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Synthesis of Organic-Inorganic Perovskite $CH_3NH_3PbI_3$ Using Dimethyl Sulfoxide (DMSO) Solvent

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Abstract

Organic-inorganic perovskites are unstable materials to external conditions that prevent their widespread use to convert solar energy. Changing the starting reagents ratio and the solvent can affect the structural and electrical properties of perovskites. Films of organic-inorganic perovskites $CH_3NH_3PbI_3$ at different ratios of starting reagents (PbI_2:CH_3NH_3I) in solvent dimethyl sulfoxide (DMSO) has been synthesized. It was found that regardless of the initial reagent ratio (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_2·2DMSO, PbI_2·DMSO. It was found that the use of DMSO and the ratio of initial reagents 1:3 at the synthesis of organic-inorganic perovskite leads to the formation of more stable films compared with the use of DMF solvent. It was found that under the influence of moisture for 80 days, perovskite films obtained at a ratio of 1:2 and 1:3 in DMSO, were degraded by 45 and 22%, respectively. The films obtained in DMF at a ratio of 1:2 and 1:3 were degraded by 62 and 57%, respectively. This difference shown is associated with the formation of different intermediate phases, which are templates in the crystallization of perovskite.

Keywords: Perovskite solar cells; Film deposition; Microstructural morphology; Intermediate products; Stability improvement.
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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 power 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.[14-17] 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.[18,19] The process of nucleation and

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formation of crystals is determined by the chemical interaction of the organic cation, the coordinating solvent, and the inorganic component.[20] 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.[21] The type of solvent can affect both the phase transformations in the synthesis and the properties of organic-inorganic perovskite films. That is why the phase transformations that occur when using solvents other than DMF are of interest. This work aimed to study the processes of the formation of intermediate phases in the synthesis of films of organic-inorganic perovskites $CH_3NH_3PbI_3$ at different ratios of starting reagents, which dissolve in DMSO and study their properties.

2. Experimental section

2.1 Material preparation

Lead iodide (PbI_2) and methylammonium iodide (CH_3NH_3I) 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.[20] Dried dimethyl sulfoxide (DMSO) was used as the solvent.

To obtain $CH_3NH_3PbI_3$ films, solutions of starting reagents PbI_2 and CH_3NH_3I in ratios of 1:1, 1:2, 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. To obtain the films, we used a solution of the starting reagents, which was applied to the glass substrate by spin coating at a speed of 1200 rpm for 30 seconds. Heat treatment of the films was performed on an electric stove, which was preheated in the temperature range from 25 to 205 °C for 15 minutes.

2.2 Material characterization

Determination of the microstructure of organic-inorganic perovskites $CH_3NH_3PbI_3$ was performed on a scanning electron microscope SEC miniSEM SNE 4500MB. For perovskite films, the elemental composition was studied using an EDAX Element PV6500/00 F spectrometer.

Using the X-ray powder diffractometry (XRPD), the phase composition of the organic-inorganic perovskites $CH_3NH_3PbI_3$ films was determined by a DRON-4-07 diffractometer (CuK_α radiation, 30 kW, 30 mA) at 2θ = 5-50º, a step of 0.03aº and a reference time of 3 sec.

The kinetics of fluorescence was studied on a spectrofluorometer 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 affect the morphology of the synthesized films. At a ratio of starting reagents of 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 centre 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 starting reagents can significantly affect the formation of $CH_3NH_3PbI_3$ precursors and, accordingly, the further growth of perovskite crystals and their form.[21]

