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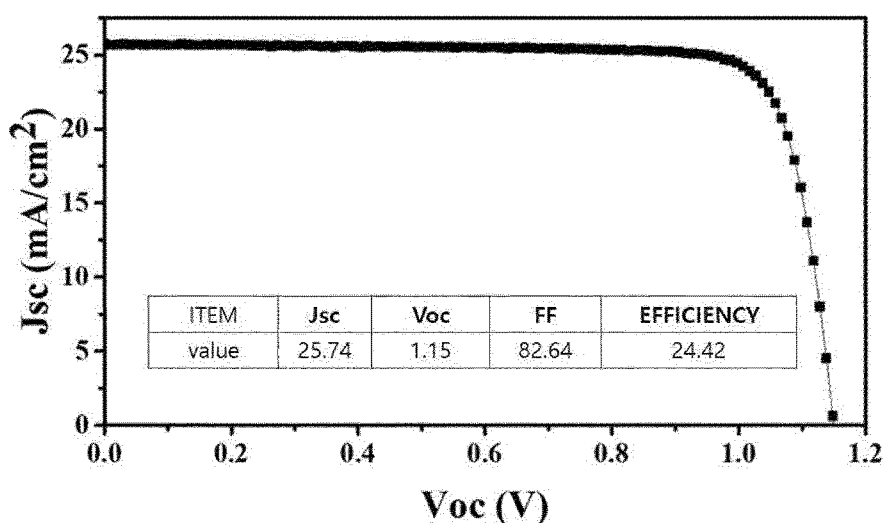
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(54) Title: PEROVSKITE COMPOUND CONTAINING DIVALENT ORGANIC CATION AND DEVICE CONTAINING THE SAME



(57) Abstract: A perovskite compound according to the present invention contains an organic cation, a metal cation, and a non-metal anion, wherein a monovalent amidinium group cation and a divalent organic cation are contained as the organic cation. The perovskite compound according to the present invention has an excellent power conversion efficiency of more than 24% and has significantly improved stability with respect to heat and moisture itself.



Description

Title of Invention: PEROVSKITE COMPOUND CONTAINING DIVALENT ORGANIC CATION AND DEVICE CONTAINING THE SAME

Technical Field

- [1] The following disclosure relates to a perovskite compound containing a divalent organic cation and a device containing the same.

Background Art

- [2] An inorganic-organic hybrid halide perovskite crystal having a perovskite structure that is called an inorganic/organic perovskite compound is a material consisting of an organic cation (A), a metal cation (M), and a halogen anion (X) and represented by a chemical formula of AMX_3 .
- [3] An inorganic-organic hybrid having a perovskite structure has excellent light absorbing properties, a long charge carrier diffusion length, a high absorption coefficient, a low trap density, and a small exciton binding energy. Therefore, an interest in the inorganic-organic hybrid having a perovskite structure has increased in various fields such as a light emitting device, a photovoltaic device, and a semiconductor device.
- [4] Currently, a perovskite solar cell using an inorganic-organic hybrid material as a light absorber is the most commercialized solar cell among next solar cells including dye-sensitized and organic solar cells. It has been reported that the perovskite solar cell has an efficiency of about 20%, which is second only to that of a silicon solar cell.
- [5] The inorganic-organic hybrid material having a perovskite structure is very low in price and is usable in a low temperature process or a low-priced solution process, and thus has excellent commerciality.
- [6] However, although the inorganic-organic hybrid having a perovskite structure has such commercial and physical advantages, the inorganic-organic hybrid having a perovskite structure has very poor stability with respect to light, heat, and moisture. Thus, in order to commercialize the inorganic-organic hybrid, the development of a technology capable of improving stability has been required.
- [7] Meanwhile, an inorganic-organic hybrid which is currently known to have the most excellent power conversion efficiency is based on an amidinium group cation. However, an amidinium group cation-based inorganic-organic hybrid material having the highest efficiency has instability with respect to light, heat, and moisture as well as phase instability (formation of a δ -phase which is inactive to light and phase transition from an α -phase to a δ -phase).

- [8] In order to solve the phase instability, a technology of mixing an amidinium group cation with small amounts of methylammonium and bromine ions to obtain a stabilizer that stabilizes the α -phase has been suggested. However, methylammonium is very easily decomposed by heat or moisture, which significantly degrades moisture and heat stability of the amidinium group cation-based inorganic-organic hybrid material. In addition, a band gap of the inorganic-organic hybrid material is increased by the addition of bromine ions, and thus a light absorption region is reduced.

Disclosure of Invention

Technical Problem

- [9] An embodiment of the present invention is directed to providing an amidinium group cation-based perovskite compound having improved stability.
- [10] Another embodiment of the present invention is directed to providing an amidinium group cation-based perovskite compound having improved heat, moisture, and/or α -phase stability.
- [11] Still another embodiment of the present invention is directed to providing an amidinium group cation-based perovskite compound capable of implementing a solar cell having improved stability, capable of absorbing solar light with a wide range by a small band gap, and having an improved power conversion efficiency.
- [12] Still another embodiment of the present invention is directed to providing a device based on an amidinium group cation-based perovskite compound having improved stability and efficiency.

Solution to Problem

- [13] In one aspect, a perovskite compound contains an organic cation, a metal cation, and a non-metal anion, wherein a monovalent amidinium group cation and a divalent organic cation are contained as the organic cation.
- [14] The divalent organic cation may be an ammonium group organic cation.
- [15] The ammonium group organic cation may be an aliphatic ammonium group cation.
- [16] The aliphatic ammonium group cation may satisfy the following Chemical Formula 1.
- [17] Chemical Formula 1
- [18] $\text{NH}_3^+-\text{L}_1-\text{NH}_3^+$
- [19] In Chemical Formula 1, L_1 is C1-C3 alkylene.
- [20] The aliphatic ammonium group cation may be a methylenediammonium ion.
- [21] The divalent organic cation may be contained in an amount of more than 0% to 15% or less based on a total number of moles (100%) of the organic cation contained in the perovskite compound.
- [22] When a band gap energy (eV) of a reference perovskite compound consisting of the

same cation and anion as those of the perovskite compound except that the divalent organic cation is not contained is 1, a band gap energy of the perovskite compound may be 0.95 to 1.30.

[23] The non-metal anion may be a halogen anion, a chalcogen anion, or a complex anion of a halogen anion and a chalcogen anion.

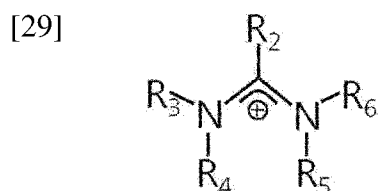
[24] The halogen anion may be I^- , Cl^- , Br^- , or a mixed anion thereof.

[25] The metal cation may be one or two or more selected from a divalent metal cation, a monovalent metal cation, and a trivalent metal cation.

[26] The metal cation may be a divalent metal cation, and the divalent metal cation may be one or two or more selected from Cu^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+} , Cr^{2+} , Pd^{2+} , Cd^{2+} , Ge^{2+} , Sn^{2+} , Pb^{2+} , and Yb^{2+} .

[27] The amidinium group cation may satisfy the following Chemical Formula 2.

[28] Chemical Formula 2



[30] In Chemical Formula 2, R_2 to R_6 are each independently hydrogen, C1-C24 alkyl, C3-C20 cycloalkyl, or C6-C20 aryl.

[31] In another general aspect, a solution contains the perovskite compound and a solvent.

[32] In still another general aspect, a solution contains a monovalent amidinium group cation, a divalent organic cation, a metal ion, a non-metal anion, and a solvent.

[33] The solution may be a solution for preparing a perovskite compound.

[34] In still another general aspect, a particle contains the perovskite compound.

[35] In still another general aspect, a layer contains the perovskite compound.

[36] In still another general aspect, a device contains the perovskite compound.

[37] The device may be a light emitting device, a diode, a bipolar junction transistor (BJT), a field effect transistor (FET), or a photovoltaic cell.

[38] In still another general aspect, a perovskite solar cell contains the perovskite compound.

[39] The perovskite solar cell may include a first electrode, a first charge carrier, a light absorption layer containing the perovskite compound, a second charge carrier carrying a charge that is complementary to a charge carried by the first charge carrier, and a second electrode.

[40] In still another general aspect, there is provided an apparatus to which power is supplied by the perovskite solar cell.

[41] Other features and aspects will be apparent from the following detailed description,

the drawings, and the claims.

