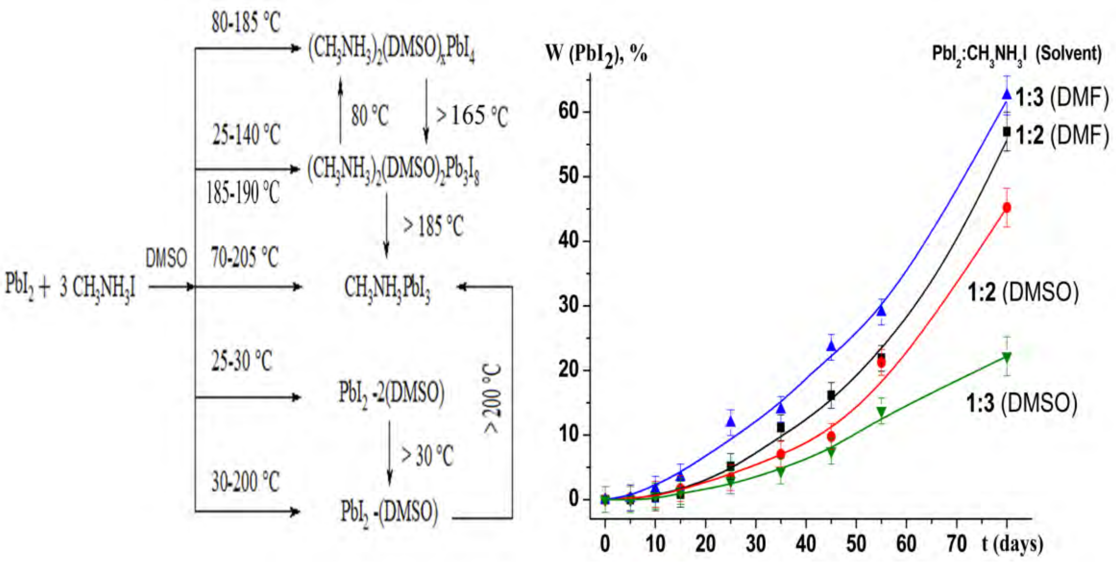
Graphical Abstract



Peculiarities of synthesis of $CH_3NH_3PbI_3$ perovskite prepared at different ratios of starting reagents PbI_2 and CH_3NH_3I in different solvents were determined. The use of DMSO and a ratio of starting reagents of 1:3 allowed the perovskite films with high resistance to moisture to be prepared.

Synthesis of organic-inorganic perovskite $CH_3NH_3PbI_3$ using DMSO solvent

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Abstract

Films of organic-inorganic perovskites $CH_3NH_3PbI_{2.98}Cl_{0.02}$ at different ratios of starting reagents (PbI_2:{CH_3NH_3I:CH_3NH_3Cl}) in solvent DMSO has been synthesized. It was found that regardless of the ratio of initial reagents PbI_2 and CH_3NH_3I (1:1, 1:2, 1:3), the formation of perovskite occurs in similar schemes: through the formation of four intermediate compounds $(CH_3NH_3)_2(DMSO)_xPbI_4$, $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, $PbI_2\cdot 2DMSO$, $PbI_2\cdot DMSO$. To study the properties of organic-inorganic perovskites, they were obtained at different ratios of starting reagents in solvent DMSO. The stability of organic-inorganic perovskite films was studied by X-ray diffractometry and fluorescence spectroscopy. It was found that the use of DMSO at the synthesis of organic-inorganic perovskite leads to the formation of more stable films compared with the use of DMF solvent.

Keywords: Organic-inorganic perovskite, Film, Microstructure, X-ray diffractometry, Intermediate compounds, Stability

1. Introduction

Energy stability is one of the priorities of modern society. The use of fossil fuels as an energy source leads to an increase in greenhouse gases, which have a detrimental effect on the environment. Overcoming this impact can be solved by developing renewable energy sources. However, the search for cost-effective and environmentally friendly renewable energy sources remains an urgent task both from a scientific and technological point of view [1]. Currently, solar elements based on silicon are mostly (89%) used [2-4]. The energy conversion efficiency of silicon solar panels is about 17.5% (theoretical limit 26%). Unfortunately, such photovoltaic cells are expensive. Significant progress has been made in the development of solar energy converters using another class of materials - thin-film devices based on amorphous silicon, CuIn, $GaSe_{2-x}S_x$, or CdTe. However, the production of inorganic thin-film solar cells requires a high vacuum and high temperatures [5-7], which leads to a significant increase in the price of the elements. In addition, the films contain toxic elements.

Methylammonium lead iodide perovskite $CH_3NH_3PbI_3$ (MAPI) 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 energy conversion efficiency (PCE) of more than 20% [8-11]. Organic-inorganic perovskites are combining some of the advantages of organic and inorganic semiconductors: high optical absorption, high mobility of charge carriers[12], and adjustable bandgap [13]. One of the main disadvantages of these materials is their low resistance to external factors. When exposed to moisture, heat treatment, or UV radiation, $CH_3NH_3PbI_3$ is easily decomposed into PbI_2 and other components [14-18]. This prevents the widespread use of solar cells based on organic-inorganic perovskites. To solve these problems, the processes of formation of the crystal structure of $CH_3NH_3PbI_3$ perovskite films and possible ways to overcome the above problems should be studied. Changes in the stoichiometry of the starting reagents and the chemistry of precursors (use of different solvents dimethylformamide (DMF), dimethyl sulfoxide (DMSO), γ-Butyrolactone , N-Methyl-2-pyrrolidone) affect the chemical, structural, and physical properties of organic-inorganic perovskites [19, 20]. The process of nucleation and formation of crystals [21] is determined by the chemical interaction of the organic cation, the coordinating solvent, and the inorganic component. The interaction between these three components affects the properties of crystalline films as a whole. However, a detailed analysis of phase transformations for samples synthesized at different ratios of starting reagents that dissolve in organic solvents and at different temperatures is practically non-existent in the literature. Earlier studies on phase transformations that occur in the synthesis of organic-inorganic perovskite $CH_3NH_3PbI_3$, where DMF was used as a solvent were published [22]. The aim of this work was to study the processes of the formation of intermediate phases in the synthesis of films of organic-inorganic perovskites $CH_3NH_3PbI_{2.98}Cl_{0.02}$ at different ratios of starting reagents, which dissolve in DMSO and study their properties.

