

INFLUENCE OF THE SOLVENT AND THE RATIO OF STARTING REAGENTS ON THE PROPERTIES OF ORGANIC-INORGANIC PEROVSKITE MAPbI_3

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The peculiarities of formation and properties of organic-inorganic MAPbI_3 perovskite films, obtained from solutions with different ratios of starting reagents (PbI_2 :MAI = 1:1, 1:2, and 1:3), in the DMF and DMSO solvents, studied. As the PbI_2 :MAI ratio increases, the temperature of the formation of a single-phase MAPbI_3 perovskite film also increases. The slight changes in the structural and electrophysical characteristics for perovskite films obtained at the different ratios of PbI_2 :MAI in DMF and DMSO were found. These changes are related to the solvent that is included in the crystalline structure of perovskite. In the same ratios of starting reagents, DMF is included in the structure of perovskite in a greater amount than DMSO.

Keywords: organic-inorganic perovskite, phase transformations, structural parameters, electrophysical characteristics.

INTRODUCTION. The global energy crisis is one of the greatest challenges facing humanity. It is necessary to develop new technologies for the successful use of energy from renewable sources due to the reduced availability of fossil fuels. Solar energy is a rich, freely available source and promising replacement for non-renewable fossil fuels.

The solar cells based on organic-inorganic perovskites have attracted the attention of scientists according to a significant increase in efficiency to 25.2%, low cost, and ease of production. [1–2]. This effect was achieved

by improving the design of solar cells, adding new conductive layers (of n- and p-type), and improving the quality of the perovskite films. Organic-inorganic perovskites combine the advantages of organic and inorganic semiconductors: high optical absorption, high mobility of charge carriers [3], and regulated bandgap [4].

Photoactive halide perovskites usually exhibit a three-dimensional crystal structure with the characteristic chemical formula ABX_3 , where A is a monovalent cation of methylammonium (CH_3NH_3^+), formamidinium ($\text{HC}(\text{NH}_2)_2^+$), cesium (Cs^+) or rubidium (Rb^+),

and B is a divalent metal cation Pb^{2+} or Sn^{2+} , and X is a halide anion (Cl^- , Br^- or I^-) [5, 6].

Achieving the high photoelectric characteristics of organic-inorganic perovskite depends on the nucleation and growth of crystal processes. As a result of the process control, it is possible to obtain a smooth and compact film of perovskite. External factors (temperature, moisture, oxygen), as well as solvent, methods of obtaining films, and annealing can significantly affect the structural and physical properties of organic-inorganic perovskite. It is known that solvents (DMF, DMSO, γ -butyrolactone (GBL), NMP) [7, 8] were used for the synthesis of perovskites can affect the properties of films.

Changes in the synthesis conditions (ratio of starting reagents and solvent) may affect the properties of perovskites. It was shown that the ratio of starting reagents PbI_2 :MAI ($\text{CH}_3\text{NH}_3\text{I}$) affects electrophysical characteristics, particularly, the bandgap [9]. Solvent replacement also affects the properties of organic-inorganic perovskite. An increase in the stability of films to moisture and the mobility of charge carriers detected by using dimethyl sulfoxide instead of dimethylformamide during the synthesis of perovskite [10].

The method of obtaining perovskites is a key factor in achieving high characteristics (surface coverage, crystallinity, thickness, and quality of films responsible for the morphological and transport properties of perovskite). Several methods can be used to obtain films of organic-inorganic perovskites. The most common methods of them are one-step and two-step deposition, spin-coating, the method of rapid deposition crystallization, and thermal evaporation.

It is known that organic-inorganic perov-

skites are unstable materials that can degrade and decompose into various components under the influence of external factors. Finding ways to increase the stability of perovskites is an urgent task, as its solution will allow them to be used in the large-scale creation of solar cells. Nowadays, the best laboratory samples of elements based on perovskite demonstrate high efficiency and a low cost of their production. However, they have relatively low stability, although some solar cells show stable operation throughout the year [11, 12].

This work aims to study the peculiarities of perovskite formation, and structural and electrophysical characteristics of organic-inorganic MAPbI_3 perovskite films depending on the solvent and the ratio of starting reagents.

EXPERIMENT AND DISCUSSION OF THE RESULTS.

Materials. Lead iodide (PbI_2) and methylammonium iodide MAI ($\text{CH}_3\text{NH}_3\text{I}$) were used as starting reagents for the synthesis of organic-inorganic perovskites. To stabilize the structure of perovskite, partial replacement of iodine with chlorine was carried out by adding chemically pure methylammonium chloride MACl ($\text{CH}_3\text{NH}_3\text{Cl}$). Dried chemically pure dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were used as solvents.

The starting reagents PbI_2 and MAI in the ratios 1:1, 1:2, 1:3 were dissolved in DMF and DMSO and stirred at 70 °C for 1 hour to obtain MAPbI_3 ($\text{CH}_3\text{NH}_3\text{PbI}_3$) films. The formation of crystalline MAPbI_3 films was performed in a dry box. A pre-prepared clear solution was deposited on cleaned glass substrates by spin-coating at a speed of 1200 rpm for 30 s. The heat treatment of the films was performed on a preheated stove at temperatures from 20 to 205 °C for 15 minutes.

The identifications of the phase composition of films and calculations of the parameters of the unit cell were performed by X-ray diffraction (XRD) using a DRON-4-07 (CuK α radiation and Ni filter, 40 kV, 18 mA) at $2\Theta = 5-50^\circ$, a step of 0.04° and a count time of 4 s.