[42]

Advantageous Effects of Invention

[43] The perovskite compound according to the present invention has an excellent power conversion efficiency of more than 24% and has significantly improved stability with respect to heat and moisture itself. Further, the amidinium group cation-based perovskite compound according to the present invention has α -phase stability and has excellent solution stability that does not cause degradation even during long-term storage in a state in which the compound is dissolved in a solvent.

[44]

Brief Description of Drawings

[45] FIG. 1 is a view illustrating a J-V curve showing a power conversion efficiency of a solar cell produced in Example 2 and a short-circuit current density (J_{sc}), an open-circuit voltage (V_{oc}), a fill factor (FF), and an efficiency obtained therefrom.

[46] FIG. 2 is a view illustrating NMR analysis results of a perovskite material prepared in Example 2.

[47] FIGS. 3A and 3B are views illustrating the results of analyzing contents of Cl ions in perovskite materials prepared in Comparative Example 1 and Example 2.

[48] FIGS. 4A and 4B are views illustrating efficiency changes over time under conditions of a relative humidity of 85%, room temperature (25°C), and 150°C.

[49]

Mode for the Invention

[50] Hereinafter, a perovskite compound of the present invention will be described in detail with reference to the accompanying drawings. The drawings to be described below are provided by way of example so that the idea of the present invention can be sufficiently transferred to those skilled in the art. Therefore, the present invention is not limited to the drawings suggested below but may be modified in many different forms. In addition, the drawings suggested below will be exaggerated in order to clear the idea of the present invention. Technical terms and scientific terms used herein have the general meanings understood by those skilled in the art to which the present invention pertains unless otherwise defined, and a description for the known function and configuration obscuring the present invention will be omitted in the following description and the accompanying drawings.

[51] A perovskite compound according to the present invention contains an organic cation, a metal cation, and a non-metal anion, and the organic cation includes a monovalent amidinium group cation and a divalent organic cation.

[52] Both of the monovalent amidinium group cation and the divalent organic cation are

contained as the organic cation, such that a binding force between a halogen anion and an organic cation is significantly increased. Therefore, the perovskite compound according to the present invention may have improved stability with respect to heat and moisture of the material as compared with an organometal halide having a perovskite structure according to the related art that contains only a monovalent organic cation.

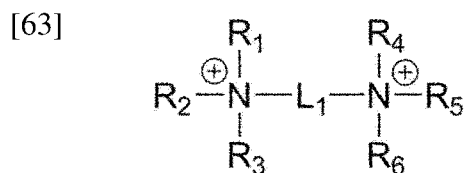
- [53] In addition, in a case where the perovskite compound contains both a monovalent amidinium group cation and a divalent organic cation, entropic stabilization may be implemented and an α -phase may be stabilized by a high δ -phase formation energy.
- [54] The perovskite compound may refer to a material including or consisting of one or more perovskite species, which encompass any perovskite structure known in the art of the present invention.
- [55] The perovskite compound may refer to an inorganic-organic hybrid material having a perovskite structure. The perovskite structure includes an organic cation (A), a metal cation (M), and an anion (X), and may refer to a three-dimensional structure in which AX_{12} having a cuboctahedral structure formed by binding the organic cation (A) and 12 anions (X) and MX_6 having an octahedral structure formed by binding the metal cation (M) and 6 anions (X) are combined. That is, the perovskite structure typically has a three-dimensional network of corner-sharing MX_6 octahedra, and A may be a cation typically located in 12-fold coordinated holes between the MX_6 octahedra.
- [56] In a specific example, the perovskite compound may be a three-dimensional material or a two-dimensional material. In an exemplary embodiment, the perovskite compound may be a three-dimensional material.
- [57] In a specific example, the perovskite compound may be represented by a chemical formula of AMX_3 , AMX_4 , A_2MX_4 , or A_3MX_5 . In a preferred exemplary embodiment, the perovskite compound may be represented by a chemical formula of AMX_3 . In this case, it should not be interpreted that the perovskite compound satisfies a molar ratio of A:M:X=1:1:3, 1:1:4, 2:1:4, or 3:1:5 by the represented chemical formula in a mathematically strict sense. The molar ratio thereof may be out of a stoichiometric ratio at a predetermined level (for example, $m \pm 0.1 m$, where m is a natural number according to a stoichiometric ratio) at which the perovskite structure is maintained against defects that may thermodynamically or spontaneously occur.
- [58] In a specific example, the perovskite compound may be an amidinium group perovskite compound. The amidinium group perovskite compound may refer to a perovskite compound in which a content (the number of moles) of a monovalent amidinium group cation contained in an organic cation is at least 80% or more, and specifically, 90% or more, based on a total number of moles (100%) of the organic cation contained in the perovskite compound.

[59] In an exemplary embodiment, the perovskite compound contains an organic cation, a metal cation, and a non-metal anion, and may be an amidinium group perovskite compound in which an organic cation includes a monovalent amidinium group cation and a divalent organic cation.

[60] In a specific example, the divalent organic cation may be an ammonium group organic cation, and may be an aliphatic ammonium group cation so that a divalent organic ammonium ion may be positioned in a crystal structure of the amidinium group perovskite compound.

[61] The aliphatic ammonium group cation may satisfy the following Chemical Formula 1.

[62] Chemical Formula 1



[64] In Chemical Formula 1, L_1 is C1-C5 alkylene, C2-C5 alkenylene, or C2-C5 alkynylene, R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are each independently hydrogen or a C1-C3 alkyl group, and at least one of R_1 , R_2 , and R_3 and at least one of R_4 , R_5 , and R_6 each are hydrogen.

[65] In a case where the divalent organic cation is an ammonium group organic cation (divalent ammonium group organic cation), spontaneous crystallization may be stably generated at a level equivalent to that of organometal halide having a perovskite structure according to the related art, and thus a crystalline perovskite compound may be prepared through a process of drying of an aqueous phase or a process of mixing (including adding dropwise) an aqueous phase with a non-solvent.

[66] In addition, in a case where the divalent organic cation is an aliphatic ammonium group cation, in particular, an aliphatic ammonium group cation satisfying Chemical Formula 1, it is advantageous because the divalent organic cation may form a dissolved solid phase substituted at a position of the organic cation (A) in a lattice structure of the perovskite compound.

[67] The divalent organic cation may be easily substituted at the position of the organic cation, and may be stably and spontaneously crystallized. In the case of the divalent organic cation, in Chemical Formula 1, L_1 may be C1-C3 alkylene, preferably C1-C2 alkylene, and more preferably C1 alkylene, and all R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 may be hydrogen so that a change of a band gap energy by introduction of the divalent organic cation may be suppressed.

[68] As known in the art, the amidinium group perovskite compound is a material having the most excellent power conversion efficiency among various perovskite compounds.

Accordingly, in a case where a divalent organic ammonium cation is dissolved and substituted at a position of an amidinium group cation having a lattice structure, it is advantageous because lattice distortion is not caused, and the band gap energy of the amidinium group perovskite compound is not increased by introduction of the divalent organic cation as much as possible.

[69] The divalent organic cation may satisfy Chemical Formula 2 so that the divalent organic cation is easily substituted at the position(site) of the organic cation, which is a position(site) of the amidinium group cation, in a crystal lattice, and lattice distortion and a band gap energy change (increase) are not caused, while having α -phase stability, heat stability, and moisture stability.

[70] Chemical Formula 2

[71] $\text{NH}_3^+ \text{-L}_1 \text{-NH}_3^+$

[72] In Chemical Formula 2, L_1 is C1-C3 alkylene, preferably C1-C2 alkylene, and more preferably C1 alkylene.

[73] Specific examples of the divalent organic ammonium cation satisfying Chemical Formula 2 may include an ethylenediammonium cation, a methylenediammonium cation, and a propylenediammonium cation.

[74] In a case where the perovskite compound contains both a monovalent amidinium group cation and a divalent organic cation satisfying Chemical Formula 2, an α -phase stabilization effect may be further improved by entropic stabilization effect and a strong dipole moment of two -NH_3^+ and an increase in the number of hydrogen bonds between a non-metal anion and hydrogen. In addition, stability of a perovskite compound material itself is significantly improved, and thus, an amidinium group cation-based perovskite compound (amidinium group perovskite compound) may be prevented from being degraded by heat and moisture.

[75] In addition, in the case where the perovskite compound contains both a monovalent amidinium group cation and a divalent organic cation satisfying Chemical Formula 2, lattice distortion is not substantially caused by introduction of the divalent organic cation, and thus light absorption degradation due to a band gap increase may be prevented. In addition, the power conversion efficiency (improved light stability) may be uniformly and stably exhibited during continuous light irradiation.

[76] Specifically, in a case where the perovskite compound contains an aliphatic ammonium group cation satisfying Chemical Formula 2 as the divalent organic cation, degradation by heat hardly occurs even in a case where a layer containing the perovskite compound is left at a temperature of 150°C for 24 hours in a state in which a surface of the layer is exposed, and thus 90% or more of properties of the perovskite compound immediately after preparation may be maintained.

[77] Specifically, in the case where the perovskite compound contains an aliphatic

ammonium group cation satisfying Chemical Formula 2 as the divalent organic cation, degradation by moisture hardly occurs even in a case where the layer containing the perovskite compound is left at a relative humidity atmosphere of 85% for 72 hours in a state in which the surface of the layer is exposed, and thus 90% or more of the properties of the perovskite compound immediately after preparation may be maintained.

- [78] In a specific example, the perovskite compound may contain the divalent organic cation in an amount of 15% or less, specifically, 13% or less, and more specifically, 10% or less, based on a total number of moles (100%) of the organic cation contained in the perovskite compound, but the present invention is not limited thereto. However, in a case where the perovskite compound contains the divalent organic cation in an amount of 15% or less, specifically, 13% or less, and more specifically, 10% or less, crystals having a perovskite structure may be further stably self-assembled by a simple solution application method in which a divalent organic cation halide, an amidinium group cation halide, and a metal halide are dissolved in a solvent to satisfy a desired composition, and then a prepared solution is applied and dried.
- [79] In a specific example, the perovskite compound may contain the divalent organic cation in an amount of more than 0%, specifically, 0.5% or more, more specifically, 1% or more, and still more preferably, 2% or more, based on the total number of moles (100%) of the organic cation contained in the perovskite compound, but the present invention is not limited thereto. However, in a case where the perovskite compound contains the divalent organic cation in an amount of more than 0%, specifically, 0.5% or more, more specifically, 1% or more, and still more preferably, 2% or more, solid α -phase stability, heat stability, moisture stability, and/or light stability may be secured.
- [80] In an exemplary embodiment, the perovskite compound may contain the divalent organic cation in an amount of more than 0% to 15% or less, 0.5% to 15%, 2% to 15%, 0.5% to 10%, 1% to 10%, 2% to 10%, 1% to 8%, 2% to 8%, or 2% to 6%, based on the total number of moles (100%) of the organic cation contained in the perovskite compound.
- [81] In an exemplary embodiment, the perovskite compound may contain the divalent organic cation in an amount of 1% to 8%, specifically, 2% to 8%, and more specifically, 2% to 6%, based on the total number of moles (100%) of the organic cation contained in the perovskite compound. In this case, excellent α -phase, light, moisture, and heat stability may be implemented by the divalent organic cation, and the perovskite compound may have a power conversion efficiency that is significantly better than that of amidinium perovskite (a perovskite compound in which A consists of a monovalent amidinium group cation) when the perovskite compound is applied as a light absorber. In a case where the perovskite compound contains the divalent

organic cation in an amount of 2% to 6% based on the total number of moles of the organic cation, the power conversion efficiency of the perovskite compound may be about 20%. In particular, in a case where the perovskite compound contains the divalent organic cation in an amount of 2.0% to 5.0%, the power conversion efficiency of the perovskite compound may be 24% or more. The power conversion efficiency of 24% or more is not reported earlier in an amidinium group perovskite compound containing no α -phase stabilization material known in the related art, such as an inorganic cation or methylammonium ion.

[82] In a specific example, the perovskite compound may not contain an α -phase stabilizer known in the related art. Examples of the α -phase stabilizer may include a monovalent organic ammonium cation such as a methylammonium cation and an alkali metal ion such as Cs^+ . In an exemplary embodiment, the organic cation may include a monovalent amidinium group cation and a divalent organic cation.

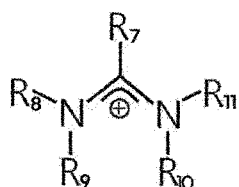
[83] The α -phase stabilizer known in the related art may be excluded by the advantageous effect in terms of the solid α -phase stability by the divalent organic cation according to a specific example of the present invention. Accordingly, it cannot be interpreted that the perovskite compound according to the present invention does not necessarily contain an α -phase stabilizer, and the perovskite compound according to the present invention may further contain an α -phase stabilizer such as Cs^+ or methylammonium, if necessary.

[84] In a specific example, the perovskite compound may contain a non-metal anion positioned at an interstitial site, a vacancy (V_A^-) of an organic cation site, or a non-metal anion positioned at an interstitial site and a vacancy (V_A^-) of an organic cation site, in the crystal structure of the perovskite compound. The non-metal anion positioned at an interstitial site may be a halogen anion, and the halogen anion may be F^- , Cl^- , Br^- , I^- , or any combination thereof. In an exemplary embodiment, the halogen anion may be Cl^- . In an exemplary embodiment, the perovskite compound containing the divalent organic cation may contain a non-metal anion positioned at an interstitial site, a vacancy (V_A^-) of an organic cation site, or a non-metal anion positioned at an interstitial site and a vacancy (V_A^-) of an organic cation site so that the perovskite compound satisfies charge neutrality.

[85] In a specific example of the present invention, the amidinium group cation may satisfy the following Chemical Formula 3.

[86] Chemical Formula 3

[87]



- [88] In Chemical Formula 3, R_7 to R_{11} are each independently hydrogen, C1-C24 alkyl, C3-C20 cycloalkyl, or C6-C20 aryl.
- [89] In Chemical Formula 3, R_7 to R_{11} may be adequately selected depending on use of the perovskite compound. Specifically, a size of a unit cell of the perovskite compound is related to a band gap of the perovskite compound, and the perovskite compound may have a band gap energy (for example, about 1.1 to 1.5 V) that is suitable for use in a solar cell having a small unit cell size. Therefore, when considering a band gap energy suitable for use in a solar cell, R_7 to R_{11} may be each independently hydrogen, amino, or C1-C24 alkyl, specifically, hydrogen, amino, or C1-C7 alkyl, and more specifically, hydrogen, amino, or methyl. Still more specifically, R_7 may be hydrogen, amino, or methyl and R_3 to R_6 may be hydrogen. Substantial examples of an amidinium group ion may include, but are not limited to, a formamidinium ($NH_2CH=NH_2^+$) ion, an acetamidinium ($NH_2C(CH_3)=NH_2^+$) ion, and a guamidinium ($NH_2C(NH_2)=NH_2^+$) ion. Such a specific example is an example considering the use of the perovskite compound, that is, the use as a light absorber for solar light. R_7 to R_{11} may be adequately selected in consideration of a design of a wavelength band of light to be absorbed, a design of a light emission wavelength band when used as a light emitting layer of a light emitting device, and an energy band gap and a threshold voltage when used as a semiconductor device of a transistor.
- [90] In a specific example, a metal of the metal cation may be one or two or more metals selected from the group consisting of metal elements belonging to Group IA, Group IIA, Group IIIB, Group IVB, Group VB, Group VIB, Group VIIB, Group VIIIB, Group IB, Group IIB, Group IIIA, Group IVA, and Group VA of the periodic table. As an example, the metal of the metal cation may be Li, Mg, Na, K, Rb, Cs, Be, Ca, Sr, Ba, Sc, Ti, V, Cr, Fe, Ni, Cu, Zn, Y, La, Zr, Nb, Tc, Ru, Mo, Rh, W, Au, Pt, Pd, Ag, Co, Cd, Hf, Ta, Re, Os, Ir, Hg, Al, Ga, In, Tl, Ge, Sn, Pb, Sb, Bi, Po, or any combination thereof.
- [91] In a specific example, the metal of the metal cation may be a transition metal selected from Group IIIB, Group IVB, Group VB, Group VIB, Group VIIB, Group VIIIB, Group IB, and Group IIB of the periodic table. As an example, the transition metal may be Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Y, Zr, Nb, Tc, Ru, Mo, Rh, W, Au, Pt, Pd, Ag, Mn, Co, Cd, Hf, Ta, Re, Os, Ir, Hg, or any combination thereof.
- [92] In a specific example, the metal cation may be a monovalent metal cation, a divalent metal cation, a trivalent metal cation, a tetravalent metal cation, or combinations thereof. The monovalent metal cation may be Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , or any combination thereof. The divalent metal cation may be Cu^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+} , Cr^{2+} , Pd^{2+} , Cd^{2+} , Ge^{2+} , Sn^{2+} , Pb^{2+} , Eu^{2+} , Yb^{2+} , or any combination thereof. The trivalent metal cation may be Sb^{3+} , Bi^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Sc^{3+} , Y^{3+} , La^{3+} , Ce^{3+} , Fe^{3+} ,

Ru³⁺, Cr³⁺, V³⁺, Ti³⁺ or any combination thereof. The tetravalent metal cation may be Ti⁴⁺, Sn⁴⁺, Ce⁴⁺, Zr⁴⁺, Mo⁴⁺, W⁴⁺ or any combination thereof.

[93] In a specific example, a non-metal of the non-metal anion may be one or more non-metals selected from the group of non-metals belonging to Group VIA and Group VIIA of the periodic table. In an example, the non-metal of the non-metal anion may be O, S, Se, Te, F, Cl, Br, I, or any combination thereof.

[94] In a specific example, the non-metal anion may include a chalcogen anion, a halogen anion, or a halogen anion and a chalcogen anion. A chalcogen of the chalcogen anion may be S, Se, Te, or any combination thereof. A halogen of the halogen anion may be F, Cl, Br, I, or any combination thereof.

[95] In a specific example, the non-metal anion may be a monovalent anion, a divalent anion, or a monovalent anion and a divalent anion. The monovalent anion may be a halogen anion, and the divalent anion may be a chalcogen anion.

[96] When considering the use of the light absorber that is the main use of the perovskite compound, the non-metal anion preferably contains I⁻ as a halogen anion. As known in the art, the non-metal anion contains two or more halogen anions, in particular, I⁻ and Br⁻, which is advantageous in terms of crystal phase stabilization. In a specific example of the present invention, the α -phase is very solidly stabilized by the divalent organic ion, and thus the halogen anion may be free from Br, which means that it is possible to implement a perovskite compound having a smaller band gap energy. However, this may be obtained by the effect according to a specific example of the present invention, and the perovskite compound may contain Br as an anion, if necessary. That is, the perovskite compound containing Br is not excluded in the present invention.

[97] In a specific example, the perovskite compound may contain: both a monovalent amidinium group cation and a divalent organic cation as an organic cation; and a divalent metal ion, monovalent and trivalent metal ions, monovalent, divalent, and trivalent metal ions, monovalent and divalent metal ions, divalent and trivalent metal ions, a trivalent metal ion, divalent and tetravalent metal ions, or a tetravalent metal ion, as a metal cation. In this case, the perovskite compound may contain a monovalent halogen anion, a divalent chalcogen anion, a non-metal anion positioned at an interstitial site, a vacancy (V_A) of an organic cation site, or combinations thereof, so that the perovskite compound satisfies charge neutrality. The charge neutrality may be charge neutrality corresponding to a chemical formula of AMX_3 , AMX_4 , A_2MX_4 , or A_3MX_5 .

[98] As an example, the perovskite compound may contain an organic cation, a metal cation, and a non-metal anion. A monovalent amidinium group cation and a divalent organic cation may be contained as the organic cation, a divalent metal cation may be

contained as the metal cation, and a halogen anion may be contained as the non-metal anion. In this case, the perovskite compound may contain a non-metal anion positioned at an interstitial site, a vacancy (V_A^-) of an organic cation site, or a non-metal anion positioned at an interstitial site and a vacancy (V_A^-) at an organic cation site so that the perovskite compound satisfies the charge neutrality corresponding to the chemical formula of AMX_3 . As a preferred example for use of a light absorber, the halogen anion may include I^- , the divalent metal cation may include Pb^{2+} , and the non-metal anion positioned at an interstitial site may include Cl^- .

- [99] As an example, the perovskite compound may contain an organic cation, a metal cation, and a non-metal anion. A monovalent amidinium group cation and a divalent organic cation may be contained as the organic cation, a divalent metal cation may be contained as the metal cation, and a halogen anion and a chalcogen anion may be contained as the non-metal anion. In this case, the perovskite compound may contain a chalcogen anion so that the perovskite compound satisfies the charge neutrality corresponding to the chemical formula of AMX_3 . On the other hand, in a case where the perovskite compound contains a chalcogen anion that is insufficient to satisfy the charge neutrality corresponding to the chemical formula of AMX_3 , the perovskite compound may contain a non-metal anion positioned at an interstitial site, a vacancy (V_A^-) at an organic cation site, or a non-metal anion positioned at an interstitial site and a vacancy (V_A^-) at an organic cation site so that the perovskite compound satisfies the charge neutrality corresponding to the chemical formula of AMX_3 . As a preferred example for use of a light absorber, the halogen anion may include I^- , the chalcogen anion may include S^{2-} , the divalent metal cation may include Pb^{2+} , and the non-metal anion positioned at an interstitial site may include Cl^- .
- [100] In a specific example, when a band gap energy (eV) of a reference perovskite compound consisting of the same cation and anion as those of the perovskite compound except that the divalent organic cation is not contained is 1, a band gap energy of the perovskite compound may be 0.95 to 1.30, specifically, 1 to 1.20, and more specifically, 1 to 1.15.
- [101] In a specific example, the perovskite compound may have a film shape or a particle shape, but the present invention is not limited thereto.
- [102] The present invention includes a layer containing the perovskite compound.
- [103] The present invention includes a particle containing the perovskite compound. In this case, the particle may include a particle having a size of the order of sub-nanometer to several hundred micrometers and a quantum dot exhibiting quantum confinement effect, and a particle phase of the particle may include a monocrystalline or polycrystalline phase.
- [104] As described above, a monovalent organic ammonium ion such as a methy-

ammonium ion (hereinafter, referred to as an MA cation) is known as a stabilizer that stabilizes a phase of an amidinium group cation-based inorganic-organic hybrid halide material. However, in a case of a perovskite solution containing both a monovalent organic ammonium ion such as an MA cation and an amidinium group ion, the MA cation is deprotonated and methylamine is gasified and then disappears over time. Therefore, an efficiency of a produced perovskite solar cell may be significantly degraded, and process stability and reproducibility may be degraded.

[105] On the other hand, the perovskite compound according to a specific example of the present invention contains both an amidinium group cation and a divalent organic ammonium ion rather than a monovalent organic ammonium ion such as an MA cation, such that solution stability may be significantly improved.

[106] The present invention includes a perovskite solution (I) containing the perovskite compound and a solvent.

[107] Independently, the present invention includes a perovskite solution (II) containing a monovalent amidinium group cation halide, a divalent organic cation halide, a metal halide, and a solvent, or a perovskite solution (II) containing a monovalent amidinium group cation halide, a divalent organic cation halide, a metal halide, a chalcogen source, and a solvent. In this case, since the monovalent amidinium group cation halide, the divalent organic cation halide, and the metal halide are crystallized into the perovskite compound through spontaneous crystallization by removing the solvent, the perovskite solution may contain a monovalent amidinium group cation halide, a divalent organic cation halide, a metal halide, and a chalcogen source so as to satisfy a composition of a desired perovskite compound. In this case, the chalcogen source may be one or two or more kinds of chalcogens selected from S, Se and Te, or a compound of chalcogens. In this case, the compound of chalcogens may be a compound of one kind of chalcogen selected from S, Se, and Te, or a compound of two or more kinds of chalcogens selected from S, Se, and Te, or a combination thereof.

[108] Independently, the present invention includes a perovskite solution (III) containing a monovalent amidinium group cation, a divalent organic cation, a metal ion, a non-metal anion, and a solvent. In this case, since the ions contained in the solution are crystallized into a perovskite compound through spontaneous crystallization by removing the solvent, the perovskite solution (III) may contain a monovalent amidinium group cation, a divalent organic cation, a metal ion, and a non-metal anion so as to satisfy a composition of a desired perovskite compound.

[109] In this case, the perovskite solutions (I, II, and III) may be solutions for preparing a perovskite compound, and may be solutions that may produce a crystalline perovskite compound by application and self-assembly of the solution.

[110] In consideration of specific use of the perovskite compound, each of the perovskite

solutions (I, II, and III) may further contain an additive known in the related art, if necessary. As a specific example, each of the perovskite solutions (I, II, and III) may further contain a surface treating agent known as an additive for improving interface properties with an electron carrier in a perovskite solar cell. As known in the art, the surface treating agent may be C1-C3 alkylammonium chloride that may be decomposed (thermally decomposed) at a temperature of 200°C or lower and may generate chlorine. A substantial example of the surface treating agent may include methylammonium chloride. The C1-C3 alkylammonium chloride may be contained in an amount of 0.20 to 1.00 mole based on 1.00 mole of a metal in the ions contained in each of the perovskite solutions (I, II, and III). However, the present invention is not limited by the specific type and content of the additive.

