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Phase formation processes in the synthesis of organic-inorganic perovskites $CH_3NH_3PbI_3$

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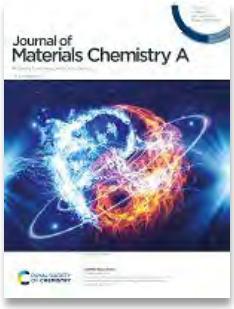

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The aim of this work was to study the processes of the formation of intermediate phases at the synthesis of organic-inorganic perovskite films $CH_3NH_3PbI_3$ at different ratios of the initial reagents in a wide temperature range. It was found that depending on the ratio of the initial reagents and heat treatment temperature of the films, the formation of organic-inorganic perovskite occurs according to different schemes. In addition to perovskite $CH_3NH_3PbI_3$, intermediate phases $(CH_3NH_3)_2(DMF)_xPbI_4$, $(CH_3NH_3)_3(DMF)PbI_5$, $(CH_3NH_3)_2(DMF)_2Pb_2I_6$ and $(CH_3NH_3)_2(DMF)_2Pb_3I_8$ in the films are formed. The presence of intermediate phases can significantly affect the morphology of the films, the degradation of films, and can affect the efficiency of solar cell based on them.

I believe that the manuscript will be of general interest for the readership of the Journal of Materials Chemistry A and encourage further detailed studies regarding the interaction between solvent and salts in the synthesis of organic-inorganic films $CH_3NH_3PbI_3$ on the properties of materials for practical applications.

I look forward to hearing your decision in due course.

Yours faithfully,

Oleg V’yunov

Phase formation processes in the synthesis of organic-inorganic perovskites $CH_3NH_3PbI_3$

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Abstract

The organic-inorganic perovskite films $CH_3NH_3PbI_3$ were synthesized from solutions with different ratios (1:1, 1:2 and 1:3) of initial reagents (PbI_2 and CH_3NH_3I). XRD and Raman spectroscopy shows that the perovskites are formed according to different schemes depending on the ratio of PbI_2 and CH_3NH_3I. At ratio 1:1 of initial reagents, three intermediate compounds are formed: $(CH_3NH_3)_2(DMF)_xPbI_4$, $(CH_3NH_3)_2(DMF)_2Pb_3I_8$, $(CH_3NH_3)_3(DMF)PbI_5$. At ratio 1:2 of initial reagents four intermediate compounds are formed: in addition to the above phases, the phase $(CH_3NH_3)_2(DMF)_2Pb_2I_6$ is found. And at ratio 1:3 of initial reagents, only two intermediate phases, $(CH_3NH_3)_2(DMF)_xPbI_4$ and $(CH_3NH_3)_3(DMF)PbI_5$, 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 sizes of films.

Introduction

Nowadays, much of the energy comes from hydrocarbons, coal and other fossil fuels. Their usage in electricity generation leads to significant 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. Active layers of these materials are relatively thick (~200 μm) for 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. 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_2ZnSnS_4 [2], organic semiconductors [3], semiconductor quantum dots [4], and organic-inorganic halides $CH_3NH_3PbI_{3-y}X_y$ with perovskite structure [5].

In recent years, the efficiency of perovskite solar cells based on $CH_3NH_3PbI_3$ has dynamically increased [5-7]. 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 large diffusion length of charge carriers [6]. Over the last 10 years, the efficiency of solar-to-electrical conversion of perovskite-based photoelectric elements has grown from 3% [7] to 25.2% [8].

However, organic-inorganic perovskites have some drawbacks. In particular, their structure degrades by the intense solar radiation and the atmospheric humidity. To overcome the above problems, the processes in the formation of perovskites films $CH_3NH_3PbI_3$ 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 $CH_3NH_3PbI_3$ perovskites [9,10,11]. The complex chemical interaction of an organic cation, a coordinating solvent, and an inorganic component determines the processes of crystal nucleation and formation [12] and consequently affects the properties of crystalline films. However, practically no data is published about the phase transformations during the synthesis of the samples in different synthesis conditions (ratios of initial reagent, solvents, heat-treatment temperatures).

The aim of this work was to study in a wide temperature range (from 20 to 175 °C) the processes at the synthesis of organic-inorganic perovskite films $CH_3NH_3PbI_3$ using the initial reagents CH_3NH_3I and PbI_2 in different ratios, which are dissolved in dimethylformamide (DMF).

Experimental section

Materials

Lead iodide (PbI_2), methylammonium chloride (CH_3NH_3Cl) and pre-synthesized methylammonium iodide (CH_3NH_3I) were used as starting materials. To stabilize the perovskite structure, the iodine was partially substituted with chlorine by the addition of methylammonium chloride (CH_3NH_3Cl) [12]. In this paper, for simplicity, the solid solution $CH_3NH_3PbI_{2.98}Cl_{0.02}$ will be further written as $CH_3NH_3PbI_3$. Dried dimethylformamide (DMF) was used as the solvent.