SiO₂ (angle standard 2Θ) and Al₂O₃ (certified intensity standard) were used as standards [13]. The parameters of the unit cell and the coordinates of atoms were determined using the FullProf program developed by Juan Rodríguez-Carvajal, Laboratoire Léon Brillouin (France) [14].

Peculiarities of phase transformations in the formation of organic-inorganic perovskite MAPbI₃ in DMF, DMSO solvents. Plots of the percentage of crystalline phases versus the film treatment temperature were constructed based on diffractograms of perovskite films obtained at different ratios of starting reagents in the DMF solvent (Fig. 1).

Figure 1 shows that the temperature ranges of the existence of intermediate compounds (MA)₂(DMF)₂Pb₃I₈, (MA)₂(DMF)_xPbI₄, (MA)₃(DMF)PbI₅, (MA)₂(DMF)₂Pb₂I₆ and organic-inorganic perovskite MAPbI₃ in the film can be determined depending on the ratio of reagents. The structure of MAPbI₃ perovskite begins to form at a temperature of 20–25 °C, regardless of the ratio of starting reagents. The formation of organic-inorganic perovskite occurs by the formation and decomposition of various amounts of intermediate compounds. At the ratio of starting reagents PbI₂:MAI – 1:1, there are three intermediate compounds, and at 1:2, 1:3 four and two intermediate compounds, respectively. In a detailed analysis of the percentage of crystalline phases and diffractograms, formation reactions of MAPbI₃ perovskite were obtained at the PbI₂:MAI = 1:1 ratio in DMF (Table 1).

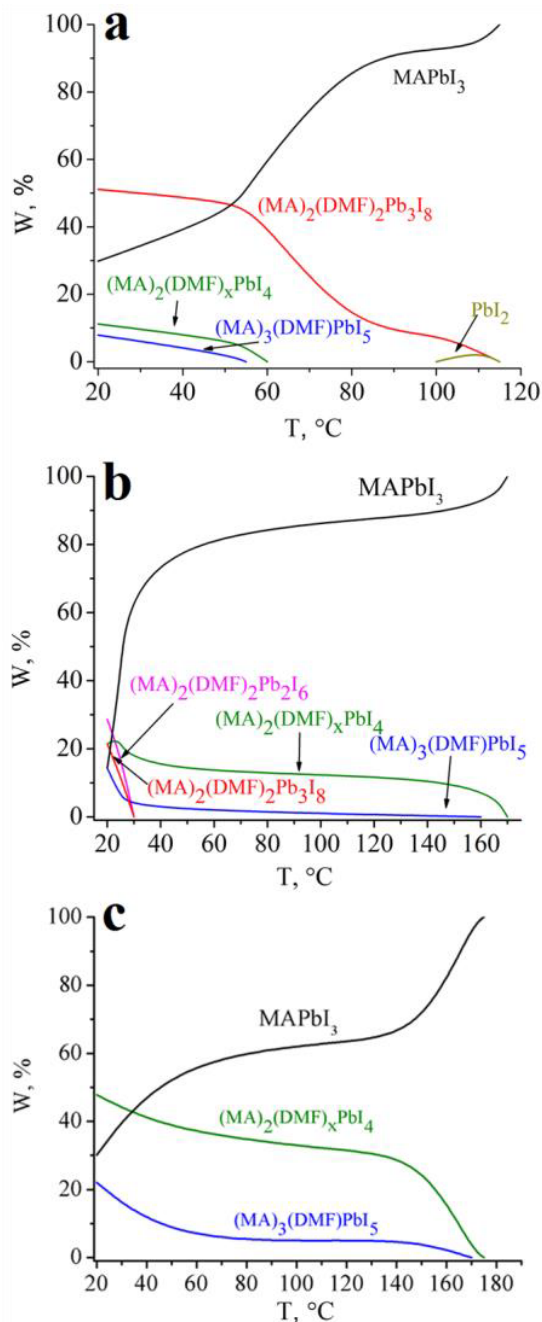


Fig. 1. The dependence of the percentage of crystalline phases on the treatment temperature of the film obtained at different ratios PbI₂:MAI in DMF: a) 1:1; (b) 1:2; (c) 1:3.

Table 1

Phase transformations in the formation of MAPbI₃ perovskite at a ratio of starting reagents of 1:1 in DMF.

Reagents	Temperature	Reaction products
13PbI ₂ + 13MAI (1:1 in DMF)	20–45 °C	(MA) ₃ (DMF)PbI ₅ + (MA) ₂ (DMF) _x PbI ₄ + 2MAPbI ₃ + 3(MA) ₂ (DMF) ₂ Pb ₃ I ₈
	50 °C	0.5(MA) ₃ (DMF)PbI ₅ + 0.75(MA) ₂ (DMF) _x PbI ₄ + 1.25MAI + 3(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + 2.75MAPbI ₃
	55 °C	0.5(MA) ₂ (DMF) _x PbI ₄ + 2.5(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + 2MAI + 5MAPbI ₃
	> 55–105 °C	(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + 10MAPbI ₃ + MAI
	>105–110 °C	0.5(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + 11MAPbI ₃ + MAI + 0.5PbI ₂
	> 110–115 °C	13 MAPbI ₃
13PbI ₂ + 13MAI	20–45 °C	(MA) ₃ (DMF)PbI ₅ + (MA) ₂ (DMF) _x PbI ₄ + 2MAPbI ₃ + 3(MA) ₂ (DMF) ₂ Pb ₃ I ₈
(MA) ₃ (DMF)PbI ₅	50 °C	0.5(MA) ₃ (DMF)PbI ₅ + 0.5(MA) ₂ (DMF) _x PbI ₄ + 0.5MAI + (0.5–0.5x)DMF
2(MA) ₂ (DMF) _x PbI ₄		0.25(MA) ₂ (DMF) _x PbI ₄ + 0.75MAPbI ₃ + 0.75MAI + 1.5xDMF
0.5(MA) ₃ (DMF)PbI ₅	55 °C	0.5(MA) ₂ (DMF) _x PbI ₄ + 0.5MAI + (0.5–0.5x)DMF
0.75(MA) ₂ (DMF) _x PbI ₄		0.75MAPbI ₃ + 0.75MAI + 0.75xDMF
3(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + 0.5MAI		2.5(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + 1.5MAPbI ₃ + 2DMF
0.5(MA) ₂ (DMF) _x PbI ₄	>55–105 °C	0.5MAPbI ₃ + 0.5MAI + 0.5xDMF
2.5(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + 0.5MAI		(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + 4.5MAPbI ₃ + 3DMF
(MA) ₂ (DMF) ₂ Pb ₃ I ₈	> 105–110 °C	0.5(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + MAPbI ₃ + 0.5PbI ₂ + DMF
0.5(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + 0.5MAI	> 110–115 °C	1.5MAPbI ₃ + DMF
0.5PbI ₂ + 0.5MAI		0.5MAPbI ₃