[111] Even after each of the perovskite solutions (I, II, and III) according to a specific example of the present invention is left at a relative humidity of 25% and a temperature of 50°C for 8 days under a yellow light (dominant wavelength: 635 to 590 nm, indoor light intensity), it is possible to prepare a perovskite compound having substantially almost the same physical properties as those of a perovskite compound produced by using a perovskite solution immediately after preparation (before leaving).

[112] In each of the perovskite solutions (I, II, and III) according to a specific example of the present invention, any polar organic solvent may be used as long as it may dissolve a perovskite compound and may be easily volatilized and removed when being dried. As an example, the polar organic solvent may be one or two or more selected from γ -butyrolactone, formamide, N,N-dimethylformamide, diformamide, acetonitrile, tetrahydrofuran, dimethyl sulfoxide, diethylene glycol, 1-methyl-2-pyrrolidone, N,N-dimethylacetamide, acetone, α -terpineol, β -terpineol, dihydro terpineol, 2-methoxy ethanol, acetylacetone, methanol, ethanol, propanol, butanol, pentanol, hexanol, ketone, and methyl isobutyl ketone, but the present invention is not limited by a specific material. In addition, in a case where each of the perovskite solutions (I, II, and III) contains a chalcogen source or a chalcogen ion, the solvent may further contain a hydrazine-based solvent together with the polar organic solvent. The hydrazine-based solvent may be hydrazine anhydride, hydrazine hydrate, hydrazine derivative, hydrazine derivative hydrate, or combinations thereof, but the present invention is not limited by a specific material of the solvent contained in each of the perovskite solutions (I, II, and III).

[113] The present invention includes a method of preparing a perovskite compound by using each of the perovskite solutions (I, II, and III).

[114] As a specific example, according to the present invention, a layer containing the perovskite compound may be produced by applying and drying the perovskite solution. A specific application and drying method for producing a layer containing a perovskite

compound may be performed with reference to a solution application method according to the related art (for example, Korean Patent No. 1547870 or the like). However, in a case where the perovskite solution further contains a surface treating agent such as methylammonium chloride, annealing of the layer produced by using the perovskite solution at a temperature equal to or higher than a pyrolysis temperature of the surface treating agent may be performed. As an example, in a case where the perovskite solution further contains methylammonium chloride as a surface treating agent, annealing may be performed at 100 to 160°C.

[115] As a specific example, in the present invention, quantum dots or nano particles of the perovskite compound may be prepared by adding the perovskite solution to an aprotic solvent. In the case of preparing quantum dots, the perovskite solution may be added dropwise to an aprotic solvent in the presence of a surfactant. In this case, the surfactant may be contained in the aprotic solvent or in the perovskite solution. Any surfactant may be used as long as it is a material typically used in the preparation of quantum dots of a perovskite compound, and examples thereof may include C1-C18 carboxylic acid, C1-C18 alkylamine, or C1-C18 carboxylic acid and C1-C18 alkylamine, but the present invention is not limited thereto. The surfactant may be contained in an amount typically used for preparing quantum dots of a perovskite compound in the related art. As a specific example, the surfactant may be contained in an amount of 5 to 20 moles based on 1 mole of a metal halide, but the present invention is not limited thereto. Examples of the aprotic solvent may include, but are not limited to, one or two or more solvents selected from dichloroethylene, trichloroethylene, chloroform, chlorobenzene, dichlorobenzene, styrene, xylene, toluene, and cyclohexene.

[116] The present invention includes a device provided with the perovskite compound (containing the perovskite compound).

[117] A perovskite-based device may refer to a device provided with a perovskite compound as a light emitting material, a light absorbing material that absorbs light and generates excitons, or a semiconductor material.

[118] As a specific example, the perovskite-based device includes an optical device containing the perovskite compound as a light emitting material. In this case, the optical device may include a light emitting film, a light emitting diode (LED), an LED package, as well as a display device including them.

[119] As a specific example, the perovskite-based device includes a photovoltaic device containing the perovskite compound (hereinafter, referred to as a perovskite solar cell) as a light absorber. In this case, the perovskite solar cell may include a solar cell in which the perovskite compound is attached to a porous support in a form of a particle (quantum dot or nano particle), and a solar cell including a layer containing of the

perovskite compound.

[120] As a substantial example of the perovskite solar cell, the perovskite solar cell may include a first electrode, a first charge carrier, a light absorption layer containing the perovskite compound, a second charge carrier carrying a charge that is complementary to a charge carried by the first charge carrier, and a second electrode.

[121] At least one of the first electrode and the second electrode may be a transparent electrode.

[122] As the electrode (the first electrode or the second electrode), any conductive electrode in ohmic contact with a charge carrier may be used, and a material typically used as an electrode material for a front electrode or a back electrode in a solar cell may be used. As a non-limiting example, in a case where the electrode (the first electrode or the second electrode) is an electrode material for a back electrode, the second electrode may be one or more materials selected from gold, silver, platinum, palladium, copper, aluminum, carbon, cobalt sulfide, copper sulfide, nickel oxide, and a composite thereof. As a non-limiting example, in a case where the electrode (the first electrode or the second electrode) is a transparent electrode, the electrode may be an inorganic-based conductive electrode such as a fluorine doped tin oxide (FTO), indium doped tin oxide (ITO), ZnO, carbon nanotube (CNT), or graphene, or an organic-based conductive electrode such as PEDOT:PSS.

[123] The first charge carrier and the second charge carrier may carry charges complementary to each other. In a case where the first charge carrier is an electron carrier, the second charge carrier may be a hole carrier. In a case where the first charge carrier is a hole carrier, the second charge carrier may be an electron carrier. In addition, the charge carrier (the first charge carrier or the second carrier) may be a porous layer, a non-porous layer (dense layer), or a stacked layer of a non-porous layer and a porous layer.

[124] The hole carrier may be an organic hole carrier, an inorganic hole carrier, or a stacked layer thereof. The inorganic hole carrier may be an oxide semiconductor, a sulfide semiconductor, a halide semiconductor, or a mixture thereof, that has hole conductivity, that is, a p-type semiconductor. Specifically, examples of the oxide semiconductor may include NiO, CuO, CuAlO₂, and CuGaO₂, an example of the sulfide semiconductor may include PbS, and an example of the halide semiconductor may include PbI₂, but the present invention is not limited by an inorganic hole carrier material. A thickness of the inorganic hole carrier may be 50 nm to 10 μm, specifically, 10 nm to 1,000 nm, and more specifically, 50 nm to 1,000 nm. In a case where the hole carrier has a porous structure, a specific surface area thereof may be 10 to 100 m²/g, and an average diameter of p-type semiconductor particles constituting the hole carrier may be 5 to 500 nm. A porosity (apparent porosity) of the porous hole

carrier may be 30% to 65%, and specifically, 40% to 60%.

- [125] In a case where the hole carrier includes an organic hole carrier, the organic hole carrier may contain an organic hole carrying material, specifically, a monomolecular or high molecular organic hole carrying material (hole conductive organic material). The organic hole carrying material may be any organic hole carrying material used in a general inorganic semiconductor-based solar cell using an inorganic semiconductor quantum dot as a dye. Non-limiting examples of the monomolecular or high molecular hole carrying material may include, but are not limited to, one or two or more materials selected from pentacene, coumarin 6,3-(2-benzothiazolyl)-7-(diethylamino)coumarin, zinc phthalocyanine (ZnPC), copper phthalocyanine (CuPC), titanium oxide phthalocyanine (TiOPC), 2,2',7,7'-tetrakis(N,N-p-dimethoxyphenylamino)-9,9'-spirobifluorene (Spiro-MeOTAD), copper(II) 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluoro-29H,31H-phthalocyanine (F16CuPC), boron subphthalocyanine chloride (SubPc), and cis-di(thiocyanato)-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid)-ruthenium(II) (N3).
- [126] In a case where the organic hole carrying material is a high molecule, as a hole conductive high molecule, one or two or more materials selected from a thiophene-based material, a p-phenylene vinylene-based material, a carbazole-based material, and a triphenylamine-based material may be used, but the present invention is not limited thereto. The hole carrier may be a thin film formed of an organic hole carrying material, and a thickness of the thin film may be 10 to 500 nm, but is not limited thereto.
- [127] The electron carrier may be an organic electron carrier, an inorganic electron carrier, or a stacked layer thereof. The electron carrier may be an electron conductive organic layer, an electron conductive inorganic layer, or a stacked layer thereof.
- [128] An electron conductive organic material may be an organic material used as an n-type semiconductor in a general organic solar cell. As a specific example, the electron conductive organic material may include fullerene (C₆₀, C₇₀, C₇₄, C₇₆, C₇₈, C₈₂, and C₉₅), fullerene-derivatives including [6,6]-phenyl-C₆₁butyric acid methyl ester (PCBM), C₇₁-PCBM, C₈₄-PCBM, and [6,6]-phenyl C₇₀-butyric acid methyl ester (PC₇₀BM), polybenzimidazole (PBI), 3,4,9,10-perylenetetracarboxylic bisbenzimidazole (PTCBI), tetrafluorotetracyanoquinodimethane (F4-TCNQ), or a mixture thereof, but the present invention is not limited thereto.
- [129] An electron conductive inorganic material may be an electron conductive metal oxide used for electron carrying in a general quantum dot-based solar cell or dye-sensitized solar cell. As a specific example, the electron conductive metal oxide may be an n-type metal oxide semiconductor. Examples of the n-type metal oxide semiconductor may

include, but are not limited to, one or two or more materials selected from Ti oxide, Zn oxide, In oxide, Sn oxide, W oxide, Nb oxide, Mo oxide, Mg oxide, Ba oxide, Zr oxide, Sr oxide, Yr oxide, La oxide, V oxide, Al oxide, Y oxide, Sc oxide, Sm oxide, Ga oxide, In oxide, and SrTi oxide, and may include a mixture or composite oxide thereof.