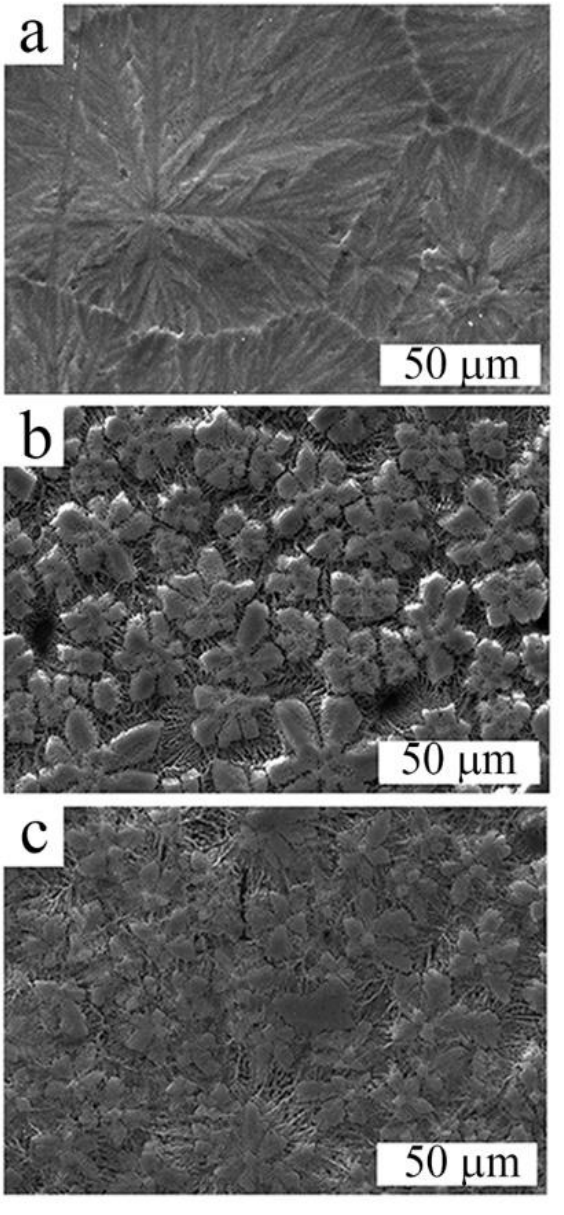

Fig. 1 The surface of the perovskite films $CH_3NH_3PbI_3$ obtained at different ratios of the starting reagents PbI_2 and CH_3NH_3I: 1:1 (a), 1:2 (b), and 1:3 (c).

The elemental composition of the $CH_3NH_3PbI_3$ 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.[22] 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, which indicates the formation of organic-inorganic perovskite of the same chemical composition. The difference in the intensities of the elements Si and Ca is related to the film thickness, which is 800 nm and 600 nm for $CH_3NH_3PbI_3$ films obtained at a ratio of starting reagents 1:2 and 1:3, respectively.

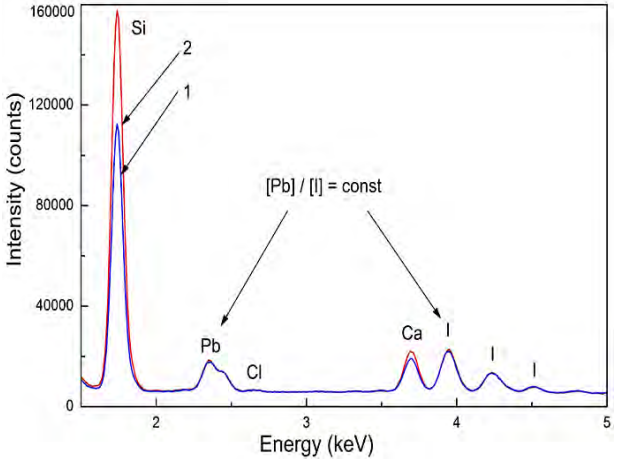

Fig. 2 EDX of films $CH_3NH_3PbI_3$ obtained at a ratio of starting reagents (PbI_2 and CH_3NH_3I): 1:2 (1) and 1:3 (2).

Table 1 shows the literature data[23-29] 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.

Fig. 3 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 different temperatures of heat treatment.

X-ray diffraction patterns of the films show the peaks corresponding to $CH_3NH_3PbI_3$ (14.1° and 19.9°) (denoted in Fig. 3 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. 3 as "*") can be attributed to the intermediate phase $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$.[25] The peak at 2θ: 11.48° (denoted in Fig. 3 as "□") corresponds to the compound $(CH_3NH_3)_2(DMSO)_xPbI_4$,[29] the peaks at 2θ: 12.88°, 14.5° (denoted in Fig. 3 as "●") correspond to the compound PbI_2-2DMSO.[25] The compound PbI_2-DMSO is characterized by a peak at 2θ = 12.72° (denoted in Fig. 3 as "○").[25] 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_2·2DMSO, and PbI_2·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. Analysis of the literature also indicates that when the ratio of starting reagents (PbI_2 and CH_3NH_3I) 1:1 and the use of DMSO solvent are always present impurities of the additional phase.[30] This result differs from the situation when DMF was used as a solvent and a single-phase perovskite phase can be obtained at a ratio of starting reagents (PbI_2 and CH_3NH_3I) of 1:1.[22] The change in the solvent (DMF to DMSO) also changes the chemical composition of the intermediate phases that are formed during the formation of the perovskite structure.

