The organic-inorganic perovskite films \(\text{CH}_3\text{NH}_3\text{PbI}_3\) were synthesized from solutions with different ratios (1:1, 1:2 and 1:3) of initial reagents (\(\text{PbI}_2\) and \(\text{CH}_3\text{NH}_3\text{I}\)) in a DMF solvent. XRD and Raman spectroscopy shows that the perovskites are formed according to different schemes depending on the ratio of \(\text{PbI}_2\) and \(\text{CH}_3\text{NH}_3\text{I}\). At the ratio 1:1 of initial reagents, three intermediate compounds are formed: \((\text{CH}_3\text{NH}_3)_2(\text{DMF})\text{PbI}_4\), \((\text{CH}_3\text{NH}_3)_2(\text{DMF})_2\text{Pb}_3\text{I}_8\) and \((\text{CH}_3\text{NH}_3)_3(\text{DMF})\text{PbI}_5\). At the ratio 1:2 of initial reagents four intermediate compounds are formed: in addition to the above phases, the phase \((\text{CH}_3\text{NH}_3)_2(\text{DMF})\text{Pb}_2\text{I}_6\) is found. And at the ratio 1:3 of initial reagents, only two intermediate phases, \((\text{CH}_3\text{NH}_3)_2(\text{DMF})_x\text{PbI}_4\) and \((\text{CH}_3\text{NH}_3)_3(\text{DMF})\text{PbI}_5\), are observed. The morphology of the perovskite films was established to depend primarily on the ratio of the initial reagents. The temperature of heat treatment changes only the grain size of films.

Keywords: organic-inorganic perovskite, X-ray diffraction analysis, Raman spectroscopy, intermediate compounds, stability.

INTRODUCTION. Nowadays, much of the energy comes from hydrocarbons, coal and other fossil fuels. Their usage in electricity generation leads to significant \(\text{CO}_2\) emissions in the atmosphere, increases the greenhouse effect and changes the climate across the globe in disastrous proportions. The increase of energy produced by photovoltaic elements contributes to solving the problem of global warming [1]. Today, most solar panels are manufactured based on indirect band gap silicon. The active layers of these materials are relatively thick (~200 \(\mu\text{m}\)) for the complete absorption of solar radiation in the visible and near-infrared ranges. This increases their cost and holds back the growth of solar power plants. Therefore, the direct band gap semiconductors with a high absorption coefficient in the visible spectral range based on environmentally friendly and economically attractive materials are of interest. They are characterized by a high level of properties, which allows them to be considered as promising materials for next-generation PV technologies: high electron mobility.
(800 cm$^2$/Vs) [2], long carrier diffusion length (over 1 μm) [3, 4], ambipolar nature of moving charges [5], high absorption coefficient (greater than 105 cm$^{-1}$) [3], etc. The search for such materials is going in several directions. In particular, the following materials are investigated as an active layer of solar cells: multicomponent metal chalcogenides Cu$_2$ZnSnS$_4$ [6], organic semiconductors [7], semiconductor quantum dots [8], and organic-inorganic halides CH$_3$NH$_3$PbI$_{3-y}$X$_y$ with perovskite structure [9].

In recent years, the efficiency of perovskite solar cells based on CH$_3$NH$_3$PbI$_3$ has dynamically increased [9-11]. Indeed, they are quite promising materials for producing solar cells. The organic-inorganic perovskite films are relatively easy to synthesize, they have high light absorption coefficients in the visible spectral range and a large diffusion length of charge carriers [10]. Over the last 10 years, the efficiency of solar-to-electrical conversion of perovskite-based photoelectric elements has grown from 3% [11] to 25.2% [12].

However, organic-inorganic perovskites have some drawbacks. In particular, their structure degrades due to atmospheric humidity. To overcome the above problems, the processes in the formation of CH$_3$NH$_3$PbI$_3$ perovskite films have to be clearly described.

The ratio of starting reagents and the chemistry of precursors are the main factors affecting the structural and, as a result, physical and chemical properties of CH$_3$NH$_3$PbI$_3$ perovskites [13–18]. The complex chemical interaction of an organic cation, a coordinating solvent, and an inorganic component determines the processes of crystal nucleation and formation [19] and consequently affects the properties of crystalline films. However, practically no data is published about the phase transformations during the synthesis of samples in different synthesis conditions (ratios of initial reagents, solvents, heat-treatment temperatures).

The aim of this work was to study in a wide temperature range (from 20 to 175 °C) the processes in the synthesis of organic-inorganic CH$_3$NH$_3$PbI$_3$ perovskite films using the initial reagents CH$_3$NH$_3$I and PbI$_2$ in different ratios, which are dissolved in dimethylformamide (DMF).

**EXPERIMENT AND DISCUSSION OF THE RESULTS.** *Materials.* Lead iodide (PbI$_2$), methylammonium chloride (CH$_3$NH$_3$Cl) and pre-synthesized methylammonium iodide (CH$_3$NH$_3$I) were used as starting materials. To stabilize the perovskite structure, iodine was partially substituted with chlorine by the addition of methylammonium chloride (CH$_3$NH$_3$Cl) [19]. In this paper, for simplicity, the solid solution CH$_3$NH$_3$PbI$_{2.98}$Cl$_{0.02}$ will be further written as CH$_3$NH$_3$PbI$_3$. Dried dimethylformamide (DMF) was used as the solvent.

**Synthesis of methylammonium iodide and organic-inorganic perovskites.** Methylammonium iodide (CH$_3$NH$_3$I) was synthesized by the dropwise addition of aqueous HI (Sigma Aldrich, 57%, 1.0eq) into methylamine (Sigma Aldrich, aqueous, 40%, 1.05eq) under stirring at 10 °C. The solution was stirred for two hours, then the solvent was removed by rotary evaporation. The yellow-white crystals were washed three times with methyl tert-butyl ether, filtered, and dried overnight under vacuum to yield white crystals of CH$_3$NH$_3$I.

For the deposition of CH$_3$NH$_3$PbI$_3$ films, the initial reagents, PbI$_2$ and CH$_3$NH$_3$I with molar ratios of 1:1; 1:2; 1:3 were dissolved in DMF and stirred at 70 °C for 1 hour. The crystalline CH$_3$NH$_3$PbI$_3$ films were formed in a dry
box. The previously prepared clear solution was deposited on to a purified glass substrate by spin-coating with a speed of 2400 rpm for 30 seconds. The films were thermally treated on a preheated hot plate at temperatures from 20 to 180 °C for 15 min.

The microstructure and the elemental composition of organic-inorganic perovskites were controlled using a scanning electron microscope SEC miniSEM SNE 4500MB equipped with EDAX Element PV6500/00 F spectrometer.

The phase composition of films was identified by X-ray diffractometry (XRD) using a DRON-4-07 diffractometer (CuKα-radiation, 40 kW, 20 mA) at 2Θ = 5–50°, a step of 0.04° and a count time of 4 s.

