3BV.1.29. SYNTHESIS OF PEROVSKITE FILMS FOR PHOTOVOLTAICS: INFLUENCE OF THE REAGENTS' RATIO ON THE MATERIAL PROPERTIES

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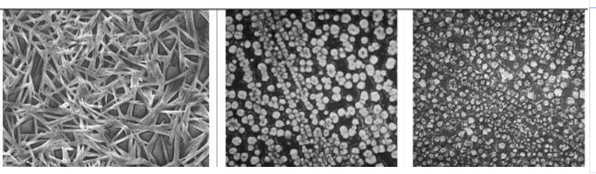
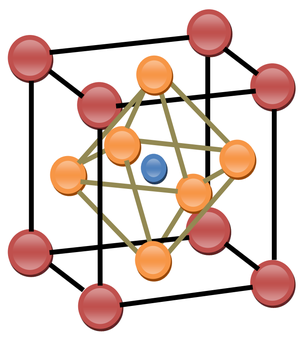


Typical perovskite structure

The general formula is ABX_3

where X (X = F, Cl, Br, I) is an anion, and A and B are cations of different sizes (A is larger than B). Cation A is mainly methylammonium ($CH3NH3^+$), and B is Pb or Sn.



$CH_3NH_3PbI_{2.98}Cl_{0.02}$

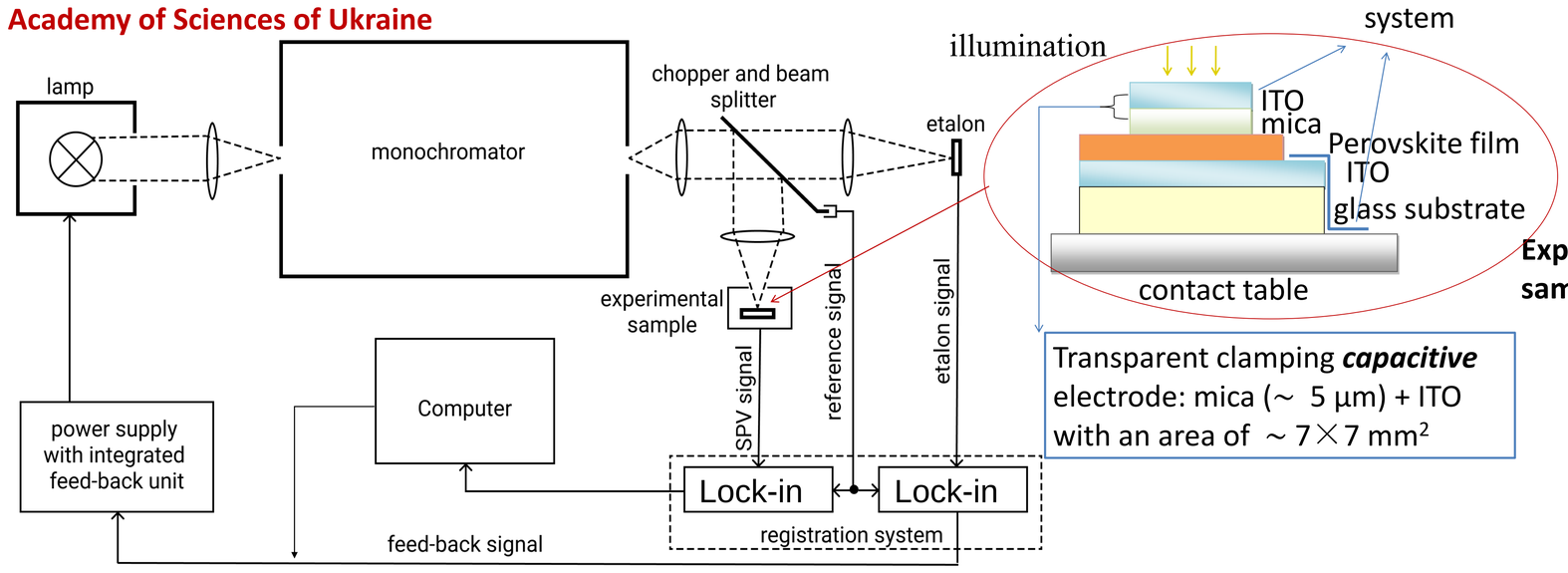
($CH3NH3^+$) Cl, I Pb

- Perovskite solar cells (SCs) have recently emerged as a promising candidate for the next generation thin film photo-voltaics (PV) (see, e.g., [1]).
- The perovskites advantages are due to a suitable direct bandgap with large absorption coefficients, and solution based fabrication process.