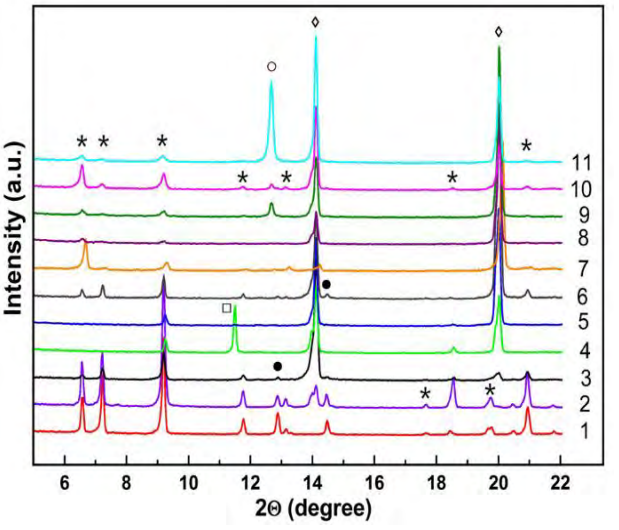

Fig. 3 X-ray diffraction pattern of films prepared with ratio 1:1 of the initial reagents PbI_2 and CH_3NH_3I with heat treatment at different temperatures: 25 °C (1), 60 °C (2), 80 °C (3), 90 °C (4), 100 °C (5), 110 °C (6), 140 °C (7), 150 °C (8), 165 °C (9), 180 °C (10) and 190 °C (11). Phases are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

Fig. 4 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 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 ° and 19.9 °) and peaks from other intermediate phases are observed.

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. 4 as "*") correspond to the intermediate compound $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$.[25] 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. 4 as "□"), [29] peaks at 2θ: 12.88° and 14.5° (denoted in Fig. 4 as "●") correspond to the compound PbI_2·2DMSO,[25] and peaks at 2θ = 9.93° and 12.72° (denoted in Fig. 4 as "○") correspond to PbI_2·DMSO.[25] 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_2·2DMSO. At a ratio of starting reagents of 1:2, a single-phase sample of organic-inorganic perovskite was obtained at a temperature T ≥ 190 °C.

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 $P\bar{3}m1$ (№ 164)	a = 4.558 Å c = 6.986 Å	[23]
CH_3NH_3I		a = 5.120 Å c = 9.000 Å	[24]
PbI_2·DMSO	Orthorhombic Pnma (№ 62)	a = 17.796(3) Å b = 11.1352(17) Å c = 4.5144(6) Å α = β = γ = 90 ° Z = 4 V = 894.6(2) Å^3	[25]
PbI_2·2DMSO	Orthorhombic Pccn (№ 56)	a = 13.6978(4) Å b = 10.8575(4) Å c = 8.7607(3) Å α=β=γ= 90 ° Z = 4 V= 1302.93(7) Å^3	[25]
$(CH_3NH_3)_2(DMSO)_2Pb_3I_8$	Orthorhombic $Pca2_1$ (№ 29)	a = 4.6212(6) Å b = 27.129(7) Å c = 26.841(4) Å α = β = γ = 90 ° Z = 4 V = 3376.2(12) Å^3	[25]
$(CH_3NH_3)_3(DMSO)PbI_5$	Monoclinic C2/c (№ 15)	a = 20.641(2) Å b = 12.4157(9) Å c =19.0841(19) Å α = γ = 90 ° β = 113.122(12) Z = 8 V = 4497.9(8) Å^3	[25]
$CH_3NH_3PbI_3$	Tetragonal I4/mcm (№ 140)	a = 8.870(2) Å c = 12.669 (8) Å V = 996.8(7) Å^3	[26]
$CH_3NH_3PbI_3$·H_2O	Monoclinic $P2_1/m$ (№ 11)	a = 10.46 Å, b = 4.63 Å, c = 11.10 Å α = γ = 90 ° β = 101.50 ° Z = 2 V = 536.05 Å^3	[27]
$(CH_3NH_3)_4PbI_6$·$2H_2O$	Monoclinic $P2_1/c$ (№ 14)	a = 10.421(3) Å b = 11.334(2) Å c = 10.668(2) Å α = γ = 90 ° β = 91.73(2) ° Z = 2 V = 1259.4(5) Å^3	[28]
$(CH_3NH_3)_2(DMSO)_xPbI_4$	-	-	[29]