Experimental Raman scattering spectra were studied at room temperature in the back-scattering geometry with an MDR-23 single-stage spectrometer equipped with a CCD detector (Andor) using λ_{exc} = 457 nm (diode-pumped solid-state laser, CNILaser). The laser excitation power was kept as low as possible, to avoid the damage of molecules under investigation either due to heating or photochemical reactions.

Figure 1 shows SEM images of the surface of the synthesized films obtained on glass substrates at different ratios of the initial PbI_2 and CH_3NH_3I reagents and heat treatment temperatures of 25 °C (a, b, c) and 75 °C (d, e, f). The ratio of the starting reagents PbI_2 and CH_3NH_3I has a decisive influence on the morphology of the synthesized films. The ratio of the initial components significantly affects the formation of CH_3NH_3PbI_3 precursors and, accordingly, the subsequent growth of perovskite crystals and their shape [19, 20]. The heat treatment of films at different temperatures also affects their morphology. As the temperature of the heat treatment of films increases, the shape of the characteristic structures (grains) on their surface remains similar, although their dimensions are significantly reduced.

Fig. 1. SEM image of the surface of CH_3NH_3PbI_3 perovskite films deposited on glass substrates at different ratios of the initial reagents: PbI_2 : CH_3NH_3I = 1:1 (a, d); 1:2 (b, e); 1:3 (c, f), and at the temperatures: 25 °C (a, b, c) and 75 °C (d, e, f).
Table 1 shows literature data [21–28] on the unit cell parameters of the initial reagents, probable intermediate and terminal compounds in the films formed in a DMF solvent at different ratios of the initial reagents PbI$_2$ and CH$_3$NH$_3$I.

### Table 1

| Compound | Symmetry and space group | Unit cell parameters | References |
|----------|--------------------------|----------------------|------------|
| (CH$_3$NH$_3$)$_2$(DMF)$_2$Pb$_2$I$_6$ | Monoclinic P2$_1$/c (№ 14) | a = 4.5647(9) Å  
b = 25.446(5) Å  
c = 12.119(2) Å  
$\alpha = \gamma = 90^\circ$  
$\beta = 96.75(3)^\circ$  
Z = 4  
V = 1397.9(5) Å$^3$ | [21] |
| (CH$_3$NH$_3$)$_2$(DMF)$_2$Pb$_3$I$_8$ | Orthorhombic Pnnm (№ 58) | a = 17.165(9) Å  
b = 21.955(4) Å  
c = 4.5549(9) Å  
$\alpha = \beta = \gamma = 90^\circ$  
Z = 2  
V = 1716.6(6) Å$^3$ | [21] |
| (CH$_3$NH$_3$)$_3$(DMF)PbI$_5$ | Triclinic P-1 (№ 2) | a = 10.1714(15) Å  
b = 11.335(3) Å  
c = 12.394(2) Å  
$\alpha = 111.18(3)^\circ$  
$\beta = 101.11(3)^\circ$  
$\gamma = 109.80(3)^\circ$  
Z = 2  
V = 1170.0(7) Å$^3$ | [21] |
| (CH$_3$NH$_3$)$_2$(DMF)$_x$PbI$_4$ | - | - | [22] |
| (CH$_3$NH$_3$)$_4$PbI$_6$2H$_2$O | Monoclinic P2$_1$/n (№ 14) | a = 10.421(3) Å  
b = 11.334(2) Å  
c = 10.668(2) Å  
$\alpha = \beta = 90^\circ$  
$\gamma = 91.73(2)^\circ$  
Z = 2  
V = 1259.4(5) Å$^3$ | [23] |
Table 1

| Compound | Symmetry and space group | Unit cell parameters | References |
|----------|--------------------------|----------------------|------------|
| CH$_3$NH$_3$PbI$_3$H$_2$O | Monoclinic P21/m (№ 11) | a = 10.46 Å  
b = 4.63 Å  
c = 11.10 Å  
$\alpha = \beta = 90^o$  
$\gamma = 101.50^o$  
Z = 2  
V= 536.05(19) | [24,25] |
| CH$_3$NH$_3$PbI$_3$ | Tetragonal  
I4/mcm (№ 140) | a = 8.870(2) Å  
c = 12.669(8) Å  
V = 996.8(7) Å$^3$ | [26] |
| PbI$_2$ | Trigonal  
P-3m1 (№ 164) | a = 4.558 Å  
c = 6.986 Å  
V = 125.69 Å$^3$ | [27] |
| CH$_3$NH$_3$I | Tetragonal  
P4/nmm (№ 129) | a = 5.12729(1) Å  
c = 9.01794(2) Å  
V = 237.074(1) Å$^3$ | [28] |

Fig. 2. X-ray diffraction pattern of films prepared with the ratio 1:1 of the initial reagents PbI$_2$ and CH$_3$NH$_3$I with heat treatment at different temperatures. The second phases are denoted by “□” – (CH$_3$NH$_3$)$_2$(DMF)PbI$_4$; “*” – (CH$_3$NH$_3$)$_2$(DMF)$_2$PbI$_6$; “●” – (CH$_3$NH$_3$)$_3$(DMF)PbI$_5$; “o” – PbI$_2$; and “◊” – CH$_3$NH$_3$PbI$_3$.

Figure 2 shows the results of an XRD analysis of CH$_3$NH$_3$PbI$_3$ perovskite films prepared at a ratio of the initial reagents PbI$_2$ and CH$_3$NH$_3$I of 1:1 and at different temperatures of heat treatment.

The X-ray diffraction patterns of the films show the peaks corresponding to CH$_3$NH$_3$PbI$_3$ (14.1 °) and second phases. In particular, the peaks at 2$\Theta$ = 6.53 °, 8.04 °, 9.5 °, 10.03 °, 6.53 °, 11.06 °, 13.08 °, 17.46 °, 19.18 °, and 19.68 ° (denoted in Fig. 1 as “*”) correspond to the phase (CH$_3$NH$_3$)$_2$(DMF)$_2$PbI$_4$ [21]. The X-ray peaks at 2$\Theta$ = 7.71 ° and 11.48 ° (denoted in Fig. 2 as “□”) correspond to the compound (CH$_3$NH$_3$)$_2$(DMF)$_x$PbI$_4$ [22], the peaks at 2$\Theta$ = 9.15 °, 16.94 °, and 18.36 ° (denoted in Fig. 2 as “●”) correspond to the compound - (CH$_3$NH$_3$)$_3$(DMF)PbI$_5$ [21], and the peaks
at $2\Theta = 12.7^\circ$ (denoted in Fig. 2 as “o”) correspond to the PbI$_2$. Thus, depending on the temperature of heat treatment, the CH$_3$NH$_3$PbI$_3$ films prepared with the ratio 1:1 of the initial reagents PbI$_2$ and CH$_3$NH$_3$I contain three intermediate phases.