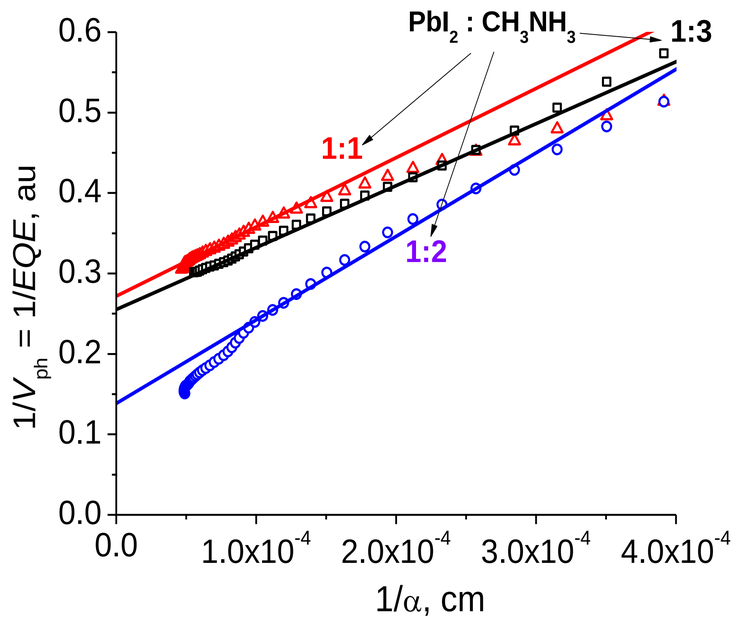
1. I. Braly, D. de Quilettes, et al. "Hybrid perovskite films approaching the radiative limit with over 90% photoluminescence quantum efficiency",Nature Photonics **12** (2018) 355

Schematic of the experimental set-up for surface photovoltage (SPV) measurement

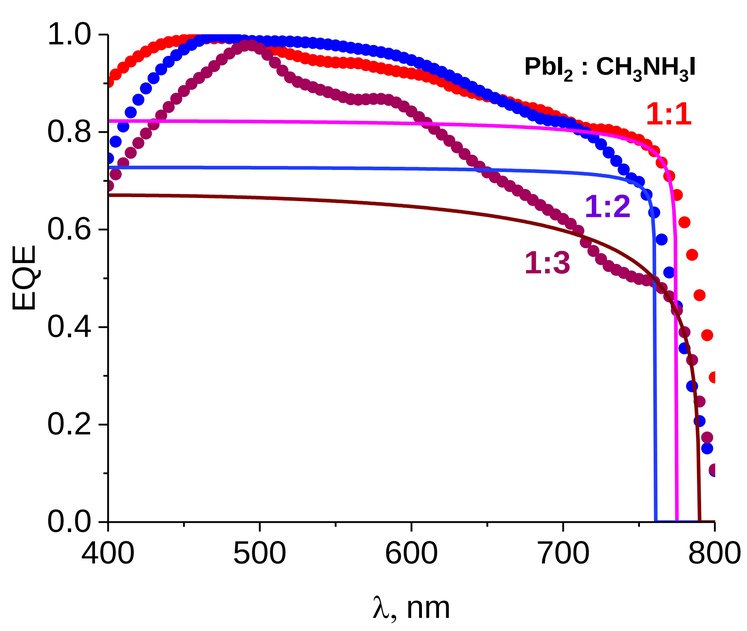
Spectral measurements were performed at the certified Testing Center for Photoconverters and Photovoltaic Batteries of the V.E.Laskaryov Institute of Semiconductor Physics National Academy of Sciences of Ukraine



Transparent clamping ***capacitive*** electrode: mica (~ 5 μm) + ITO with an area of ~ 7×7 mm²



Experimental dependencies of V_{ph}^{-1} on α^{-1} for the films with different ratio of precursors



Experimental (points) and theoretical (lines) spectra of the normalized low-signal surface photovoltage.

In **profiled surface** case, the cutoff length $1/\alpha$ equals $L_{ph} = 4n_r^2 d/b$ - the mean path length L_{ph} of the long- wavelength photon before its photoactive absorption

If the cut-off significantly exceeds the sample thickness, this indicates on a longer diffusion length of the minority carriers compared to the sample thickness. When this length significantly exceeds the sample thickness, we have to use expression for the **textured surface** $V_{ph}(\lambda)/V_{phmax}(\lambda)=EQE(\lambda)=[1+b/4\alpha(\lambda)\cdot d\cdot(n_r(\lambda))^2]^{-1}$