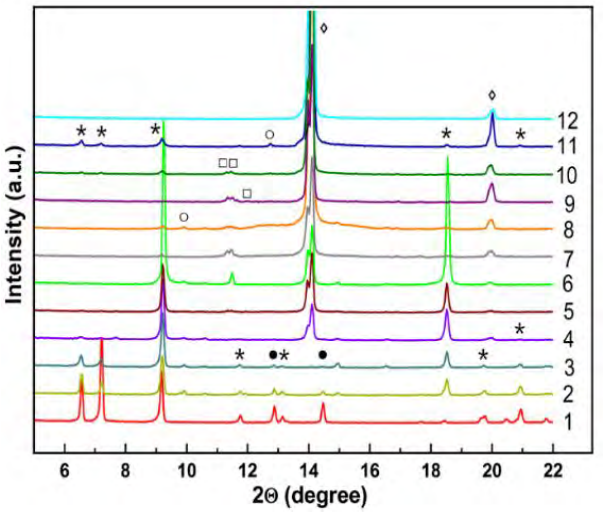

Fig. 4 X-ray diffraction pattern of films prepared with ratio 1:2 of the initial reagents PbI_2 and CH_3NH_3I with heat treatment at different temperatures: 25 °C (1), 30 °C (2), 50 °C (3), 60 °C (4), 70 °C (5), 90 °C (6) 120 °C (7), 140 °C (8), 150 °C (9), 165 °C (10), 185 °C (11) and 190 °C (12). Phases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

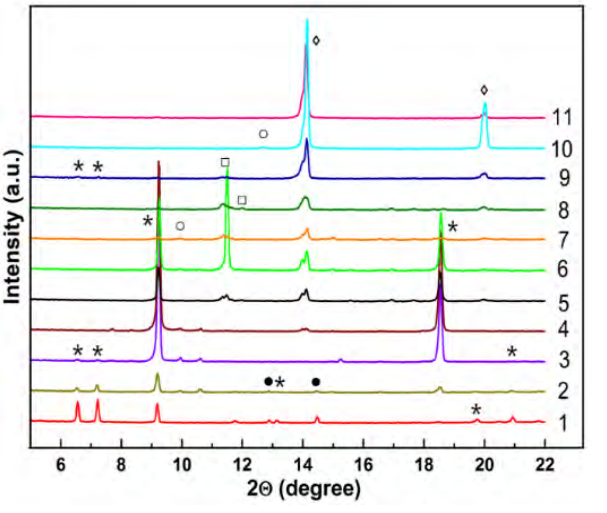

Fig. 5 X-ray diffraction pattern of films prepared with ratio 1:3 of the initial reagents PbI_2 and CH_3NH_3I with heat treatment at different temperatures: 25 °C (1), 30 °C (2), 60 °C (3), 70 °C (4), 80 °C (5), 90 °C (6), 100 °C (7), 165 °C (8), 185 °C (9), 200 °C (10) and 205 °C (11). Phases are denoted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

Fig. 5 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° and 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 $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$.[25] Peaks at 2θ = 11.35°, 11.48° and 11.67° (denoted in Fig. 5 as "□") correspond to the compound $(CH_3NH_3)_2PbI_4$ or $(CH_3NH_3)_2(DMSO)_xPbI_4$,[29] peaks at 2θ: 12.88° and 14.5° (denoted in Fig. 5 as "●") indicate the formation of the compound PbI_2·2DMSO,[25] and the peak at 2θ = 12.72° (denoted in Fig. 5 as "○") can be attributed to PbI_2·DMSO. [25] 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 in the films: $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$ and PbI_2·2DMSO. At a ratio of starting reagents of 1:3, a single-phase organic-inorganic perovskite was obtained at a temperature T ≥ 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).

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.[21]

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	25-140 °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

Therefore, in this study, we used the results of X-ray diffraction. Fig. 6 shows 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.

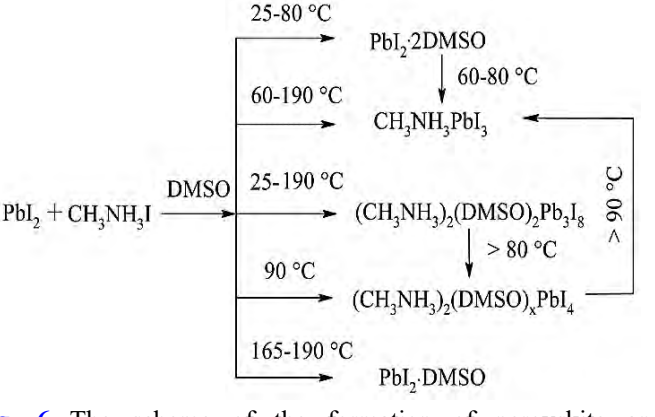

Fig. 6 The scheme of the formation of perovskite and intermediate compounds at the ratio 1:1 of the initial reagents PbI_2 and CH_3NH_3I and using DMSO.