At a ratio of 1:1, a single-phase perovskite film is formed at 115 °C. There is a gradual decomposition of the intermediate compound (MA)₃(DMF)PbI₅ into (MA)₂(DMF)_xPbI₄, which completely decomposes into MAPbI₃ at T > 55 °C. The compound (MA)₂(DMF)₂Pb₃I₈ is completely decomposed into MAPbI₃ perovskite at T > 110 °C.

When the ratio of starting reagents is 1:2 in

DMF, a single-phase MAPbI₃ perovskite film is formed at 170 °C (Table 2). At this ratio, similar transformations of the intermediate compounds (MA)₃(DMF)PbI₅, (MA)₂(DMF)_xPbI₄, (MA)₂(DMF)₂Pb₃I₈ are observed for the ratio 1:1, but the temperatures of transformations are greatly different. In addition, the conversion of the intermediate (MA)₂(DMF)₂Pb₃I₈ to MAPbI₃ is observed in this system at T > 30 °C.

Table 2

Phase transformations in the formation of MAPbI₃ perovskite at a ratio of starting reagents of 1:2 in DMF.

Reagents	Temperature	Reaction products
24PbI ₂ + 48MAI (1:2 in DMF)	20 °C	4(MA) ₂ (DMF) ₂ Pb ₂ I ₆ + 2(MA) ₃ (DMF)PbI ₅ + 20MAI + 3(MA) ₂ (DMF) _x PbI ₄ + 3(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + 2MAPbI ₃
	25 °C	3(MA) ₂ (DMF) ₂ Pb ₂ I ₆ + (MA) ₃ (DMF)PbI ₅ + 20MAI + 4(MA) ₂ (DMF) _x PbI ₄ + 2(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + 7MAPbI ₃
	>30–130 °C	3(MA) ₂ (DMF) _x PbI ₄ + 0.5(MA) ₃ (DMF)PbI ₅ + 20MAI + 20.5MAPbI ₃
	>130–160 °C	2.5(MA) ₂ (DMF) _x PbI ₄ + 21.5MAPbI ₃ + 21.5MAI
	>160–170 °C	24MAPbI ₃ + 24MAI
24PbI ₂ + 48MAI	20 °C	4(MA) ₂ (DMF) ₂ Pb ₂ I ₆ + 2(MA) ₃ (DMF)PbI ₅ + 3(MA) ₂ (DMF) _x PbI ₄ + 3(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + 2MAPbI ₃ + 20MAI
4(MA) ₂ (DMF) ₂ Pb ₂ I ₆ 2(MA) ₃ (DMF)PbI ₅	25 °C	3(MA) ₂ (DMF) ₂ Pb ₂ I ₆ + 2MAPbI ₃ + 2DMF
		(MA) ₃ (DMF)PbI ₅ + (MA) ₂ (DMF) _x PbI ₄ + MAI + (1-x)DMF
3(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + MAI		2(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + 3MAPbI ₃ + 2DMF
3(MA) ₂ (DMF) ₂ Pb ₂ I ₆ (MA) ₃ (DMF)PbI ₅	>30–130 °C	6MAPbI ₃ + 6DMF
		0.5(MA) ₃ (DMF)PbI ₅ + 0.5(MA) ₂ (DMF) _x PbI ₄ + 0.5MAI + (0.5-0.5x)DMF
4(MA) ₂ (DMF) _x PbI ₄		2.5(MA) ₂ (DMF) _x PbI ₄ + 1.5MAPbI ₃ + 1.5MAI + 1.5xDMF
2(MA) ₂ (DMF) ₂ Pb ₃ I ₈ + 2MAI		6MAPbI ₃ + 4DMF
3(MA) ₂ (DMF) _x PbI ₄	>130–160 °C	2(MA) ₂ (DMF) _x PbI ₄ + MAPbI ₃ + MAI + xDMF
0.5(MA) ₃ (DMF)PbI ₅		0.5(MA) ₂ (DMF) _x PbI ₄ + 0.5MAI + (0.5-0.5x)DMF
2.5(MA) ₂ (DMF) _x PbI ₄	>160–170 °C	2.5MAPbI ₃ + 2.5MAI + 2.5xDMF

Table 3

Phase transformations in the formation of MAPbI₃ perovskite at a ratio of starting reagents of 1:3 in DMF.