2. Material and methods

Lead iodide (PbI_2), methylammonium iodide (CH_3NH_3I), and methylammonium chloride (CH_3NH_3Cl) were used as initial reagents for the synthesis of organic-inorganic perovskites. To stabilize the structure of perovskite, iodine was partially replaced by chlorine, for this purpose methylammonium chloride CH_3NH_3Cl was added [21]. For simplicity, the solid solution $CH_3NH_3PbI_{2.98}Cl_{0.02}$ will be written as $CH_3NH_3PbI_3$. Dried dimethyl sulfoxide (DMSO) was used as the solvent.

To obtain $CH_3NH_3PbI_3$ films, solutions of starting reagents PbI_2, CH_3NH_3I and CH_3NH_3Cl in ratios of 1:0.98:0.02 (hereinafter 1:1); 1:1.98:0.02 (1:2); 1:2.98:0.02 (1:3) in DMSO were preliminarily prepared. In order to completely dissolve the reagents, the above solutions were stirred at a temperature of 70 °C for 1 hour. Crystalline films were formed in a dry box. The previously obtained solution was deposited to the purified glass substrate by spin-coating with speed 1200 rpm for 30 seconds. The thermal treatment of films was carried out on a preheated hot plate at temperatures from 25 to 205 °C for 30 minutes.

The microstructure of organic-inorganic perovskites $CH_3NH_3PbI_3$ obtained at different ratios of the starting reagents was studied on a scanning electron microscope SEC miniSEM SNE 4500MB. The elemental composition of the films was studied using an EDAX Element PV6500/00 F spectrometer, which is included in the set of this microscope.

The phase composition of films was identified by X-ray powder diffractometry (XRPD) using a DRON-4-07 diffractometer (CuKα-radiation, 40 kW, 18 mA) over $2\Theta = 5\text{–}50^{\circ}$, a step of 0.03° and a count time of 3 sec.

The kinetics of fluorescence was studied on a spectrofluorimeter CM 2203 (Belarus) under excitation by radiation with a wavelength of 470 nm in the absorption band of perovskite and recording the fluorescence intensity in the region of its radiation maximum (780 nm).

3. Results and discussion

3.1. Investigation of films

Fig. 1 shows the image of the surface of the films obtained on glass substrates at different ratios of starting reagents PbI_2 and CH_3NH_3I (1:1, 1:2, 1:3) in DMSO solvent. The ratio of the starting reagents PbI_2 and CH_3NH_3I strongly affects the morphology of the synthesized films.

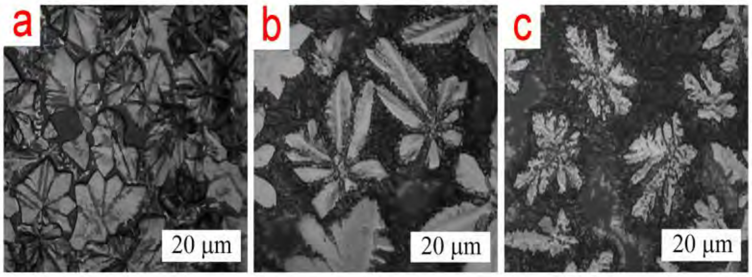


Fig. 1. The surface of the perovskite films $CH_3NH_3PbI_3$, obtained at different ratios of the starting reagents PbI_2 and CH_3NH_3I: 1:1 - (a) ; 1:2 - (b); 1:3 - (c).

At a ratio of starting reagents of 1:1, the particles grow in the form of leaves with a particle size of 30 µm, at a ratio of 1:2 and 1:3 the particles grow from the center of crystallization in 8 and 6 directions, respectively. As the ratio of starting reagents increases, the particle sizes decrease from 30 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 starting reagents can significantly affect the formation of $CH_3NH_3PbI_3$ precursors and, accordingly, the further growth of perovskite crystals and their form [22].

The elemental composition of the $CH_3NH_3PbI_{2.98}Cl_{0.02}$ films deposited from solutions with different ratios of the starting reagents PbI_2 and CH_3NH_3I (1:2, and 1:3) was studied by the energy-dispersive X-ray spectroscopy (EDX) method (Fig. 2). The spectrum exhibits peaks of Ca, Si, which is contained in the glass substrate [23]. It is shown that the ratio of the intensity of the Pb and I peaks is equal to the same for samples at different ratios of PbI_2 and CH_3NH_3I.