- [130] A thickness of the electron carrier may be 50 nm to 10 μm , and specifically, 50 nm to 1,000 nm. In a case where the electron carrier has a porous structure, a specific surface area thereof may be 10 to 100 m^2/g , and an average diameter of metal oxide particles constituting the electron carrier may be 5 to 500 nm. A porosity (apparent porosity) of the porous electron carrier may be 30% to 65%, and specifically, 40% to 60%.
- [131] In a case where the electron carrier has a porous structure, an electron conductive inorganic or organic layer is further provided between the first electrode and the electron carrier, and may serve to prevent the light absorber from being directly in contact with the electrode in advance and to carry the electrons.
- [132] A thickness of the light absorption layer may be 1 to 2,000 nm, specifically, 10 to 1,000 nm, and more specifically, 50 to 800 nm. Within this thickness range, a photoactive region absorbing light to generate a photoelectron and a photohole may be sufficiently secured while preventing a photocurrent from disappearing by recombination at the time of movement of the photocurrent, and irradiated light may be sufficiently absorbed.
- [133] The present invention includes a solar cell module in which the solar cell described above is used as a unit cell and two or more cells are arranged and electrically connected to each other. The solar cell module may have a cell arrangement and structure typically used in the solar cell field, and may further include a general light concentration unit, and a general light block guiding a path of solar light.
- [134] The present invention includes an apparatus to which power is supplied by the solar cell or the solar cell module.
- [135] As another specific example, the device includes an electronic device containing the perovskite compound as a semiconductor material. The electronic device may include a diode (p-n diode, p-i-n diode, or the like), a bipolar junction transistor (BJT), a field effect transistor (FET), and the like.
- [136] As another specific example, the device includes a sensor containing the perovskite compound.
- [137] Hereinafter, superiority of the perovskite compound according to the present invention will be experimentally described based on a perovskite solar cell which is the most representative use of the perovskite compound, but the present invention is not limited by the presented examples.
- [138] Examples 1 to 3

- [139] On a cut and partially etched fluorine doped tin oxide (FTO) glass substrate, a TiO_2 thin film having a dense structure with a thickness of about 50 nm was produced by a spray pyrolysis method, as an electron carrying layer. The spray pyrolysis method was carried out using a titanium acetylacetonate (TAA):ethanol (1:9 v/v%) solution, and a thickness of the film was adjusted in a manner of repeating a process of spraying the solution for 3 seconds and stopping spraying for 10 seconds, on the FTO substrate placed on a hot-plate maintained at 450°C.
- [140] An ethyl cellulose solution in which 10 wt% of ethyl cellulose was dissolved in ethyl alcohol was added to TiO_2 powder having an average particle size of about 50 to 60 nm (prepared by hydrothermal treatment of an aqueous solution in which 1 wt% (based on TiO_2) of titanium peroxocomplex was dissolved at 250°C for 12 hours), at 5 ml per 1 g of TiO_2 powder, terpinol was added thereto and mixed at 5 g per 1 g of TiO_2 powder, and the ethyl alcohol was removed therefrom by distillation under reduced pressure, thereby preparing a TiO_2 paste. The prepared paste was diluted with 2-methoxyethanol, was coated by spin coating (at 500 RPM for 10 seconds, and thereafter at 1,500 RPM for 40 seconds), and then was subjected to a heat treatment at 500°C for 1 hour, thereby producing a TiO_2 electron carrying layer having a thickness of about 150 to 200 nm formed on the FTO glass substrate.
- [141] To a mixed solvent in which N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were mixed at a volume ratio (DMF:DMSO) of 8:1, formamidinium iodide (hereinafter, formamidinium is denoted by FA, and formamidinium iodide is denoted by FAI) and PbI_2 were added at a molar ratio of 1(FAI):1(PbI_2), and 1.9 mol% (Example 1), 3.8 mol% (Example 2), and 5.7 mol% (Example 3) of methylenediammonium chloride (hereinafter, methylenediammonium is denoted by MDA, and methylenediammonium chloride is denoted by MDACl_2) were added based on FAI. A molar concentration of the prepared solution was about 1.26 M based on FAPbI_3 and MDACl_2 . Methylammonium chloride (MACl) which is a surface treating agent was added to the prepared solution in an amount of 50 mol% based on PbI_2 , thereby preparing a perovskite solution.
- [142] The prepared perovskite solution was added dropwise to the thin electron carrying layer in a predetermined amount, a thin film obtained by a spin coating method (performed at 500 rpm for 5 seconds, at 1,000 rpm for 5 seconds, and thereafter at 5,000 rpm for 10 seconds, and then diethylether is quickly dropped to an upper portion of the electron carrying layer) was annealed at 150°C for 10 minutes and then was annealed again at 100°C for 10 minutes, thereby producing a light absorption layer containing the perovskite solution. As known in the art, MACl which is an additive was entirely evaporated and disappeared together with the solvent remaining in the layer after the annealing process.

[143] Thereafter, a surface of the prepared light absorption layer was spin-coated with a solution in which 5 mg of phenylethylammonium iodide (hereinafter, denoted by PEAI) was dissolved in 1 ml of isopropyl alcohol (at 5,000 rpm for 30 seconds), an organic hole carrying layer was formed by spin-coating the light absorption layer with a hole carrying solution (90 mg of (spiro-OMeTAD)/1 mL of chloro benzene, addition of small amounts of Li-TFSI and TBP) in which spiro-OMeTAD was dissolved (at 3,000 rpm for 30 seconds), and then Au (70 nm) was subjected to thermal evaporation to form a second electrode, thereby producing a solar cell. The efficiency of the produced solar cell was measured at 1 sun with a solar simulator. The results are shown in Table 1.

[144] Comparative Example 1

[145] A solar cell was produced in the same manner as that of Example 1, except that a perovskite solution was prepared so that the composition of FAPbI_3 was satisfied without addition of MDACl_2 , and adding 50 mol% of MACl based on PbI_2 . The efficiency of the solar cell is shown in Table 1.

[146] Comparative Example 2

[147] A solar cell was produced in the same manner as that of Example 1, except that a perovskite solution was prepared by adding FAI , PbI_2 , MABr , and PbBr_2 so that a composition of 0.95 mol of FAPbI_3 and 0.05 mol of methylammonium (MA) PbBr_3 was satisfied, and adding 50 mol% of MACl based on PbI_2 . The efficiency of the solar cell is shown in Table 1.

[148] Table 1

[149]	FAPbI ₃ :xMDACl ₂ (x: mol%)	Efficiency (%)
Example 1	x=1.9	23.5
Example 2	x=3.8	24.4
Example 3	x=5.6	23.2
Comparative Example 1	x=0	22.6
Comparative Example 2	0.95 (FAPbI ₃) 0.05 (MAPbBr ₃)	22.9

[150] From the power conversion efficiency (PCE) of each of the solar cells produced in Comparative Examples 1 and 2 and Examples 1 to 3 shown in Table 1, it could be appreciated that in a case where both a monovalent ammonium group cation and a divalent organic ammonium ion were contained as the cation, the power conversion efficiency was increased. Specifically, it could be appreciated that when the content of the divalent organic ammonium ion was 1 to 6 mol%, the power conversion efficiency was significantly increased, and in particular, when the content of the divalent organic ammonium ion was 2 to 5 mol%, the power conversion efficiency was 24% or higher.