Reagents	Temperature	Reaction products
9PbI ₂ + 27MAI (1:3 in DMF)	20–150 °C	4(MA) ₂ (DMF) _x PbI ₄ + (MA) ₃ (DMF)PbI ₅ + 4MAPbI ₃ + 12MAI
	>150–170 °C	2(MA) ₂ (DMF) _x PbI ₄ + 7MAPbI ₃ + 16MAI
	>170–175 °C	9MAPbI ₃ + 18MAI
9PbI ₂ + 27MAI	20–150 °C	4(MA) ₂ (DMF) _x PbI ₄ + (MA) ₃ (DMF)PbI ₅ + 4MAPbI ₃ + 12MAI
4(MA) ₂ (DMF) _x PbI ₄ + (MA) ₃ (DMF)PbI ₅	>150–170 °C	2(MA) ₂ (DMF) _x PbI ₄ + 4MAI + 3MAPbI ₃ + (2x+1)DMF
2(MA) ₂ (DMF) _x PbI ₄	>170–175 °C	2MAPbI ₃ + 2MAI + 2xDMF

At the ratio $\text{PbI}_2:\text{MAI} = 1:3$, the formation of a single-phase MAPbI_3 perovskite film occurs at 175 °C (Table 3).

There is a gradual decomposition of the intermediate compound $(\text{MA})_3(\text{DMF})\text{PbI}_5$ into 4MAI and $(\text{MA})_2(\text{DMF})_x\text{PbI}_4$; the latter completely decomposes into MAPbI_3 at $T > 170$ °C.

Thus, the ratio of starting reagents in DMF significantly affects the number of intermediate compounds that are formed during the synthesis. As the ratio of reagents increases, the temperature of formation of single-phase MAPbI_3 perovskite film increases. The MAPbI_3 phase is present in the film after heat treatment at 20 °C in amounts of 15-30 wt. %. However, at higher temperatures of 40-60 °C, the intermediate phases begin to decompose, and in this temperature range, the transformation of the intermediate phases into perovskite is not completed.

For the perovskite films synthesized at different ratios of starting reagents in the DMSO solvent, plots of the crystalline phase content versus the film treatment temperature were constructed (Fig. 2).

Figure 2 shows that the structure of MAPbI_3 perovskite begins to form at 60 °C for the ratios 1:1, 1:2, and at 70 °C for the ratio 1:3. At a ratio of 1:1, the perovskite film obtained at $T > 160$ °C begins to degrade, which is accompanied by a decrease in the percentage of perovskite MAPbI_3 and an increase in the percentage of the intermediate $\text{PbI}_2 \cdot \text{DMSO}$ (Fig. 2a). At this ratio of starting reagents, a single-phase film is not formed. At a ratio of 1:2, 1:3, intermediate compounds completely decompose and a single-phase MAPbI_3 film is formed at 190 and 205 °C, respectively.

The quantitative content of the phases $(\text{MA})_2(\text{DMSO})_2\text{Pb}_3\text{I}_8$, $(\text{MA})_2(\text{DMSO})_x\text{PbI}_4$, $\text{PbI}_2 \cdot \text{DMSO}$, $\text{PbI}_2 \cdot 2\text{DMSO}$, and organic-inor-

ganic perovskite MAPbI_3 in the film depends on the ratio of reagents and treatment temperature.

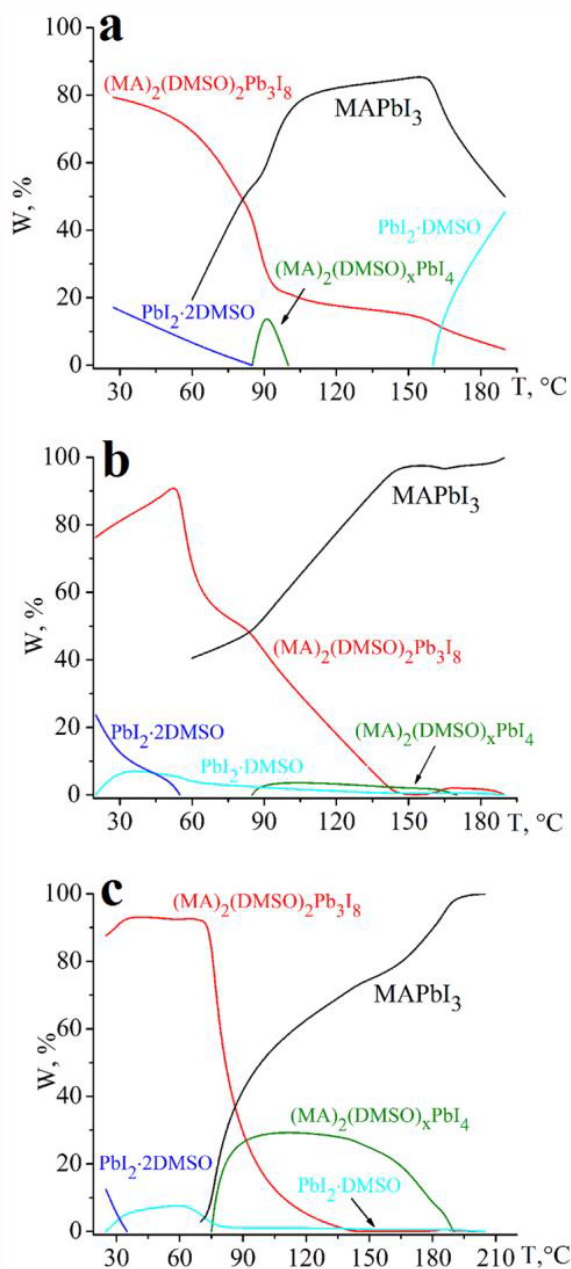


Fig. 2. The dependence of the percentage of crystalline phases on the treatment temperature of the film obtained at different ratios $\text{PbI}_2:\text{MAI}$ in DMSO: (a) 1:1; (b) 1:2; (c) 1:3.

