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**(54) Title:** METHODS FOR PRODUCING LIGHT-ABSORBING MATERIALS WITH PEROVSKITE STRUCTURE AND LIQUID POLYHALIDES OF VARIABLE COMPOSITION FOR THEIR IMPLEMENTATION

**(57) Abstract:** The invention relates to the organic-inorganic light-absorbing materials with perovskite structure, being used in perovskite solar cells production. The objective of the invention is to provide the possibility of obtaining perovskite using precursors that are in a liquid state without the use of additional substances and reagents. The concept of the invention is based on the fact that a light-absorbing material with perovskite structure with general formula $ADB_3$, where A stands for methylammonium $MA^+$ ($CH_3NH_3^+$), formamidinium, $FA^+$ ($(NH_2)_2CH^+$), guanidinium Gua ($C(NH_2)_3^+$), cesium $Cs^+$ or a mixture thereof, B stands for $Cl^-$, $Br^-$, $I^-$ or a mixture thereof, while the component D represents Sn, Pb, Bi or a mixture thereof, is obtained by mixing composition $AB$-$nB_2$ and a component containing D, where the component containing D is chosen from elemental Sn, Pb, Bi and/or their salts, mixtures, alloys, whereas the composition $AB$-$nB_2$ is deposited onto the component D followed by subsequent removal of the excessive components, n is greater than or equal to one, the component $B_2$ represents $Cl_2$, $Br_2$, $I_2$ or a mixture thereof. 3 c, 7 C.

WO 2018/124938 A1

# METHODS FOR PRODUCING LIGHT-ABSORBING MATERIALS WITH PEROVSKITE STRUCTURE AND LIQUID POLYHALIDES OF VARIABLE COMPOSITION FOR THEIR IMPLEMENTATION

## Field of the invention

The invention relates to organic-inorganic substances with variable composition, serving as an initial reagent for obtaining organic-inorganic perovskites as well as to the methods of obtaining organic-inorganic light-absorbing materials with perovskite structure, being used in perovskite solar cells production.

## State of the art

Methods of obtaining organic-inorganic light-absorbing materials with perovskite structure as well as compositions used for organic-inorganic light-absorbing materials with perovskite structure producing are known from the state of the art.

For example, methods synthesis of precursors of photoactive materials organic-inorganic perovskites, which are known from the state of the art, e.g. MAI (methylammonium iodide) and FAI (formamidinium iodide) precursors::

The published work of Qiu, Jianhang; Qiu, Yongcai; Yan, Keyou; Zhong, Min; Mu, Cheng; Yan, He; Yang, Shihe (2013), "All-solid-state hybrid solar cells based on a new organometal halide perovskite sensitizer and one-dimensional TiO2 nanowire arrays", Nanoscale, 5 (8): 3245–3248 discloses the method of MAI precursor's synthesis by mixing methylamine and hydrogen iodide (57% aqueous solution) in equimolar quantities and stirring under 0°C during 120 minutes with subsequent rotary evaporator-based crystallization under 60°C temperature;

In the report (Hu, M.; Liu, L.; Mei, A.; Yang, Y.; Liu, T.; Han, H. Efficient Hole-Conductor-Free, Fully Printable Mesoscopic Perovskite Solar Cells with a Broad Light Harvester NH2(CH)NH2PbI3. J. Mater. Chem. A 2014, 2 (40), 17115–17121) the method of FAI precursor synthesis by mixing formamidinium acetate and hydrogen iodide (57% aqueous solution) and stirring under 50°C during 30 minutes with subsequent rotary evaporator-based crystallization is disclosed.

The disadvantage of the afore-mentioned precursors is that they require the use of a solvent and special reaction conditions to ensure reaction proceeding to obtain organic-inorganic perovskite because they are solid-state materials and thus complicate technological process, increase production and environmental risks and have a negative impact on the health of employees, involved in organic-inorganic perovskite production process.