[151] FIG. 1 is a view illustrating the results of measuring a current density-voltage of the solar cell produced in Example 2. As illustrated in FIG. 1, the maximum power conversion efficiency of the solar cell produced in Example 2 was 24.44%, which is a

value increased by about 2% as compared to that of the solar cell produced in Comparative Example 1. In addition, as shown in the table added to FIG. 1, Jsc, Voc, and FF of the solar cell produced in Example 2 were 26.5 mA/cm², 1.14 V, and 81.77%, respectively, and Jsc, Voc, and FF of the solar cell produced in Comparative Example 1 were 26.1 mA/cm², 1.11 V, and 0.78, respectively. It could be appreciated from the results that in a case where both a monovalent ammonium group cation and a divalent organic ammonium ion were contained as the cation, all of the properties (Jsc, Voc, and FF) that represent the performance of the solar cell were improved. In addition, in the case of the solar cell produced by the method of Comparative Example 2 with a well-known composition by which the α -phase is stabilized, Jsc, Voc, and FF were 24.9 mA/cm², 1.14 V, and 0.807, respectively. By comparing Example 2 and Comparative Example 2, it can be appreciated that MDACl₂ stabilizes the α -phase with almost no change in the band gap of FAPbI₃, which leads to significantly increase Jsc.

[152] FIG. 2 illustrates the results obtained by dissolving, in a deuterated dimethylformamide (DMF) solvent for nuclear magnetic resonance (NMR), a perovskite compound obtained by adding MDACl₂ in an amount of Example 2 (Target (3.8 mol%) of FIG. 2) or by adding MDACl₂ after the amount was artificially increased to 10 mol% (Target (10 mol%) of FIG. 2) or 25 mol% (Target (25 mol%) of FIG. 2), and performing a heat treatment at 150°C for 10 minutes, a perovskite compound produced in Comparative Example 2 (Control of FIG. 2), and MDACl₂ (MDACl₂ of FIG. 2), and then performing 1H-NMR analysis. It was confirmed from the results that MDA was not decomposed even after annealing and remained well, whereas, a peak by MA was not observed. Therefore, it could be confirmed that MA was entirely decomposed and disappeared during the heat treatment.

[153] FIG. 3A illustrates the results of analyzing the content of Cl in the perovskite compound prepared by the methods of Example 2 and Comparative Example 1 with XPS. FIG. 3B illustrates the results of analyzing the distribution of Cl by ToF-SIMS. It could be appreciated from the results that the content of Cl in the perovskite compound prepared by the method of Example 2 was high. This means that in the case of the perovskite compound in which the divalent MDACl₂ cation is introduced by the method of Example 2, a large amount of Cl ions are contained in the structure of the perovskite compound as compared with the case of the perovskite compound in which MDACl₂ is not added as in Comparative Example 1, which means that a perovskite compound having a new composition in which I and Cl coexist is produced.

[154] FIG. 4A illustrates the results of observing the change in efficiency of the perovskite solar cells produced in Example 2 and Comparative Examples 1 and 2 by exposing the perovskite solar cells at room temperature (25°C) and a relative humidity of 85%. FIG. 4B illustrates the results of observing the change in efficiency of the perovskite solar

cells depending on the time of the heat treatment at 150°C in atmosphere. As illustrated in FIGS. 4A and 4B, it could be appreciated that the perovskite solar cell produced in Example 2 had very excellent moisture and heat stability as compared with the perovskite solar cells produced in Comparative Examples 1 and 2.

[155] In order to perform a solution stability test, the perovskite solutions prepared in Examples 1 to 3 were left at a relative humidity of 25% and a temperature of 50°C under yellow light (dominant wavelength: 635 to 590 nm, indoor light intensity), and the solar cells were produced in the same manner as those of Examples 1 to 3 by using the perovskite solutions that were left. It was confirmed that the power conversion efficiency of the solar cell produced by using the perovskite solution on the 8th day after the perovskite solution was left was 96% of the efficiency (initial efficiency) of the solar cell produced by using the perovskite solution immediately after preparation.

[156] As a result of the solution stability test, it could be appreciated that the long-term solution stability of the perovskite solution was excellent by the divalent organic ion contained together with the monovalent amidinium ion as the cation. Therefore, the perovskite compound-based device obtained by a solution process may be reproducibly and stably produced by the long-term solution stability, and the perovskite compound-based device may be produced through easy process management.

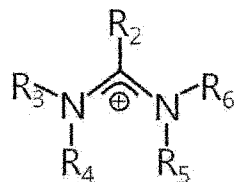
[157] Hereinabove, although the present invention has been described by specific matters, exemplary embodiments, and drawings, they have been provided only for assisting in the entire understanding of the present invention. Therefore, the present invention is not limited to the exemplary embodiments. Various modifications and changes may be made by those skilled in the art to which the present invention pertains from this description.

[158] Therefore, the spirit of the present invention should not be limited to these exemplary embodiments, but the claims and all of modifications equal or equivalent to the claims are intended to fall within the spirit of the present invention.

Claims

- [Claim 1] A perovskite compound comprising:
an organic cation;
a metal cation; and
a non-metal anion,
wherein a monovalent amidinium group cation and a divalent organic cation are contained as the organic cation.
- [Claim 2] The perovskite compound of claim 1, wherein the divalent organic cation is an ammonium group organic cation.
- [Claim 3] The perovskite compound of claim 2, wherein the ammonium group organic cation is an aliphatic ammonium group cation.
- [Claim 4] The perovskite compound of claim 3, wherein the aliphatic ammonium group cation satisfies the following Chemical Formula 1,
Chemical Formula 1
$$\text{NH}_3^+-\text{L}_1-\text{NH}_3^+$$

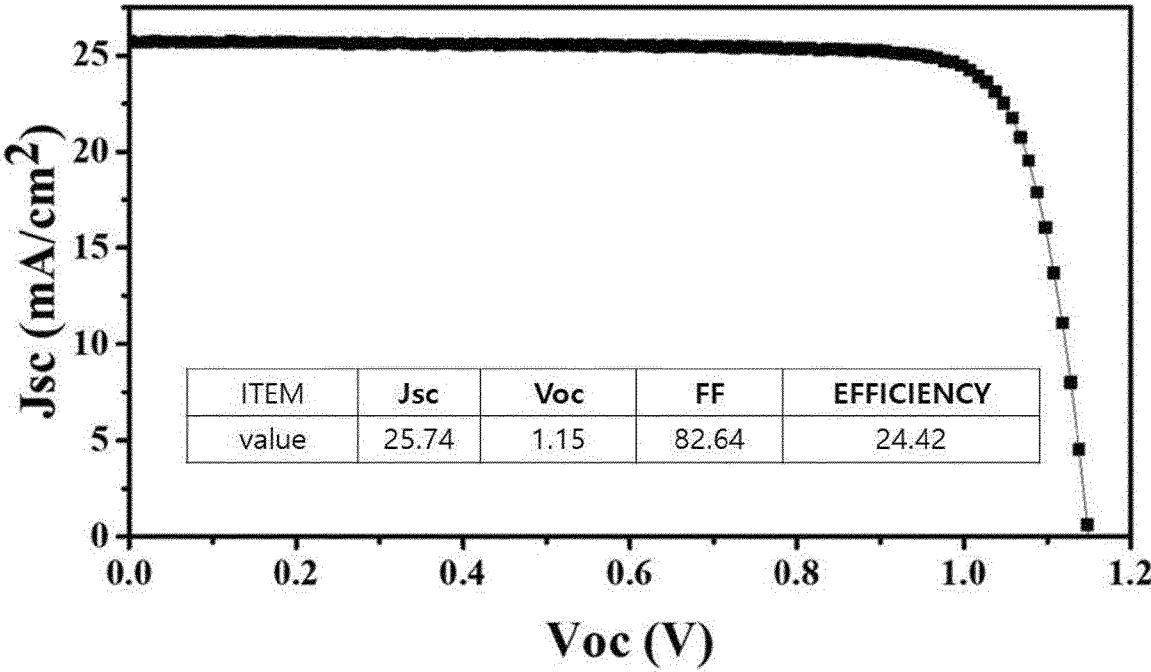
in Chemical Formula 1, L_1 is C1-C3 alkylene.
- [Claim 5] The perovskite compound of claim 1, wherein the divalent organic cation is contained in an amount of more than 0% to 15% or less based on a total number of moles (100%) of the organic cation contained in the perovskite compound.
- [Claim 6] The perovskite compound of claim 1, wherein when a band gap energy (eV) of a reference perovskite compound consisting of the same cation and anion as those of the perovskite compound except that the divalent organic cation is not contained is 1, a band gap energy of the perovskite compound is 0.95 to 1.30.
- [Claim 7] The perovskite compound of claim 1, wherein the non-metal anion is a halogen anion, a chalcogen anion, or a complex anion of a halogen anion and a chalcogen anion.
- [Claim 8] The perovskite compound of claim 1, wherein the non-metal anion is I^- , Cl^- , Br^- , or a mixed anion thereof.
- [Claim 9] The perovskite compound of claim 1, wherein the metal cation is one or two or more selected from Cu^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+} , Cr^{2+} , Pd^{2+} , Cd^{2+} , Ge^{2+} , Sn^{2+} , Pb^{2+} , and Yb^{2+} .
- [Claim 10] The perovskite compound of claim 1, wherein the amidinium group cation satisfies the following Chemical Formula 2,
Chemical Formula 2