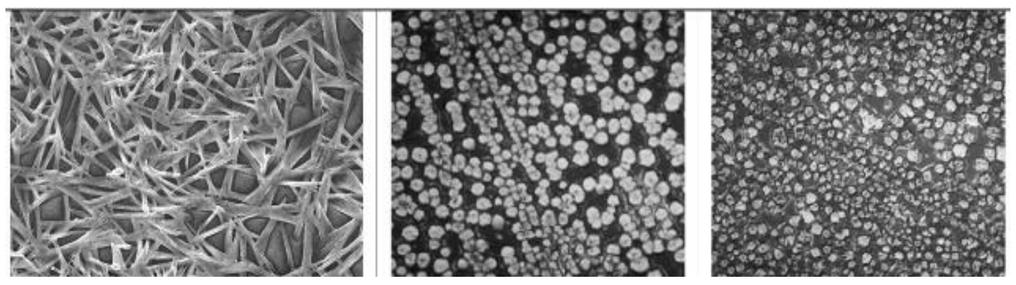
$b>1$ is a non-dimensional parameter equal to the ratio of the longest photon path length possible, $4n_r^2 d$ at ideal Lambertian light trapping to its real value

Parameters of films (thickness d = 400nm)

PbI_2:CH_3NH_3I	E_g, eV	E_0, meV	$\alpha_{ur0}\cdot10^4$, cm^{-1}	Cut-off values $1/\alpha$, μm
1:1	1.59	18	4.5	4.415
1:2	1.62	19	1.6	1.19
1:3	1.57	22	3.6	4.75

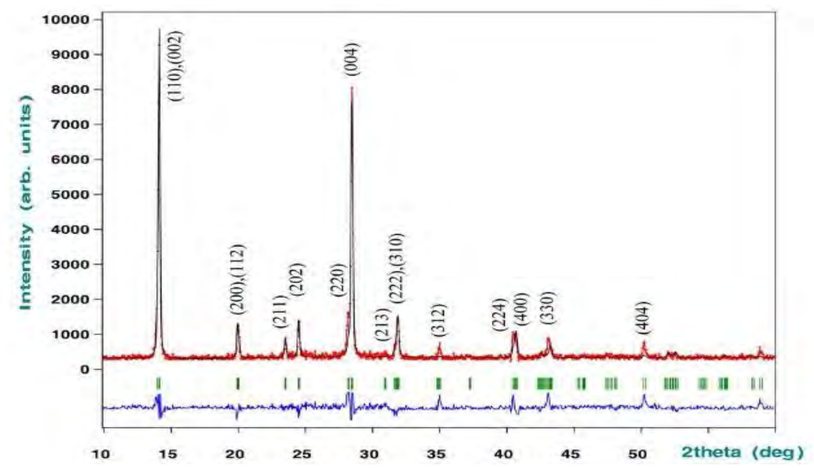
Microstructure of the $CH_3NH_3PbI_{2.98}Cl_{0.02}$ films with PbI_2 and CH_3NH_3I ratios equal to 1:1, 1:2, and 1:3

(a) 1:1; (b) 1:2; (c) 1:3



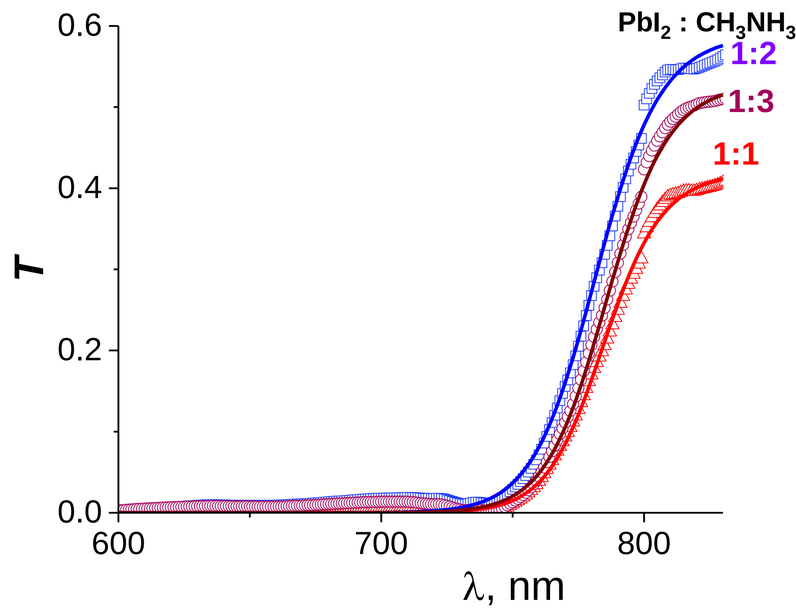
Lattice parameters of $CH_3NH_3PbI_{2.98}Cl_{0.02}$:
a = 0.8870(2) Å,
c = 1.2669 (8) Å,
V = 0.9968(7) Å^3

Experimental (symbols) and theoretical (curves) X-ray diffractograms of a $CH_3NH_3PbI_{2.98}Cl_{0.02}$ sample after the thermal processing at 90°C. The vertical lines indicate peak locations, with Miller indices given in the brackets.