Moreover, methods of synthesis of liquid at room temperature polyiodides are known from the state of the art:

In the report of Stegemann, H.; Rohde, A.; Reiche, A.; Schnittke, A.; Füllbier, H. Room Temperature Molten Polyiodides. Electrochim. Acta 1992, 37 (3), 379–383 method of synthesis of polyiodides $CH_3(CH_3CH_2)_3I_5$ by making $CH_3(CH_3CH_2)_3I$ out of triethylamine and methylammonium iodide in isopropanol and subsequent mixing of $CH_3(CH_3CH_2)_3I$ with iodine, as well as similar methods for synthesis of polyiodides $(Oc)_4I_5$, $(Oc)_4I_7$ and $(Oc)_4I_9$ is disclosed.

The disadvantage of afore-mentioned polyiodides is the use of cations which are not suitable for obtaining light-absorbing material for perovskite solar cells.

The methods of obtaining perovskites $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$, which are known from the state of the art, are the closest to the claimed technical solution.

The patent CN104250723, 09/09/2014, Zhi Zheng, Cheng Camry, Lei Yan, Jia Huimin, Ho Wei Wei, He Yingying "Chemical method for in-situ large-area controlled synthesis of perovskite type $CH_3NH_3PbI_3$ membrane material based on lead simple-substance membrane" discloses a method of synthesis of perovskite $CH_3NH_3PbI_3$ by means of dipping of the metallic lead into solution of iodine and methylammonium iodide in organic solvent, for example, ethanol.

The patent CN105369232, 16/02/2015, Zhi Zheng, He Yingying, Lei Yan, Cheng Camry, Jia Huimin, Ho Wei Wei, "Lead-based perovskite-type composite elemental thin-film in-situ wide area control $CH_3NH_3PbBr_3$ film material chemical method" describes a method of synthesis of perovskite $CH_3NH_3PbBr_3$ by dipping metallic lead into solution of methylammonium bromide in organic solvent, for example isopropanol.

The disadvantage of the above-mentioned methods is the mandatory use of solvent, that complicates the process of organic-inorganic perovskite formation and leading to production-related, environmental and health risks. Thus organic-inorganic compounds with variable composition serving as a liquid at room temperature starting reagent for obtaining organic-inorganic perovskites as well as the methods of obtaining organic-inorganic light-absorbing materials with perovskite structure, being used in perovskite solar cells production are warranted.

**The Objective** of the claimed technical solution is the development of simple, quick and low-waste method of obtaining organic-inorganic light-absorbing materials with perovskite structure in a solvent-free way as well as the synthesis of a composition to be used for afore-said methods implementation, which allows obtaining materials suitable for the use in solar cells.

**The technical outcome**, to be achieved as a result of application of the claimed invention, is the simplification and acceleration of obtaining organic-inorganic light-absorbing materials with perovskite structure, including organic-inorganic perovskites and perovskite-like compounds containing Pb, Sn, Bi, in a solvent-free way, particularly, at room temperature, with capability of the use of the obtained materials in solar cells.

The technical result in the realization of the method is achieved by the fact that a material with perovskite structure can be obtained by mixing two reagents

Realization of the method enables technical outcome achievement, owing to the fact that the material with perovskite structure can be obtained by mixing two reagents $AB\text{-}nB_2$ and D with subsequent elimination of the excessive reagents, where the first reagent is a variable composition $AB\text{-}nB_2$, where $n \geq 1$, A stands for methylammonium $MA^+$ ($CH_3NH_3^+$), formamidinium, $FA^+$ ($(NH_2)_2CH^+$), guanidinium Gua ($C(NH_2)_3^+$), cesium $Cs^+$ or a mixture thereof, B stands for $Cl^-$, $Br^-$, $I^-$ or a mixture thereof, whereas $Cl_2$, $Br_2$, $I_2$ or a mixture thereof can be used as component $B_2$, while the second reagent D is chosen from elemental Sn, Pb, Bi and/or their salts, mixtures, alloys.