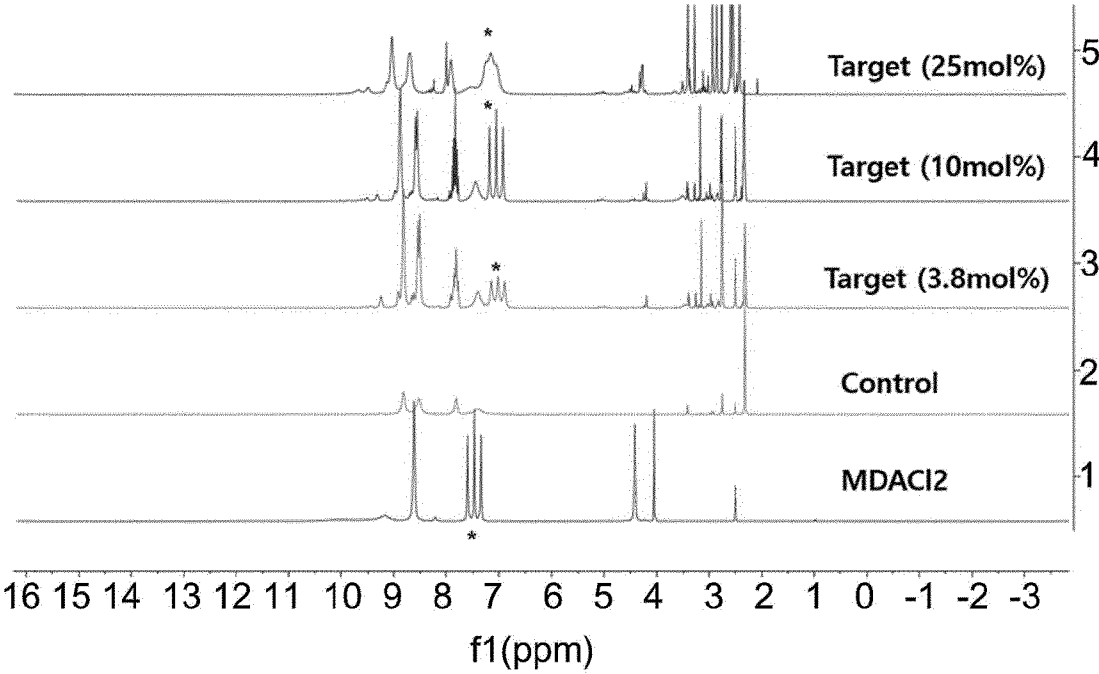
in Chemical Formula 2, R_2 to R_6 are each independently hydrogen, C1-C24 alkyl, C3-C20 cycloalkyl, or C6-C20 aryl.

- [Claim 11] A solution comprising:
the perovskite compound of any one of claims 1 to 10; and
a solvent.
- [Claim 12] A solution comprising:
a monovalent amidinium group cation;
a divalent organic cation;
a metal ion;
a non-metal anion; and
a solvent.
- [Claim 13] A particle comprising the perovskite compound of any one of claims 1 to 10.
- [Claim 14] A layer comprising the perovskite compound of any one of claims 1 to 10.
- [Claim 15] A device comprising the perovskite compound of any one of claims 1 to 10.
- [Claim 16] The device of claim 15, wherein the device is a light emitting device, a diode, a bipolar junction transistor (BJT), a field effect transistor (FET), or a photovoltaic cell.
- [Claim 17] A perovskite solar cell comprising:
a first electrode;
a first charge carrier;
a light absorption layer containing the perovskite compound of any one of claims 1 to 10;
a second charge carrier carrying a charge that is complementary to a charge carried by the first charge carrier; and
a second electrode.
- [Claim 18] An apparatus to which power is supplied by the perovskite solar cell of claim 17.

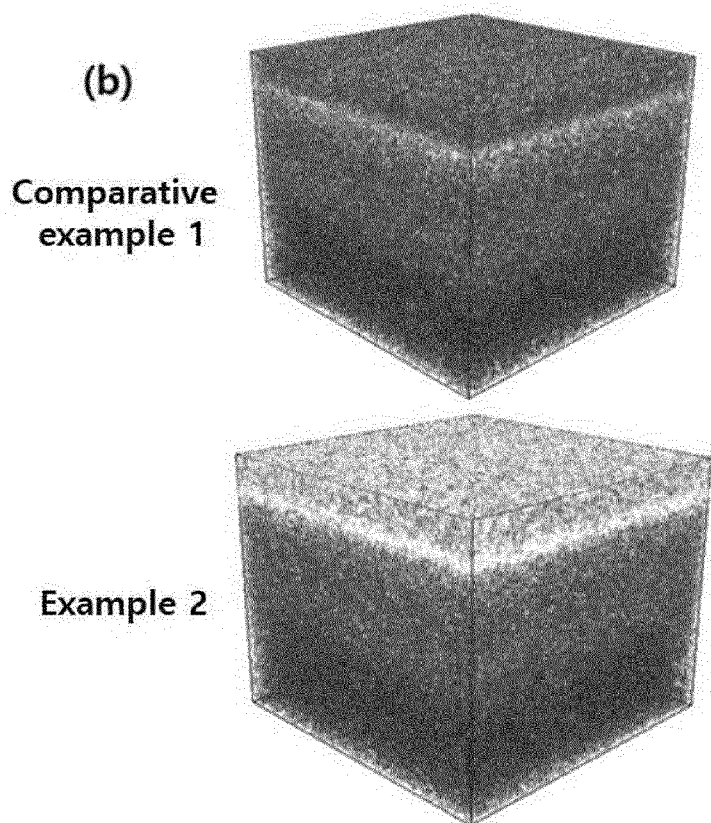
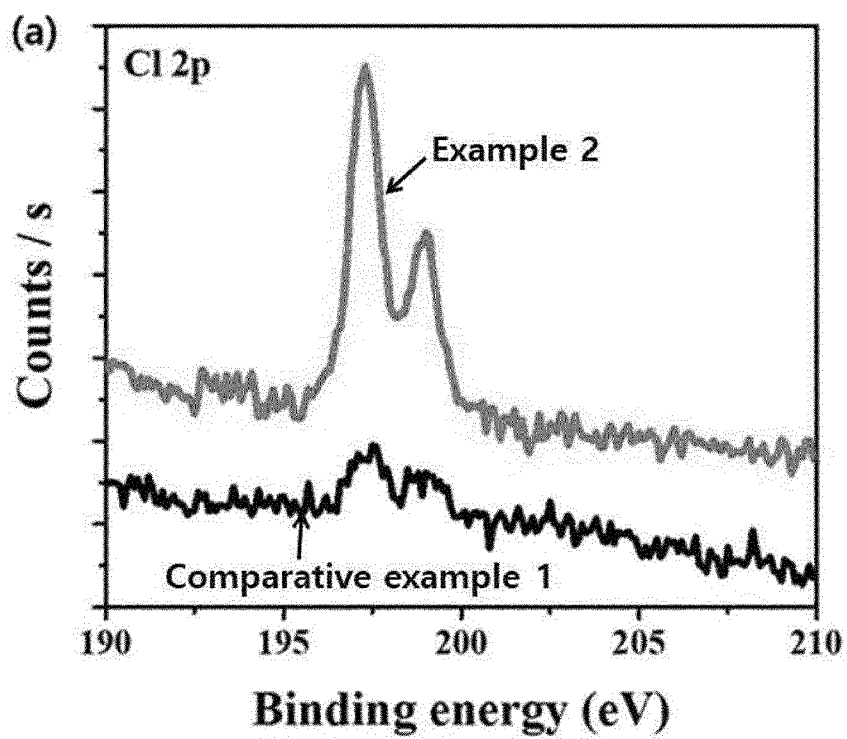
[Fig. 1]



[Fig. 2]



[Fig. 3]



[Fig. 4]