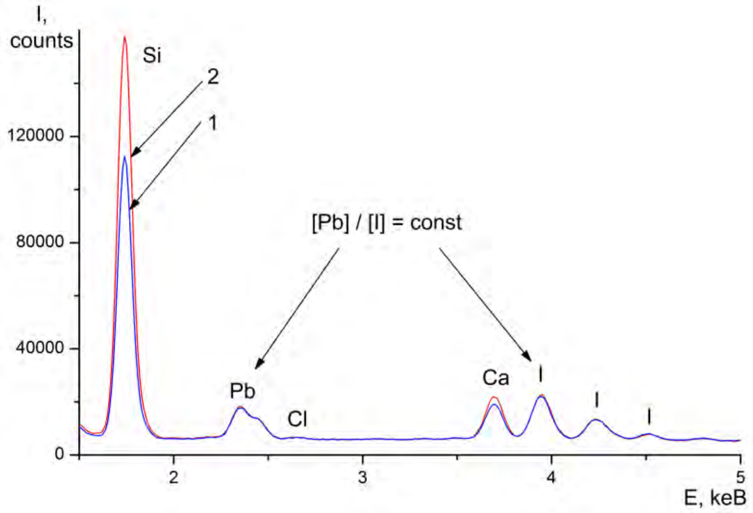


Fig. 2. EDX films $CH_3NH_3PbI_{2.98}Cl_{0.02}$ obtained at a ratio of starting reagents (PbI_2 and CH_3NH_3I) 1:2 (1) and 1:3 (2).

The crystallinity of the films (K) was determined by the formula: $K = \frac{I_1}{I_2} \cdot 100\%$, where I_1 is the area under peaks of the crystalline phase, I_2 is the total area of the whole XRD spectra. Fig. 3 shows the percent crystallinity as a function of deposition temperature of organic-inorganic films $CH_3NH_3PbI_3$ synthesized at different ratios of PbI_2 to CH_3NH_3I in DMSO solutions. The increasing temperature from room temperature to ~ 80 °C increases crystallinity. The maximum value of the crystallinity of the films obtained at different ratios of the starting reagents (1:1, 1:2, 1:3) from a solution of DMSO has observed at 80 °C. A further increase in temperature decreases the crystallinity. When the ratio of starting reagents increases the crystallinity of the films decreases. Therefore, crystallinity can significantly affect the properties of the films.

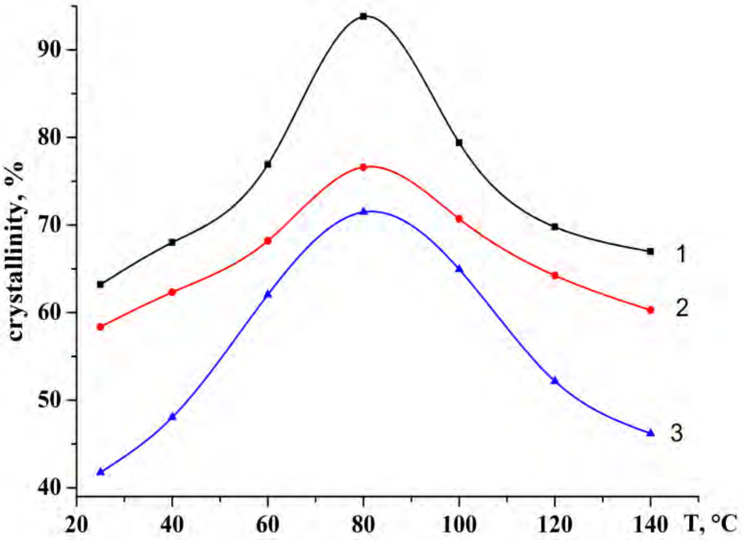


Fig. 3. Crystallinity as a function of deposition temperature of organic-inorganic films $CH_3NH_3PbI_{2.98}Cl_{0.02}$ synthesized at ratios of PbI_2 and CH_3NH_3I 1:1 (1), 1:2 (2), and 1:3 (3).

Table 1 shows the literature data [24-30] on the unit cell parameters of the initial reagents, probable intermediate and terminal compounds in the films formed in DMSO solvent at different ratios of the initial reagents, PbI_2 and CH_3NH_3I.

Table 1. Unit cell parameters at room temperature of the initial reagents, probable intermediate, and terminal compounds in the synthesis of organic-inorganic perovskite films.

Compound	Symmetry and space group	Unit cell parameters	References
PbI_2	Trigonal P-3m1 (№164)	$a = 4.558$ Å $c = 6.986$ Å	[24]
CH_3NH_3I		$a = 5.120$ Å $c = 9.000$ Å	[25]
$PbI_2 \cdot DMSO$	Orthorhombic Pnma (№62)	$a = 17.796(3)$ Å $b = 11.1352(17)$ Å $c = 4.5144(6)$ Å $\alpha = \beta = \gamma = 90°$ $Z = 4$ $V = 894.6(2)$ Å^3	[26]
$PbI_2 \cdot 2DMSO$	Orthorhombic Pccn (№56)	$a = 13.6978(4)$ Å $b = 10.8575(4)$ Å $c = 8.7607(3)$ Å $\alpha=\beta=\gamma= 90°$ $Z = 4$ $V= 1302.93(7)$ Å^3	[26]
$(CH_3NH_3)_2(DMSO)_2Pb_3I_8$	Orthorhombic $Pca2_1$ (№29)	$a = 4.6212(6)$ Å $b = 27.129(7)$ Å $c = 26.841(4)$ Å	[26]

		$\alpha = \beta = \gamma = 90°$ Z = 4 V = 3376.2(12) $Å^3$	
$(CH_3NH_3)_3(DMSO)PbI_5$	Monoclinic C2/c (№15)	a = 20.641(2) Å b = 12.4157(9) Å c =19.0841(19) Å $\alpha = \gamma =$ 90° β = 113.122(12) Z = 8 V = 4497.9(8) $Å^3$	[26]
$CH_3NH_3PbI_3$	Tetragonal I4/mcm (№140)	a = 0.8870(2) Å c = 1.2669 (8) Å V = 0.9968(7) $Å^3$	[27]
$CH_3NH_3PbI_3{\cdot}H_20$	Monoclinic $P2_1/m$ (№11)	a = 10.46 Å, b = 4.63 Å, c = 11.10 Å $\alpha = \gamma = 90°$ β = 101.50° Z = 2 V = 536.05(19) $Å^3$	[28]
$(CH_3NH_3)_4PbI_6{\cdot}2H_20$	Monoclinic $P2_1/c$ (№14)	a = 10.421(3) Å b = 11.334(2) Å c = 10.668(2) Å $\alpha = \gamma = 90°$ β = 91.73(2)° Z = 2 V = 1259.4(5) $Å^3$	[29]
$(CH_3NH_3)_2(DMSO)_xPbI_4$	-	-	[30]