When the ratio of starting reagents PbI_2 and CH_3NH_3I = 1:1 and using DMSO solvent depending on the heat treatment temperature, the films contain 4 intermediate compounds: $(CH_3NH_3)_2(DMSO)_xPbI_4$, $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, $PbI_2{\cdot}2DMSO$, and $PbI_2{\cdot}DMSO$. 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 $PbI_2{\cdot}DMSO$ 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 $PbI_2{\cdot}2DMSO$ decomposes, reacts with other compounds, and forms an organic-inorganic perovskite. At the same time, at a ratio of starting reagents (PbI_2 and CH_3NH_3I) 1:1 and using DMF solvent intermediate compounds $(CH_3NH_3)_2(DMF)_xPbI_4$, $(CH_3NH_3)_3(DMF)PbI_3$, and $(CH_3NH_3)_2(DMF)_2Pb_3I_8$ are formed.

Fig. 7 shows the scheme of the formation reaction of perovskite and intermediate phases at the ratio 1:2 of the initial reagents PbI_2 and CH_3NH_3I and using DMSO solvent. When the ratio of starting reagents PbI_2 and CH_3NH_3I = 1:2, the films contain 4 intermediate compounds: $(CH_3NH_3)_2(DMSO)_xPbI_4$, $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, $PbI_2{\cdot}2DMSO$, and $PbI_2{\cdot}DMSO$. 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 the compound $PbI_2{\cdot}2DMSO$ was present. The compound $PbI_2{\cdot}DMSO$ 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. Compound $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$ is present in the films of organic-inorganic perovskite at temperatures of 25-140 °C (Table 2). However, when the DMF solvent was used, other intermediates, $(CH_3NH_3)_2(DMF)_xPbI_4$, $(CH_3NH_3)_3(DMF)PbI_5$, $(CH_3NH_3)_2(DMF)_2Pb_2I_6$ and $(CH_3NH_3)_2(DMF)_2Pb_3I_8$ are formed.[31]

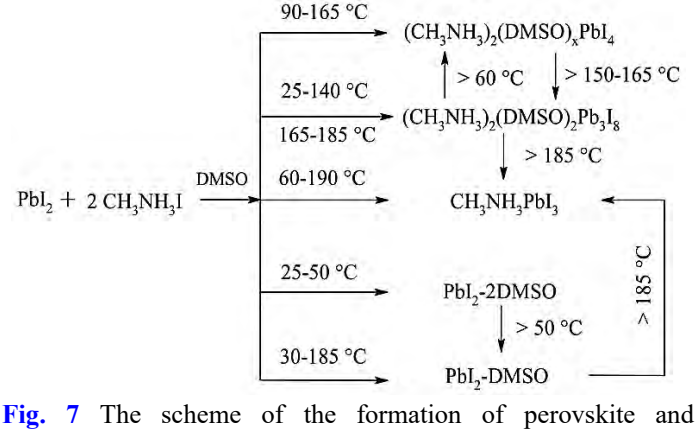

Fig. 7 The scheme of the formation of perovskite and intermediate compounds at the ratio 1:2 of the initial reagents PbI_2 and CH_3NH_3I and using DMSO.

Fig. 8 shows 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 and using DMSO solvent. When the ratio of starting reagents PbI_2 and CH_3NH_3I = 1:3, the films contain 4 intermediate compounds: $(CH_3NH_3)_2(DMSO)_xPbI_4$, $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, $PbI_2{\cdot}2DMSO$, and $PbI_2{\cdot}DMSO$. At temperatures of 25-30 °C, the existence of the compound $PbI_2{\cdot}2DMSO$ in the films of organic-inorganic perovskite 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. Compound $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$ is present in the films of organic-inorganic perovskite at temperatures of 25-140 °C (Table 2). At the same time, when DMF solvent was used, the intermediate compounds $(CH_3NH_3)_2(DMF)_xPbI_4$ and $(CH_3NH_3)_3(DMF)PbI_5$ are formed which significantly affect the formation of the structure of organic-inorganic perovskite.[错误!未定义书签。]

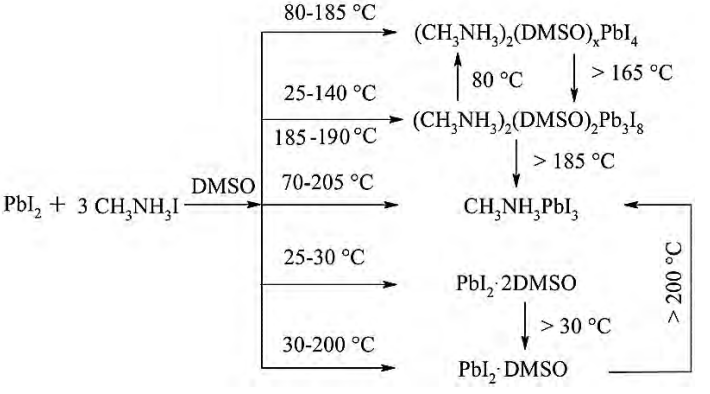

Fig. 8 The scheme of the formation of perovskite and intermediate compounds at the ratio 1:3 of the initial reagents PbI_2 and CH_3NH_3I and using DMSO.

