

MORPHOLOGICAL AND X-Ray DIFFRACTION ANALYSIS OF CH₃NH₃PbI₃ PEROVSKITE SEMICONDUCTOR

Plesco I.¹, Ghimpu L.¹, Ciobanu V.¹, Volodina G.², Tighineanu I.³

¹Electronics, Engineering and Nanotechnologies Institute D. Ghițu, Academy of Sciences of Moldova

²Institute of Applied Physics, Academy of Sciences of Moldova

³Academy of Sciences of Moldova

CH₃NH₃PbI₃ perovskite semiconductor is considered very promising for use in photovoltaics. Large family of perovskites includes insulating, antiferromagnetic, piezoelectric, thermoelectric, superconductive, conductive and semiconductive materials. Semiconductive perovskites used in photovoltaics have important advantages such as processability from solutions at room temperature, low price, and tunability of optical and electrical properties by chemical methods, including color tunability. Therefore, the initial study of this material was focused on Röntgen phase analysis. It was observed that at perovskite concentration of 40 % wt. with 1:1 rate of PbI₂:CH₃NH₃I just a part of lead-iodide has reacted and it wasn't completely compensated. A comparison of the obtained results with literature data is presented.

Keywords: perovskite, semiconductor, morphological analysis, diffraction analysis, photovoltaics.

Perovskit semiconductor CH₃NH₃PbI₃ este considerat foarte promițător pentru utilizarea în fotovoltaică. Familie mare de perovskite include materiale izolatoare, antiferomagnetice, piezoelectrice, termoelectrice, supraconductoare, conductoare și semiconductoare. Perovskite semiconductoare utilizate în fotovoltaică au avantaje importante, cum ar fi prelucrabilitate din soluții la temperatura camerei, preț scăzut și setarea proprietăților optice și electrice prin metode chimice, inclusiv și setarea culorii. Prin urmare, studiul inițial al acestui material a fost concentrat pe analiza fazică Röntgen. A fost observat că pentru concentrația masică a perovskitului de 40 % cu proporția 1:1 de PbI₂:CH₃NH₃I doar o parte din iodură de plumb a reacționat și el nu a fost compensat în totalitate. Este prezentată comparația rezultatelor obținute cu datele din literatură.

Cuvinte-cheie: perovskit, semiconductor, analiza morfologică, analiza difracțională, fotovoltaică.

INTRODUCTION

Each year the world population consumes 15-20 TW of energy. According to International Energy Agency Statistics (IEA), oil, coal and natural gas still account for the highest energy supply and consumption. From 1971 to 2012 energy consumption doubled. Only a fraction (3.5%) of energy was produced by renewable sources in 2012. The emission of CO₂ produced by fuel burning has dramatically grown since 1971 by 2.3 times [1, 2]. These facts reveal the acuteness of energy deficiency problem and environmental pollution as well as the importance of developing ecological methods for energy supply.

Solar power is gaining mass appeal as photovoltaic panel prices fall and efficiencies improve. Perovskite with its extraordinary properties provides a potential pathway to that aim, and it has set the solar research world ablaze.

The best crystalline silicon solar cells, which form most of today's commercial panels, have efficiencies around 25%. Cadmium telluride and copper indium gallium selenide thin-film solar cells are around 20% efficient. Gallium arsenide yields thin-film devices with efficiencies over 28%, but it is too expensive for the market. Perovskites, materials with the crystal structure of calcium titanate, have only been intensely studied for solar cells since 2012. The perovskite solar cells power conversion efficiency has soared from a few percent to a certified 17.9% in only two years [5].

One of the pioneer studies on the perovskite structure was conducted in the 1920. The crystal structure of the ideal perovskite (the 3D perovskite crystal structure) is cubic ABX₃ consisting of corner sharing (BX₆) octahedra with the A cation occupying 12-fold coordination site, 'A' and 'B' are two cations of very different sizes, and X is an anion that bonds to both.