Fig. 4 shows the results of the XRD analysis of perovskite films $CH_3NH_3PbI_3$ obtained at a ratio 1:1 of the initial reagents PbI_2 and CH_3NH_3I and at different temperatures of heat treatment

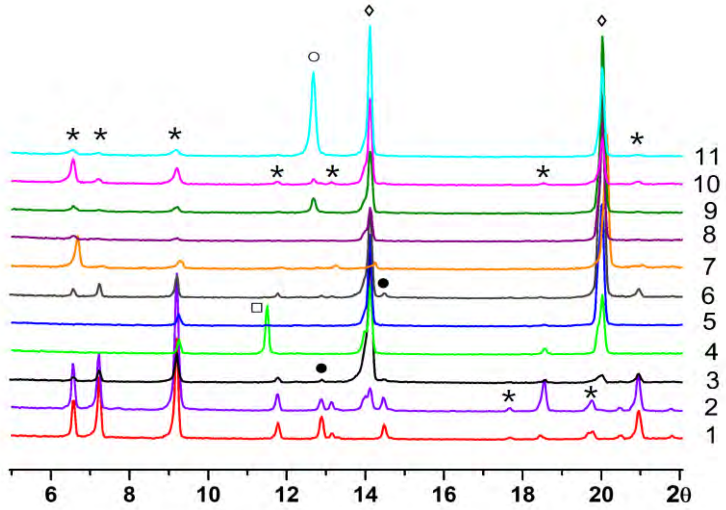


Fig. 4. X-ray diffraction pattern of films prepared with ratio 1:1 of the initial reagents PbI_2 and CH_3NH_3I with heat treatment at different temperatures: 25 °C (1), 60 °C (2), 80 °C (3), 90 °C (4), 100 °C (5), 110 °C (6), 140 °C (7), 150 °C (8), 165 °C (9), 180 °C (10) and 190 °C (11). Phases are denoted by "□" – $(CH_3NH_3)_2(DMSO)_xPbI_4$, "*" – $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, "●" – $PbI_2 \cdot 2DMSO$, "○" – $PbI_2 \cdot DMSO$ and "◊" – $CH_3NH_3PbI_3$.

X-ray diffraction patterns of the films show the peaks corresponding to $CH_3NH_3PbI_3$ (14.1 °, 19.9°) (denoted in Fig. 4 as "◊") and second phases. In particular, the peaks at 2Θ: 6.56°, 7.19°, 9.19°, 11.75°, 13.13°, 17.68°, 18.55°, 19.76° and 20.96° (denoted in Fig. 4 as "*") can be attributed to the intermediate phase $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$ [26]. The peak at 2Θ: 11.48° (denoted in Fig. 4 as "□") corresponds to the compound $(CH_3NH_3)_2(DMSO)_xPbI_4$ [30], the peaks at 2Θ: 12.88°, 14.5° (denoted in Fig. 4 as "●") correspond to the compound PbI_2-2DMSO [26]. The compound PbI_2-DMSO is characterized by a peak at 2Θ = 12.68 ° (denoted in Fig. 3 as "○") [26]. At temperatures below 60 °C, organic-inorganic perovskite $CH_3NH_3PbI_3$ is not formed. At these temperatures (25-60 °C) in the films, there are 3 intermediate phases: $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, $PbI_2 \cdot 2DMSO$, $PbI_2 \cdot DMSO$. When the ratio of starting reagents is 1:1, the films of organic-inorganic perovskite contain additional phases after heat treatment in a wide temperature range.

Fig. 5 shows the results of the XRD analysis of perovskite films $CH_3NH_3PbI_3$ obtained at a ratio 1:2 of the initial reagents PbI_2 and CH_3NH_3I and at different temperatures of heat treatment in the temperature range from 25 to 190 °C. Intense peaks of perovskite phase $CH_3NH_3PbI_3$ (14.1°, 19.9°) and peaks from other intermediate phases are observed.

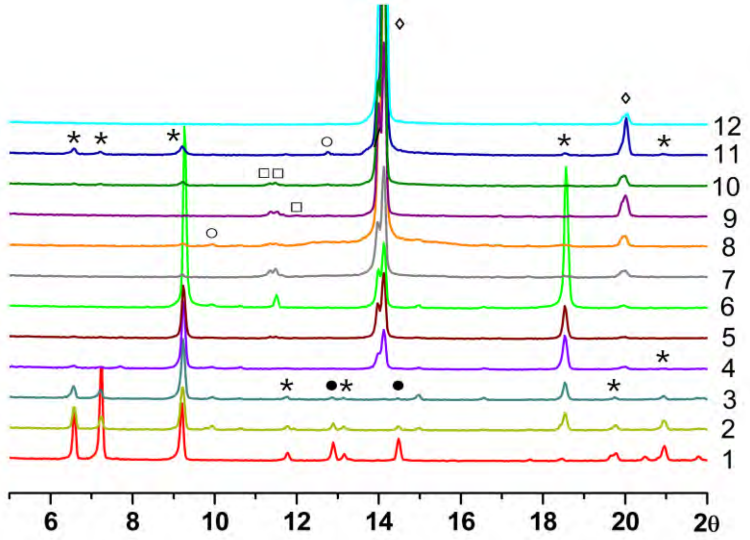


Fig. 5. X-ray diffraction pattern of films prepared with ratio 1:2 of the initial reagents PbI_2 and CH_3NH_3I with heat treatment at different temperatures: 25 °C (1), 30 °C (2), 50 °C (3), 60 °C (4), 70 °C (5), 90 °C (6) 120 °C (7), 140 °C (8), 150 °C (9), 165 °C (10), 185 °C (11) and 190 °C (12). Phases are denoted by "□" – $(CH_3NH_3)_2(DMSO)_xPbI_4$, "*" – $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, "●" – $PbI_2 \cdot 2DMSO$, "○" – $PbI_2 \cdot DMSO$ and "◊" – $CH_3NH_3PbI_3$.