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.

The crystallinity of the films (K) was determined by the equation $K= I_1*100/I_2$, where I_1 is the area under peaks of the crystalline phase, I_2 is the total area of the whole XRD spectra. Fig. 9 shows the per cent 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 values of the crystallinity of the films obtained at different ratios of the starting reagents (1:1, 1:2, and 1:3) from a solution of DMSO have been observed at 80 °C and 160-200 °C (Fig. 9). The first maximum of crystallinity is observed due to the contribution of both the crystalline phase of perovskite and the crystalline phases of intermediate compounds. At T > 80 °C, the content of the crystalline phases of intermediate compounds decreases.

In the temperature range (80 °C < T <140 °C) the crystallinity decreases in the film. At temperatures above 140 °C, crystallinity increases due to an increase in the content of the perovskite phase (the second maximum).

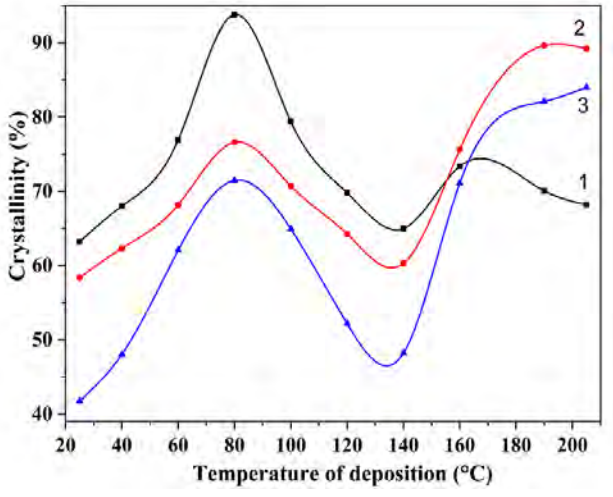

Fig. 9 Crystallinity as a function of deposition temperature of organic-inorganic films $CH_3NH_3PbI_3$ synthesized at ratios of PbI_2 and CH_3NH_3I 1:1 (1), 1:2 (2), and 1:3 (3).

The processes of crystallization of the intermediate phases and the formation of a single-phase perovskite film are separated in temperature. The maximum crystallinity is observed at a temperature of 80 °C (Fig. 9), and single-phase perovskites are formed at temperatures above 190 °C (Figs. 4, 5). Therefore, the intermediate phases are templates in the crystallization of perovskite. At a ratio of starting reagents of 1:2, the intermediate compound is $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, and at a ratio of 1:3 is $(CH_3NH_3)_2(DMSO)_xPbI_4$. The formation of various compounds can affect the properties of perovskite films.

Comparison of the sequence of perovskite formation using different solvents (DMF and DMSO) (Figs. 7-10) shows that in addition to similar for both systems intermediates ($(CH_3NH_3)_2(solvent)_xPbI_4$ and $(CH_3NH_3)_2(solvent)_2Pb_3I_8$), in the case of DMF, intermediate compounds $(CH_3NH_3)_3(DMF)PbI_5$ and $(CH_3NH_3)_2(DMF)_2Pb_2I_6$ are formed, while in the case of DMSO, lead iodide complexes $PbI_2 \cdot 2DMSO$ and $PbI_2 \cdot DMSO$ are formed.

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. 11). 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.