Table 4

Phase transformations in the formation of MAPbI₃ perovskite at a ratio of starting reagents of 1:1 in DMSO.

Reagents	Temperature	Reaction products
10PbI ₂ + 10MAI (1:1 in DMSO)	20–50 °C	3(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + PbI ₂ ·2DMSO + 4MAI
	60–85 °C	2(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + PbI ₂ ·2DMSO + 3MAPbI ₃ + 3MAI
	90 °C	(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + (MA) ₂ (DMSO) _x PbI ₄ + 6MAPbI ₃
	> 90–100 °C	(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 7MAPbI ₃ + MAI
	110 °C	0.5(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 0.5PbI ₂ ·2DMSO + MAI + 8MAPbI ₃
	> 110–160 °C	0.5(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 8.5MAPbI ₃ + 0.5MAI
	> 165–180 °C	0.25(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 9MAPbI ₃ + 0.5MAI + 0.25PbI ₂ ·DMSO
	190 °C	0.25(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 7MAPbI ₃ + 2.25PbI ₂ ·DMSO + 2.5MAI
10PbI ₂ + 10MAI	20–50 °C	3(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + PbI ₂ ·2DMSO + 4MAI
3(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + MAI	60–85 °C	2(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 3 MAPbI ₃ + 2DMSO
2(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 2MAI	90 °C	(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + (2-x)DMSO + (MA) ₂ (DMSO) _x PbI ₄ + 2MAPbI ₃
PbI ₂ ·2DMSO + MAI		MAPbI ₃ + 2DMSO
(MA) ₂ (DMSO) _x PbI ₄	> 90–100 °C	MAPbI ₃ + MAI + xDMSO
(MA) ₂ (DMSO) ₂ Pb ₃ I ₈	110 °C	0.5(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + MAPbI ₃ + 0.5PbI ₂ ·2DMSO
0.5PbI ₂ ·2DMSO + MAI	> 110–160 °C	0.5 MAPbI ₃ + 0.5 MAI + DMSO
0.5(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 0.5MAI	> 165–180 °C	0.25(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 0.5MAPbI ₃ + 0.25PbI ₂ ·DMSO + 0.25DMSO
0.25PbI ₂ ·DMSO + 2MAPbI ₃	190 °C	2 MAI + 2.25PbI ₂ ·DMSO

In a detailed analysis of diffractograms and the phase content of the film, formation reactions of MAPbI₃ perovskite at the ratio PbI₂:MAI = 1:1 in DMSO were obtained (Table 4).

At a ratio of starting reagents of 1:1 in DMSO, the formation of organic-inorganic perovskite MAPbI₃ occurs through the formation and decomposition of 4 intermediates (MA)₂(DMSO)₂Pb₃I₈, (MA)₂(DMSO)_xPbI₄,

PbI₂·DMSO, PbI₂·2DMSO. It was shown that the intermediate compound (MA)₂(DMSO)₂Pb₃I₈ at 90 °C decomposes into the compound (MA)₂(DMSO)_xPbI₄, from which perovskite formation takes place.

At a ratio of 1:2 in DMSO, a single-phase perovskite film is formed at 190 °C (Table 5). In this case, the same 4 intermediate compounds are also formed, which are formed at a ratio of 1:1.

Table 5

Phase transformations in the formation of MAPbI₃ perovskite at a ratio of starting reagents of 1:2 in DMSO.

Reagents	Temperature	Reaction products
8PbI ₂ + 16MAI (1:2 in DMSO)	20–55 °C	3(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + PbI ₂ ·2DMSO + PbI ₂ ·DMSO + 12MAI
	60–85 °C	2(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + PbI ₂ ·DMSO + MAPbI ₃ + 11MAI
	90–140 °C	(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + PbI ₂ ·DMSO + 3MAPbI ₃ + 9MAI + (MA) ₂ (DMSO) _x PbI ₄
	>140–160 °C	PbI ₂ ·DMSO + 2(MA) ₂ (DMSO) _x PbI ₄ + 5MAPbI ₃ + 7MAI
	165 °C	0.5(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 0.5PbI ₂ ·DMSO + 5MAPbI ₃ + (MA) ₂ (DMSO) _x PbI ₄ + 8MAI
	>165–185 °C	0.75(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 5.25MAPbI ₃ + 0.5PbI ₂ ·DMSO + 9.25MAI
	190 °C	8MAPbI ₃ + 8MAI
8PbI ₂ + 16MAI	20–55 °C	2(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + PbI ₂ ·2DMSO + PbI ₂ ·DMSO + 12MAI
PbI ₂ ·2DMSO	60–85 °C	PbI ₂ ·DMSO + DMSO
PbI ₂ ·DMSO + MAI		MAPbI ₃ + DMSO
2(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 2MAI	90–140 °C	(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 2MAPbI ₃ + (2-x)DMSO + (MA) ₂ (DMSO) _x PbI ₄
(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 2MAI	>140–160 °C	(MA) ₂ (DMSO) _x PbI ₄ + 2MAPbI ₃ + (2-x)DMSO
2(MA) ₂ (DMSO) _x PbI ₄ + PbI ₂ ·DMSO	165 °C	0.5(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 0.5PbI ₂ ·DMSO + (MA) ₂ (DMSO) _x PbI ₄ + MAI + (x-0.5)DMSO
0.5(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + (MA) ₂ (DMSO) _x PbI ₄	>165–185 °C	0.75(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 0.25MAPbI ₃ + 1.25MAI + (x-0.5)DMSO
0.75(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 1.25MAI	190 °C	2.25 MAPbI ₃ + 1.5DMSO + 0.5MAI
0.5PbI ₂ ·DMSO + 0.5MAI		0.5MAPbI ₃ + 0.5DMSO