In particular, the peaks at 2Θ: 6.56°, 7.19°, 9.19°, 11.75°, 13.13°, 18.55°, 19.76° and 20.96° (denoted in Fig. 5 as "*") correspond to the intermediate compound $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$ [26]. The compound $(CH_3NH_3)_2PbI_4$ or $(CH_3NH_3)_2(DMSO)_xPbI_4$ is characterized by peaks at 2Θ: 11.35 °, 11.48 °, 11.67 ° (denoted in Fig. 5 as "□")[30], peaks at 2Θ: 12.88 °, 14.5 ° (denoted in Fig. 5 as "●") correspond to the compound - $PbI_2 \cdot 2DMSO$ [26], and peaks at 2Θ - 9.93° and 12.68° (denoted in Fig. 5 as "○") correspond to $PbI_2 \cdot DMSO$ [26]. At temperatures below 60 °C, organic-inorganic perovskite $CH_3NH_3PbI_3$ is not formed. At these temperatures (< 60 °C) there are 2 intermediate compounds, $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$ and $PbI_2 \cdot 2DMSO$. At a ratio of starting reagents of 1:2, a single-phase sample of organic-inorganic perovskite was obtained at a temperature $T \geq 190$ °C.

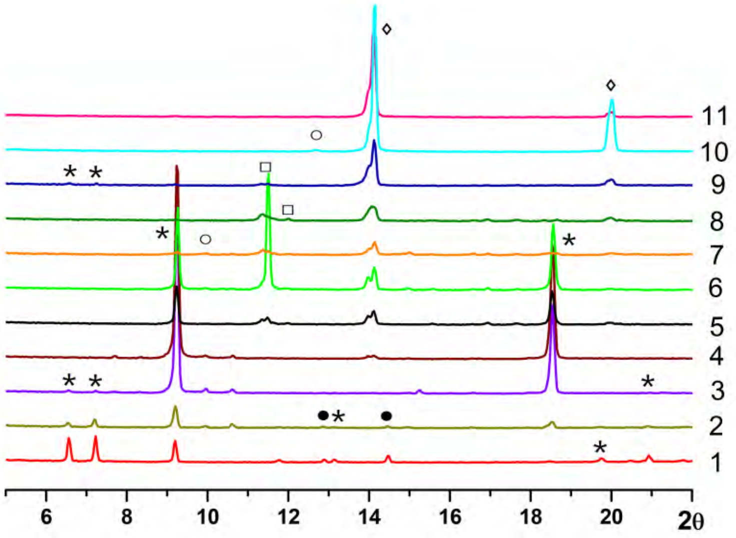


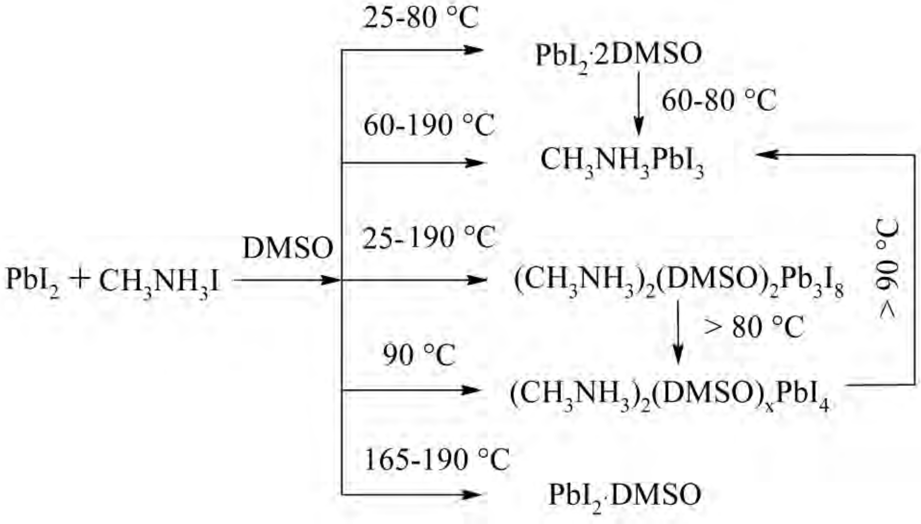
Fig. 6. X-ray diffraction pattern of films prepared with ratio 1:3 of the initial reagents PbI_2 and CH_3NH_3I with heat treatment at different temperatures: 25 °C (1), 30 °C (2), 60 °C (3), 70 °C (4), 80 °C (5), 90 °C (6), 100 °C (7), 165 °C (8), 185 °C (9), 200 °C (10) and 205 °C (11). Phases are denoted by "□" – $(CH_3NH_3)_2(DMSO)_xPbI_4$, "*" – $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, "●" – $PbI_2{\cdot}2DMSO$, "○" – $PbI_2{\cdot}DMSO$ and "◊" – $CH_3NH_3PbI_3$.