Synthesis of methylammonium iodide and organic-inorganic perovskites

Methylammonium iodide (CH_3NH_3I) 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 by methyl tert-butyl ether, filtered, and dried overnight under vacuum to yield white crystals of CH_3NH_3I.

For the deposition of $CH_3NH_3PbI_3$ films, the initial reagents, PbI_2 and CH_3NH_3I with ratios of 1:1; 1:2; 1:3 was dissolved in DMF and stirred at 70 °C for 1 hour. The crystalline $CH_3NH_3PbI_3$ films were formed in a dry box. The previously prepared clear solution was deposited to the purified glass substrate by spin-coating with speed 1200 rpm for 30 seconds. The films were thermally treated on a preheated hot plate at temperatures from 20 to 180 °C for 30 min.

Characterization

The microstructure and the element 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 (Cu*K*α-radiation, 40 kW, 20 mA) over $2\Theta = 5–50^{o}$, a step of 0.04^{o} 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 CCD detector (Andor) using λ_{exc} = 457 nm (diode-pumped solid-state laser, CNILaser). The exciting laser power was kept as low as possible, to avoid the damage of molecules under investigation either due to heating or photochemical reactions.

Results and Discussion

Fig. 1 shows the 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 at 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 [12,13]. Heat treatment of films at different temperatures also affects their morphology, but not as critical as the previous factor. As the temperature of the heat treatment of the films increases, the shape of the characteristic structures (grains) on their surface remains similar, although their dimensions are significantly reduced.

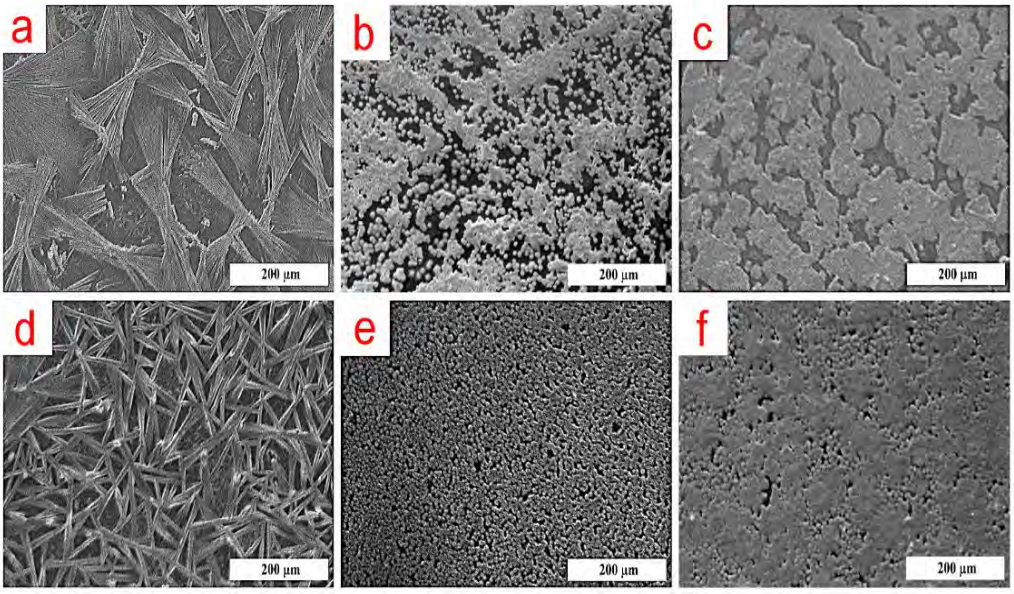


Fig. 1. SEM image of the surface of perovskite films $CH_3NH_3PbI_3$ deposited on glass substrates at different ratios of the initial reagents: PbI_2 : CH_3NH_3I = 1:1 (a, d); 1:2 (b, e); 1:3 (c, f), and at temperatures: 25 °C (a, b, c) and 75 °C (d, e, f).

Table 1 shows the literature data [14-21] on the unit cell parameters of the initial reagents, probable intermediate and terminal compounds in the films formed in DMF solvent at different ratios of the initial reagents, PbI_2 and CH_3NH_3I.