At a ratio of 1:2, interconversion of compounds (MA)₂(DMSO)₂Pb₃I₈ ↔ (MA)₂(DMSO)_xPbI₄ is observed. At low temperatures (90–160 °C) the preceding reaction proceeds in the forward direction with the formation of (MA)₂(DMSO)_xPbI₄, while a part of (MA)₂(DMSO)₂Pb₃I₈ is converted into MAPbI₃. At T > 165–185 °C, the reaction proceeds in the

reverse direction, while a part of (MA)₂(DMSO)_xPbI₄ is converted into MAPbI₃. A conversion of the compound PbI₂·2DMSO to PbI₂·DMSO is also observed, which in interaction with MAI forms perovskite MAPbI₃.

When increasing the ratio of starting reagents to 1:3, a single-phase perovskite film is formed at 205 °C (Table 6). The formation of

perovskite occurs through the formation and decomposition of 4 intermediate compounds. At a ratio of 1:3, interconversion of compounds $(MA)_2(DMSO)_2Pb_3I_8 \leftrightarrow (MA)_2(DMSO)_xPbI_4$ is also observed, but in a wider temperature

range. There is also a conversion of the compound $PbI_2 \cdot 2DMSO$ to $PbI_2 \cdot DMSO$, which when interacting with MAI forms perovskite $MAPbI_3$ as for the ratio 1:2.

Table 6

Phase transformations in the formation of $MAPbI_3$ perovskite at a ratio of starting reagents of 1:3 in DMSO.

Reagents	Temperature	Reaction products
8PbI ₂ + 24MAI (1:3 in DMSO)	20–30 °C	2(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + PbI ₂ ·2DMSO + PbI ₂ ·DMSO + 20MAI
	>30–65 °C	2(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 2PbI ₂ ·DMSO + 20MAI
	70–75 °C	2(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + PbI ₂ ·DMSO + MAPbI ₃ + 19MAI
	80–140 °C	(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + PbI ₂ ·DMSO + 3MAPbI ₃ + (MA) ₂ (DMSO) _x PbI ₄ + 17MAI
	>140–160 °C	3(MA) ₂ (DMSO) _x PbI ₄ + 5MAPbI ₃ + 13MAI
	>165–185 °C	0.5(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 0.5(MA) ₂ (DMSO) _x PbI ₄ + 6MAPbI ₃ + 16MAI
	>185–200 °C	PbI ₂ ·DMSO + 7MAPbI ₃ + 17MAI
	205 °C	8MAPbI ₃ + 16MAI
8PbI ₂ + 24MAI	20–30 °C	2(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + PbI ₂ ·2DMSO + PbI ₂ ·DMSO + 20MAI
PbI ₂ ·2DMSO + PbI ₂ ·DMSO	>30–65 °C	2PbI ₂ ·DMSO + DMSO
2PbI ₂ ·DMSO + MAI	70–75 °C	PbI ₂ ·DMSO + MAPbI ₃ + DMSO
2(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 2MAI	80–140 °C	(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 2MAPbI ₃ + (2-x)DMSO + (MA) ₂ (DMSO) _x PbI ₄
(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 3MAI	>140–165 °C	MAPbI ₃ + 2(MA) ₂ (DMSO) _x PbI ₄ + (2-2x) DMSO
PbI ₂ ·DMSO + MAI		MAPbI ₃ + DMSO
3(MA) ₂ (DMSO) _x PbI ₄	>165–185 °C	0.5(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + MAPbI ₃ + 3MAI + 0.5(MA) ₂ (DMSO) _x PbI ₄ + (2.5x-1) DMSO
0.5(MA) ₂ (DMSO) ₂ Pb ₃ I ₈ + 0.5(MA) ₂ (DMSO) _x PbI ₄	>185–200 °C	PbI ₂ ·DMSO + MAPbI ₃ + MAI + 0.5xDMSO
PbI ₂ ·DMSO + MAI	205 °C	MAPbI ₃ + DMSO

Thus, regardless of the ratio of starting reagents in DMSO, the formation of MAPbI₃ perovskite occurs through the formation of 4 intermediate compounds. When the ratio of reagents increases, the temperature of formation of single-phase MAPbI₃ film increases.

Crystallographic and electrophysical charac-

teristics of organic-inorganic perovskites MAPbI₃, obtained at different ratios PbI₂:MAI in DMF, and DMSO. The calculation of the unit cell parameters of organic-inorganic MAPbI₃ perovskite films was performed by the Rietveld full-profile analysis method using X-ray diffraction patterns (Fig. 3).