Fig. 6 shows the results of the XRD analysis of perovskite films $CH_3NH_3PbI_3$ prepared at ratio 1:3 of the initial reagents PbI_2 and CH_3NH_3I at different temperatures of heat treatment. The analysis of the X-ray diffraction pattern of films shows that in addition to peaks of the perovskite phase (14.1°, 19.9°), the peaks of other intermediate compounds are present. In particular, peaks at 6.56°, 7.19°, 9.19°, 13.13°, 18.55°, 19.76°, and 20.96° indicate the formation of the intermediate compound of $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$ [26]. Peaks at 2Θ = 11.35°, 11.48° and 11.67° (denoted in Fig. 6 as "□") correspond to the compound $(CH_3NH_3)_2PbI_4$ or $(CH_3NH_3)_2(DMSO)_xPbI_4$ [30], peaks at 2Θ: 12.88°, 14.5° (denoted in Fig. 6 as "●") indicate the formation of to the compound - $PbI_2{\cdot}2DMSO$ [26], and the peak at 2Θ = 12.68° (denoted in Fig. 6 as "○") can be attributed to $PbI_2{\cdot}DMSO$ [26]. At temperatures below 70 °C, the formation of organic-inorganic perovskite $CH_3NH_3PbI_3$ is not observed. At these temperatures (< 70 °C) there are 2 intermediate compounds: $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, $PbI_2{\cdot}2DMSO$ in the films. At a ratio of starting reagents of 1:3, a single-phase organic-inorganic perovskite was obtained at a temperature $T \geq 205$ °C. XRD investigation has shown the presence of certain intermediate compounds in the synthesized film depends on the ratio of the starting reagents and the processing temperature of the film (Table 2).

Table 2. Temperature interval of existence of intermediate compounds at different ratios of starting reagents.

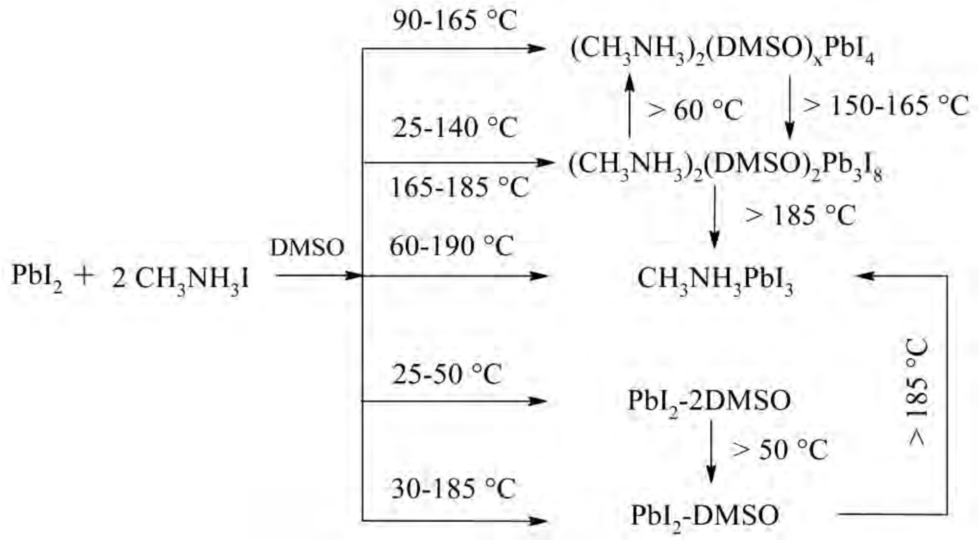
Compound	Temperature interval of existence		
	1:1	1:2	1:3
$(CH_3NH_3)_2(DMSO)_2Pb_3I_8$	25-190 °C	25-140 °C 165-185 °C	25-140 °C 185-190°C
$(CH_3NH_3)_2(DMSO)_xPbI_4$	90-95 °C	90-165 °C	80-185 °C
$PbI_2{\cdot}2DMSO$	25-80 °C	25-50 °C	25-30 °C
$PbI_2{\cdot}DMSO$	165-190 °C	30-185 °C	30-200 °C
$CH_3NH_3PbI_3$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

The results of X-ray diffraction can be used to note the reaction schemes of the formation of perovskite $CH_3NH_3PbI_3$ and intermediate compounds at different ratios of the starting reagents PbI_2 and CH_3NH_3I. Earlier, we studied the formation of intermediate compounds at the synthesis of organic-inorganic films from DMF solutions by Raman spectroscopy and XRD analysis [22]. Therefore, in this study, we used the results of X-ray diffraction. The scheme of the reaction of formation of perovskite and intermediate phases at the ratio 1:1 of the initial reagents PbI_2 and CH_3NH_3I can be represented as:



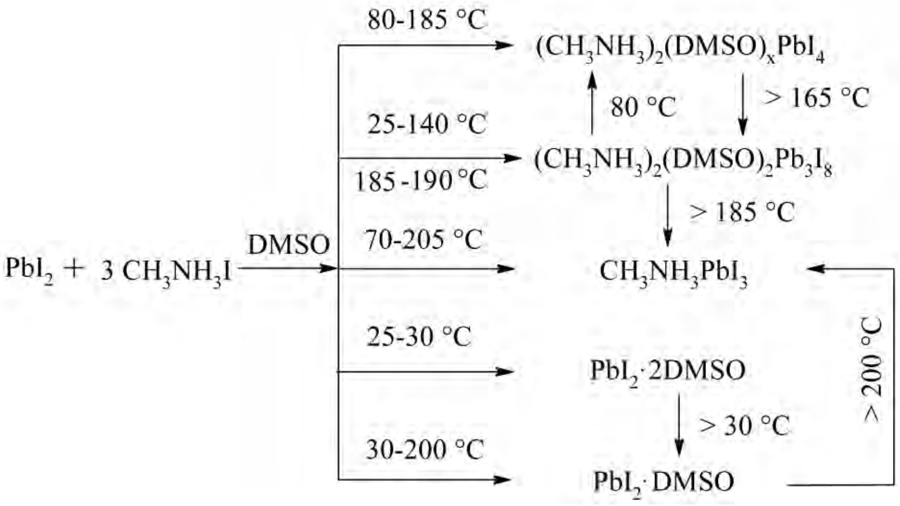
When the ratio of starting reagents PbI_2 and CH_3NH_3I = 1:1 depending on the heat treatment temperature, the films contain 4 intermediate compounds: $(CH_3NH_3)_2(DMSO)_xPbI_4$, $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, PbI_2·2DMSO, PbI_2·DMSO. At temperatures of 25-80 °C in the films of organic-inorganic perovskite, the existence of the compound PbI_2-2DMSO was established, at temperatures of 25-190 °C the compound $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$ is present. The compound PbI_2·DMSO is formed at temperatures of 165-190 °C (Table 2). At T >80 °C there is a partial decomposition of the compound $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$. The compound $(CH_3NH_3)_2(DMSO)_xPbI_4$ is formed at 90 °C. The compound is unstable and with increasing temperature turns into perovskite. Also at temperatures T= 60-80 °C, the compound PbI_2·2DMSO decomposes, reacts with other compounds, and forms an organic-inorganic perovskite.