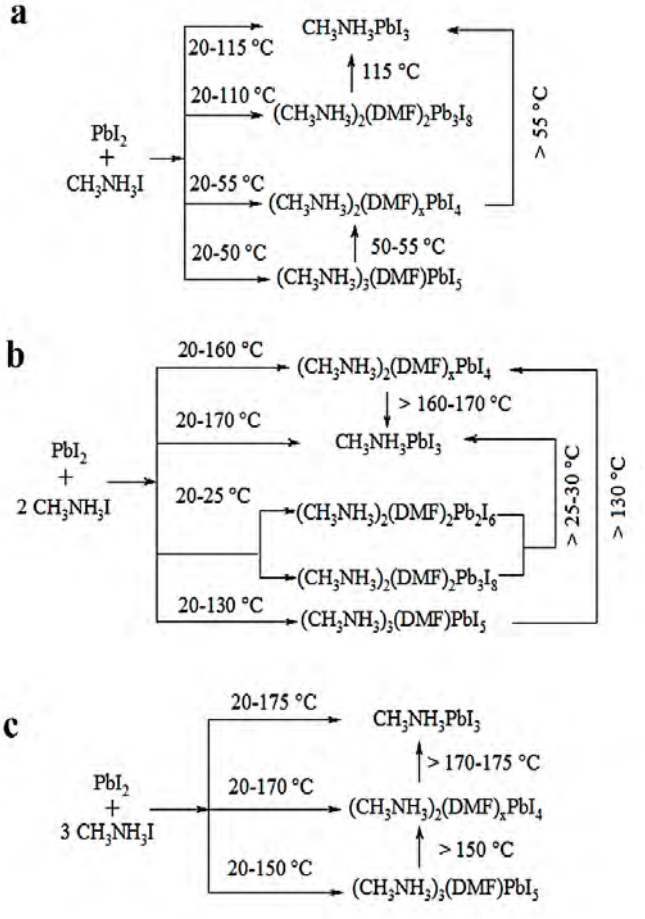

Fig. 10 The scheme of the formation reactions of perovskite and intermediate compounds at the ratio PbI_2:CH_3NH_3I 1:1 (a), 1:2 (b), 1:3 (c) and using DMF.

Films of organic-inorganic perovskite $CH_3NH_3PbI_3$, obtained from solutions with different ratios of starting reagents (1:2 and 1:3) in different solvents (DMF and DMSO), show different stability to moisture. This can be explained by the change in structural parameters for organic-inorganic perovskites (Table 3). In particular, for films obtained using DMSO solvent, smaller unit cell volume values are observed than when using DMF. Regardless of the solvent, there is an increase in unit cell volume with an increasing ratio of starting reagents. This increase in volume may be due to an increase in the organic component (namely included solvent) in the crystal structure of the perovskite.

Regardless of the ratio of starting reagents at the synthesis of perovskites, the films obtained from DMF solution are less stable (Fig. 12, curves 1, 2) and are characterized by higher values of the lattice parameters a, c, and the unit cell volume. Organic-inorganic perovskite films obtained from DMSO solution are more stable to moisture (Fig. 12, curves 3, 4). It should be noted that the unit cell volume is smaller for the film deposited at the ratio of the initial reagents of 1:1.

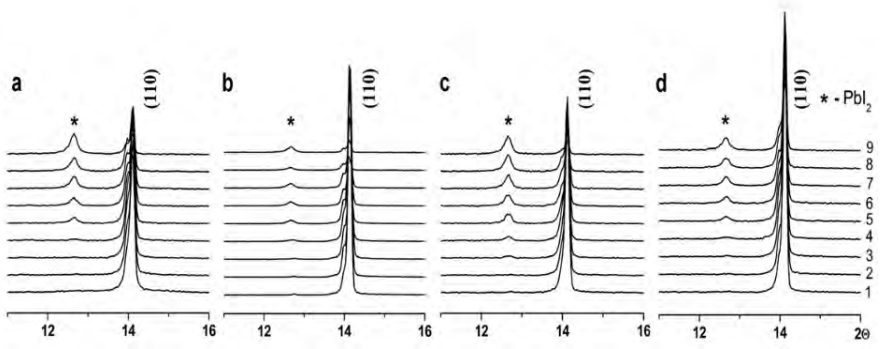

Fig. 11 XRD of organic-inorganic perovskite films synthesized with a ratio of starting reagents PbI_2 and CH_3NH_3I =1:2 (a, b) and 1:3 (c, d) in different solvents DMF (a, c) and DMSO (b, d): 1 - after synthesis; 2-9 - after 5, 10, 15, 25, 35, 45, 55, 80 days, respectively. Phase PbI_2 is denoted by "*".

Table 3. 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 DMF and DMSO as a solvent.

DMF	1:1	1:2	1:3
Unit cell parameters			
a, Å	8.8657(9)	8.878(1)	8.884(1)
c, Å	12.653(2)	12.669(6)	12.638(4)
V, Å^3	994.5(3)	998.6(5)	997.5(4)
Deposition temperature	115 °C	170 °C	175 °C
DMSO	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

Films obtained with a ratio of starting reagents 1:3 are more stable than films with a ratio of 1:2. Perovskite film obtained at a ratio of starting reagents 1:2, 1:3 in DMSO, was degraded by 45 and 22%, under the influence of moisture for 80 days. When using DMF, the film obtained at a ratio of 1:2, 1:3 was degraded by 62 and 57%, respectively.

Fluorescence spectroscopy showed that regardless of the ratio of starting reagents (1:1 and 1:3) irradiation of perovskite films obtained when using DMSO as a solvent leads to gradual changes in the fluorescence intensity of the films over time (Fig. 13).