Methods for bringing together the components $AB - nB_2$ and D can be different: dip–coating – dropping one substance onto another or immersing the substance D in the composition $AB - nB_2$, spray–coating - spraying one substance onto another, spin coating - applying one substance in a liquid state on a rotating substrate with another substance, doctor blade – applying one substance onto another by means of a dosing blade, roll-to-roll – roll-to-roll technology of application of substances, screen printing – screen printing of the substance AB-n$B_2$ on the surface of the substance D.

Excess of the component B (Cl, Br, I) can be removed by one of the following methods: washing in a solvent, dropping the solvent on the surface, annealing at an elevated temperature, evaporation under reduced pressure, using a substance that absorbs component $B_2$.

The technical result in case of using the composition and the method for its preparation is achieved by mixing the two solid components AB and $B_2$ in the form of powders to obtain a liquid composition AB-n$B_2$ of variable composition with various molar ratios of the components AB and $B_2$, where n≥1, A stands for methylammonium $MA^+$ ($CH_3NH_3^+$), formamidinium, $FA^+$ ($(NH_2)_2CH^+$), guanidinium Gua ($C(NH_2)_3^+$), cesium $Cs^+$ or a mixture thereof, B stands for $Cl^-$, $Br^-$, $I^-$ or a mixture thereof, whereas $B_2$ stands for $Cl_2$, $Br_2$, $I_2$ or a mixture thereof.

The main feature of a new composition for light absorbing material with perovskite structure preparation which can be used for implementation of the process according to the invention is its quick and simple production without the use of a solvent according to the following reaction: $AB - nB_2 + D = ADB_3 + (n-1)B_2$.

A more general approach to produce a light absorbing material with perovskite structure and chemical formula $ADB_3$ (wherein A is chosen from the cations $CH_3NH_3^+$, $(NH_2)_2CH^+$, $C(NH_2)_3^+$, $Cs^+$ and the mixtures of thereof, B is chosen from the from the anions $Cl^-$, $Br^-$, $I^-$ or mixtures of thereof and D is chosen from elements Sn, Pb, Bi or mixtures of thereof) is to mix the composition $AB - nB_2$ and reagent that contains D, wherein the component that contains D is chosen from elemental Sn, Pb, Bi and/or their salts, mixtures, alloys, B is chosen from $Cl_2$, $Br_2$, $I_2$ and mixtures of thereof, for which, the reactant with the composition $AB - nI_2$ (n≥1) is brought into contact with the component D and the excess of this composition is removed.

Moreover, the mixing of the composition $AB - nB_2$ with the reagent that contains D is performed by means of dissolution of D in the mixture that contains components A and B with a consequent thermal treatment or the mixing of the composition $AB - nB_2$ with the reagent that contains D is performed by means of dissolution of D in the mixture that contains components A and B with a consequent pressure decrease or the mixing of the composition $AB - nB_2$ with the reagent D is performed by means of dissolution of D in the mixture that contains components A, B and D with the consequent with a consequent thermal treatment or the mixing of the composition AB - $nB_2$ with the reagent D is performed by means of dissolution of D in the mixture that contains components A, B and D with a consequent pressure decrease.

Furthermore, the mixing of reagents AB-$nB_2$ and the reagent that contains D can be performed by means of any of the methods listed below or a combination thereof: spin-coating, spray-coating, immersion, blade coating, drop-casting, roll-to-roll deposition, screen printing, while the excess of the component B from the composition AB-$nB_2$ is removed by means of any of the methods listed below or a combination thereof: washing with a solvent, thermal treatment of the substrate, removal under the reduced pressure, removal using sorbent.

In a particular embodiment of the process, the method for preparation of a liquid reagent for the fabrication of an organic-inorganic perovskite is to mix the components that contain cations A and B within the temperature range from 0 to 150 °C that results in the formation of the mixture AB-$nB_2$, ($n \geq 1$), wherein A is chosen from $CH_3NH_3^+$, $(NH_2)_2CH^+$, $C(NH_2)_3^+$, or mixture of thereof, B is chosen from $Cl^-$, $Br^-$, $I^-$ anions or mixture of thereof, as well as a mixture of these components with $Cs^+$ ions while the A to B ratio lies within the range from 1:1 to 1: 5.