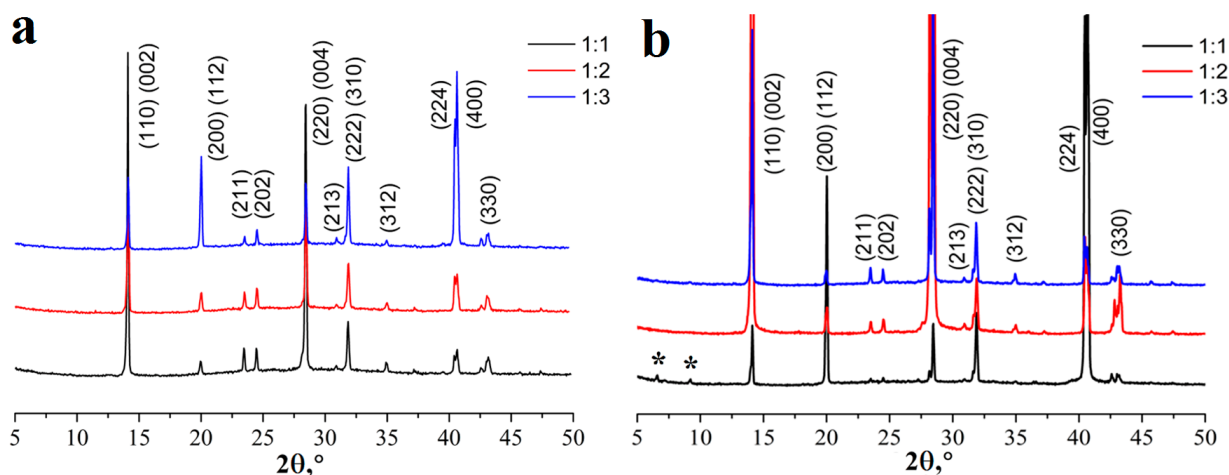


Fig. 3. Experimental X-ray diffraction patterns of samples of MAPbI₃ films obtained at different ratios of starting reagents in the DMSO solvent. The Miller indices are given in parentheses. * – (MA)₂(DMSO)₂Pb₃I₈.

It was found that depending on the ratio of starting reagents and solvent, there are slight changes in the volume of the cell for perovskite films (Table 7). The changes in the unit cell volume are associated with a small amount of the solvent that is part of the crystalline structure of perovskite. It was proved that the solvent DMSO can replace the cation MA⁺ in the structure of organic-inorganic perovskite MAPbI₃ [15]. The radius of DMSO and DMF molecules are 3.05 Å and 3.13 Å, respectively [16], and the radius of the cation

MA⁺ is 2.17 Å [17]. Since DMF and DMSO molecules are close in size, it can be assumed that DMF enters into the crystal structure, creating deformations. To test this assumption, we will calculate the changes in volume and solvent concentration.

From literature, it is known that the volume of the unit cell for perovskite is $V_{\text{perovskite}} = 990 \text{ Å}^3$ [18], or $V_{\text{perovskite}}/Z = 990/4 = 247.5 \text{ Å}^3$. Table 7 shows that the experimental values of unit cell volume are slightly larger than the theoretical value of unit cell volume of 990 Å^3 .

Table 7

Structural parameters of organic-inorganic perovskites MAPbI₃, obtained at different ratios PbI₂:MAI (1:1, 1:2, 1:3) in the DMF and DMSO solvents.

Parameters	DMF			DMSO		
	1:1	1:2	1:3	1:1	1:2	1:3
V, Å ³	994.5(3)	998.6(5)	997.5(4)	991.3(1)	994.7(4)	994.5(2)
Deposition temperature	115 °C	170 °C	175 °C	150 °C	190 °C	205 °C

The calculation of the amount of solvent in the structure of perovskite was performed according to formula (1) using the unit cell vo-

lumes of the starting reagents, and perovskite, as well as the volumes of DMF, DMSO solvent molecules, and methylammonium cation MA⁺:

$$\frac{V_{\text{perovskite}}}{Z_1} = \frac{V(\text{PbI}_2)}{Z_2} + \frac{V(\text{MAI})}{Z_3} + (V_{\text{solvent}} - V_{(\text{MA}^+)}) \cdot x, \quad (1)$$

where Z_1 , Z_2 , and Z_3 are the formula unit for perovskite, PbI₂, and MAI, respectively, x is the amount of solvent included in the structure of perovskite, $V(\text{PbI}_2)$ is the unit cell volume of PbI₂, $V(\text{MAI})$ is the unit cell volume of MAI, V_{solvent} is the volume of the solvent molecule, $V(\text{MA}^+)$ is the volume of the methylammonium cation MA⁺. Taking into account the values of the volumes of compounds and their formula units, we obtain $V(\text{PbI}_2)/Z_2 = 125.69/1 = 125.69 \text{ Å}^3$, $V(\text{MAI})/Z_3 = 235.93/2 = 117.965 \text{ Å}^3$,

The calculation of the volume of the solvent (V_{solvent}) was performed according to formula (2) under the assumption that the solvent molecule has a spherical shape [18].

$$V = \frac{4}{3}\pi R^3, \quad (2)$$

where R is the radius of the solvent molecule.

A similar volume calculation was performed for the MA⁺ cation. The volume of the DMF and DMSO solvents is $V_{(\text{DMF})} = 128.4 \text{ Å}^3$, and $V_{(\text{DMSO})} = 118.8 \text{ Å}^3$, respectively. The volume of the cation MA⁺ is $V(\text{MA}^+) = 42.8 \text{ Å}^3$.

The replacement of a smaller MA⁺ cation with a larger molecule of DMF or DMSO leads to minor changes in structural and electro-physical characteristics, which is confirmed by the following calculations.

The solvent content of the structure (x) was determined from formula (3), which was derived from formula (1):

$$x = \frac{\frac{V_{\text{perovskite}}}{Z_1} - \frac{V(\text{PbI}_2)}{Z_2} - \frac{V(\text{MAI})}{Z_3}}{V_{\text{solvent}} - V_{(\text{MA}^+)}}. \quad (3)$$

The results of the calculations are summarized in table 8.