Figure 3 shows the results of an XRD analysis of CH$_3$NH$_3$PbI$_3$ perovskite films obtained at a ratio of the initial reagents PbI$_2$ and CH$_3$NH$_3$I 1:2 after heat treatment in the temperature range from 20 to 170 °C.

Fig. 4. X-ray diffraction pattern of films prepared with the ratio 1:3 of the initial reagents PbI$_2$ and CH$_3$NH$_3$I with heat treatment at different temperatures. The second phases are denoted by “□” – (CH$_3$NH$_3$)$_2$(DMF)$_x$PbI$_4$; “●” – (CH$_3$NH$_3$)$_3$(DMF)PbI$_5$; and “◊” – CH$_3$NH$_3$PbI$_3$.

Intense peaks of the perovskite phase (14.1°) and peaks from other intermediate phases are observed. In particular, the peaks at $2\Theta$ angles of 11.35 °, 11.48 °, 11.64 °, 12 °, and 15.59 ° can be attributed to the intermediate phase (CH$_3$NH$_3$)$_2$(DMF)PbI$_4$; at $2\Theta$ angles of 9.16 °, 10.1 °, 16.94 °, 17.75 °, 18.36 °, and 18.66 ° to (CH$_3$NH$_3$)$_3$(DMF)PbI$_5$.

To determine the temperature ranges of the formation of the intermediate compounds in the synthesized films, Raman spectroscopy was used. It should be noted that the interac-
tion of laser excitation with the sample results in several types of radiation: inelastic (Raman) scattering, elastic (Rayleigh) scattering, and photoluminescence (PL). The intensity of Rayleigh scattering depends significantly on the morphology of films, which, like PL, interferes with the recording of Raman spectra of perovskite films [29,30]. In the presence of intense PL, it is not possible at all to record the Raman spectrum of these films. The PL band of perovskites is quite wide (675–850 nm), so to excite Raman spectra, the laser radiation in the spectral regions before and after the PL band should be used [31,32]. However, if the film consists of several compounds, it is difficult to consider all of these factors. That is why a change in the film composition may not result in the appearance/disappearance of Raman bands of a particular compound. In this case, the spectrum changes as a whole due to the overlapping of the contribution of Raman and Rayleigh scattering, and PL. The analysis of such changes allows us to evaluate the phase, component and morphological changes that occurred during the formation of the film at different ratios of the initial reagents and temperature of heat treatment.

Fig. 5. Raman spectra of a film obtained at a ratio of the starting reagents PbI₂ and CH₃NH₃I of 1:1 at a temperature of 90 °C with intensive laser treatment (laser radiation density ∼1.5·10⁴ W/cm²) and varying the irradiation time from 1 to 60 minutes.

Fig. 6. Raman spectra of films prepared at the ratio 1:1 of initial reagents PbI₂ and CH₃NH₃I and with heat treatment at different temperatures. (a) Raman spectra in the low-frequency range, (b) Raman spectra in the high-frequency range.
Figure 5 shows that in the spectrum of the original film (curve 1) there is a low-intensity band in the region of 58 cm$^{-1}$, which corresponds to I-Pb-I vibrations [33]. As the irradiation time increases, perovskite decomposes into CH$_3$NH$_3$I and PbI$_2$, as evidenced by an increase in the intensity of the bands of the latter compound over time. Subsequently, to record the Raman spectra of perovskite films, the intensity of laser excitation radiation was chosen such that it did not lead to degradation of the film under investigation, even prolonged action.

Figure 6 shows Raman spectra of the synthesized films prepared at the ratio 1:1 of the initial reagents PbI$_2$ and CH$_3$NH$_3$I after heat treatment at different temperatures.

The Raman spectrum of a film formed at 20 to 30 °C contains intense bands of Pb-I vibrations (59 and 110 cm$^{-1}$), CH$_3$NH$_3$ vibrations (110 and 138 cm$^{-1}$) corresponding to CH$_3$NH$_3$PbI$_3$ perovskite and intermediate compounds, and bands of the DMF solvent (864, 982, 1103 cm$^{-1}$, etc.). Increasing the temperature of the film heat treatment to 30 °C leads to the disappearance of the bands at 59 and 110 cm$^{-1}$ and the emergence of a low-frequency band with a maximum of 51 cm$^{-1}$ and intense photoluminescence (PL).

The emergence of intensive PL is most likely associated with the compound (CH$_3$NH$_3$)$_2$(DMF)$_2$Pb$_3$I$_8$. According to X-ray diffraction data at temperatures above 30 °C, the content of the compound in the film increases due to the decomposition of the compounds (CH$_3$NH$_3$)$_3$(DMF)PbI$_5$ and (CH$_3$NH$_3$)$_2$(DMF)$_2$PbI$_4$.

At temperatures of 50–100 °C, in the spectra there appear bands at 51, 250, 752, 838 cm$^{-1}$, which can be assigned to the compound (CH$_3$NH$_3$)$_2$(DMF)$_2$Pb$_3$I$_8$. When the temperature rises to 100 °C, the intensity of PL decreases, which is associated with a decrease in the content of (CH$_3$NH$_3$)$_2$(DMF)$_2$Pb$_3$I$_8$ in the film of organic-inorganic perovskite. At temperatures of 50–100 °C, the CH$_3$NH$_3$PbI$_3$ perovskite content increases. During the formation of films at a temperature of 100 °C, bands with frequencies of 110 and 96 cm$^{-1}$, which are characteristic of PbI$_2$, appear in the Raman spectrum. According to X-ray diffraction at a temperature of 100 °C, in addition to perovskite, phases of PbI$_2$ and (CH$_3$NH$_3$)$_2$(DMF)$_2$Pb$_3$I$_8$ are present in the film. At 115 °C, a single-phase film of organic-inorganic CH$_3$NH$_3$PbI$_3$ perovskite is formed. At temperatures above 120 °C, PbI$_2$ bands (51, 59 and 110 cm$^{-1}$) have appeared, and their intensity increases.

When using starting reagents with a ratio of PbI$_2$ and CH$_3$NH$_3$I of 1:1 for the synthesis of perovskite film, the single-phase perovskite is formed at 115 °C, which degrades at temperatures above 115 °C with the formation of PbI$_2$.

Figure 7 shows Raman spectra of films prepared at a ratio of 1:2 of the initial reagents PbI$_2$ and CH$_3$NH$_3$I and heat-treated at different temperatures. As for the films obtained at a ratio of PbI$_2$ and CH$_3$NH$_3$I of 1:1, bands of Pb-I vibrations (∼65–106 cm$^{-1}$) corresponding to perovskite, intermediate compounds, and the DMF solvent (864, 982, 1103 cm$^{-1}$) are present in the Raman spectra of films obtained at temperatures from 20 to 30 °C. At higher temperatures, bands of DMF do not appear in the spectra. Instead, in the temperature range of 40 to 90 °C in the low-frequency region of the Raman spectra, bands appear with maxima in the region of 80 and 106 cm$^{-1}$, which are characteristic of perovskites and other phases. At the same time, in the high-frequency part of the spectrum for films formed in the tem-
perature range from 50 to 120 °C, bands with a frequency of \( \sim 1207 \text{ cm}^{-1} \) appear, which most likely correspond to the phases \((\text{CH}_3\text{NH}_3)_3(\text{DMF})\text{PbI}_5\) and \((\text{CH}_3\text{NH}_3)_2(\text{DMF})_x\text{PbI}_4\).