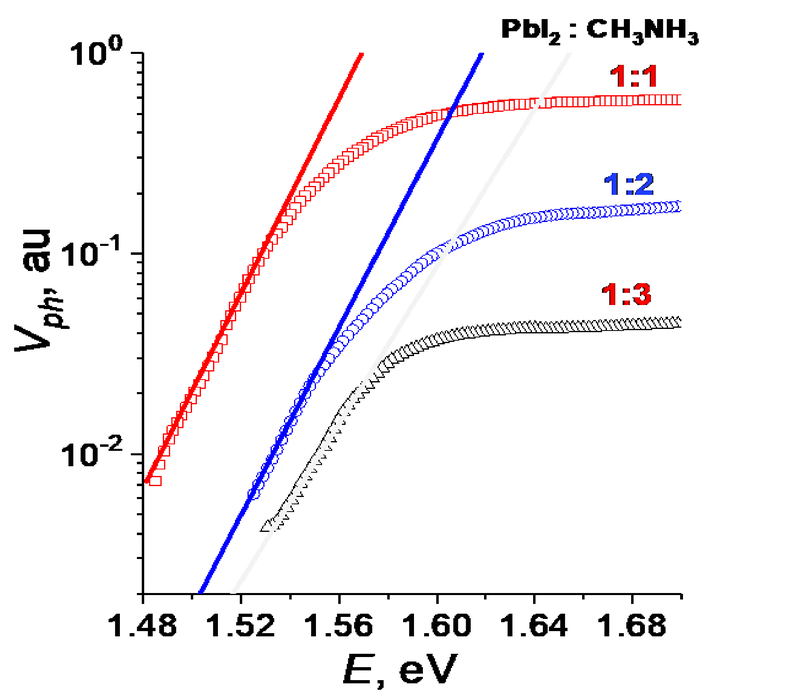


Features:

-- low-signal surface photovoltage $V_{ph}(\lambda)<<kT/q$
--constant photons flux of the monochromatic light
-- wavelength range $\Delta\lambda$ = 400 ÷ 900 nm
-- modulation frequency of 20 Hz
-- $V_{ph}(\lambda)$ did not exceed 40 μV



Experimental (symbols) and theoretical (lines) spectral dependencies of the samples' transmission for different ratios of the precursors for perovskites with PbI_2 and CH_3NH_3I ratios of 1:1, 1:2 and 1:3.



Urbach parameters determination. Experimental surface photovoltage $V_{ph}(E)$ spectra for the synthesized $CH_3NH_3PbI_{0.98}Cl_{0.02}$ films (points). Lines: theory, calculated using equation $\alpha_{ur} = \alpha_{ur0}\exp(E_{ph}/E_0)$

Conclusions

- The microstructure of perovskite films depends significantly on on the ratio of PbI_2:CH_3NH_3I precursors despite the fact that the elemental composition of the perovskite film remains stoichiometric.
- For the ratio of precursors 1:1, the structure is needle-shaped. At a ratio of 1:2, the films consist of faceted crystallites in an amorphous matrix, and contain smaller crystallites at the 1:3 ratio.
- This leads to the surface microrelief appea-rance, which improves the light capture in the long-wavelength spectral region.
- The best capture is achieved in the films with a precursors ratio of 1:1, and the worst at 1:2.
- The perovskite films' bandgap depends on the precursors ratio. It equals to 1.59 eV; 1.62 eV and 1.57 eV for the films with PbI_2 to CH_3NH_3I ratio of 1:1, 1:2 and 1:3, respectively.
- The films investigated have longer diffusion length of the minority charge carriers as compared to the films thickness and are promising for applications in photovoltaics and optoelectronics.
- The low-signal surface photovoltage $V_{ph}(\lambda)$ decrea-ses with increasing the proportion of CH_3NH_3I from 1 to 3 during the synthesis of the films.
- The $V_{ph}(\lambda)$ values are 8.1μV at (1:1), 0.96 μV at (1:2) and 0.41 μV at (1:3), which indicates on decrease of the surface charge and the initial surface band bending.
- It is established that the spectral dependencies of the low-signal surface photovoltage $V_{ph}(\lambda)$ are much more sensitive to the microstructure and electronic structure in the region of the absorption edge, compared to the optical transmission spectra.