Table 8

Determination of the amount of solvent in the structure of perovskite depending on the ratios of starting reagents PbI₂:MAI in the DMF, DMSO solvent.

PbI ₂ :MAI	V _{perovskite} · Å ³	Z ₁	V _{perovskite} /Z ₁ · Å ³	V _{solvent} · Å ³		x. %
MAPbI ₃	990.0	4	247.5	–	–	0
1:1	991.3(1)	4	247.8	DMSO	118.8	5.5
1:2	994.7(4)	4	248.7			6.6
1:3	994.5(2)	4	248.6			6.5
1:1	994.5(3)	4	248.6	DMF	128.4	5.8
1:2	998.6(5)	4	249.6			7.0
1:3	997.5(4)	4	249.4			6.7

It was found that at the same ratios of starting reagents, the structure of perovskite included the DMF solvent in a greater amount than DMSO.

The fact that the solvent is part of the structure of perovskite affects not only the structural parameters but also the electrophysical characteristics, in particular, the width of the bandgap (Table 9).

Table 9

Influence of the solvent on the electrophysical characteristics of perovskite MAPbI₃.

Solvent		DMF			DMSO		
PbI ₂ :MAI		1:1	1:2	1:3	1:1	1:2	1:3
Solvent content, %	0	5.8	7	6.7	5.5	6.6	6.5
Bandgap, eV	1.55 [18]	1.59	1.62	1.57	1.57	1.53	1.54

The bandgap for the perovskites obtained at different ratios of starting reagents in DMSO is less than for the films obtained using DMF.

CONCLUSIONS

The peculiarities of formation and properties of organic-inorganic MAPbI₃ perovskite

films have been studied as a function of the ratio of starting reagents in DMF and DMSO solvents. As the PbI₂:MAI ratio increases, the temperature of the formation of single-phase MAPbI₃ perovskite film increases. It was found that when using the DMF solvent, the number of crystalline phases in the film depends on

the ratio of starting reagents. At a ratio of 1:1 in DMF, the number of phases is 4 and at 1:2, 1:3, 5, and 3, respectively. When using DMSO, regardless of the ratio of starting reagents, there are 5 crystalline phases in the film.

Plots of the percentage of crystalline phases in the film versus the treatment temperature have been constructed for perovskite films synthesized at different ratios of starting reagents in the DMF, and DMSO solvents. It was shown that the formation of organic-inorganic perovskite occurs through the formation and decomposition of intermediate compounds (phases). Reactions of MAPbI₃ perovskite formation at different ratios PbI₂:MAI in DMF and DMSO have been obtained.

It was found that for the perovskite films obtained at different ratios PbI₂: MAI in DMF and 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 found that at the same ratios of starting reagents, DMF is included in the structure of perovskite in a greater amount than DMSO.



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ВПЛИВ РОЗЧИННИКА ТА СПІВВІДНОШЕННЯ ВИХІДНИХ РЕАГЕНТІВ НА ВЛАСТИВОСТІ ОРГАНО-НЕОРГАНІЧНОГО ПЕРОВСЬКІТУ MAPbI₃

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Синтезовано органо-неорганічний перовскіт MAPbI₃ (CH₃NH₃PbI₃) методом одностадійного осадження за різного співвідношення вихідних реагентів (PbI₂ та MAI, які брали у співвідношенні 1:1, 1:2, 1:3) у розчиннику ДМФА та ДМСО. Для отримання плівок органо-неорганічного перовскіту MAPbI₃ використовували метод spin-coating.

Досліджено особливості утворення та властивості плівок органо-неорганічного перовскіту MAPbI₃ залежно від співвідношення вихідних реагентів у розчиннику DMF, DMSO. Зі збільшенням співвідношення PbI₂:MAI зростає температура утворення однофазної плівки перовскіту MAPbI₃. Показано, що утворення органо-неорганічного перовскіту відбувається через утворення та розкладання проміжних сполук (фаз). Отримано реакції утворення перовскіту MAPbI₃ за різного співвідношення PbI₂:MAI у DMF, DMSO.

Встановлено, що структура перовськіту MAPbI_3 починає формуватися за температури 20–25 °C незалежно від співвідношення вихідних реагентів у DMF. При використанні DMSO структура перовськіту MAPbI_3 починає формуватися за температури 60 °C для співвідношень 1:1, 1:2, та при 70 °C для співвідношення 1:3.

Встановлено, що при використанні розчинника DMF кількість кристалічних фаз у плівці залежить від співвідношення вихідних реагентів. При співвідношенні 1:1 у DMF кількість фаз становить 4, а при 1:2, 1:3 – 5 та 3 відповідно. При використанні DMSO незалежно від співвідношення вихідних реагентів у плівці присутні 5 кристалічних фаз.

Для плівок перовськіту, отриманих за різного співвідношення вихідних реагентів у розчиннику DMF, DMSO, було побудовано залежність вмісту кристалічних фаз у плівці від температури оброблення. Встановлено, що для плівок перовськіту, отриманих за різного співвідношення PbI_2 :MAI у DMF, DMSO спостерігаємо незначні зміни в структурних (об'єм елементарної комірки) та електрофізичних (ширина забороненої зони) характеристиках. Ці зміни пов'язані з розчинником, який входить у кристалічну структуру перовськіту. Встановлено, що за однакових співвідношень вихідних реагентів DMF входить в структуру перовськіту у більшій кількості, ніж DMSO.

Ключові слова: органо-неорганічний перовскіт, фазові перетворення, структурні параметри, електрофізичні характеристики.

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