The luminescence intensity increased when excited by both visible radiation (470 nm) and UV (370 nm) for organic-inorganic perovskite, obtained at the ratio of 1:1 (Fig. 13, curves 1, 2). Similar changes are observed for perovskite obtained at a ratio of 1:3. Moreover, the increase in luminescence intensity at excitation of 470 nm (visible radiation) is more than at excitation by UV radiation (370 nm) although the energy of light is less at a wavelength of 470 nm than at 370 nm. Changes in luminescence intensity can be explained by the change in the morphology of the perovskite film due to crystallization processes under the influence of light.[32]

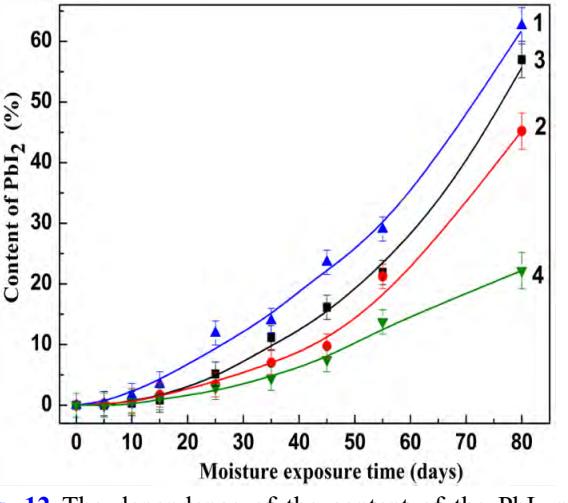

Fig. 12 The dependence of the content of the PbI_2 phase, which is formed during the decomposition of perovskite obtained from a solution of DMF (1, 3) and DMSO (2, 4) with different ratios of starting reagents: 1:2 (1, 2); 1:3 (3, 4).

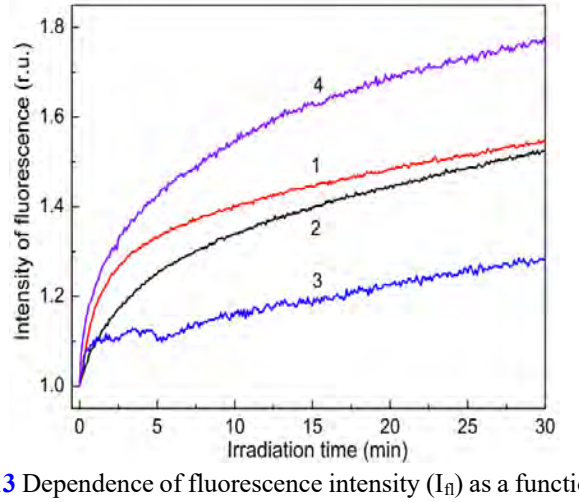

Fig. 13 Dependence of fluorescence intensity (I_{fl}) as a function of time irradiation of organic-inorganic perovskites films obtained from a solution of DMSO with different ratios of starting reagents: 1:1 (1, 2) and 1:3 (3, 4). Excitation wavelength λ = 370 nm (1, 3) and 470 nm (2, 4).

4. Conclusions

In summary, we report that 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 centre of crystallization in 6 and 5 directions, respectively.

It was found that depending on the ratio of starting reagents (1:1, 1:2, 1:3) and heat treatment temperature, 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: $(CH_3NH_3)_2(DMSO)_xPbI_4$, $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$, $PbI_2{\cdot}2DMSO$, and $PbI_2{\cdot}DMSO$. The intermediates $(CH_3NH_3)_2(solvent)_xPbI_4$ and $(CH_3NH_3)_2(solvent)_2Pb_3I_8$ are similar for systems with DMF and DMSO. However, other intermediates differ significantly. The compounds $(CH_3NH_3)_3(DMF)PbI_5$ and $(CH_3NH_3)_2(DMF)_2Pb_2I_6$ are formed when using DMF, and lead iodide complexes $PbI_2{\cdot}2DMSO$ and $PbI_2{\cdot}DMSO$ are formed when using DMSO. This difference significantly affects the formation of the structure of organic-inorganic perovskites. Investigation of the stability of organic-inorganic perovskite films obtained using DMF and DMSO solvents were determined by XRD. 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, which is confirmed by changes in unit cell parameters. 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. The stability of films can be explained by the template process of perovskite formation throughout intermediate compound $(CH_3NH_3)_2(DMSO)_2Pb_3I_8$ at a ratio of starting reagents of 1:2 and throughout $(CH_3NH_3)_2(DMSO)_xPbI_4$ at a ratio of 1:3.

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Conflict of interest

There are no conflicts to declare.

Supporting information

Not applicable.

Abbreviations

DMF: dimethylformamide
DMSO: dimethyl sulfoxide
PCE: power conversion efficiency
MAPI: methylammonium lead iodide perovskites
XRD: X-ray diffractometry.

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