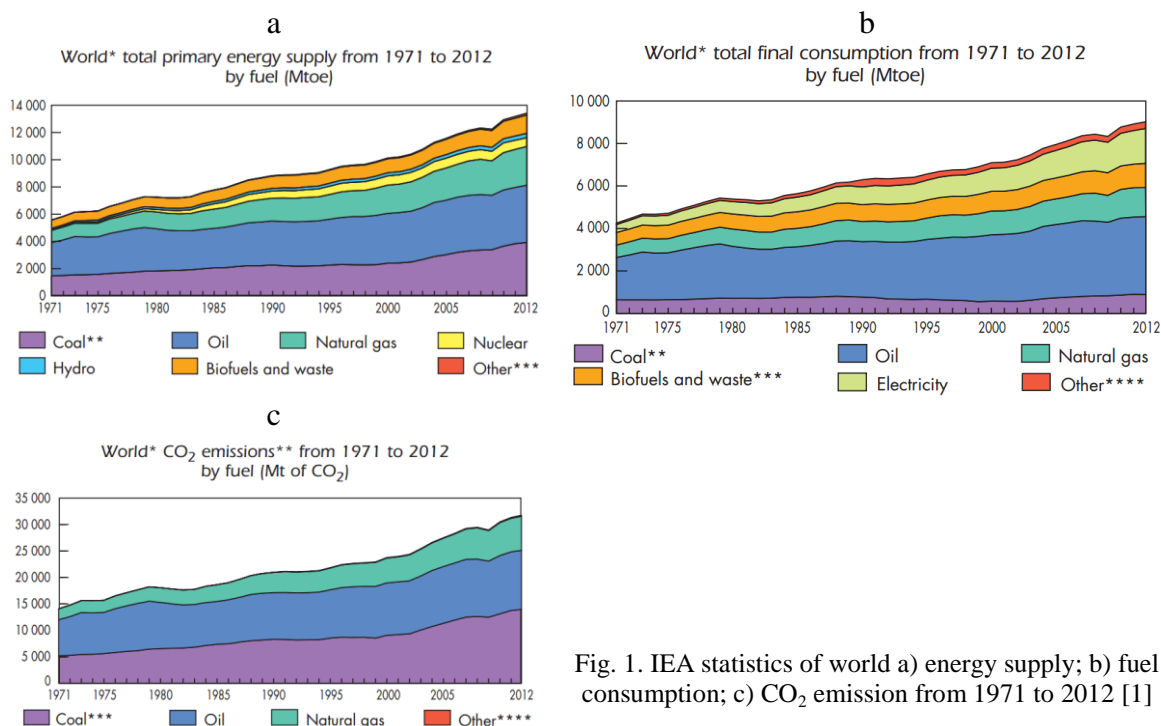
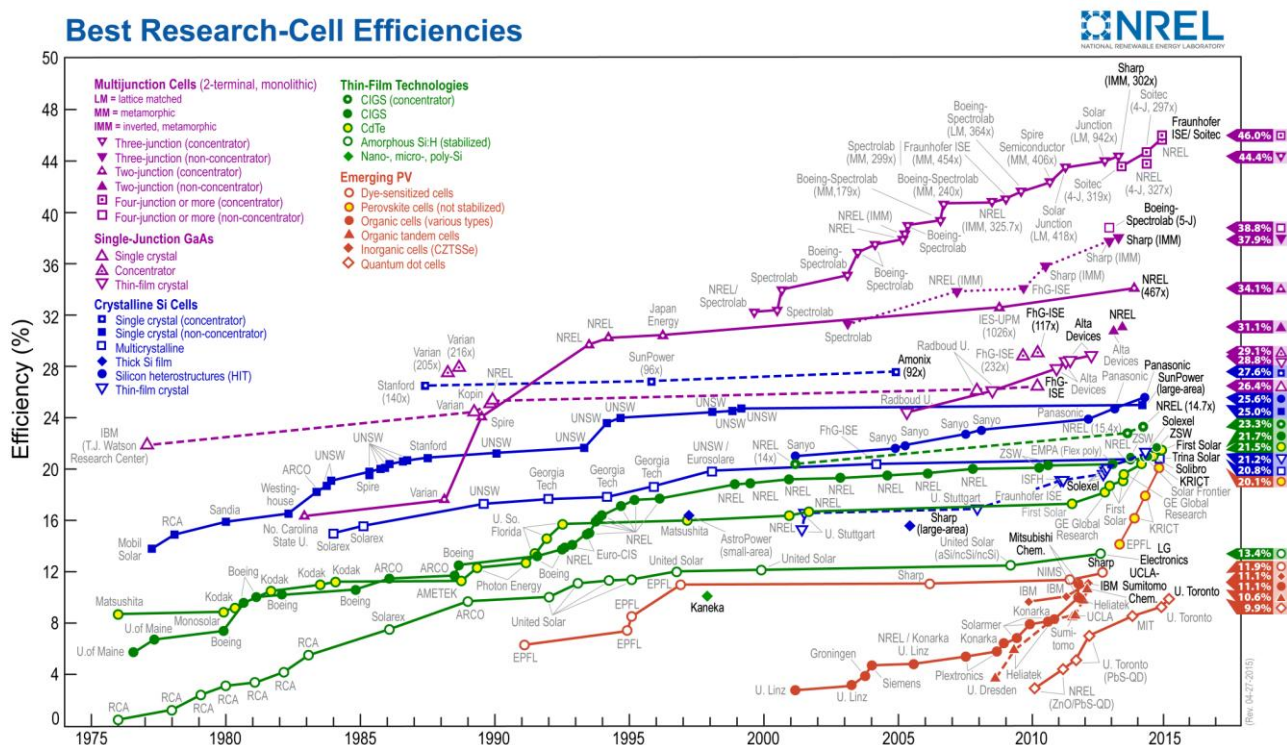


Fig. 1. IEA statistics of world a) energy supply; b) fuel consumption; c) CO₂ emission from 1971 to 2012 [1]



The B cation is a divalent metal, which satisfies the charge balancing. Examples for the metal cation include: Cu²⁺, Ni²⁺, Co²⁺, Fe²⁺, Mn²⁺, Cr²⁺, Pd²⁺, Cd²⁺, Ge²⁺, Sn²⁺, Pb²⁺, Eu²⁺, or Yb²⁺. The basic structures of organometallic perovskite are (R-NH₃)₂MX₄ and (NH-R-NH)MX; (X=Cl⁻, Br⁻, or I⁻).

Moreover, the organic component can consist of a bilayer or a monolayer of organic cations (Fig. 3). The ammonium head (in dye case of monoammonium) of the cation component bonds to the halogens in one inorganic layer, and the organic group extends into the space between the inorganic layers.

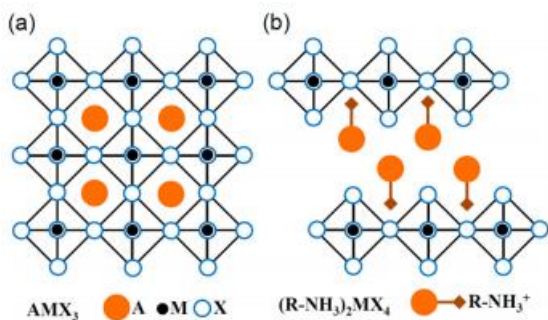


Fig. 3 a) The 3D cubic ABX_3 perovskite structure with the corner-sharing octahedral and b) the 2D layered structure of $(R-NH_3)_2MI_4$ perovskite [6]

The organic groups are optically inert and function as "spacer" groups by that allowing the ABX_3 lattice to be maintained. However, they have a major influence on the properties of the perovskite. The organic component tunes the exciton binding energy as it influences the dielectric constant. By changing the halides, the optical properties of the perovskite can be tuned, achieving absorption at different wavelengths.

Organometallic halide perovskite has good potential to be used as a light harvester in the solar cell due to its direct band gap, large absorption coefficients and high carrier mobility [6, 7, 9].

EXPERIMENTAL SECTION

For the further study, three types of perovskite precursors were prepared and bladed on the glass. For their fabrication, we chose a polar solvent Dimethylformamide (DMF). We observed fast reaction between dry precursors and their good solubility in DMF. The $CH_3NH_3PbI_3$ perovskite precursor solution was prepared by dissolving CH_3NH_3I (Solaronix SA) and PbI_2 (homemade) in the following molar ratios: sample 1 – 1:1,

sample 2 – 2:1, sample 3 – 3:1. In all cases, precursors were dissolved completely in DMF with concentration of 40 wt%. The precursor solution was then bladed on the cleaned glass and heated at $50^\circ C$. The crystallization has occurred in time of heating. A color change from yellow to brown was observed after crystallization.

For lead iodide preparation we dissolved 300 g of $Pb(CH_3COO)_2 \cdot 3H_2O$ in 600 ml H_2O and added to 260 g of KI in 600 ml of H_2O . The solution was agitated and filtered; the remaining yellow-gold precipitate was washed with distilled water. Then the precipitate was exsiccated and grinded. As a result, the yellow-gold powder with plate hexagonal particles with diameters of 5-50 μm was obtained.

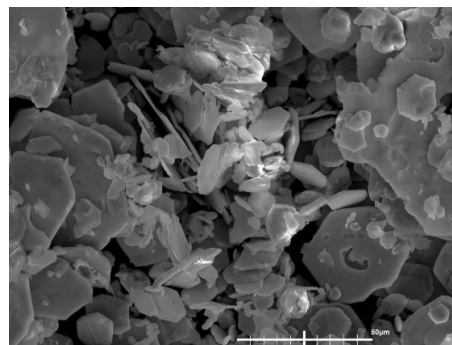


Fig. 4. SEM image of PbI_2 powder obtained in laboratory

RESULTS AND DISCUSSIONS

Surface morphology study was performed by Vega TeScan Scanning Electron Microscope (SEM). The instrument uses an electron beam accelerated to 30 kV. Good crystallinity of the films with crystallite diameter in ranges of 0.5-3 μm can be seen here.

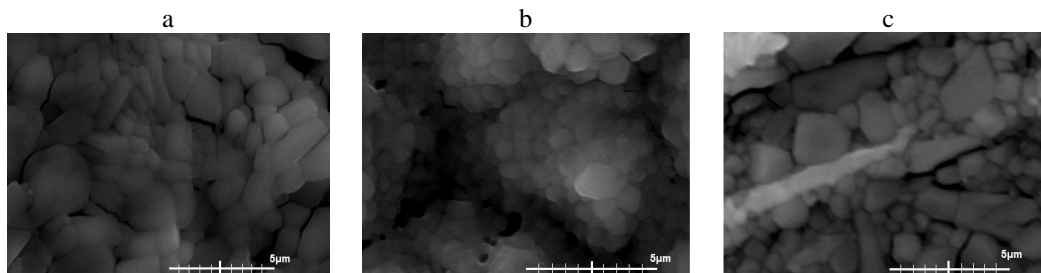


Fig. 5. Top-view SEM images for a) sample 1; b) sample 2; c) sample 3

In the samples 1 and 3 crystallites with variable sizes form a uniform layer; in contrast, in the sample 2 crystallites have the same sizes but form columnar agglomerates on the surface. Hence, by changing composition or concentration of liquid precursor the crystallite sizes and surface morphology can be modified on purpose. For instance, Mingzhen Liu et. al. [9] obtained similar layers with grain sizes about 300 nm,

Cristina Roldan-Carmona et. al. [10] – about 200 nm. In these research studies specimens were prepared with evaporation technology, unlike our samples obtained by blading or spin-coating methods. In addition, Bat-El Cohen et. al. [11] obtains perovskite with grains of micrometer ranges by dipping method. These films attain such morphology with sharply defined grains just after thermal annealing [9, 10, 11].

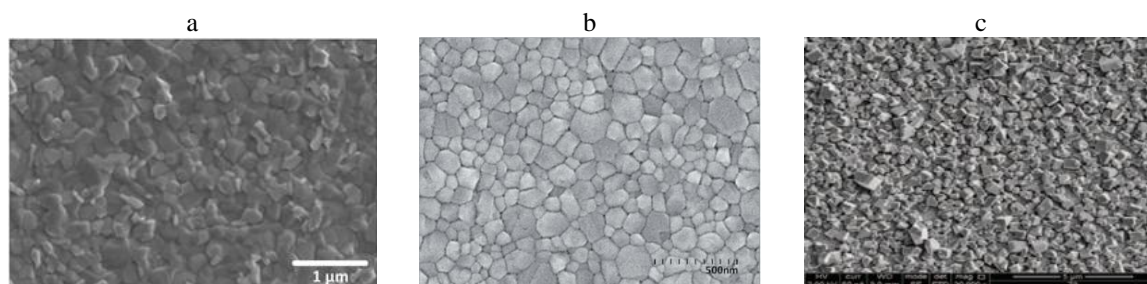


Fig. 6. Top-view SEM images for the a) [9] b) [10] vapor-deposited and c) [11] by dipping made perovskite films

“Its widespread demand has caused an improvement in the crystallinity of the material,” Snaith said. “The crystal domain size is increasing, and their quality is getting higher.” Larger, more uniform crystal grains mean fewer boundaries and defects at which electrons and holes can recombine. This results in more charge-carriers getting out of the device, boosting efficiency. [11] Further steps in perovskite development will be taken to obtain larger crystals and even monocrystalline material.

For X-ray Diffraction Spectroscopy (EDX) we used DRON UM1 with Fe $K\alpha$ ($\lambda=1.939973 \text{ \AA}$) irradiation source and Mn filter, $\theta/2\theta$ method. It was defined that all investigated samples represent perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals with tetragonal cell ($a=8.85 \text{ \AA}$, $c=12.60 \text{ \AA}$).

The crystallographic orientations were defined based on the results of other researchers. The strongest $\text{CH}_3\text{NH}_3\text{PbI}_3$ peaks are at 17.52° (110) and 35.71° (220). With

growth of organic component concentration, peaks at 51.27° (224), 40.20° (114) and 54.69° (314) appear, and in the last at 25.34° (200), 30.71° (202), 44.25° (024), 64.24° (404) and 75.31° (440). Nevertheless, three phases (110), (220) and (224) predominate in material [13].

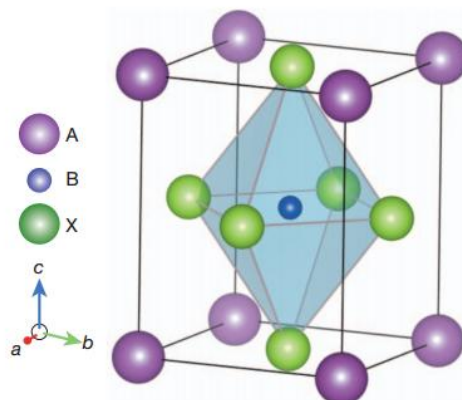


Fig. 7. Model of the perovskite tetragonal cell, where $A=\text{CH}_3\text{NH}_3^+$, $B=\text{Pb}^{2+}$, $X=\text{I}$ [9]

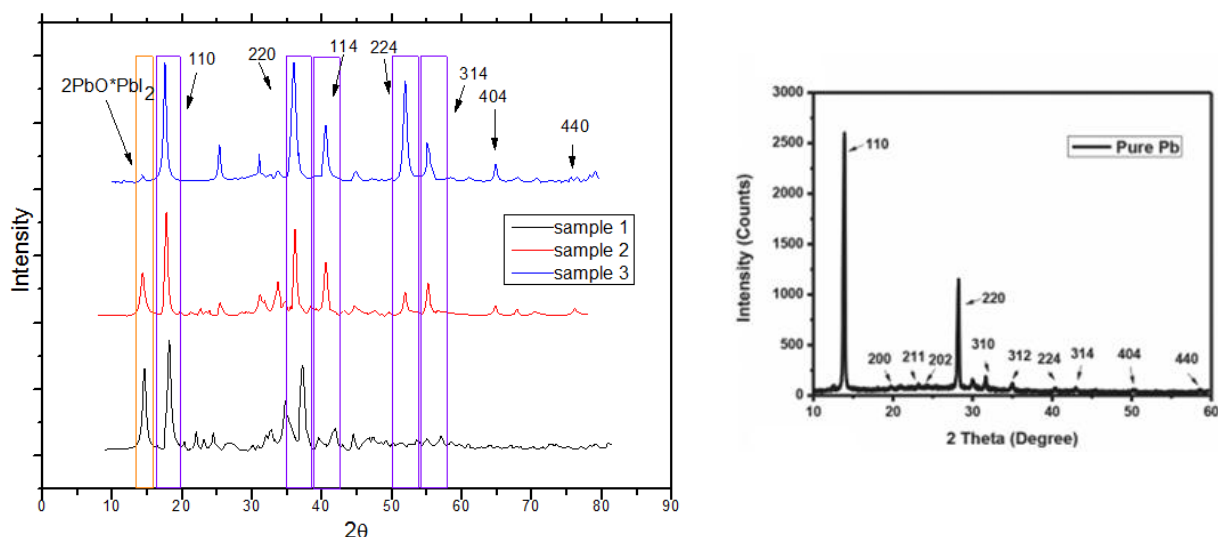


Fig. 8. XRD Spectra of a) tetragonal perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ samples 1, 2, 3; b) tetragonal perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ studied by Fan Zuo et.al. [13]

Besides, $\text{CH}_3\text{NH}_3\text{PbI}_3$ phase samples also contain $2\text{PbO}^*\text{PbI}_2$ with peak at 14.36° , its intensity is high in sample 1 and almost disappears in sample 3.