The scheme of the reaction of formation of perovskite and intermediate phases at the ratio 1:2 of the initial reagents PbI_2 and CH_3NH_3I can be represented as:



When the ratio of starting reagents PbI_2 and CH_3NH_3I = 1:2, the films contain 4 intermediate compounds: $(CH_3NH_3)_2(DMSO)_xPbI_4$, $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, PbI_2·2DMSO, PbI_2·DMSO. With the increasing amount of CH_3NH_3I in the initial solution, the temperature intervals of the existence of intermediates differ significantly. At a temperature of 25-50 °C in the films of organic-inorganic perovskite PbI_2·2DMSO compound was present. The compound PbI_2·DMSO is formed at temperatures of 30-185 °C. Compound $(CH_3NH_3)_2(DMSO)_xPbI_4$ is present in films of organic-inorganic perovskite at temperatures of 90-165 °C. For the compound $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, two intervals of existence were established at temperatures of 25-140 °C and 165-185 °C (Table 2).

The scheme of the reaction of formation of perovskite and intermediate compounds at the ratio 1:3 of the initial reagents PbI_2 and CH_3NH_3I can be represented as:



When the ratio of starting reagents PbI_2 and CH_3NH_3I = 1:3, the films contain 4 intermediate compounds: $(CH_3NH_3)_2(DMSO)_xPbI_4$, $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, $PbI_2 \cdot 2DMSO$, $PbI_2 \cdot DMSO$. At temperatures of 25-30 °C in the films of organic-inorganic perovskite, the existence of the compound $PbI_2 \cdot 2DMSO$ was established. The compound $PbI_2 \cdot DMSO$ is formed at temperatures of 30-200 °C. Compound $(CH_3NH_3)_2(DMSO)_xPbI_4$ is present in the films of organic-inorganic perovskite at temperatures of 80-185 °C. For the compound $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, two intervals of existence were established at temperatures of 25-140 °C and at 185-190 °C (Table 2). X-ray analysis of films obtained with different ratios of starting reagents PbI_2 and CH_3NH_3I in DMSO shows that formed films in addition to perovskite $CH_3NH_3PbI_3$ contain 4 intermediate compounds.

3.2. Investigation of films stability

Changing the conditions of the synthesis of organic-inorganic perovskites can significantly affect the properties of the films. To study the properties of perovskite films, films with different ratios of starting reagents PbI_2 and CH_3NH_3I (1:2 and 1:3) in DMF and DMSO solvents were synthesized.

The influence of moisture and irradiation on the stability of organic-inorganic perovskite has been studied. The stability of organic-inorganic perovskite films was determined by XRD and fluorescence spectroscopy. The stability of perovskites to moisture was studied using XRD analysis. X-ray diffraction of films was studied at regular intervals for

80 days (Fig. 7). The stability of the films was evaluated by the content of the PbI_2 phase, which is formed as a result of the degradation of the film of organic-inorganic perovskite.

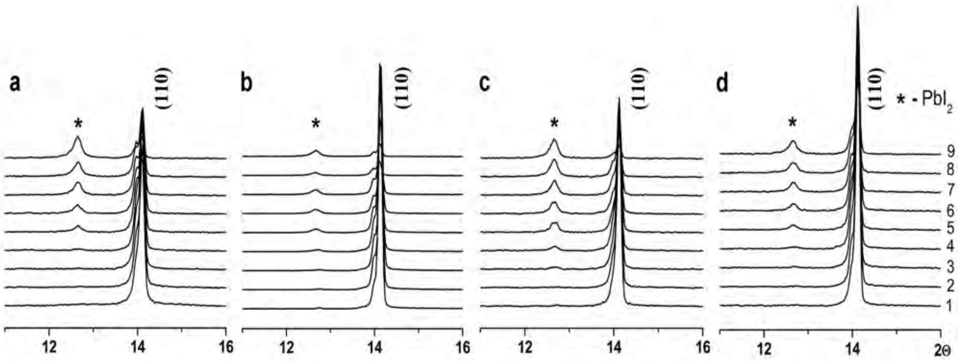


Fig. 7. XRD of organic-inorganic perovskite films synthesized with a ratio of starting reagents PbI_2 and CH_3NH_3I =1:2 (a, b) and 1:3 (c, d) in different solvents DMF (a, c) and DMSO (b, d): 1 - after synthesis; 2-9 - after 5, 10, 15, 25, 35, 45, 55, 80 days respectively. Phase PbI_2 is denoted by “*”.

