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INVESTIGATION OF MICROSTRUCTURE AND SPECTRAL LUMINESCENCE PROPERTIES OF PEROVSKITE FILMS $CH_3NH_3PbI_3$

Ibrayev N.Kh., Afanasyev D.A., Mirzoev K.Yu., Smagulov G.K.

Institute of Molecular Nanophotonics, E.A. Buketov Karaganda State University,
Universitetskaya Str. 28, Karaganda, 100028, Kazakhstan, a_d_afanasyev@mail.ru

Investigation of microstructure and spectral-luminescent properties perovskite films ($CH_3NH_3PbI_3$) was shown in this work. Perovskite films were made by two-step method synthesis with using the porous films of TiO_2. Microscopic measurements show that the penetration depth of $CH_3NH_3PbI_3$ film is 275 nm in TiO_2 films. Spectral-luminescent properties of $CH_3NH_3PbI_3$ films were investigated. Luminescence spectra indicate that on the surface of TiO_2 film formed $CH_3NH_3PbI_3$ films. Using of 35 μl of CH_3NH_3I solution leads to more quality perovskite films with fewer defects. The anneling temperature affects on luminescence intensity $CH_3NH_3PbI_3$ of films has been studied.

Keywords: perovskite film, luminescence, microstructure properties, microstructure.

Introduction

Investigation in field of using organic material for creating of transformers of solar energy to electrical energy has led to making of two new types of solar cells – dye-sensitized solar cells (DSC) and polymer solar cells (PSC) [1, 2]. There are different new types of solar cells, for example, elements based on semiconducting quantum dots [3] or based on low molecular organic compounds [4]. But only DSC and PSC cells can do efficiency more than 10% [5, 6]. The new type of solar cells – perovskite solar cells were obtained on fabrication technology of DSC. Perovskite solar cells based on organic-inorganic compounds $MAPbX_3$, where MA – methylammonium, X – halogen Br, I or Cl. Since 2009 till 2014 perovskite solar cells increased own efficiency from 3.8 % to 19 % [7].

Using of organic-inorganic compounds for transformation solar energy to electrical energy in solar cells proposed recently. Many properties of such materials are unknown and need further investigation. Spectral-luminescent properties of perovskite films need investigation too. Spectral-luminescent data allows determine very important parameters. There is a band gap, charge carrier lifetime etc. Understanding of these parameters and ability to manage it will speed up creating of highly effective transformers of solar energy to electrical energy based on perovskite solar cells.

In this work are given results of a study of microstructure and spectral-luminescent properties of methyl ammonium lead iodide $CH_3NH_3PbI_3$ films.

1. Experimental part

$CH_3NH_3PbI_3$ film was synthesized in porous film of titanium dioxide TiO_2. Paste based on 20 nm particles of TiO_2. Ethylene glycol as solvent used for the preparation of porous film. The paste deposited on substrate by spin coating. Concentration of TiO_2 and conditions of deposition were chosen so that the thickness of film was minimum and surface was homogeneous. The thickness of films wasn't higher than 1 μm.

Perovskite film $CH_3NH_3PbI_3$ applied by two. On the first step applied PbI_2 by spin coating. Than substrate dried with 50 °C and 100 °C. On the second step on the film applied solution of methylammonium iodide CH_3NH_3I. After that films heated with 25°C, 100°C, 150°C temperature. Microstructural properties of synthesized films explored with SEM TESCAN Mira 3.