CONCLUSIONS

Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ studied in this work has well defined crystallinity in micrometer range and grain dimensions can be further increased. The best quality perovskite suitable for photovoltaic application needs increase of crystal domain size and high phase purity. XRD analysis showed improvement of phase purity and intensification of major phases with (110), (220) and (224) orientations, varying proportions of organic and inorganic components. It is proved that the obtained material has 3D structure with tetragonal cell. It may also be orthorhombic or cubic and good for highly effective optoelectronic devices.

BIBLIOGRAPHY

1. Key World Energy Statistics, <http://www.iea.org/publications/freepublications/publication/keyworld2014.pdf>
2. Richard E. Smalley, Future Global Energy Prosperity: The Terawatt Challenge, cohesion.rice.edu/naturalsciences/smalley/emplibary/120204%20mrs%20boston.pdf

3. Kangning Liang, David B. Mitzi, Michael T. Prikas, Synthesis and Characterization of Organic-Inorganic Perovskite Thin Films Prepared Using a Versatile Two-Step Dipping Technique, *Chem. Mater.* 1998, 10, 403-411.
4. <http://energyinformative.org/nrel-efficiency-record-two-junction-solar-cell>
5. Prachi Patel, Perovskites in the spotlight *MRS Bulletin*, V 39, September 2014.
6. Nam-Gyu Park, Organometal Perovskite Light Absorbers Toward a 20% Efficiency Low-Cost Solid-State Mesoscopic Solar Cell, [dx.doi.org/10.1021/jz400892a](https://doi.org/10.1021/jz400892a) | *J. Phys. Chem. Lett.* 2013, 4, 2423–2429.
7. Jacob Tse-Wei Wang, James M. Ball, Eva M. Barea, Antonio Abate, Jack A. Alexander-Webber, Jian Huang, Michael Saliba, Ivan Mora-Sero, Juan Bisquert, Henry J. Snaith, and Robin J. Nicholas, Low-Temperature Processed Electron Collection Layers of Graphene/ TiO_2 Nanocomposites in Thin Film Perovskite Solar Cells, [dx.doi.org/10.1021/nl403997a](https://doi.org/10.1021/nl403997a) | *Nano Lett.*
8. Shany Gamliel and Lioz Etgar, Organometal perovskite based solar cells: sensitized versus planar architecture, *RSC Adv.*, 2014, 4, 29012.
9. Mingzhen Liu, Michael B. Johnston & Henry J. Snaith, Efficient planar heterojunction perovskite solar cells by vapour deposition, doi: 10.1038/nature12509.
10. Cristina Roldan-Carmona, Olga Malinkiewicz, Rafael Betancur, Giulia Longo,

Cristina Momblona, Franklin Jaramillo, Luis Camacho and Henk J. Bolink, High efficiency single-junction semitransparent perovskite solar cells, *Energy Environ. Sci.*, 2014, 7, 2968.

11. Bat-El Cohen, Shany Gamliel, and Lioz Etgar, Parameters influencing the deposition of methylammonium lead halide iodide in hole conductor free perovskite-based solar cells, *APL MATERIALS* 2, 081502 (2014).

12. Paolo Umari, Edoardo Mosconi & Filippo De Angelis, Relativistic GW

calculations on $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{SnI}_3$ Perovskites for Solar Cell Applications, 10.1038/srep04467.

13. Fan Zuo, Spencer T. Williams, Po-Wei Liang, Chu-Chen Chueh, Chien-Yi Liao, and Alex K.-Y. Jen, Binary-Metal Perovskites Toward High-Performance Planar-Heterojunction Hybrid Solar Cells, 10.1002/adma.201401641.

Prezentat la redacție la 13 decembrie 2014