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

Compound	Symmetry and space group	Unit cell parameters	References
$(CH_3NH_3)_2(DMF)_2Pb_2I_6$	Monoclinic $P2_1/c$ (№ 14)	a = 4.5647(9) Å b = 25.446(5) Å c = 12.119(2) Å $\alpha = \gamma = 90$ ° $\beta = 96.75(3)$ ° Z = 4 V=1397.9(5) Å^3	[14]
$(CH_3NH_3)_2(DMF)_2Pb_3I_8$	Orthorhombic Pnnm (№ 58)	a = 17.165(9) Å b = 21.955(4) Å c = 4.5549(9) Å $\alpha = \beta = \gamma = 90$ ° Z = 2 V =1716.6(6) Å^3	[14]
$(CH_3NH_3)_3(DMF)PbI_5$	Triclinic P-1 (№ 2)	a = 10.1714(15) Å b = 11.335(3) Å c =12.394(2) Å $\alpha = 111.18(3)$ ° $\beta = 101.11(3)$ ° $\gamma = 109.80(3)$ ° Z = 2 V = 1170.0(7) Å^3	[14]
$(CH_3NH_3)_2(DMF)_xPbI_4$	-	-	[15]
$(CH_3NH_3)_4PbI_6{\cdot}2H_2O$	Monoclinic $P2_1/n$ (№ 14)	a = 10.421(3) Å b = 11.334(2) Å c = 10.668(2) Å $\alpha = \beta = 90°$ $\gamma = 91.73(2)$ Z = 2 V=1259.4(5) Å^3	[16]
$CH_3NH_3PbI_3{\cdot}H_2O$	Monoclinic P21/m	a = 10.46 Å b = 4.63 Å	[17,18]

	(№ 11)	c = 11.10 Å α = β = 90° γ = 101.50° Z = 2 V=536.05(19)	
$CH_3NH_3PbI_3$	Tetragonal I4/mcm (№ 140)	a = 8.870(2) Å c = 12.669(8) Å V = 996.8(7) Å^3	[19]
PbI_2	Trigonal P-3m1 (№ 164)	a = 4.558 Å c = 6.986 Å V = 125.69 Å^3	[20]
CH_3NH_3I	Tetragonal P4/nmm (№ 129)	a = 5.12729(1) Å c = 9.01794(2) Å V = 237.074(1) Å^3	[21]

Fig. 2 shows the results of the XRD analysis of perovskite films $CH_3NH_3PbI_3$ prepared at a ratio of the initial reagents PbI_2 and CH_3NH_3I 1:1 and at different temperatures of heat treatment.

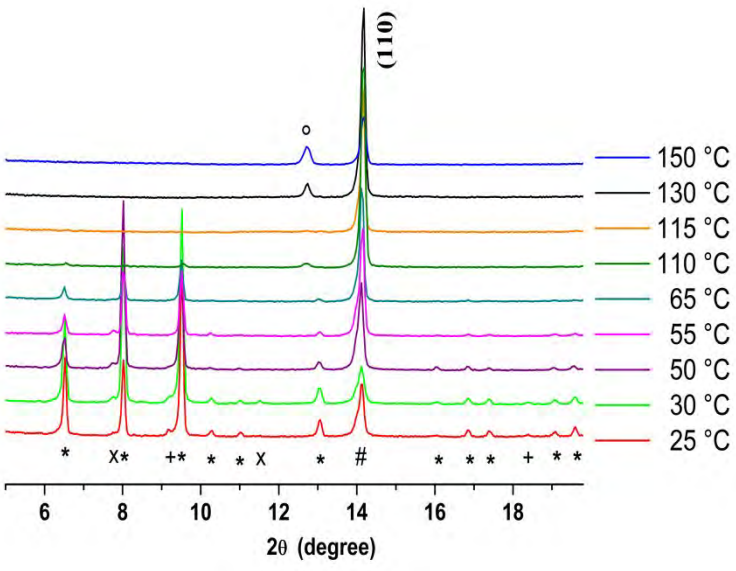


Fig. 2. X-ray diffraction pattern of films prepared with ratio 1:1 of the initial reagents PbI_2 and CH_3NH_3I with heat treatment at different temperatures. Second phases are denoted by "X" – $(CH_3NH_3)_2(DMF)_xPbI_4$, "*" – $(CH_3NH_3)_2(DMF)_2Pb_3I_8$, "+" – $(CH_3NH_3)_3(DMF)PbI_5$, "o" – PbI_2 and "#" – $CH_3NH_3PbI_3$.

X-ray diffraction patterns of the films show the peaks corresponding to $CH_3NH_3PbI_3$ (14.1 °) and second phases. In particular, peaks at 2Θ: 6.53 °, 8.04 °, 9.5 °,

10.03 °, 6.53 °, 11.06 °, 13.08 °, 16.13 °, 17.46 °, 19.18 ° and 19.68 ° (denoted in Fig. 1 as "*") correspond to the phase $(CH_3NH_3)_2(DMF)_2Pb_3I_8$ [14]. X-ray peaks at 2Θ: 7.71 ° and 11.48 ° (denoted in Fig. 2 as "X") correspond to compound $(CH_3NH_3)_2(DMF)_xPbI_4$ [14], peaks at 2Θ: 9.15 °, 16.94 ° and 18.36 ° (denoted in Fig. 2 as " +") correspond to compound - $(CH_3NH_3)_3(DMF)PbI_5$ [14], and peaks at 2Θ to 12.7° (denoted in Fig. 2 as "o") correspond to PbI_2. Thus, depending on the temperature of heat treatment, the $CH_3NH_3PbI_3$ films prepared with ratio 1:1 of the initial reagents PbI_2 and CH_3NH_3I contain three intermediate phases.

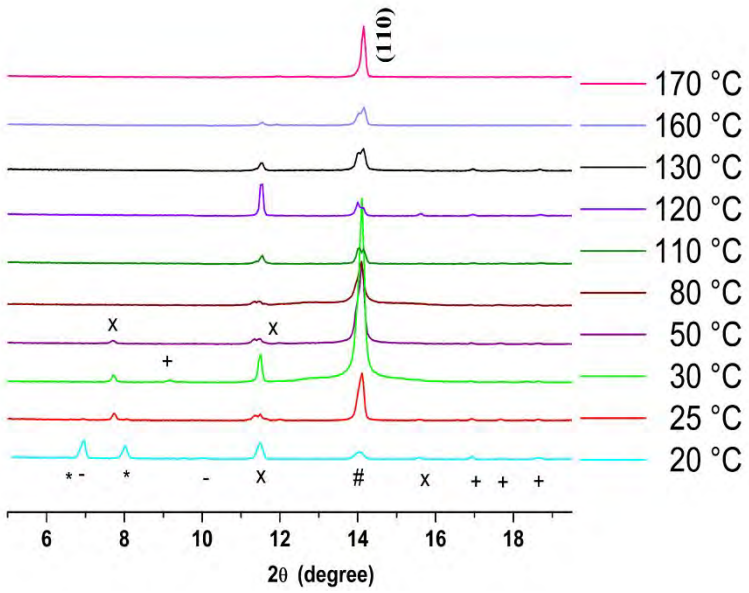


Fig. 3. X-ray diffraction pattern of films prepared with the ratio 1:2 of the initial reagents PbI_2 and CH_3NH_3I with heat treatment at different temperatures. Second phases are denoted by "X" – $(CH_3NH_3)_2(DMF)_xPbI_4$, "*" – $(CH_3NH_3)_2(DMF)_2Pb_3I_8$, "+" – $(CH_3NH_3)_3(DMF)PbI_5$, "-" – $(CH_3NH_3)_2(DMF)_2Pb_2I_6$ and "#" – $CH_3NH_3PbI_3$.

Fig. 3 shows the results of XRD analysis of perovskite films $CH_3NH_3PbI_3$ obtained at a ratio of the initial reagents PbI_2 and CH_3NH_3I 1:2 after heat treatment in the temperature range from 20 to 170 °C. The analysis of the X-ray diffraction pattern of films shows that in addition to peaks of the perovskite phase (14.1°), the peaks of other intermediate compounds are present. In particular, peaks at 7.71 °, 11.35 °, 11.48 °, 12 °, and 15.59 ° indicate the formation of the intermediate compound of $(CH_3NH_3)_2PbI_4$ or $(CH_3NH_2)_2(DMF)_xPbI_4$. Peaks with 2Θ: 9.16 °, 16.94 °, 17.75 °, and 18.66 ° indicate the formation of compound $(CH_3NH_3)_3(DMF)PbI_5$; with 2θ: 6.94° and 10.1° for the

formation of $(CH_3NH_3)_2(DMF)_2Pb_2I_6$ and with 2Θ: 6.53° and 8.04° for the formation of $((CH_3NH_3)_2(DMF)_2Pb_2I_8$ compounds.

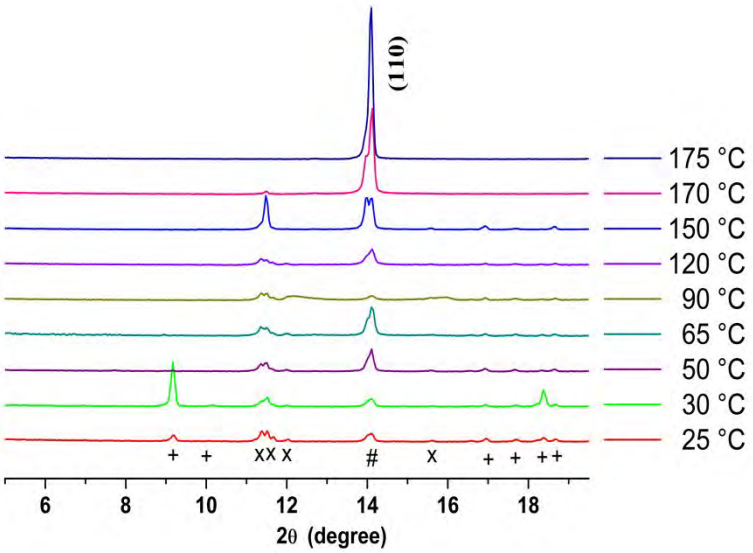


Fig. 4. X-ray diffraction pattern of films prepared with the ratio 1:3 of the starting reagents PbI_2 and CH_3NH_3I with heat treatment at different temperatures. The second phases are denoted by "X" – $(CH_3NH_3)_2(DMF)_xPbI_4$, "+" – $(CH_3NH_3)_3(DMF)PbI_5$ and "#" – $CH_3NH_3PbI_3$.

Fig. 4 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. Intense peaks of perovskite phase (14.1°) and peaks from other intermediate phases are observed. In particular, peaks at 2Θ angles: 7.71 °, 11.35 °, 11.48 °, 11.64 °, 12 °, and 15.59 ° can be attributed to the intermediate phase $(CH_3NH_3)_2(DMF)_xPbI_4$, at 2Θ angles: 9.16 °, 10.1 °, 16.94 °, 17.75 °, 18.36 °, and 18.66 ° to $(CH_3NH_3)_3(DMF)PbI_5$, and peaks at 2Θ angles: 6.94 ° and 10.1 ° to the intermediate phase $(CH_3NH_3)_2(DMF)_2Pb_2I_6$.

To clarify the temperature ranges of the formation of the intermediate compounds in the synthesized films Raman spectroscopy was used. It should be noted that the interaction 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 the films. The latter, like PL, interfere with the recording of Raman spectra of perovskite films

[22,23]. In the presence of intense PL, it is not possible at all to register the Raman spectrum from 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 [24,25]. However, if the film consists of several compounds, it is difficult to consider all of these factors. That is why the change in the film composition may not result in the appearance/disappearance of Raman bands of a particular compound. In this case, the spectrum is changing as a whole due to the overlapping of 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 the temperature of the heat treatment.

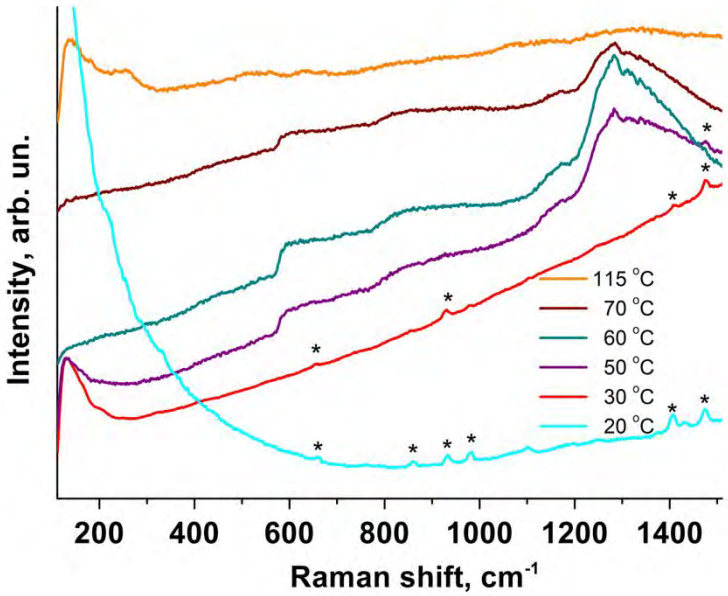


Fig. 5. Raman spectra of films prepared at the ratio 1:1 of initial reagents PbI_2 and CH_3NH_3I and heat treatment at different temperatures. DMF bands denoted by asterisks.

Fig. 5 shows the Raman spectra of the synthesized films prepared at ratio 1:1 of the initial reagents PbI_2 and CH_3NH_3I after heat treatment at different temperatures. The Raman spectrum of a film formed at 20 °C contains intense bands from $CH_3NH_3PbI_3$ perovskite in the low-frequency region (~135 cm^{-1}) and narrow bands from DMF solvent (the most intense are ~930 and ~1475 cm^{-1}). Increasing the temperature of the film heat treatment to 30°C leads to the emergence of intense photoluminescence (PL), which

arises most likely due to the increase in the fraction of the perovskite phase in the film. In this case, all DMF bands in the Raman spectrum of the film remain. At 50 – 60 °C, the contribution from DMF in the Raman spectra of films decreases and disappear above 60 °C. At 50-70 °C, broad bands appear in the spectra at 620, 870, and 1280 cm^{-1}. These bands are possibly due to the formation of compound $(CH_3NH_3)_2(DMF)_xPbI_4$. Above 70 °C, these features in the spectrum decrease, and the intensity of the perovskite bands (low-frequency region ~135 cm^{-1}) increase.

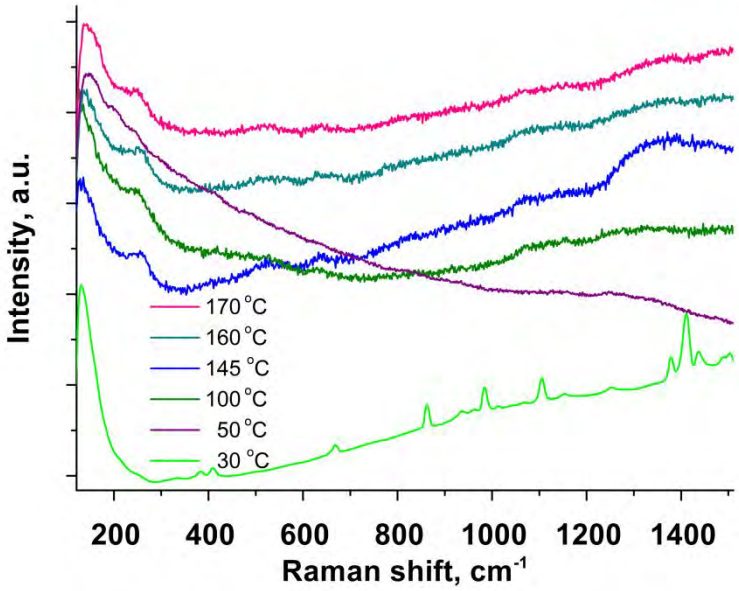


Fig. 6. Raman spectra of films prepared at the ratio 1:2 of initial reagents PbI_2 and CH_3NH_3I and heat-treated at different temperatures.

Fig. 6 shows the Raman spectra of the films prepared at a ratio 1:2 of the initial reagents PbI_2 and CH_3NH_3I and heat treated at different temperatures. For the films prepared at 30 °C, bands characteristic of perovskite $CH_3NH_3PbI_3$ and DMF appear in the spectrum. Increasing the heat treatment temperature to 50 °C leads to significant changes in the spectrum. The low-frequency bands characteristic of perovskite remain, however, the DMF bands disappear and a wide band in the region of 1300 cm^{-1}, referred to $(CH_3NH_3)_2(DMF)_xPbI_4$, appears. The absence of the DMF band in the spectrum does not indicate that there is no solvent at all in the film. DMF bands may not appear in the spectrum against the background of more intense scattering from other structural units of the intermediate compounds. Increasing the temperature of the film heat treatment to 100 °C and above leads to an increase in the bands intensity of $CH_3NH_3)_2(DMF)_xPbI_4$ and

$CH_3NH_3PbI_3$. In addition, intense PL is observed due to a significant percentage of perovskite in the prepared films.

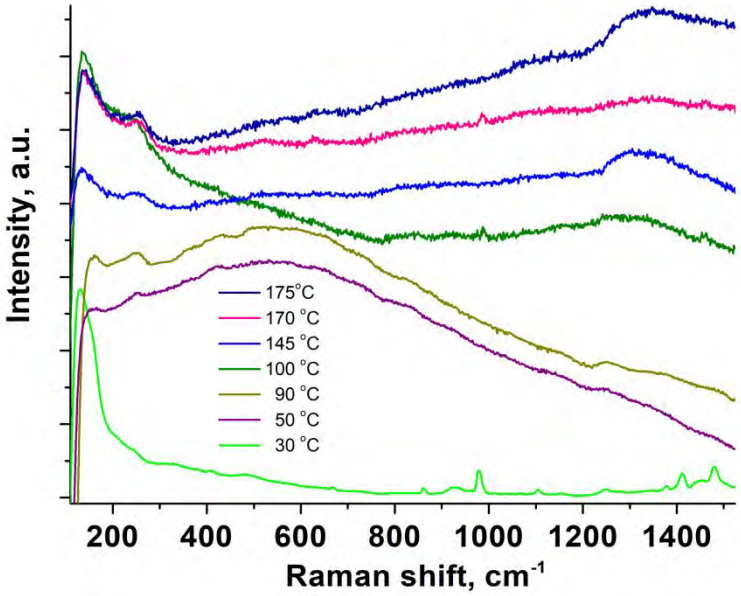
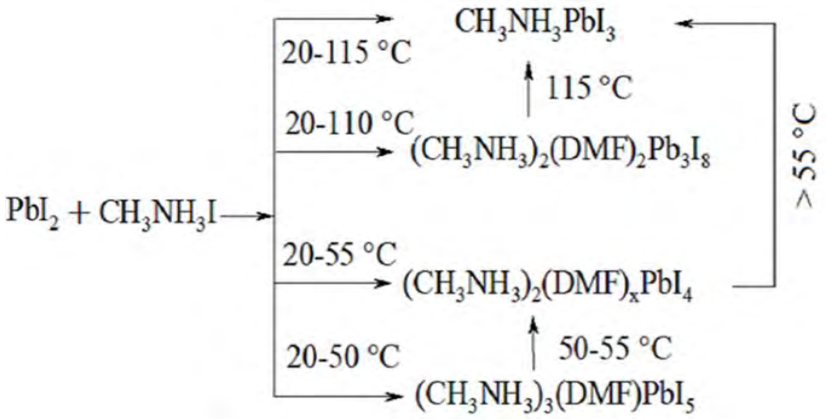


Fig. 7. The Raman spectra of films prepared at the ratio 1:3 of initial reagents PbI_2 and CH_3NH_3I and heat-treated at different temperatures.

Fig. 7 shows the Raman spectra of films prepared at the ratio 1:3 of initial reagents PbI_2 and CH_3NH_3I and the variation of the heat treatment temperature from 30 to 175 °C. The low-frequency bands characteristic of perovskite $CH_3NH_3PbI_3$ and DMF appeared in Raman spectra at heat treatment temperatures in the range of 20 to 50 °C. At 50–90 °C, the spectra of films show low-frequency bands of perovskite $CH_3NH_3PbI_3$ and a broad band with a maximum of 600 cm^{-1} of $(CH_3NH_3)_3(DMF)PbI_5$. At 100–170 °C, Raman spectra of the films contain bands from $CH_3NH_3PbI_3$ and $(CH_3NH_3)_2(DMF)_xPbI_4$. For all films prepared at temperatures above 100 °C PL is observed. With increasing heat treatment temperature above 170 °C, DMF bands in the spectra are no longer visible.

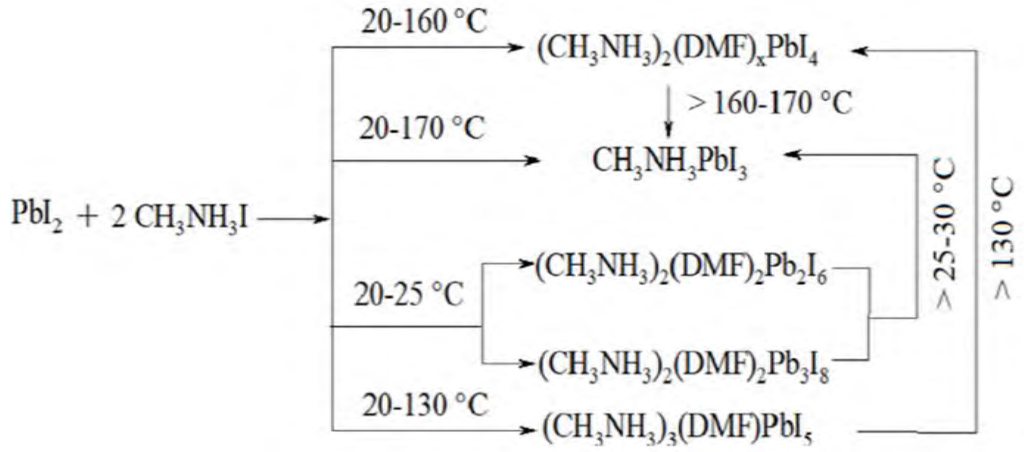
XRD and Raman spectroscopy data allows the reaction schemes of the formation of perovskite $CH_3NH_3PbI_3$ and intermediate compounds at different ratios of initial reagents PbI_2 and CH_3NH_3I to be recorded.

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



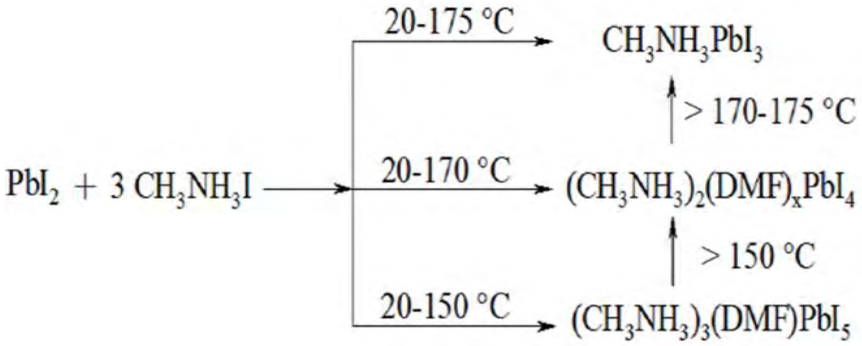
The intermediate phases in this case are $(CH_3NH_3)_2(DMF)_2Pb_3I_8$, $(CH_3NH_3)_2(DMF)_xPbI_4$ and $(CH_3NH_3)_3(DMF)PbI_5$.

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



In this case, among the intermediate phases, in addition to $(CH_3NH_3)_2(DMF)_2Pb_3I_8$, $(CH_3NH_3)_2(DMF)_xPbI_4$ and $(CH_3NH_3)_3(DMF)PbI_5$, the phase $(CH_3NH_3)_2(DMF)_2Pb_2I_6$ is additionally observed.

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



The intermediate phases in this case are only $(CH_3NH_3)_2(DMF)_xPbI_4$ and $(CH_3NH_3)_3(DMF)PbI_5$.

At 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 their conversion sequence in the perovskite depends on their properties. The difference in temperature stability can be shown based on the enthalpies of intermediate compounds formation (Table 2). Compound $(CH_3NH_3)_2(DMF)_2Pb_3I_8$ is the most stable at the ratio 1:1 of the initial components of PbI_2 and CH_3NH_3I. Increasing the ratio of the initial reagents decreases the temperature of interval of the existence of this compound. In contrast to $(CH_3NH_3)_2(DMF)_2Pb_3I_8$, the temperature interval of existence of low-stable compound $(CH_3NH_3)_3(DMF)PbI_5$ is increased with an increase in CH_3NH_3I amount (Table 2).

Table 2. 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		
		1:1	1:2	1:3
$(CH_3NH_3)_2(DMF)_2Pb_3I_8$	-180.1	20-110 °C	20-25 °C	–
$(CH_3NH_3)_2(DMF)_2Pb_2I_6$	-177.6	–	20-25 °C	–
$(CH_3NH_3)_3(DMF)PbI_5$	-133.8	20-50 °C	20-130 °C	20-150 °C
$(CH_3NH_3)_2(DMF)_xPbI_4$	–	20-55 °C	20-160 °C	20-170 °C

XRD shows that $CH_3NH_3PbI_3$ films prepared on glass substrates at different ratios of the initial reagents PbI_2 and CH_3NH_3I 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 portion of perovskite and, on the other hand, can contribute to its stability both under the intense solar radiation and the surrounding atmosphere. Raman spectroscopy confirms the formation of the intermediate

compounds and clarifies the temperature intervals of their existence. The ratio of the initial reagents and the temperature of the 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 the films, the processes of their degradation and the solar-to-electricity conversion efficiency.

Conclusions

The formation of $CH_3NH_3PbI_3$ perovskite films at different ratios (1:1, 1:2 and 1:3) of the initial reagents PbI_2 and CH_3NH_3I dissolved in the DMF and after heat treatment at different temperatures from 20 to 175 °C were 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 characteristic structures of the 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 heat treatment temperature of the 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 1:1, 1:2 or 1:3, respectively. The intermediate phases $(CH_3NH_3)_2(DMF)_xPbI_4$, $(CH_3NH_3)_3(DMF)PbI_5$, $(CH_3NH_3)_2(DMF)_2Pb_2I_6$ and $(CH_3NH_3)_2(DMF)_2Pb_3I_8$ in the films were found. The presence of intermediate compounds can significantly affect the degradation of films and the efficiency of converting solar energy into electrical energy.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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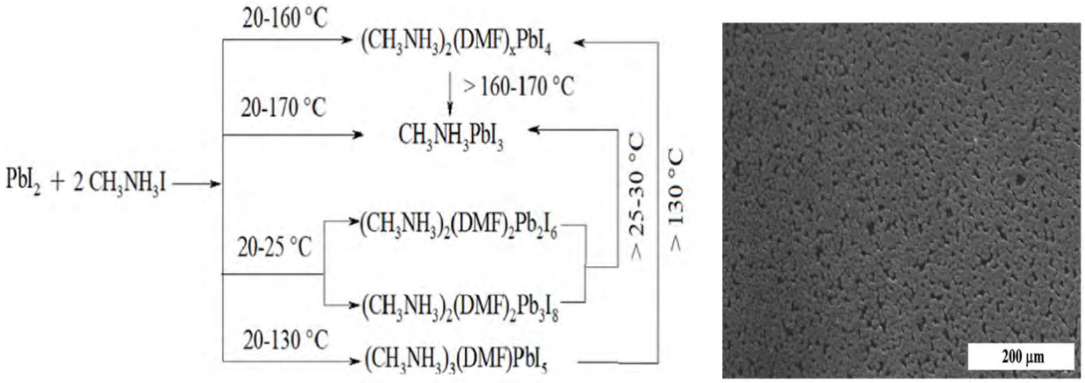
Table of Content



The formation processes of perovskite films $CH_3NH_3PbI_3$ at different ratios (1:1, 1:2 and 1:3) of the initial reagents PbI_2 and CH_3NH_3I in DMF solvent have been investigated. The intermediate compounds determine the morphology of the films and can affect the processes of their degradation and the solar-to-electricity conversion efficiency.