According to X-ray data, these phases are present in the perovskite film in this temperature range. Heating such films even to 175 °C does not lead to their decomposition into \(\text{CH}_3\text{NH}_3\text{I}\) and \(\text{PbI}_2\). The presence of the \((\text{CH}_3\text{NH}_3)_2(\text{DMF})_x\text{PbI}_4\) phase in the film may lead to greater stability of perovskite.

Fig. 7. Raman spectra of films prepared at the ratio 1:2 of the initial reagents \(\text{PbI}_2\) and \(\text{CH}_3\text{NH}_3\text{I}\) and heat-treated at different temperatures. (a) Raman spectra in the low-frequency range, (b) Raman spectra in the high-frequency range.

Fig. 8. Raman spectra of films prepared at the ratio 1:3 of the initial reagents \(\text{PbI}_2\) and \(\text{CH}_3\text{NH}_3\text{I}\) and heat-treated at different temperatures. (a) Raman spectra in the low-frequency range, (b) Raman spectra in the high-frequency range.
Figure 8 shows Raman spectra of films prepared at the ratio 1:3 of the initial reagents PbI$_2$ and CH$_3$NH$_3$I and the variation of the heat treatment temperature from 20 to 175 °C. In the temperature range from 20 to 30 °C, bands characteristic of DMF (861, 982, 1103 cm$^{-1}$) appear in the spectra. At temperatures above 30 °C, DMF bands in the spectra are no longer visible. For films formed at temperatures in the range from 20 to 100 °C, bands characteristic of perovskite and other phases appear in the Raman spectra. Indeed, when the film formation temperature changes, the intensity of the bands is redistributed in the range from 80 to 110 cm$^{-1}$, which is characteristic of the vibrations of different phases, both CH$_3$NH$_3$PbI$_3$ and (CH$_3$NH$_3$)$_3${(DMF)}PbI$_5$ and (CH$_3$NH$_3$)$_2${(DMF)}PbI$_4$. At temperatures above 120 °C, bands characteristic of perovskite with a maximum of 106 cm$^{-1}$ appear in the spectra and, as in the case of film synthesis using the starting components in a ratio of 1:2, degradation of the perovskite phase to PbI$_2$ and CH$_3$NH$_3$I is not observed. The band at 980 cm$^{-1}$ can be assigned to the compounds (CH$_3$NH$_3$)$_2${(DMF)}PbI$_4$, (CH$_3$NH$_3$)$_2${(DMF)}PbI$_3$, and (CH$_3$NH$_3$)$_2${(DMF)}PbI$_3$. At a temperature of 175 °C, this band is not observed, which indicates the decomposition of compounds and the formation of a single-phase film of CH$_3$NH$_3$PbI$_3$ perovskite.

XRD and Raman spectroscopy data allows the reaction schemes of the formation of CH$_3$NH$_3$PbI$_3$ perovskite and intermediate compounds at different ratios of the initial reagents PbI$_2$ and CH$_3$NH$_3$I to be recorded.

Figure 9 shows the scheme of the formation reaction of perovskite and intermediate phases at the ratio 1:1 of the initial reagents PbI$_2$ and CH$_3$NH$_3$I and using DMF.

In this case, the intermediate phases are (CH$_3$NH$_3$)$_2${(DMF)}PbI$_4$, (CH$_3$NH$_3$)$_2${(DMF)}PbI$_3$, and (CH$_3$NH$_3$)$_3${(DMF)}PbI$_5$. Figure 10 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$_3$NH$_3$I and using the DMF solvent.

In this case, among the intermediate phases, besides (CH$_3$NH$_3$)$_2${(DMF)}PbI$_4$, (CH$_3$NH$_3$)$_2${(DMF)}PbI$_3$, and (CH$_3$NH$_3$)$_3${(DMF)}PbI$_5$, the phase (CH$_3$NH$_3$)$_2${(DMF)}PbI$_2$ is additionally observed.

Figure 11 shows the scheme of the formation reaction of perovskite and intermediate phases at the ratio 1:3 of the initial reagents PbI$_2$ and CH$_3$NH$_3$I and using the DMF solvent.
Fig. 11. The scheme of the formation of perovskite and intermediate compounds at the ratio 1:3 of the initial reagents PbI$_2$ and CH$_3$NH$_3$I and using DMF.

In this case, the intermediate phases are only (CH$_3$NH$_3$)$_2$(DMF)$_x$PbI$_4$ and (CH$_3$NH$_3$)$_3$(DMF)PbI$_5$.

At the first glance, the schemes presented above are contradictory, while they show that the same intermediate phases may exist at different temperatures depending on the initial reaction conditions. However, XRD proves this fact. Indeed, the stability of the intermediate compounds and the sequence of their conversion to perovskite depend on their properties. The difference in temperature stability can be shown based on the enthalpies of intermediate compounds formation (Table 2). The compound (CH$_3$NH$_3$)$_2$(DMF)$_2$PbI$_3$ is the most stable at the ratio 1:1 of the initial components PbI$_2$ and CH$_3$NH$_3$I. Increasing the ratio of the initial reagents decreases the temperature of interval of the existence of this compound. In contrast to (CH$_3$NH$_3$)$_2$(DMF)$_2$PbI$_3$, the temperature interval of existence of the unstable compound (CH$_3$NH$_3$)$_3$(DMF)PbI$_5$ increased with an increase in CH$_3$NH$_3$I amount (Table 2).

XRD shows that CH$_3$NH$_3$PbI$_3$ films prepared on glass substrates at different ratios of the initial reagents PbI$_2$ and CH$_3$NH$_3$I may contain other intermediate compounds after heat treatment at different temperatures. The phase composition of the film depends on the ratio of the initial reagents and the temperature of heat treatment. The presence of other compounds in the film, on the one hand, reduces the proportion of perovskite and, on the other hand, can contribute to its stability in the surrounding atmosphere.

Enthalpy of formation [14] and temperature interval of existence of intermediate compounds at different ratios of starting reagents.

| Compound | Enthalpy of formation (kcal/mol) | Temperature interval of existence |
|----------|----------------------------------|----------------------------------|
| (CH$_3$NH$_3$)$_2$(DMF)$_2$PbI$_3$ | -180.1 | 20-110 ºC | 20-25 ºC | – |
| (CH$_3$NH$_3$)$_2$(DMF)$_2$PbI$_6$ | -177.6 | – | 20-25 ºC | – |
| (CH$_3$NH$_3$)$_3$(DMF)PbI$_5$ | -133.8 | 20-50 ºC | 20-130 ºC | 20-150 ºC |
| (CH$_3$NH$_3$)$_3$(DMF)PbI$_4$ | – | 20-55 ºC | 20-160 ºC | 20-170 ºC |

The influence of moisture on the stability of organic-inorganic perovskite has been studied. The stability of organic-inorganic perovskite films was determined by X-ray diffractometry.
results are analyzed and presented as the dependence of the PbI$_2$ phase content on the time of exposure to moisture (Fig. 12.).