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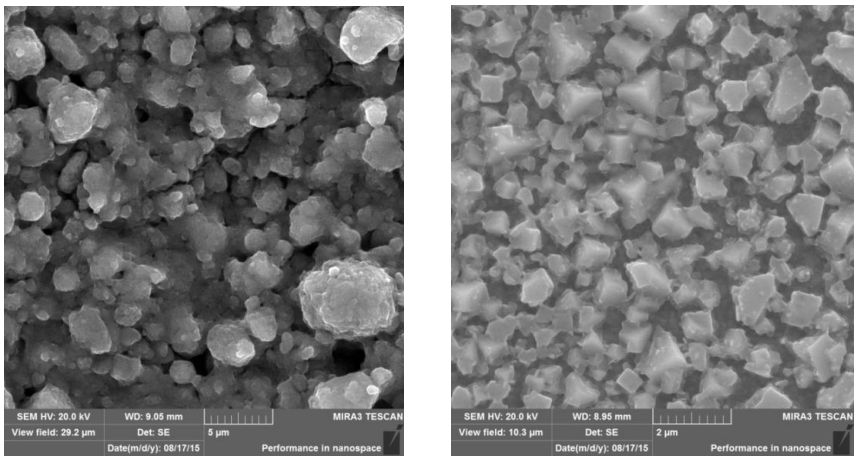
Spectrophotometer Agilent Cary 300 was used for registration of the absorption spectra of the films. The fluorescence spectra were measured on a Cary Eclipse spectro-fluorimeter of Agilent company. Kinetics of fast luminescense of films was measured using a pulsed spectro-fluorometer with picosecond resolution and registration with time-correlated photon counting mode (Becker & Hickl). Excitation of fluorescence was performed pulsed semiconductor laser with a wavelength $\lambda gen = 488$ nm with full width at half maximum of pulse $\tau = 80$ ps.

2. Results and their discussion

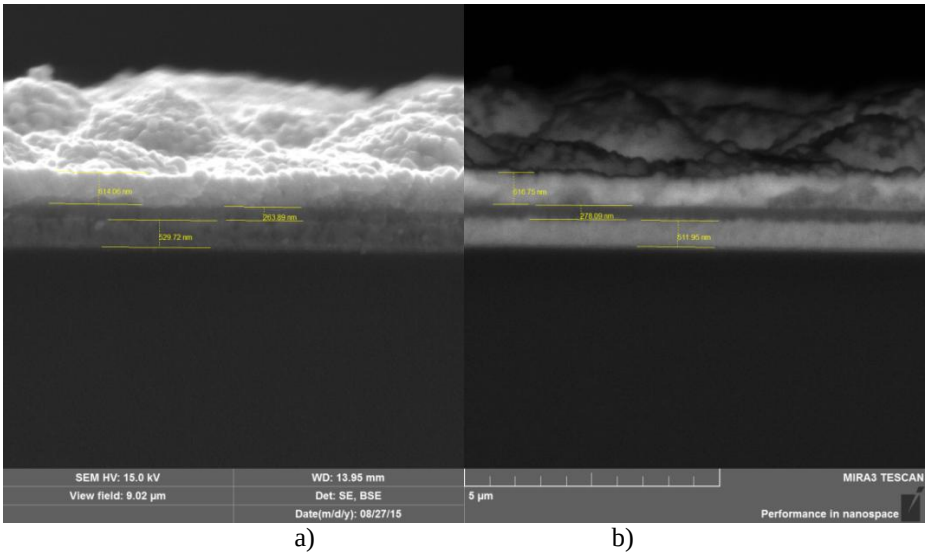
Figure 1 shows electron microscopic images of the surface of film TiO_2 (a) and $CH_3NH_3PbI_3$ perovskite film (b).



a) b)

Fig.1. An electron microscopic image of the surface of the TiO_2 film (a) and $CH_3NH_3PbI_3$ perovskite film (b)

Comparison of images in Figure 1 shows that the staged applying of PbI_2 and CH_3NH_3I on the surface of TiO_2 film formed structures different from the surface of TiO_2. However, the properties of the TiO_2 film surface greatly affect the properties of the forming film. So in CH_3NH_3I film detected formed granules perovskites. There is a great distance between grains in contrast with the data presented in [8]. Cleavage of film TiO_2-$CH_3NH_3PbI_3$ when measured in the secondary (SE) and backscattered electron (BSE) is shown in Figure 2.



a) b)

Fig. 2. Split of TiO_2 film - $CH_3NH_3PbI_3$ registering the signal from the secondary electron detector (a) and backscattered electrons (b)

Absence of differences of microscopic data in the SE and BSE measurement modes indicate the uniformity of TiO_2 and $CH_3NH_3PbI_3$ films. The figure 2 shows that for TiO_2- $CH_3NH_3PbI_3$ structures occur formation of 3-layer film. The lower layer film is a porous film of TiO_2. It has thickness is about 510 nm. The higher film is $CH_3NH_3PbI_3$ with different thickness (maximum 610 nm). Between the films TiO_2 and $CH_3NH_3PbI_3$ has porous transition layer with TiO_2 formed $CH_3NH_3PbI_3$ film in it. The thickness of the transition layer is about 260-275 nm. From these microscopic data, we can say that with this method of synthesis $CH_3NH_3PbI_3$ film depth of its penetration into the pores of TiO_2 does not exceeding 275 nm. So for creating of perovskite solar cell need formation of film TiO_2 with thickness not higher than 250 nm.