Below the particular embodiments of the fabrication of the light absorbing material with a perovskite structure with the general formula $ADB_3$ are provided.

Information on the application of the claimed method for obtaining a perovskite solar cell is given as an example of a specific implementation.

Example 1:

A reagent $MAI\text{-}2I_2$ is obtained by mixing 159 mg MAI and 508 mg $I_2$ which is then spin-coated on top of the substrate of the following configuration: $FTO/TiO_2/Pb$ with a metallic lead layer 250nm thick (FTO stands for fluorine-doped tin oxide). The substrate is then heated and kept at a temperature of 115 °C for 30 minutes. As a result, a perovskite layer $MAPbI_3$ is formed on the substrate.

Example 2:

A powder of metallic lead (20mg) is added to the reagent AB - $nB_2$ (A = MA; B = I, Br; $n \geq 1$) that is obtained by mixing 127 mg MAI, 22mg MABr, and 508 mg $I_2$ and this mixture is stirred for 12 hours. The mixture is then filtered using the syringe filter (PTFE, 0.45μm pore-diameter) and spin-coated on top of metallic lead 50nm-thick on glass substrate. After the spin-coating process, the substrate is immersed into the isopropanol bath, removed and dried. As a result, a perovskite layer $MAPbI_xBr_{3-x}$ is formed on the glass substrate.

Example 3.

A reagent AB - $nB_2$ (A = MA, FA; B = I, Br; $n \geq 1$) is obtained by mixing FAI (137mg), MABr (22mg) and $I_2$ (508mg) which is then spin-coated on top of metallic lead 250nm-thick on glass substrate. Just 15 seconds before the rotation of the sample-holder ends, 100μl of the isopropyl alcohol is dropped onto the surface of the sample. As a result, a perovskite layer $MA_xFA_{1-x}PbI_{3y}Br_{3-3y}$ ($0 \leq x \leq 1$; $0 \leq y \leq 1$) is formed on the glass substrate.

See below the ways of preparation of liquid polyhalides composition with a general formula AB-$nB_2$.

Example 4.

1016 mg (4 mmol) of crystalline iodine in the form of a solid powder is added at room temperature to 318 mg (2 mmol) of crystalline MAI in the form of a solid powder. After that, the mixture is stirred for 3 minutes at room temperature, resulting in the formation of a dark brown liquid with a composition $MAI\text{-}2I_2$. After preparation, the composition retains its properties for at least a month at room temperature.

Example 5.

1270 mg (5 mmol) of crystalline iodine in the form of a solid powder is added at room temperature to 318 mg (2 mmol) of crystalline MAI in the form of a solid powder. After that, the mixture is stirred for 3 minutes at 40°C and cooled down to room temperature, resulting in the formation of a dark brown liquid with a composition $MAI\text{-}2.5I_2$. After preparation, the composition retains its properties for at least a month at room temperature.

Example 6.

2540 mg (10 mmol) of crystalline iodine in the form of a solid powder is heated in a closed vial up to 120°C which causes iodine melting. Then, 318 mg (2 mmol) of crystalline MAI in the form of a solid powder is added in the vial. After that, the mixture is stirred for 3 minutes and cooled down to 70°C, resulting in the formation of dark brown liquid with a composition $MAI\text{-}5I_2$. After preparation, the composition retains its properties for at least a month at 70°C.