Raman spectroscopy confirms the formation of the intermediate compounds and determines the temperature intervals of their existence. The ratio of initial reagents and the temperature of heat treatment should be controlled at the synthesis of perovskite films since it affects the presence of intermediate phases and, as a result, the morphology of films and the processes of their degradation.

**CONCLUSIONS.** The formation of CH$_3$NH$_3$PbI$_3$ perovskite films at different ratios (1:1, 1:2 and 1:3) of the initial reagents PbI$_2$ and CH$_3$NH$_3$I dissolved in the DMF and after heat treatment at different temperatures from 20 to 175 °C has been investigated. SEM established that the morphology of the films mainly depends on the ratio of the initial reagents. The temperature of heat treatment changes only the dimensions of the characteristic structures of films. The presence of other compounds in the film influences the morphology of the film and, as a result, the reflection and absorption of solar radiation.

XRD and Raman spectroscopy show that depending on the ratio of the initial reagents and the heat treatment temperature of films, the formation of organic-inorganic perovskite occurs according to different schemes: through the formation of 3, 4 or 2 intermediate compounds at the ratio of the initial reagents of 1:1, 1:2 or 1:3, respectively. The intermediate phases (CH$_3$NH$_3$)$_2$(DMF)$_x$PbI$_{4-y}$, (CH$_3$NH$_3$)$_3$(DMF)$_x$Pb$_2$I$_6$ and (CH$_3$NH$_3$)$_2$(DMF)$_x$Pb$_3$I$_8$ in the films were found. The presence of intermediate compounds can significantly affect the degradation of films. It has been established that moisture significantly affects the stability of organic-inorganic perovskite films. The films obtained at a ratio of starting reagents of 1:3 are the most stable.
Acknowledgements

The authors acknowledge the support from the Targeted Program of Basic Research of the National Academy of Sciences of Ukraine “Advanced fundamental research and innovative development of nanomaterials and nanotechnologies for the needs of industry, healthcare, and agriculture” (State registration № 0120U102242).

ПЛІВКИ ОРГАНО-НЕОРГАНИЧНИХ ПЕРОВСКИТІВ CH₃NH₃PbI₅ ПРИ ВИКОРИСТАННІ РОЗЧИННИКА ДМФА

П. В. Торчинюк¹, О. І. В’юнов²*, В. О. Юхимчук², О. М. Грещук², С. В. Вакаров¹, А. Г. Білоус¹

¹Інститут загальної та неорганічної хімії імені В. І. Вернадського НАН України, просп. Академіка Палладіна, 32/34, Київ 03142, Україна
²Інститут фізики напівпровідників імені В. Є. Лашкарьова НАН України, просп. Наук, 41, Київ 03028, Україна
* e-mail: vyunov@ionc.kiev.ua

Плівки органо-неорганічних перовсikitів CH₃NH₃PbI₅ було синтезовано з розчинів із різним співвідношенням (1:1, 1:2 та 1:3) вихідних реагентів (PbI₂ та CH₃NH₃I) у розчиннику ДМФА. Методами рентгеновського аналізу та раманівської спектроскопії було показано, що органо-неорганічні перовсikitи утворюються за різними схемами залежно від співвідношення PbI₂ та CH₃NH₃I.

При співвідношенні вихідних реагентів 1:1, крім органо-неорганічного перовскиту CH₃NH₃PbI₅, утворюються три проміжні сполуки: (CH₃NH₃)ₓ(DMF)ᵧPbI₄, (CH₃NH₃)ₓ(DMF)ᵧPbI₃, (CH₃NH₃)ₓ(DMF)ᵧPbI₂. При співвідношенні вихідних реагентів 1:2 утворюються чотири проміжні сполуки: крім зазначених фаз, виявляється солода (CH₃NH₃)ₓ(DMF)ᵧPbI₃. При співвідношенні вихідних реагентів до 1:3 спостерігають лише дві проміжні фази (CH₃NH₃)ₓ(DMF)ᵧPbI₂ та (CH₃NH₃)ₓ(DMF)ᵧPbI₃. Встановлено, що морфологія плівок перовсikitів залежить, перш за все, від співвідношення вихідних реагентів. Температура оброблення змінює лише розміри зерен плівок.

Наявність проміжних сполук при синтезі органо-неорганічних перовсikitів може суттєво впливати на властивості плівок. Методом РФА було досліджено вплив вологи на стійкість плівок органо-неорганічних перовсikitів CH₃NH₃PbI₅, отриманих при співвідношенні PbI₂:CH₃NH₃I = 1:1, 1:2, 1:3. Стійкість плівок оцінювали за вмістом фази PbI₂, яка утворюється в результаті деконденсації плівки органо-неорганічного перовскиту. Показано, що стійкість плівок залежить від кількості проміжних сполук, які утворюються при синтезі перовскиту. Плівки перовскиту, які утворюються при співвідношенні 1:3 через формування та розпад двох проміжних сполук, є найстійчішими до дії вологи. Плівки перовскиту, отримані при співвідношенні 1:2 і в яких утворення перовскиту відбувається через утворення чотирьох проміжних сполук, є найменш стійкими до дії вологи.

Для синтезу плівок органо-неорганічних перовсikitів необхідно контролювати
співвідношення вихідних реагентів і температуру оброблення плявки, оскільки це впливає на кількість проміжних фаз і, як результат, морфологію плявок, процеси їхньої деградації.

Ключові слова: органо-неорганічний перовскит, рентгенофазовий аналіз, раманівська спектроскопія, проміжні сполуки, стабільність.

ЛІТЕРАТУРА

1. Noh J. H., Im S. H., Heo J. H., Mandal T. N., Seok S. I., Chemical management for colorful, efficient, and stable inorganic-organic hybrid nanostructured solar cells. Nano Letters, 2013, 13 (4). P. 1764–1769.
2. Valverde-Chávez D. A., Ponseca C. S., Stoumpos C. C., Yartsev A., Kanatzidis M. G., Sundström V., Cooke D. G., Intrinsic femtosecond charge generation dynamics in single crystal CH₃NH₃PbI₃. Energy & Environmental Science, 2015, 8 (12). P. 3700–3707.
3. Miyata A., Mitioglu A., Plochocka P., Portugall O., Wang J. T.-W., Stranks S. D., Snaith H. J., Nicholas R. J., Direct measurement of the exciton binding energy and effective masses for charge carriers in organic-inorganic tri-halide perovskites. Nature Physics, 2015, 11 (7). P. 582–587.
4. Xing G., Mathews N., Sun S., Lim S. S., Lam Y. M., Grätzel M., Mhaisalkar S., Sum T. C., Long-range balanced electron-and hole-transport lengths in organic-inorganic CH₃NH₃PbI₃. Science, 2013, 342 (6156). P. 344–347.
5. Gonzalez-Pedro V., Juarez-Perez E. J., Arsyad W.-S., Barea E. M., Fabregat-Santigao F., Mora-Sero I., Bisquert J., General working principles of CH₃NH₃PbX₃ perovskite solar cells. Nano Letters, 2014, 14 (2). P. 888–893.
6. Valakh M. Y., Kolomys O. F., Ponomaryov S. S., Yukhymchuk V. O., Babichuk I. S., Izquierdo-Roca V., Saucedo E., Perez-Rodriguez A., Morante J. R., Schorr S., Raman scattering and disorder effect in Cu₂ZnSnS₄. Physica status solidi (RRL) – Rapid Research Letters, 2013, 7 (4). P. 258–261.
7. Abdulrazzaq O. A., Saini V., Bourdo S., Dervishi E., Biris A. S., Organic solar cells: a review of materials, limitations, and possibilities for improvement. Particulate science and technology, 2013, 31 (5). P. 427–442.
8. Nozik A. J., Quantum dot solar cells. Physics E: Low-dimensional Systems and Nanostructures, 2002, 14 (1–2). P. 115–120.
9. Della Gaspera E., Peng Y., Hou Q., Spiccia L., Bach U., Jasieniak J. J., Cheng Y.-B., Ultra-thin high efficiency semitransparent perovskite solar cells. Nano Energy, 2015, 13. P. 249–257.
10. Baig H., Kanda H., Asiri A. M., Nazeeruddin M. K., Mallick T., Increasing efficiency of perovskite solar cells using low concentrating photovoltaic systems. Sustainable Energy & Fuels, 2020, 4 (2). P. 528–537.
11. Rajagopal A., Yao K., Jen A. K. Y., Toward perovskite solar cell commercialization: a perspective and research roadmap based on interfacial engineering. Advanced Materials, 2018, 30 (32). P. 1800455.
12. Zhao W., Yang D., Liu S. F., Organic–inorganic hybrid perovskite with controlled dopant modification and application in
photovoltaic device. *Small*, 2017, **13** (25). P. 1604153.

13. Kojima A., Teshima K., Shirai Y., Miyasaka T., Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society*, 2009, **131** (17). P. 6050–6051.

14. Best Research-Cell Efficiency Chart. In *National Renewable Energy Laboratory*, 2020, Vol. 2020.

15. Xie H., Liu X., Lyu L., Niu D., Wang Q., Huang J., Gao Y., Effects of precursor ratios and annealing on electronic structure and surface composition of \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) perovskite films. *The Journal of Physical Chemistry C*, 2016, **120** (1). P. 215–220.

16. Cui D., Yang Z., Yang D., Ren X., Liu Y., Wei Q., Fan H., Zeng J., Liu S., Color-tuned perovskite films prepared for efficient solar cell applications. *The Journal of Physical Chemistry C*, 2016, **120** (1). P. 42–47.

17. V’yunov O. I., Belous A. G., Kobylianska S. D., Kovalenko L. L., Impedance Analysis of Thin Films of Organic-Inorganic Perovskites \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) with Control of Microstructure. *Nanoscale Research Letters*, 2018, **13** (1). P. 98.

18. Belous A. G., V’yunov O. I., Kobylyanskaya S. D., Ishchenko A. A., Kulichin A. V., Influence of Synthesis Conditions on the Morphology and Spectral-Luminescent Properties of Films of Organic-Inorganic Perovskite \( \text{CH}_3\text{NH}_3\text{PbI}_3\cdot\text{Cl}_{0.02}\cdot\text{H}_2\text{O} \). *Russian Journal of General Chemistry*, 2018, **88** (1). P. 114–119.

19. Belous A., Kobylianska S., V’yunov O., Torchyniuk P., Yukhymchuk V., Hreshchuk O., Effect of non-stoichiometry of initial reagents on morphological and structural properties of perovskites \( \text{CH}_3\text{NH}_3\text{PbI}_3 \). *Nanoscale Research Letters*, 2019, **14** (4). P. 1–9.

20. Торчинюк П. В., В’юнов О. І., Іщенко О. О., Курдюкова І. В., Власюк В. М., Костильов В. П., Білоус А. Г. Органо-неорганічний перовскит \( \text{CH}_3\text{NH}_3\text{PbI}_3 \): морфологічні, структурні та електрофізичні властивості. *Український хімічний журнал*, 2019, **85** (9). P. 31–43.

22. Petrov A. A., Sokolova I. P., Belich N. A., Peters G. S., Dorovatovskii P. V., Zubavichus Y. V., Khrustalev V. N., Petrov A. V., Grätzel M., Goodlin E. A., Crystal structure of DMF-intermediate phases uncovers the link between \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) morphology and precursor stoichiometry. *The Journal of Physical Chemistry C*, 2017, **121** (38). P. 20739–20743.

23. Roghabadi F. A., Ahmadi V., Aghmiuni K. O., Organic–Inorganic Halide Perovskite Formation: In Situ Dissociation of Cation Halide and Metal Halide Complexes during Crystal Formation. *The Journal of Physical Chemistry C*, 2017, **121** (25). P. 13532–13538.

24. Vincent B. R., Robertson K. N., Cameron T. S., Knop O., Alkylammonium lead halides. Part I. Isolated \( \text{PbI}_6^{4–} \) ions in \( (\text{CH}_3\text{NH}_3)_4\text{PbI}_6\cdot2\text{H}_2\text{O} \). *Canadian Journal of Chemistry*, 1987, **65** (5). P. 1042–1046.

25. Kye Y.-H., Yu C.-J., Jong U.-G., Chen Y., Walsh A., Critical Role of Water in Defect Aggregation and Chemical Degradation of Perovskite Solar Cells. *The journal of physical chemistry letters*, 2018, **9** (9). P. 2196–2201.

26. Imler G. H., Li X., Xu B., Dobereiner G. E., Dai H.-L., Rao Y., Wayland B. B., Solid state transformation of the crystalline monohydrate \( (\text{CH}_3\text{NH}_3)_4\text{PbI}_6\cdot(\text{H}_2\text{O}) \) to
the \((\text{CH}_3\text{NH}_3)\text{PbI}_3\) perovskite. \textit{Chemical Communications}, 2015, 51 (56). P. 11290–11292.

27. Kawamura Y., Mashiyama H., Hasebe K., Structural study on cubic-tetragonal transition of \(\text{CH}_3\text{NH}_3\text{PbI}_3\). \textit{Journal of the Physical Society of Japan}, 2002, 71 (7). P. 1694–1697.