Absorption spectra of $CH_3NH_3PbI_3$ films are shown on figure 3. For comparison, the figure shows the absorption spectra of the PbI_2 films and $CH_3NH_3PbI_3$ film, obtained by using different amounts CH_3NH_3I reagent. Analysis of the data shows that the absorption spectrum of PbI_2 film differs from the absorption spectrum $CH_3NH_3PbI_3$ film. Thus, in a second step, adding CH_3NH_3I leads to formation of $CH_3NH_3PbI_3$ film. In this case 20 μl of CH_3NH_3I solution allows to obtain a film with higher optical density than using 35 μl solution.

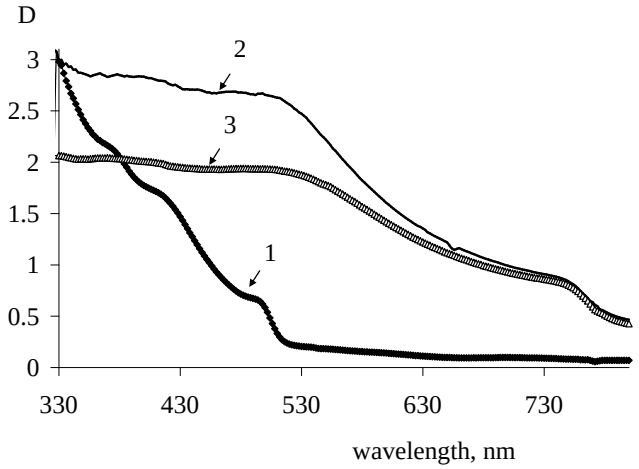


Fig.3.The absorption spectrum of the film PbI_2 (1) and films $CH_3NH_3PbI_3$ synthesized by adding 20 (2) and 35 (3) μl CH_3NH_3I solution

Thermal heating of films was made after the two-step synthesis. Effect of thermal heating on the absorption spectra of the films $CH_3NH_3PbI_3$ was studied in our work. Absorption specters were measured with 50 °C, 100 °C, 150 °C.

$CH_3NH_3PbI_3$ absorption spectra of the films obtained by applying different amounts CH_3NH_3I solution are shown in Figure 4. Figure 4 shows that the thermal annealing differently affect the films obtained by using different volumes of CH_3NH_3I solution. A shift of the absorption edge of the spectrum is observed for thermal heating of film with using of 20 μl CH_3NH_3I. Increase of the optical density in maximum absorption (350-550 nm) of the film is observed for thermal heating of film with using of 35 μl CH_3NH_3I.

The absorption spectra of $CH_3NH_3PbI_3$ films were used for the determination of the band gap (Eg) perovskite films. Figure 5 and Table 1 shows the results of determination Eg depending on the volume of CH_3NH_3I solution and annealing temperature. The value of Eg for $CH_3NH_3PbI_3$ films correlated with literature data [9]. Analysis of the data in Table 1 shows that different heating affects the width of the forbidden zone $CH_3NH_3PbI_3$ films obtained by using different volumes of CH_3NH_3I solution. The increase in the value of Eg for the film with 35 μl of CH_3NH_3I point out a decrease in film defects with increasing heating temperature. Incomplete transformation of PbI_2 in $CH_3NH_3PbI_3$ films take place probably in the case changing of Eg value with increasing heating

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temperature for film with 20 microliters of CH_3NH_3I solution. Even with the increasing of the heating temperature does not occur on reduction of defects in this film. CH_3NH_3I solution is used necessary to obtain better films of $CH_3NH_3PbI_3$.

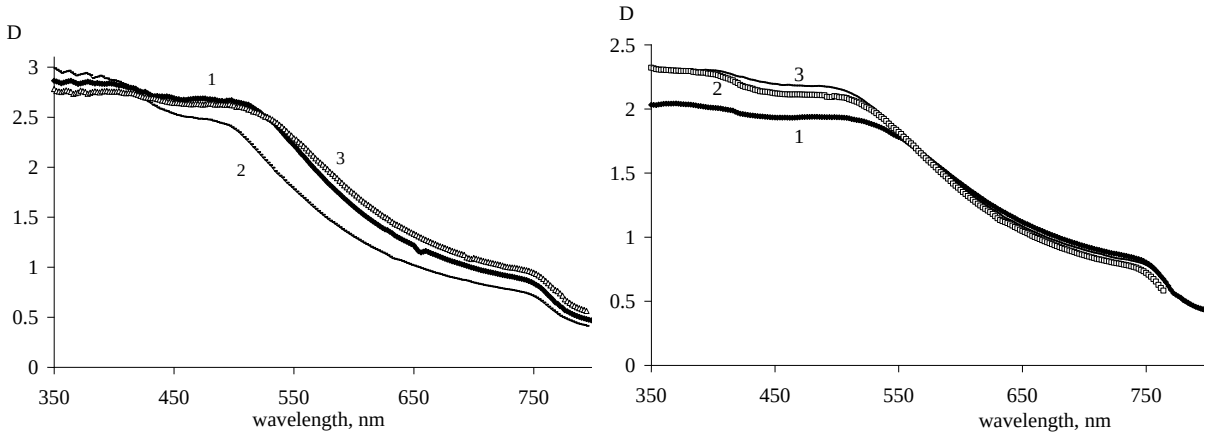

Fig.4. Effects of thermal annealing on the absorption spectra of $CH_3NH_3PbI_3$ films with 20 (a) and 35 (b) μl of CH_3NH_3I solution. Annealing temperature: 1 - 50 ° C; 2- 100 ° C; 3 - 150 ° C

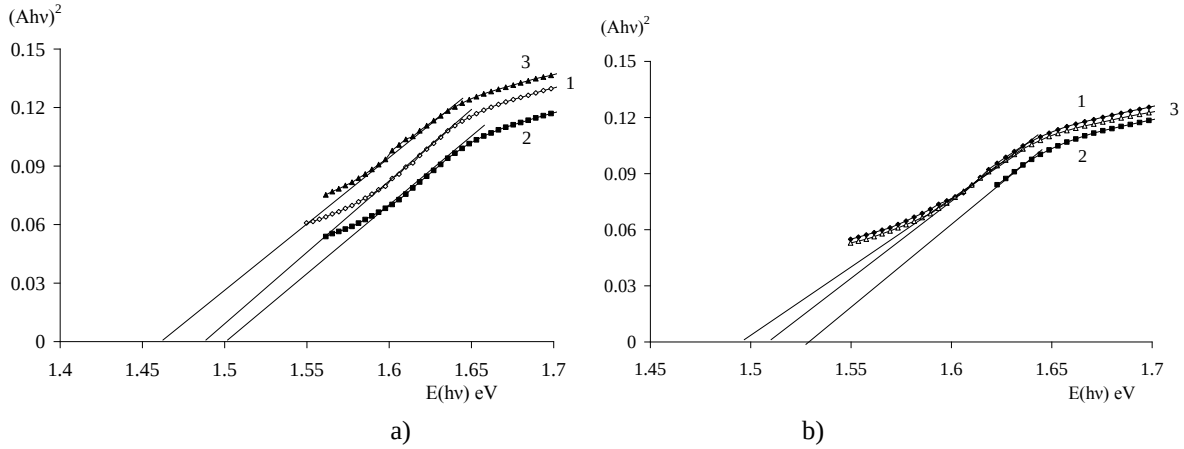

Fig.5. The spectral dependence of the optical absorption edge for $CH_3NH_3PbI_3$ films with 20 (a) and 35 (b) μl of CH_3NH_3I solution and annealing temperature: 1 - 50 ° C; 2 - 100 ° C; 3 - 150 ° C

Table 1 - Effect of thermal heating on the value of the band gap of $CH_3NH_3PbI_3$ films

Annealing temperature (°C)	Band gap of (eV) film $CH_3NH_3PbI_3$ (eV) (20 μl CH_3NH_3I)	Band gap of film $CH_3NH_3PbI_3$ (eV) (35 μl CH_3NH_3I)
50	1.48	1.50
100	1.50	1.51
150	1.46	1.53

The luminescence spectra of $CH_3NH_3PbI_3$ films measured after measurement and analysis of the absorption spectra. Figure 6 shows the spectrum of the luminescence of $CH_3NH_3PbI_3$ films depending on using of the volume of CH_3NH_3I solution. The resulting luminescence spectra correspond with spectra shown in [9, 10]. The luminescence intensity of $CH_3NH_3PbI_3$ films

increases with increasing of volume of CH_3NH_3I solution. The maximum of the luminescence intensity of $CH_3NH_3PbI_3$ obtained by using 35 µl of CH_3NH_3I solution.

Thermal heating of $CH_3NH_3PbI_3$ films obtained by using different volumes of CH_3NH_3I solution also leads to a change in the fluorescence intensity of the spectra (Figure 7). Form of fluorescence spectra of films $CH_3NH_3PbI_3$ under heating doesn't change. Reduction of intensity of luminescence spectra was with increase heating temperature for $CH_3NH_3PbI_3$ film with 35 µl of CH_3NH_3I solution. As is well known [11], intensity of luminescence is higher in perovskite films with a lot of defects. Thus, a decrease in the luminescence intensity in these films indicates a decrease in defects of $CH_3NH_3PbI_3$ structure. Increasing of heating temperature leads to initially increasing fluorescence intensity then decreasing of fluorescence intensity of $CH_3NH_3PbI_3$ film (20 µl). One of the possible reasons for these changes may be considerable structural defects of synthesized $CH_3NH_3PbI_3$ film.

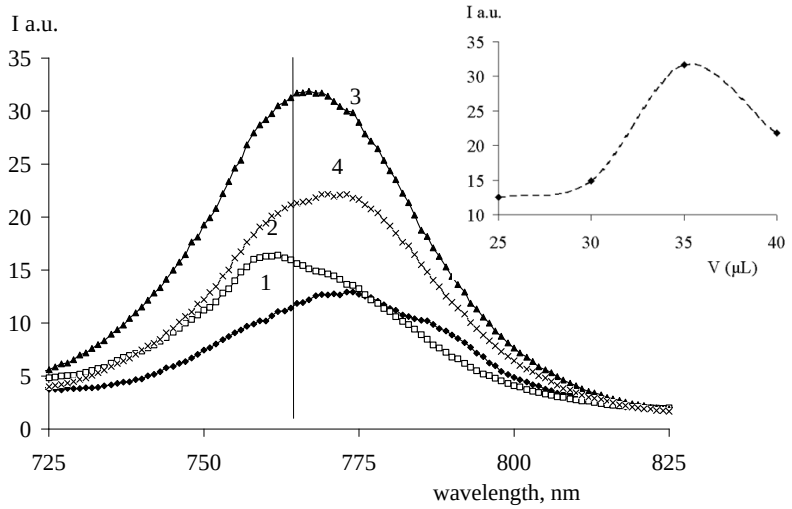

Fig.6. The luminescence spectra of $CH_3NH_3PbI_3$ films depending on the volume of CH_3NH_3I solution: 1 - 25 µl; 2 - 30 µl; 3 - 35 µl; 4 - 40 µl. The inset shows the dependence of the luminescence intensity on the concentration of the solution CH_3NH_3I at λ_{REG} = 770 nm.

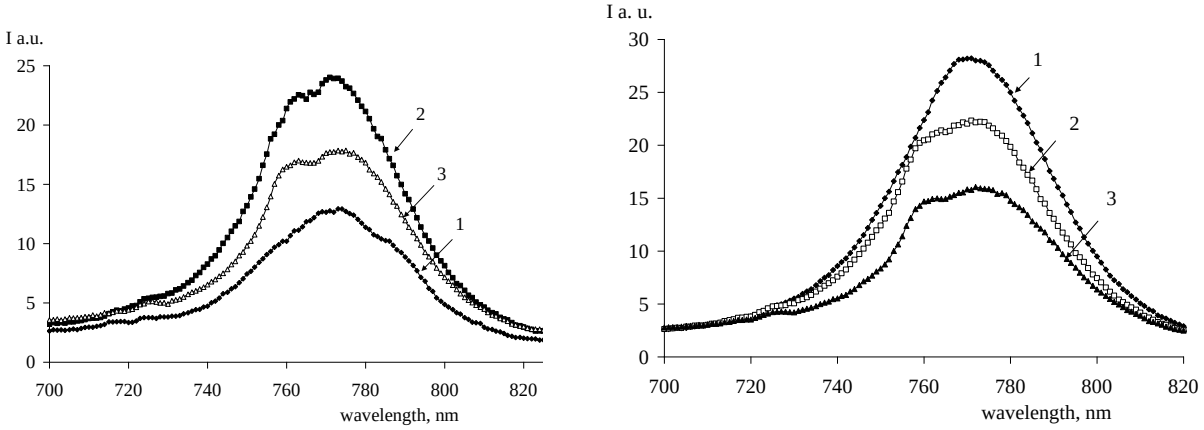

Fig.7. Fluorescence spectrum of $CH_3NH_3PbI_3$ films with 20 µl (a) and 35 µl (b) of CH_3NH_3I solution. Annealing temperature: 1 - 50 ° C; 2- 100 ° C; 3 - 150 ° C

The kinetics of luminescence perovskite films investigated in the nanosecond time range. Example of fluorescence kinetics shown in Figure 8. We studied the effect of time of registration on the time of the luminescence life. We made measurements immediately after synthesis and with an interval of 24 hours during the week. These results show that major changes in the luminescence lifetime occurs after 1 day after the measurement. Time stability luminescence of perovskite films studied. Measuring of the luminescence lifetime (τ_{lum}.) right after the synthesis and further at intervals of 24 hours. These studies have shown that the major changes in the luminescence lifetime τ_{lum}. occur through 1 day after the synthesis. Lifetime of perovskite films decreased by 15% compared with the lifetime, measured immediately after synthesis of films.

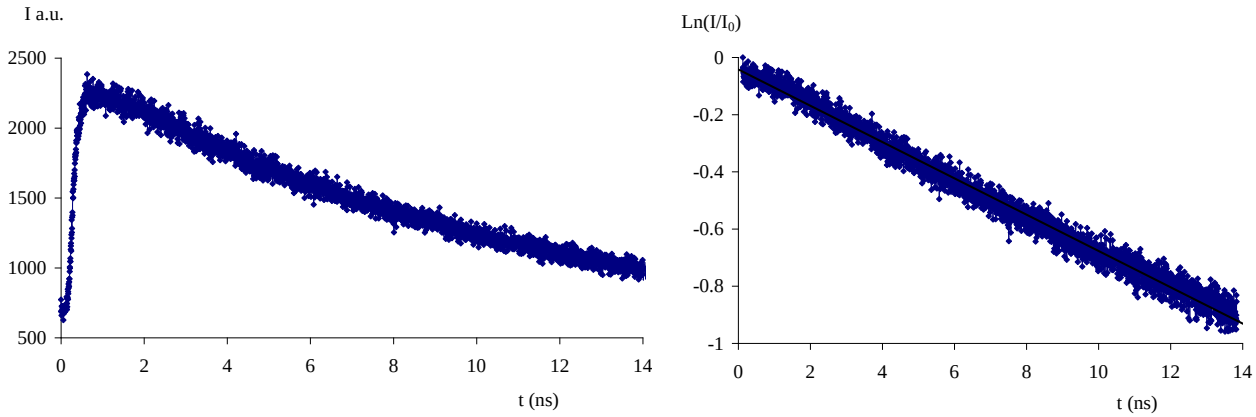

Fig.8. Kinetics luminescence of MAPbI3 film (τ = 15.7 ns)

Conclusions

According to the results of the investigation, we can do some conclusions. The technology of synthesis of perovskite films ($CH_3NH_3PbI_3$) by two-step method synthesis with using the porous films of TiO_2 was perfected. Microscopic measurements show that the penetration depth of $CH_3NH_3PbI_3$ film is 275 nm. Therefore, for the fabrication of perovskite solar cells need TiO_2 film with a thickness less than 250 nm. Spectral-luminescent properties of $CH_3NH_3PbI_3$ films were investigated. Detected, that for need to using of 35 μl of CH_3NH_3I solution leads to more quality perovskite films with fewer defects. Luminescence spectra also indicate that on the surface of TiO_2 film formed $CH_3NH_3PbI_3$ films. The anneling temperature effects on luminescence intensity of $CH_3NH_3PbI_3$ films has been studied.

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