Claims:

1. A method for producing a light absorbing material with the perovskite structure and chemical formula $ADB_3$ (wherein A is chosen from the cations $CH_3NH_3^+$, $(NH_2)_2CH^+$, $C(NH_2)_3^+$, $Cs^+$ and the mixtures of thereof, B is chosen from the from the anions Cl-, Br-, I- or mixtures of thereof and D is chosen from elements Sn, Pb, Bi or mixtures of thereof) is to mix the composition $AB - nB_2$ and component D, wherein the component that contains D is chosen from elemental Sn, Pb, Bi and/or their salts, alloys, B is chosen from $Cl_2$, $Br_2$, $I_2$ and mixtures of thereof, for which, the reactant with the composition $AB - nI_2$ ($n \geq 1$) is brought into contact with the component D and the excess of this reactant is removed.
2. The method according to claim 1, wherein the mixing of the composition $AB - nB_2$ with the reagent that contains D is performed by means of dissolution of D in the mixture that contains components A and B with a consequent thermal treatment.
3. The method according to claim 1 or claim 2, wherein the mixing of the composition $AB - nB_2$ with the reagent that contains D is performed by means of dissolution of D in the mixture that contains components A and B with a consequent pressure decrease.
4. The method according to claim 1, wherein the mixing of the composition $AB - nB_2$ with the reagent D is performed by means of dissolution of D in the mixture that contains components A, B and D with the consequent with a consequent thermal treatment.
5. The method according to claim 1 or claim 4, wherein the mixing of the composition $AB - nB_2$ with the reagent D is performed by means of dissolution of D in the mixture that contains components A, B and D with a consequent pressure decrease.
6. The method according to claim 1, wherein the mixing of the reagents $AB - nB_2$ with the reagent that contains D is performed by means of deposition of $AB - nB_2$ on the reagent that contains D.
7. The method according to claim 4, wherein the deposition of $AB-nB_2$ and the reagent that contains D can be performed by means of any of the methods listed below or a combination thereof: spin-coating, spray-coating, immersion, blade coating, drop-casting, roll-to-roll deposition, screen printing.

8. The method according to claim 1, wherein the excess of the component B from the composition $AB\text{-}nB_2$ is removed by means of any of the methods listed below or a combination thereof: washing with a solvent, thermal treatment of the substrate, removal under the reduced pressure, removal using sorbent.
9. Method for preparation of the liquid precursor for obtaining organic-inorganic perovskite based on the mixing of the components with A and B, A being at least one of the following cations: $CH_3NH_3^+$, $(NH_2)_2CH^+$, $C(NH_2)_3^+$, or a mixture thereof, B being at least one of the following anions $Cl^-$, $Br^-$, $I^-$ or a mixture thereof, as well as their mixture with $Cs^+$ ions, A to B molar ratio being varied within the range from 1:1 to 1:5 within temperature range from 0 to 150°C and where $n \geq 1$.
10. Liquid precursor $AB - nB_2$ for obtaining organic-inorganic perovskite, where $n \geq 1$, A being at least one of the following cations: $CH_3NH_3^+$, $(NH_2)_2CH^+$, $C(NH_2)_3^+$, or a mixture thereof, B being at least one of the following anions Cl-, Br , I- or a mixture thereof, as well as their mixture with $Cs^+$ ions, while mixing of the components with A cations and B anions with A to B molar ratio varying within the range from 1:1 to 1:5 is performed within the temperature range from 0 to 150°C.

# INTERNATIONAL SEARCH REPORT

International application No
PCT/RU2017/000946

**A. CLASSIFICATION OF SUBJECT MATTER**
INV. H01L51/42
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | CN 104 250 723 A (UNIV XUCHANG; ZHENG ZHI) 31 December 2014 (2014-12-31) cited in the application abstract; example 1 | 1-10 |
| A | BAHRAM ABDOLLAHI NEJAND ET AL: "Novel Solvent-free Perovskite Deposition in Fabrication of Normal and Inverted Architectures of Perovskite Solar Cells", SCIENTIFIC REPORTS, vol. 6, no. 1, 19 September 2016 (2016-09-19), XP055480060, DOI: 10.1038/srep33649 abstract | 1-10 |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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1

# INTERNATIONAL SEARCH REPORT

**Information on patent family members**

International application No

PCT/RU2017/000946

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
| --- | --- | --- | --- |
| CN 104250723 A | 31-12-2014 | NONE | |