28. Palosz B., The structure of PbI\(_2\) polytypes 2H and 4H: a study of the 2H-4H transition. \textit{Journal of Physics: Condensed Matter}, 1990, 2 (24). P. 5285.

29. Yamamuro O., Matsuo T., Suga H., David W., Ibberson R., Leadbetter A., Neutron diffraction and calorimetric studies of methylammonium iodide. \textit{Acta Crystallographica Section B: Structural Science}, 1992, 48 (3). P. 329–336.

30. Srimath Kandada A. R., Petrozza A., Photophysics of hybrid lead halide perovskites: The role of microstructure. \textit{Accounts of Chemical Research}, 2016, 49 (3). P. 536–544.

31. Antoniadou M., Siranidi E., Vaenas N., Kontos A. G., Statthatos E., Falaras P., Photovoltaic Performance and Stability of \(\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x\) Perovskites. \textit{Journal of Surfaces and Interfaces of Materials}, 2014, 2 (4). P. 323–327.

32. Merdasa A., Bag M., Tian Y., Källman E., Dobrovolsky A., Scheblykin I. G., Super-resolution luminescence microspectroscopy reveals the mechanism of photoinduced degradation in \(\text{CH}_3\text{NH}_3\text{PbI}_3\) perovskite nanocrystals. \textit{The Journal of Physical Chemistry C}, 2016, 120 (19). P. 10711–10719.

33. Barugkin C., Cong J., Duong T., Rahman S., Nguyen H. T., Macdonald D., White T. P., Catchpole K. R., Ultralow absorption co-efficient and temperature dependence of radiative recombination of \(\text{CH}_3\text{NH}_3\text{PbI}_3\) perovskite from photoluminescence. \textit{The journal of physical chemistry letters}, 2015, 6 (5). P. 767–772.

34. Niemann R. G., Kontos A. G., Palles D., Kamitsos E. I., Kaltzoglou A., Brivio F., Falaras P., Cameron P. J., Halogen effects on ordering and bonding of \(\text{CH}_3\text{NH}_3^+\) in \(\text{CH}_3\text{NH}_3\text{PbX}_3\) \((X = \text{Cl, Br, I})\) hybrid perovskites: a vibrational spectroscopic study. \textit{The Journal of Physical Chemistry C}, 2016, 120 (5). P. 2509–2519.

REFERENCES

1. Noh J. H., Im S. H., Heo J. H., Mandal T. N., Seok S. I., Chemical management for colorful, efficient, and stable inorganic-organic hybrid nanostructured solar cells. \textit{Nano Letters}. 2013, 7 (4): 1764–1769. https://doi.org/10.1021/nl400349b.

2. Valverde-Chávez D. A., Ponseca C. S., Stoumpos C. C., Yartsev A., Kanatzidis M. G., Sundström V., Cooke D. G., Intrinsic femtosecond charge generation dynamics in single crystal \(\text{CH}_3\text{NH}_3\text{PbI}_3\). \textit{Energy & Environmental Science}. 2015, 8 (12): 3700–3707. https://doi.org/10.1039/c5ee02503f.

3. Miyata A., Mitioglu A., Plochocka P., Portugall O., Wang J. T.-W., Stranks S. D., Snaith H. J., Nicholas R. J., Direct measurement of the exciton binding energy and effective masses for charge carriers in organic-inorganic tri-halide perovskites. \textit{Nature Physics}. 2015, 11 (7): 582–587. https://doi.org/10.1038/nphys3357.

4. Xing G., Mathews N., Sun S., Lim S. S., Lam Y. M., Grätzel M., Mhaisalkar S., Sum
T. C., Long-range balanced electron-and hole-transport lengths in organic-inorganic CH$_3$NH$_3$PbI$_3$. *Science*. 2013. 342 (6156): 344–347. https://doi.org/10.1126/science:1243167.

5. Gonzalez-Pedro V., Juarez-Perez E. J., Arsyad W.-S., Barea E. M., Fabregat-Santiago F., Mora-Sero I., Bisquert J., General working principles of CH$_3$NH$_3$PbX$_3$ perovskite solar cells. *Nano Letters*. 2014. 14 (2): 888–893. https://doi.org/10.1021/nl404252e.

6. Valakh M. Y., Kolomys O. F., Ponomaryov S. S., Yukhymchuk V. O., Babichuk I. S., Izquierdo Roca V., Saucedo E., Perez Rodriguez A., Morante J. R., Schorr S., Raman scattering and disorder effect in Cu$_2$ZnSnS$_4$. *Physica status solidi (RRL)–Rapid Research Letters*. 2013. 7 (4): 258–261. https://doi.org/10.1002/pssr.201307073.

7. Abdulrazzaq O. A., Saini V., Bourdo S., Dervishi E., Biris A. S., Organic solar cells: a review of materials, limitations, and possibilities for improvement. *Particulate science and technology*. 2013. 31 (5): 427–442. https://doi.org/10.1080/02726351.2013.769470.

8. Nozik A. J., Quantum dot solar cells. *Physica E: Low-dimensional Systems and Nanostructures*. 2002. 14 (1–2): 115–120. https://doi.org/10.1016/S1386-9477(02)00374-0.

9. Della Gaspera E., Peng Y., Hou Q., Spiccia L., Bach U., Jasieniak J. J., Cheng Y.-B., Ultra-thin high efficiency semitransparent perovskite solar cells. *Nano Energy*. 2015. 13: 249–257. https://doi.org/10.1016/j.nanoen.2015.02.028.

10. Baig H., Kanda H., Asiri A. M., Naezeruddin M. K., Mallick T., Increasing efficiency of perovskite solar cells using low concentrating photovoltaic systems. *Sustainable Energy & Fuels*. 2020. 4 (2): 528–537. https://doi.org/10.1039/c9se00550a.

11. Rajagopal A., Yao K., Jen A. K. Y., Toward perovskite solar cell commercialization: a perspective and research roadmap based on interfacial engineering. *Advanced Materials*. 2018. 30 (32): 1800455. https://doi.org/10.1002/adma.201800455.

12. Zhao W., Yang D., Liu S. F., Organic-inorganic hybrid perovskite with controlled dopant modification and application in photovoltaic device. *Small*. 2017. 13 (25): 1604153. https://doi.org/10.1002/smll.201604153.

13. Kojima A., Teshima K., Shirai Y., Miyasaka T., Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society*. 2009. 131 (17): 6050–6051. https://doi.org/10.1021/ja809598r.

14. Best Research-Cell Efficiency Chart. In *National Renewable Energy Laboratory*, 2020. Vol. 2020.

15. Xie H., Liu X., Lyu L., Niu D., Wang Q., Huang J., Gao Y., Effects of precursor ratios and annealing on electronic structure and surface composition of CH$_3$NH$_3$PbI$_3$ perovskite films. *The Journal of Physical Chemistry C*. 2016. 120 (1): 215–220. https://doi.org/10.1021/acs.jpcc.5b07728.

16. Cui D., Yang Z., Yang D., Ren X., Liu Y., Wei Q., Fan H., Zeng J., Liu S., Color-tuned perovskite films prepared for efficient solar cell applications. *The Journal of Physical Chemistry C*. 2016. 120 (1): 42–47. https://doi.org/10.1021/acs.jpcc.5b09393.

17. V’yunov O. I., Belous A. G., Kobylianska S. D., Kovalenko L. L., Impedance Analysis of Thin Films of Organic-Inorganic...
Perovskites CH$_3$NH$_3$PbI$_3$ with Control of Microstructure. *Nanoscale Research Letters.* 2018. 13 (1): 98. https://doi.org/10.1186/s11671-018-2509-2.

18. Belous A. G., V’yunov O. I., Kobylyanskaya S. D., Ishchenko A. A., Kulinich A. V., Influence of Synthesis Conditions on the Morphology and Spectral-Luminescent Properties of Films of Organic-Inorganic Perovskite CH$_3$NH$_3$PbI$_3$ with Control of Microstructure. *Russian Journal of General Chemistry.* 2018. 88 (1): 114–119. https://doi.org/10.1134/S1070363218010188.

19. Belous A., Kobylianska S., V’yunov O., Torchyniuk P., Yukhymchuk V., Hreshchuk O., Effect of non-stoichiometry of initial reagents on morphological and structural properties of perovskites CH$_3$NH$_3$PbI$_3$. *Nanoscale Research Letters.* 2019. 14 (4): 1–9. https://doi.org/10.1186/s11671-018-2841-6.

20. Torchyniuk P., V’yunov O., Ishchenko A., Kurdyukova I., Vlasyuk V., Kostylyov V., Belous A., Organic-inorganic perovskite CH$_3$NH$_3$PbI$_3$: morphological, structural and photoelectrophysical properties. *Ukrainian Chemistry Journal.* 2019. 85 (9): 31–43. https://doi.org/10.33609/0041-6045.85.9.2019.31–41.

22. Petrov A. A., Sokolova I. P., Belich N. A., Peters G. S., Dorovatovskii P. V., Zubavichus Y. V., Krustalev V. N., Petrov A. V., Grätzel M., Goodlin E. A., Crystal structure of DMF-intermediate phases uncovers the link between CH$_3$NH$_3$PbI$_3$ morphology and precursor stoichiometry. *The Journal of Physical Chemistry C.* 2017. 121 (38): 20739–20743. https://doi.org/10.1021/acs.jpcc.7b08468.

23. Roghabadi F. A., Ahmadi V., Aghmiuni K. O., Organic–Inorganic Halide Perovskite Formation: In Situ Dissociation of Cation Halide and Metal Halide Complexes during Crystal Formation. *The Journal of Physical Chemistry C.* 2017. 121 (25): 13532–13538. https://doi.org/10.1021/acs.jpcc.7b03311.

24. Vincent B. R., Robertson K. N., Cameron T. S., Knop O., Alkylammonium lead halides. Part 1. Isolated PbI$_6$– ions in (CH$_3$NH$_3$)$_4$PbI$_6$·2H$_2$O. *Canadian Journal of Chemistry.* 1987. 65 (5): 1042–1046. https://doi.org/10.1139/v87-176.

25. Kye Y.-H., Yu C.-J., Jong U.-G., Chen Y., Walsh A., Critical Role of Water in Defect Aggregation and Chemical Degradation of Perovskite Solar Cells. *The journal of physical chemistry letters.* 2018. 9 (9): 2196–2201. https://doi.org/10.1021/acs.jpclett.8b00406.

26. Imler G. H., Li X., Xu B., Dobereiner G. E., Dai H.-L., Rao Y., Wayland B. B., Solid state transformation of the crystalline monohydrate (CH$_3$NH$_3$)$_4$PbI$_6$·(H$_2$O) to the (CH$_3$NH$_3$)$_4$PbI$_6$ perovskite. *Chemical Communications.* 2015. 51 (56): 11290–11292. https://doi.org/10.1039/C5CC03741G.

27. Kawamura Y., Mashiyama H., Hasebe K., Structural study on cubic-tetragonal transition of CH$_3$NH$_3$PbI$_3$. *Journal of the Physical Society of Japan.* 2002. 71 (7): 1694–1697. https://doi.org/10.1143/jpsj.71.1694.

28. Palosz B., The structure of PbI$_2$ polytypes 2H and 4H: a study of the 2H-4H transition. *Journal of Physics: Condensed Matter.* 1990. 2 (24): 5285. https://doi.org/10.1088/0953-8984/2/24/001.

29. Yamamuro O., Matsuo T., Suga H., David W., Iberson R., Leadbetter A., Neutron diffraction and calorimetric studies of
methylammonium iodide. *Acta Crystallographica Section B: Structural Science.* 1992. 48 (3): 329–336. https://doi.org/10.1107/S0108768192000260.

30. Srimath Kandada A. R., Petrozza A., Photophysics of hybrid lead halide perovskites: The role of microstructure. *Accounts of Chemical Research.* 2016. 49 (3): 536–544. https://doi.org/10.1021/acs.accounts.5b00464.

31. Antoniadou M., Siranidi E., Vaenas N., Kontos A. G., Stathatos E., Falaras P., Photovoltaic Performance and Stability of CH$_3$NH$_3$PbI$_3$–Cl Perovskites. *Journal of Surfaces and Interfaces of Materials.* 2014. 2 (4): 323–327. https://doi.org/10.1166/jsim.2014.1060.

32. Merdasa A., Bag M., Tian Y., Källman E., Dobrovolsky A., Scheblykin I. G., Super-resolution luminescence microspectroscopy reveals the mechanism of photoinduced degradation in CH$_3$NH$_3$PbI$_3$ perovskite nanocrystals. *The Journal of Physical Chemistry C.* 2016. 120 (19): 10711–10719. https://doi.org/10.1021/acs.jpcc.6b03512.

33. Barugkin C., Cong J., Duong T., Rahman S., Nguyen H. T., Macdonald D., White T. P., Catchpole K. R., Ultralow absorption coefficient and temperature dependence of radiative recombination of CH$_3$NH$_3$PbI$_3$ perovskite from photoluminescence. *The Journal of Physical Chemistry Letters.* 2015. 6 (5): 767–772. https://doi.org/10.1021/acs.jpclett.5b00044.

34. Niemann R. G., Kontos A. G., Palles D., Kamitsos E. I., Kaltzoglou A., Brivio F., Falaras P., Cameron P. J., Halogen effects on ordering and bonding of CH$_3$NH$_3^+$ in CH$_3$NH$_3$PbX$_3$ (X = Cl, Br, I) hybrid perovskites: a vibrational spectroscopic study. *The Journal of Physical Chemistry C.* 2016. 120 (5): 2509–2519. https://doi.org/10.1021/acs.jpcc.5b11256.

Стаття надійшла 23.07.2021.