Films of organic-inorganic perovskite $CH_3NH_3PbI_3$, obtained from solutions with different ratios of starting reagents (1:2, 1:3) in different solvents (DMF, DMSO), show different stability to moisture. Regardless of the ratio of starting reagents at the synthesis of perovskites, the films obtained from DMF solution are less stable (Fig. 8, curves 1, 2). Organic-inorganic perovskite films obtained from DMSO solution are more stable to moisture (Fig. 8, curves 3, 4). Films obtained with a ratio of starting reagents 1:3 are more stable than films with a ratio of 1:2.

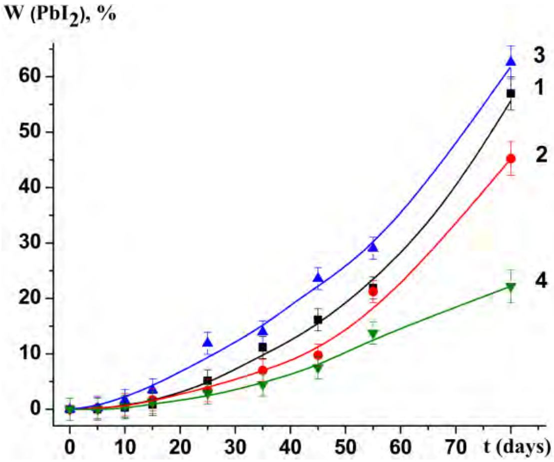


Fig. 8. The dependence of the content of the PbI_2 phase, which is formed during the decomposition of perovskite obtained from a solution of DMF (1,3) and DMSO (2,4) with different ratios of starting reagents: 1, 2 - 1:2; 3, 4 - 1:3.

Fluorescence spectroscopy showed that regardless of the ratio of starting reagents (1:2, 1:3) irradiation of perovskite films obtained when using DMF as a solvent leads to gradual changes in the fluorescence intensity of the films over time, which indicating the changes in its morphology (Fig. 9, curves 1,3). At the same time, under similar conditions in the films obtained from DMSO, the fluorescence intensity does not change (Fig. 9, curves 2,4), which indicates their much higher resistance to irradiation.

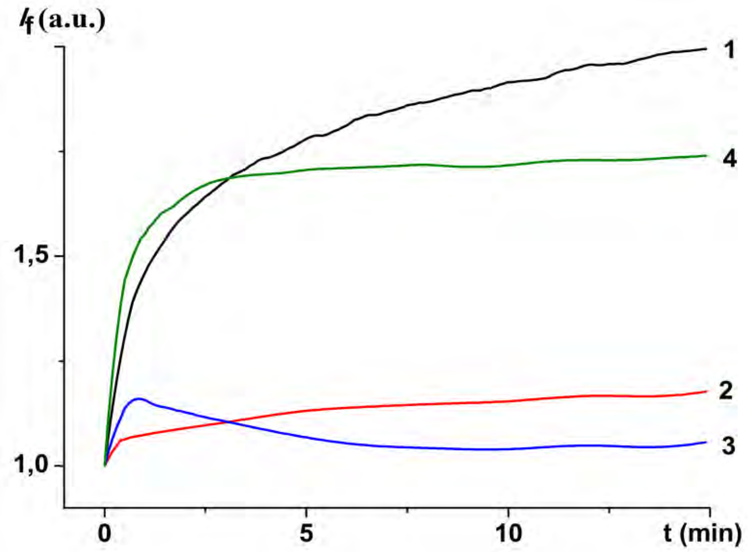


Fig. 9. Dependence of fluorescence intensity (I_f) as a function of time irradiation of organic-inorganic perovskites films obtained from a solution of DMF (1,3) and DMSO (2,4) with different ratio of starting reagents: 1, 2 - 1:2; 3, 4 - 1:3.

4. Conclusions

The formation of intermediate phases in the synthesis of $CH_3NH_3PbI_3$ films at different ratios of starting reagents PbI_2 and CH_3NH_3I (1:1, 1:2, and 1:3) in DMSO solvent was studied. The change in the ratio of the starting 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 starting reagents are characterized by different morphology. At a ratio of starting reagents of 1:1, leaf-shaped particles are observed, at a ratio of 1:2 and 1: 3, the growth of particles occurs from the center of crystallization in 8 and 6 directions, respectively.

It was found that depending on the ratio of starting reagents and heat treatment temperature, the formation of organic-inorganic perovskite occurs according to similar schemes: through the formation of 4 intermediate compounds (1:1, 1:2, 1:3). In addition to $CH_3NH_3PbI_3$ perovskite, other intermediates may be present in the films: $(CH_3NH_3)_2(DMSO)_xPbI_4$, $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, $PbI_2 \cdot 2DMSO$, $PbI_2 \cdot DMSO$.

Investigation of the stability of organic-inorganic perovskite films obtained using DMF and DMSO solvents were determined by XRD and fluorescence spectroscopy. It was found that the use of DMSO at the synthesis of organic-inorganic perovskite leads to the formation of more stable films than when using DMF. It was found that regardless of the solvent, perovskite films obtained with a ratio of starting reagents 1:3 are more stable to moisture and radiation than films obtained with a ratio of starting reagents 1:2.

Abbreviations

DMF: dimethylformamide, DMSO: dimethyl sulfoxide, PCE: energy conversion efficiency; MAPI: methylammonium lead iodide perovskites; XRPD: X-ray powder diffractometry.

Acknowledgements

The work was carried out with the financial support from the targeted program of fundamental research of the Ukrainian National Academy of Sciences “Promising fundamental research and innovative development of nanomaterials and nanotechnologies for the needs of industry, health and agriculture

Funding

The authors would like to thank the Ukrainian National Academy of Sciences for providing the research grant (0120U102242) to support this work.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: