



(51) International Patent Classification:

*H01L 31/0256* (2006.01)      *H01L 31/06* (2012.01)  
*H01L 31/032* (2006.01)      *H01L 31/18* (2006.01)

(21) International Application Number:

PCT/AU2017/051114

(22) International Filing Date:

13 October 2017 (13.10.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2016904157      13 October 2016 (13.10.2016)      AU

(71) Applicant: **NEWSOUTH INNOVATIONS PTY LIMITED** [AU/AU]; Rupert Myers Building, Gate 14,

Barker Street, UNSW, Sydney, New South Wales 2052 (AU).

(72) Inventors: **UDDIN, Ashraf**; 3 Rhodes Street, Hillsdale, New South Wales 2036 (AU). **ELUMALAI, Naveen Kumar**; 220/717 Anzac Parade, Maroubra, New South Wales 2035 (AU).

(74) Agent: **GRIFFITH HACK**; Level 29 Northpoint, 100 Miller Street, North Sydney, New South Wales 2060 (AU).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,

(54) Title: A METHOD OF FORMING A LIGHT ABSORBING PEROVSKITE LAYER FOR A PHOTOVOLTAIC CELL AND A PHOTOVOLTAIC CELL COMPRISING THE LIGHT ABSORBING PEROVSKITE LAYER

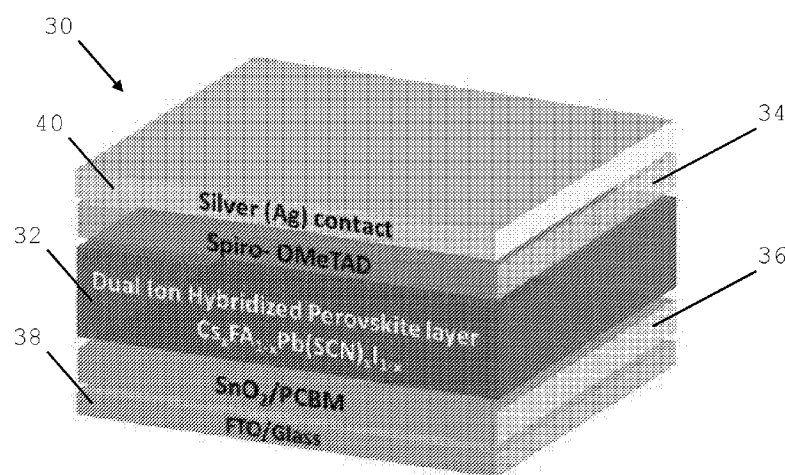


FIGURE 3

(57) Abstract: The present disclosure is directed to perovskite materials of the formula ABX<sub>3</sub> formed by simultaneous ion hybridisation via A-site cation hybridisation (metal-organic) and X-site anion hybridisation (halide-pseudohalide) and their use in stable hybrid perovskite based photovoltaic devices. In preferred embodiments the A-site cation hybridisation is done by hybridising formamidinium ion (FA<sup>+</sup>) with either caesium ion (Cs<sup>+</sup>) or rubidium ion (Rb<sup>+</sup>), the X-site anion hybridisation is done by hybridising one of iodide ion (I<sup>-</sup>), bromide ion (Br<sup>-</sup>) or chloride ion (Cl<sup>-</sup>) with one of thiocyanate ion (SCN<sup>-</sup>), selenocyanate ion (SeCN<sup>-</sup>) or cyanate ion (OCN<sup>-</sup>). In embodiments the cation B is selected to be Pb<sup>2+</sup>. Additionally contemplated are photovoltaic devices comprising: a



OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Published:**

— *with international search report (Art. 21(3))*

A METHOD OF FORMING A LIGHT ABSORBING PEROVSKITE LAYER FOR A PHOTOVOLTAIC CELL AND A  
PHOTOVOLTAIC CELL COMPRISING THE LIGHT ABSORBING PEROVSKITE LAYER

- 1 -

Field of the Invention

5 The present invention generally relates to photovoltaic thin film devices comprising a perovskite based light absorbing material.

Background of the Invention

10 The majority of commercial photovoltaic (PV) modules based on silicon solar cells utilise solar cells fabricated using high quality silicon wafer. Despite the constant drop of silicon prices over the last few years, the cost of silicon still represents a large portion of the final price of these PV modules.

15 Substantial investments have been made in the last 10 years to develop PV devices which use inexpensive materials, possibly in very small quantities. These PV devices are often referred to as thin film solar cells. Cadmium telluride cells are an example of a thin film  
20 solar cell technology which had a major commercial success and competes on the market with conventional wafer-based silicon cells.

Recently, PV devices that use perovskite based light  
absorbing materials have shown very good performance with  
25 a low production cost. A record efficiency of 22% has been demonstrated for a perovskite based solar cell in late 2016. Moreover, perovskite PVs has the lowest energy

- 2 -

payback time (EPBT) compared to any PV technology ever developed.

One of the main problems of perovskite based PV devices is related to operational stability. In other words, the  
5 time it takes before the performance of the PV device start degrading. The stability of current perovskite PV devices is in the range of ~4000 hours. This figure is not compatible with the majority of commercial PV applications.

10 There is a need in the art for perovskite based PV devices with improved stability that are compatible with today's commercial solar applications.

#### Summary of the Invention

In accordance with the first aspect, the present invention  
15 provides a method for manufacturing a stable perovskite photovoltaic device comprising the steps of:

providing a substrate;

forming an electron transport layer which facilitates the transport of electrons from the  
20 photovoltaic device to a contact structure;

forming a photon absorbing layer that comprises a material that has an  $ABX_3$  perovskite structure;

forming a hole transport layer which facilitates the transport of holes from the photovoltaic device to a  
25 contact structure; and

forming a contact arrangement for extraction of charge carriers from the photovoltaic device;

- 3 -

wherein the step of forming a photon absorbing layer comprises the steps of:

providing a first monovalent organic cation;

providing a divalent metal cation;

5 providing a monovalent halide anion;

hybridising the first monovalent organic cation with a second metal divalent cation; and

hybridising the monovalent halide anion with a pseudohalide compound; and

10 the steps of hybridising the first monovalent organic cation with a second metal divalent cation and hybridising the monovalent halide anion with a pseudohalide compound are performed in a manner such that the stability of the material that has a perovskite  
15 structure is improved.

In embodiments, the steps of hybridising the first monovalent organic cation with a second metal divalent cation and hybridising the monovalent halide anion with a pseudohalide compound are performed simultaneously in a  
20 dual-ion hybridisation process. These steps may be performed as fractional hybridisation processes.

The first monovalent organic cation is generally an A-site of the compound and may be a Formamidinium ion ( $\text{FA}^+$ ). The first monovalent organic cation may be hybridised with  
25 alkali ions, such as a Caesium ion ( $\text{Cs}^+$ ) or/and Rubidium ( $\text{Rb}^+$ ). The halide anion is generally an X-site  $\text{I}^-$ ,  $\text{Br}^-$  or  $\text{Cl}^-$  ion and may be hybridised with a thiocyanate compound, such as  $\text{SCN}^-$ ,  $\text{SeCN}^-$  or  $\text{OCN}^-$ .

- 4 -

The perovskite absorbing layer formed by following steps defined above provides an improved stability in comparison to  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite absorbers used in current thin films perovskite solar cells. The stability may be  
5 improved more than 30 times.

In embodiments, the method further comprises the step of forming a charge selective interlayer adjacent the photon absorbing layer to further improve stability of the perovskite material. The charge selective interlayer may  
10 comprise  $\text{SnO}_2$  or Spiro-OMeTAD.

In accordance with the second aspect, the present invention provides a photovoltaic device manufactured in accordance with the method of the first aspect.

In accordance with the third aspect, the present invention  
15 provides a composition for an absorber material of a solar cell, the composition comprising a perovskite material of formula (I):



wherein

20 A is a hybridised monovalent cation comprising a Formamidinium ion ( $\text{FA}^+$ ) and a Caesium ion ( $\text{Cs}^+$ );

B is a divalent metal cation selected from the group consisting of  $\text{Ge}^{2+}$ ,  $\text{Sn}^{2+}$ , or  $\text{Pb}^{2+}$ , and

X is a hybridised ion comprising a monovalent  
25 halide selected from the group consisting of  $\text{I}^-$ ,  $\text{Br}^-$  or  $\text{Cl}^-$  and a pseudohalide compound selected from the group consisting of  $\text{SCN}^-$ ,  $\text{SeCN}^-$  or  $\text{OCN}$ .

- 5 -

In accordance with the fourth aspect, the present invention provides photovoltaic device comprising:

a substrate;

an electron transport layer;

5 a light-absorbing layer comprising a perovskite material based on the composition of the third aspect; and

a hole transport layer;

a contact arrangement;

10 wherein photons absorbed in the light-absorbing layer induce generation of charge carriers that are extractable via the contact arrangement.

Advantageous embodiments of the present invention allow to substantially improve the chemical and thermodynamic stability of the absorber layer of perovskite solar cells without compromising their high performance. Embodiments use a new approach to harness the integrated benefits of simultaneous ion hybridization in perovskite materials via A-site Cation hybridization (Metal - Organic) and X-site Anion hybridization (Halide - Pseudohalide) within the highly successful framework (in terms of power conversion efficiency) of the archetypal organic-inorganic hybrid lead halide perovskite ( $ABX_3$ ) configuration. The invention is unprecedented and first of the kind to inter-combine the phase/entropic stabilization characteristics of concurrent metal and pseudohalide ion incorporation within the perovskite crystal lattice.

15  
20  
25

Embodiments of the invention provide a stable hybrid perovskite material, for the fabrication of PV devices,

- 6 -

via dual-ion hybridization that is highly photo-active as well as intrinsically robust with excellent moisture, thermal and phase stability.

#### Brief Description of the Drawings

5 Features and advantages of the present invention will become apparent from the following description of embodiments thereof, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a flow diagram outlining a series of method  
10 steps to manufacture a photovoltaic device comprising a stable hybrid perovskite material in accordance with an embodiment of the invention;

Figure 2 shows an illustration of the dual-ion hybridisation process in accordance with embodiments;

15 Figure 3 is a schematic illustration of a photovoltaic device comprising of a stable hybrid perovskite material in accordance with an embodiment;

Figure 4 shows a simulated current-voltage curve for a photovoltaic device comprising of a stable hybrid  
20 perovskite material in accordance with an embodiment;

Figure 5 shows simulated efficiencies as a function of time for a photovoltaic device comprising of a stable hybrid perovskite material and a conventional perovskite based PV device;

25 Figure 6 is a schematic view of the doping process of the Electron Transport Layer and the perovskite device

- 7 -

structure employing triple cation based perovskite as light absorbing layer with a J-V curve; and

Figure 7 is a schematic representation of fabricated PSCs (CA device and CC device) (a) and J-V curves (both FB-SC and SC-FB direction at 0.05 V/s) of the best performing CC device (b) and CA device (c).

#### Detailed Description of Embodiments

Embodiments described herein are directed to a PV device which has a photon absorbing layer that comprises a material that has an  $ABX_3$  perovskite structure. The absorber material is formed by dual-ion hybridisation of the A-site and the X-site of the perovskite. In the main embodiment, the absorber material is formed by hybridising a Formamidinium ion ( $FA^+$ ) with a Caesium ion ( $Cs^+$ ) or/and  $Rb^+$  and hybridising a  $I^-$ ,  $Br^-$  or  $Cl^-$  ion with a thiocyanate compound, such as  $SCN^-$ ,  $SeCN^-$  or  $OCN^-$ . The two hybridisation steps are performed simultaneously to provide a perovskite material with a better chemical and thermodynamic stability.

The degradation of perovskite PV devices is predominantly due to the chemical and structural instability of the light absorbing perovskite materials. Specifically, the ions at the A-site and the X-site are found to be the most vulnerable components leading to the destruction of the perovskite crystal structure, when exposed to ambient conditions or heat, moisture and light (UV). The Applicants realised that these issues require a modification of the perovskite material in addition to innovative encapsulation techniques.

- 8 -

PV devices based on the hybrid inorganic-organic lead halide perovskite materials consisting of the  $ABX_3$  crystal structure, where A is an organic cation, B is a metallic cation (typically  $Pb^{2+}$ ) and X = is a halide anion (typically  $Cl^-$ ,  $I^-$  and  $Br^-$ ) have most of the requisites for the implementation of a low cost PV device with a good energy conversion efficiency. The limitation, however, is that the as-formed hybrid lead-halide perovskite thin films lack chemical and structural stability, undergoing rapid retrograde degradation in the presence of moisture, heat or light.

Chemical degradation in a humid environment and thermal degradation of the organic component within hybrid perovskites at relatively low temperatures ( $\sim 80-90^\circ C$  for  $CH_3NH_3PbI_3$ ), are the most recognized degradation pathways for perovskite materials. In addition to the moisture and heat-related degradation, other factors or potential degradation mechanisms such as oxygen, light-induced trap state formation, and electric bias-induced ion migration are also important.

The method for forming a stable perovskite device described herein targets the thin film PV device stability problem where it originates, i.e. the chemical structure of the light absorbing perovskite layer. The Applicants are of the opinion that such a technique, used in synergy with effective encapsulation, provides a perovskite PV device with long term stability. Mere encapsulation of solar modules is insufficient to guarantee very long-term stability.

The method provides a feasible strategy to solve the intrinsic stability issue prevalent in HPSCs without

- 9 -

compromising performance efficiency, by means of dual-ion hybridization and compositional engineering of hybrid perovskite materials. The resulting perovskite addresses the degradation issues arising out of moisture, heat and  
5 light simultaneously. These simultaneous benefit have never been achieved in the art.

Further, the method will also greatly benefit the auxiliary research established on hybrid perovskite materials which include optoelectronic devices such as  
10 LEDs, Photodetectors, Laser, and FETs etc.

Referring now to figure 1, there is shown a flow diagram  
10 with steps to realise a PV device with a photon absorbing layer that comprises a material that has an  $ABX_3$  perovskite structure using the dual-ion hybridisation  
15 process.

At step 12, a substrate upon which the PV device is manufactured is provided. The substrate can be a polymer or a glass and be flexible or hard.

At step 14, an electron transport layer which facilitates  
20 the transport of electrons from the photovoltaic device to a contact structure is formed. Thin film perovskite cells do not have a semiconductor junction like traditional silicon solar cells. Therefore an electron and a hole selective layers allow to split carriers in the device.

25 At step 16, the photon absorbing layer that comprises the material with an  $ABX_3$  perovskite structure is formed. Step 16 include a number of different steps that allow for the dual-hybridisation process to be performed. At step 16a first monovalent organic cation is provided. At step 16b,  
30 a divalent metal cation is provided and, at step 16c, a

- 10 -

monovalent halide anion is provided. The first monovalent organic cation and the second metal divalent cation are hybridised at step 16d and simultaneously the monovalent halide anion the pseudohalide compound are hybridised at  
5 step 16e.

Subsequently, at step 18, a hole transport layer which facilitates the transport of holes from the photovoltaic device to a contact structure is formed before forming a contact arrangement for extraction of charge carriers.

10 Referring now to figure 2, there is shown a schematic diagram illustrating an embodiment of the dual-ion hybridisation process.

The A-site of the perovskite is hybridised with  $\text{FA}^+$  ( $\text{HC}(\text{NH}_2)_2$ ) and  $\text{Cs}^+$  or/and  $\text{Rb}^+$ .

15  $\text{Cs}^+$  or/and  $\text{Rb}^+$  allows for increased formation of the lead-X halide complex providing a good moisture stability. Further  $\text{Cs}^+$  provides high inter-ionic interaction with A site ions, enhancing thermal and light stability.  $\text{Cs}^+$  also allows removing halide segregation under light soaking and  
20 helps stabilising the physical structure of the perovskite.

$\text{FA}^+$  provides an enhanced thermal stability due to the organic cation and good photoactive and bandgap properties, enhancing the energy efficiency of the device.

25 The X-site of the perovskite is hybridised with a  $\text{I}^-$ ,  $\text{Br}^-$  or  $\text{Cl}^-$  ion and a  $\text{SCN}^-$  ion.  $\text{SCN}^-$  increases the entropic stability of the perovskite and enhances thermal stability. Further, it increases interaction between the organic cation (X hydrogen bonding) improving light

- 11 -

stability. The hybridisation process is a fractional process, the fractional substitution allows for better phase stability and reduces the moisture solvation of  $\text{FA}^+$  ions, improving moisture stability.  $\text{SCN}^-$  also allows for improved thermal stability.

Referring now to figure 3 there is shown a schematic illustration 30 of a photovoltaic device comprising of a stable hybrid perovskite material in accordance with an embodiment. The device has a dual-ion hybridised perovskite layer  $\text{Cs}_x\text{FA}_{1-x}\text{PB}(\text{SCN})_x\text{I}_{1-x}$  32 formed in accordance with the method described above. Layer 32 is positioned between a Spiro-OMeTAD electron blocking layer 34 and a  $\text{SnO}_2$ /PCBM hole blocking layer 36. The operation of the electrons and holes blocking layers have been discussed above.

Device 30 is realised on a glass substrate coated with a conductive FTO layer 38. The front contact of device 30 is realised using a silver layer 40.

The type of device shown in figure 3 offers four degrees of freedom serving as the template for developing the most stable perovskite film developed till date. Furthermore, the stability of the dual-ion hybridized perovskite absorber films can be further enhanced during fabrication by employing suitable and stable charge selective interlayers adjacent to the perovskite films thereby opening up extensive possibilities for overall stability improvement.

The rationale behind the concept of simultaneous A- and X-site ion hybridization is explained in the following section. Among the various factors that could affect the

- 12 -

stability of perovskite materials, crystal-structure transition (or phase transition) is an important one that has received less attention. Materials with  $ABX_3$  composition can adopt different crystal structures depending on the size and interaction of the A cation and the corner-sharing  $BX_6$  octahedra. Goldschmidt tolerance factor ( $t$ ) is a reliable empirical index to predict which structure is preferentially formed. The Goldschmidt tolerance factor is calculated from the ionic radius of the atoms using the following expression:

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

where  $r_A$  is the radius of the A cation,  $r_B$  is the radius of the B cation, and  $r_X$  is the radius of the anion. Any Substitution of ABX components should satisfy the requirement of Goldsmith tolerance factor,  $0.9 < t < 1$ , to maintain the stable perovskite structure; where  $t=1$  depicts ideal high-symmetry cubic structure.

Light, heat and moisture induced phase transition results in deviation of the tolerance factor from the ideal value, thereby resulting in the non-photoactive yellow phase of the perovskite. The method designed by the inventors uses dual-ion hybridization to tune the tolerance factor as a compositional design strategy which not only stabilizes the perovskite structure, but also passivates the vulnerability of the A- and X-sites. The method employs Formamidinium iodide ( $FAPbI_3$ ) serving as the archetypal or base material for ion hybridization to start with. Tuning of the tolerance factor by alloying the large-tolerance-factor  $FAPbI_3$  and small-tolerance-factor  $CsPbI_3$  in a precise stoichiometry proportion results in a stabilized

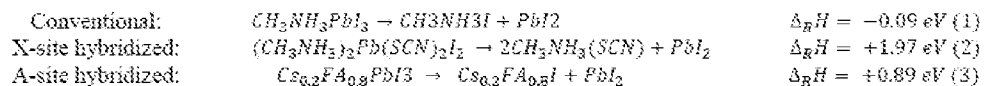
- 13 -

$\alpha$ -phase (black phase) in the mixed perovskite. Such mixed  $\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3$  alloys (where  $x$  is 0.1 - 0.2) exhibits lower  $\delta$ -to- $\alpha$  phase-transition temperature compared to pure  $\text{FAPbI}_3$  and  $\text{CsPbI}_3$ .

- 5 The Cs alloying appears to not only stabilize the perovskite phase of the  $\text{FAPbI}_3$  compound, but also suppress the decomposition to  $\text{PbI}_2$ . Incorporation of partial Cs ion in FA-site results in contraction of cubo-octahedral volume and thereby enhances (FA-I) interaction. Such metal
- 10 hybridization with the organic cation also increases the interaction between the organic cation  $\cdot X$  hydrogen bonding thereby resulting in enhancement of the stability of the perovskite crystal lattice and hindering the retrograde degradation to  $\text{PbI}_2$ . Moreover, Cs incorporation in FA site
- 15 with a fraction of  $x$  (0.1 - 0.2) results in an optimal bandgap of  $E_g \sim 1.5\text{--}1.6$  eV, much favourable for light absorption similar to that of  $\text{MAPbI}_3$ . The stability of  $\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3$  alloys could be further enhanced by replacing two of the halide ions ( $\text{I}^-$ ) with pseudohalides or
- 20 thiocyanate ( $\text{SCN}^-$ ) ions. Pseudo-halides have similar chemical behaviours and properties to true halides. The incorporation of  $\text{SCN}^-$  as a dopant opens up the fundamental band gap versus  $\text{MAPI}$  by 8 meV, and has a remarkable effect on the photoluminescence response concluding that  $\text{SCN}^-$
- 25 incorporation is a valuable addition to the hybrid halide family. The  $\text{SCN}$  incorporated films exhibited a band gap of 1.53 eV which is similar to the values calculated by DFT studies as the  $\text{SCN}$  incorporation matches the perovskite structure of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ .
- 30 Typically, the first step of degradation in moisture involves the formation of hydrated intermediate containing isolated  $\text{PbX}_6^{4-}$  octahedra. The formation constant of the

- 14 -

lead halide complex is essentially its equilibrium constant, which reflects the binding tightness between the halides and the central  $\text{Pb}^{2+}$  ion. The calculated formation constant is only 3.5 for  $\text{PbI}_4^{2-}$  which is in the range of the weak interactions between  $\text{I}^-$  and  $\text{Pb}^{2+}$ . In the case of  $\text{CH}_3\text{NH}_3\text{Pb}(\text{SCN})_2\text{I}$ , the interaction between  $\text{Pb}^{2+}$  and  $\text{SCN}^-$  is much stronger, and the formation constant is up to 7 for  $\text{Pb}(\text{SCN})_4$ . Moreover, comparing the spherical shape of  $\text{I}^-$  ions with the linear shape of  $\text{SCN}^-$  ions as indicated by their Lewis structures, the lone pairs of electrons from the S and N atoms in  $\text{SCN}^-$  can interact strongly with the Pb ion, which in turn stabilizes the frame structure of  $\text{CH}_3\text{NH}_3\text{Pb}(\text{SCN})_2\text{I}$ . Recent theoretical analysis suggests that the perovskite material is intrinsically thermodynamically unstable with respect to phase separation into  $\text{PbI}_2$  and  $\text{CH}_3\text{NH}_3\text{I}$ . The incorporation of SCN significantly enhances the energetics of resistance to decomposition when compared with conventional  $\text{MAPbI}_3$ . Based on the theoretical calculations, the decomposition energy of SCN incorporated perovskites is positive ( $\Delta_R H = +1.97 \text{ eV}$ ) whereas that of conventional  $\text{MAPbI}_3$  is negative ( $\Delta_R H = -0.09 \text{ eV}$ ). The positive value indicates that SCN based films does not spontaneously decompose, unlike  $\text{MAPbI}_3$ .



Combining (2) and (3) would result in  $\Delta_R H \approx 2.8-3 \text{ eV}$  resulting in high resistance to spontaneous decomposition of perovskite structure.

$\Delta_R H$  is the energetics required for the decomposition of perovskite structure. The negative sign indicates spontaneous decomposition. Moreover, DFT studies have also

- 15 -

shown that SCN incorporated perovskites exhibit low effective masses for both holes and electrons, and improved chemical stability against phase separation when compared to MAPI.

5 Hence, simultaneous hybridization of  $\text{Cs}^+$  (metal) ion and  $\text{FA}^+$  (organic) ion at the A-site and hybridization of the halide ions with SCN (pseudohalide) ions at the X-site combines the advantages of both strategies resulting in a highly stable perovskite structure with an optimal band  
10 gap of 1.5-1.6 eV with the cubic or pseudo-cubic structure (near ideal tolerance factor), thereby achieving high PCE as well as high stability simultaneously.

The step of forming the photon absorbing layer 32 require the preparation of a perovskite precursor solution  
15 mixture. In this embodiment, a perovskite with Iodide and SCN ions hybridised at the X-site and  $\text{Cs}^+$  and  $\text{FA}^+$  ion hybridised at A-site is used.

#### *Synthesis of $\text{Pb}(\text{SCN})_2$ .*

An aqueous solution of  $\text{Pb}(\text{BF}_4)$  (10 mL, Aldrich) and NaSCN  
20 (3.5 g, Aldrich) is mixed under stirring in deionized (DI) water (10 mL). The precipitate is filtered off and washed 6 times with DI water to obtain  $\text{Pb}(\text{SCN})_2$ . A Lewis Base adduct approach is employed for the preparation of  $\text{FA}_{1-x}\text{Cs}_x\text{Pb}(\text{SCN})_2\text{I}$  perovskite precursor solution. To begin  
25 with the precursor is primed by dissolving (200 mg) of Lead thiocyanate  $\text{Pb}(\text{SCN})_2$ , Formamidinium iodide FAI (172 mg), and DMSO (78 mg) in 600 mg of DMF under stirring at  $60^\circ\text{C}$  for 3 h. A-site hybridization (i.e. mixing  $\text{Cs}^+$  and  $\text{FA}^+$  ions) to form the desired  $\text{FA}_{1-x}\text{Cs}_x\text{Pb}(\text{SCN})_2\text{I}$  perovskite would  
30 be achieved by substitution of corresponding amount of CsI

- 16 -

(13, 26, 39, and 52 mg of CsI for  $X = 0.05, 0.10, 0.15,$   
and  $0.20$  respectively) instead of FAI. The solution is  
filtered by syringe filter having  $0.45\ \mu\text{m}$  pore size.  
Tuning of precursor stoichiometry by compositional  
5 engineering (i.e. modifying the concentration of FAI,  
 $\text{Pb}(\text{SCN})_2$ , and CsI) allows tailoring of the crystallization  
kinetics resulting in improved thin film homogeneity.  
Optimized precursor solution composition would be  
identified by successive characterization of the deposited  
10 perovskite film (via spin coating) and also by device  
characterization of fabricated perovskite solar cells with  
the as-prepared precursor involving additional post  
processing techniques as described in the device  
fabrication section. In alternative embodiments, the  
15 precursor preparation methodology may be varied  
hybridization at X-site using alternative but analogous  
material compositions, i.e. replacing I with Cl and Br,  
and even SCN with other pseudohalides such as SeCN and  
OCN.

#### 20 *Device fabrication.*

Device 30 is fabricated on fluorine-doped tin oxide (FTO)  
38 coated glass (Pilkington,  $7\Omega/\square$ ). Initially, patterned  
FTO Substrates are cleaned sequentially in Hellmanex  
detergent, acetone, isopropyl alcohol. FTO is then cleaned  
25 for 10 minutes using oxygen plasma. The hole-blocking  
layer 36 is formed by immersing the cleaned FTO substrate  
in a bath of  $40\ \text{mM}\ \text{SnCl}_4$  in aqueous solution for 30 minutes  
at  $80^\circ\text{C}$ . The substrates are then immediately rinsed with  
two consecutive deionized water baths and then sonicated  
30 for 10 s in an ethanol bath followed by drying in  
nitrogen. Subsequently, a  $7.5\ \text{mg/ml}$  of Phenyl-C60-butyric  
acid methyl ester (PCBM) solution in chlorobenzene is spin

- 17 -

coated inside a N<sub>2</sub> glovebox onto the SnO<sub>2</sub> compact layer at 2000 rpm for 45 seconds and annealed at 70°C for 10 minutes. The SnO<sub>2</sub> compact layer reduces UV induced degradation. The as-prepared precursor perovskite solution is then be spin-coated in a nitrogen-filled glovebox at 2000 rpm for 45 s, on the substrate pre-heated at 70°C. Additional processing methods such as inert gas assist, solvent annealing and heat treatment are employed to improve the film quality. Since degradation of the as-formed perovskite film is in many ways analogous to its initial formation, the additional film processing methods is employed to enhance the phase stability of the as-synthesized perovskite films. Hence, 500 µL of diethyl ether are dropped on the spinning substrate after 10 s to improve the film morphology. The films are dried inside a N<sub>2</sub> glovebox on a hot plate at a temperature of 70°C for 1 minute. The films are then annealed in an oven in an air atmosphere at 185°C for 90 minutes. The electron-blocking layer 34 is with a 96mg/ml of spiro-OMeTAD solution in chlorobenzene with additives of 32 µl of Li-TFSi (170 mg/ml 1-butanol solution) and 10 µl of 4-tertbutylpyridine per 1 ml of spiro-OMeTAD solution. Spin-coating is carried out in a nitrogen-filled glovebox at 2000 rpm for 60 s. A 120 nm silver electrode is thermally evaporated under vacuum of  $\approx 10^{-1}$  Torr, at a rate of  $\approx 0.2 \text{ nm}\cdot\text{s}^{-1}$ .

#### *Characterization.*

Hybrid perovskites are intrinsically complex materials, where the presence of various types of interactions and structural disorder may play an important role in the material properties. Ex-situ and in-situ measurements, such as UV vis, X-ray diffraction, vibrational spectroscopy, spectroscopic ellipsometry and X-ray

- 18 -

absorption spectroscopy (XAS) are essential techniques for studying optical properties, structure and phase transformations in materials.

The carrier lifetime of as-prepared perovskite materials is studied by monitoring time-resolved photoluminescence (TRPL) measurements. The influence of ion hybridization on carrier lifetime and ion migration in the fabricated devices are studied using impedance spectroscopy and novel charge transport measurement techniques, such as Resistance dependent photo-voltage (RPV) and High Intensity-RPV, incident photo-current (IPC). As charge accumulation within the bulk and at the interfaces influences the degradation stability of the devices, it is important to understand the impact of ion hybridization on these aspects. The essence of this approach is simply to measure the steady state photocurrent over the broad range of illumination intensity (9 orders of magnitude) as it reveals vital information with respect to device performance and stability under illuminated conditions. It is very important to account for these effects to address the stability issues in perovskite PV devices.

Referring now to figure 4, there is shown a simulated J-V plot for the device described above and shown in figure 3 at room temperature.

The current-voltage (I-V) graph is simulated using the standard single diode equation for the solar cell. The curves are extrapolated with theoretically calculated short circuit current density and open circuit voltage with the low series resistance and high shunt resistance values of the typical perovskite solar cell under 1 sun at AM1.5 condition and room temperature ~25°C.

- 19 -

*Stability testing.*

The Applicants have used a careful combination of stress factors and thorough analysis of PV parameter decaying curves, to understand the underlying degradation pathways of the device described above. Standardized and accelerated stress tests, as described in the standard ISOS-protocols have also been used for stability evaluations. The accelerated moisture-tolerance tests for perovskite materials is performed by monitoring the reflection of the corresponding perovskite films in air with 95% relative humidity at room temperature using an experimental tool developed by the Applicants.

Referring now to figure 5 there is shown a simulated aging trend for 500 h of a high performance dual-ion hybrid perovskite device at room temperature under constant illumination and maximum power point tracking. A trend for the existing conventional perovskite is also shown for comparison.

The simulated lifetime graphs for the dual-ion hybridized material as shown in figure 5 is extrapolated combining the calculated energy values shown in equation (1-3) and the trends obtained in the previous studies in perovskite solar cells with conventional and A-site ion hybridization under continuous illumination.

Referring now to figure 6, there is shown a schematic view of the doping process of the Electron Transport Layer and the perovskite device structure employing triple cation based perovskite as light absorbing layer. Figure 6(c) shows the J-V curve for the device with a ZnO layer.

- 20 -

In the embodiment of figure 6, Rb is used as alternative to Cs. Rb has shown promising stability figures.

The Applicants have performed Lithium (Li) doping of a low-temperature processed zinc oxide (ZnO) electron transport layer (ETL) for highly efficient, triple-cation-based  $\text{MA}_{0.57}\text{FA}_{0.38}\text{Rb}_{0.05}\text{PbI}_3$  (MA: methylammonium, FA: formamidinium, Rb: rubidium) perovskite solar cells (PSCs). Lithium intercalation in the host ZnO lattice structure is dominated by interstitial doping phenomena, which passivates the intrinsic defects in ZnO film. In addition, interstitial Li doping also downshifts the Fermi energy position of Li doped ETL by 30 meV, which contributes to the reduction of the electron injection barrier from the photoactive perovskite layer. Compared to the pristine ZnO, the power conversion efficiency (PCE) of the PSCs incorporating lithium-doped ZnO (Li-doped) is raised from 14.07 to 16.14%. The superior performance is attributed to the reduced current leakage, enhanced charge extraction characteristics, and mitigated trap-assisted recombination phenomena in Li-doped devices, thoroughly investigated by means of electrochemical impedance spectroscopy (EIS) analysis. Li-doped PSCs also exhibit lower photocurrent hysteresis than ZnO devices, which is investigated with regard to the electrode polarization phenomena of the fabricated devices.

Figure 6(c) represents the J-V characteristics of PSCs at the scan rate of 0.05 V/s employing triple-cation perovskite with Li-Doped ZnO as electron transport layer. The PCE of the best device in the FB-SC scan (forward bias to short circuit) is 16.14% with a Voc of 1026.26 mV, Jsc of 22.22 mA/cm<sup>2</sup>, and fill factor of 70.77%. Relatively, the J-V scan performed in the reverse direction SC-FB (short

- 21 -

circuit to forward bias) has slightly lower PCE of about 13.15% with a with a Voc of 940.94 mV, Jsc of 22.04 mA/cm<sup>2</sup>, and fill factor of 63.38%. The difference in the PCE values arising from the scan direction is attributed to  
5 the hysteresis phenomenon.

Figure 7 is a schematic representation of fabricated PSCs (CA device and CC device) (a) and J-V curves (both FB-SC and SC-FB direction at 0.05 V/s) of the best performing CC device (b) and CA device (c).

10 Here, CA ETL demonstrates a 50 meV upshift in Fermi level position with respect to CC ETL, contributing to higher n-type conductivity and lower electron injection barrier at the interface.

The PCE of the best device CA in the FB-SC scan (forward  
15 bias to short circuit) is 16.45% with a Voc of 1012.96 mV, Jsc of 23.61 mA/cm<sup>2</sup>, and fill factor of 68.79%. Relatively, the J-V scan performed in the reverse direction SC-FB (short circuit to forward bias) has slightly lower PCE of about 12.58% with a with a Voc of 930.47 mV, Jsc of 23.76  
20 mA/cm<sup>2</sup>, and fill factor of 56.89%. The difference in the measured photovoltaic parameters is attributed to hysteresis phenomenon arising due to the interfacial polarization issues existing at the perovskite/ZnO layer interface.

25 On the other hand, the PCE of the best device CC in the FB-SC scan is only 10.01% with a Voc of 804.02 mV, Jsc of 22.25 mA/cm<sup>2</sup>, and fill factor of 55.84%. Overall, the CA devices demonstrate about 82% higher average PCE (CA PSC: 15.14%, CC PSCs: 8.33%) compared to CC devices. Apart from  
30 the higher photovoltaic performance, CA devices also show

- 22 -

mitigated photo-current hysteresis phenomena compared to CC devices, which have been found to be correlated with suppressed electrode polarization phenomena in larger grain sized perovskite atop CA ETL.

- 5 The term "comprising" (and its grammatical variations) as used herein are used in the inclusive sense of "having" or "including" and not in the sense of "consisting only of".

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to  
10 the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

15

- 23 -

The Claims as defined in the invention are as follows:

1. A method for manufacturing a stable perovskite photovoltaic device comprising the steps of:

providing a substrate;

5                forming an electron transport layer which facilitates the transport of electrons from the photovoltaic device to a contact structure;

                 forming a photon absorbing layer that comprises a material that has an  $ABX_3$  perovskite structure;

10               forming a hole transport layer which facilitates the transport of holes from the photovoltaic device to a contact structure; and

                 forming a contact arrangement for extraction of charge carriers from the photovoltaic device;

15               wherein the step of forming a photon absorbing layer comprises the steps of:

                 providing a first monovalent organic cation;

                 providing a divalent metal cation;

                 providing a monovalent halide anion;

20               hybridising the first monovalent organic cation with a second metal divalent cation; and

                 hybridising the monovalent halide anion with a pseudohalide compound; and

- 24 -

the steps of hybridising the first monovalent organic cation with a second metal divalent cation and hybridising the monovalent halide anion with a pseudohalide compound are performed in a manner such that  
5 the stability of the material that has a perovskite structure is improved.

2. The method of claim 1 wherein the steps of hybridising the first monovalent organic cation with a second metal divalent cation and hybridising the monovalent halide  
10 anion with a pseudohalide compound are performed simultaneously in a dual-ion hybridisation process.

3. The method of claim 1 or claim 2 wherein the steps of hybridising the first monovalent organic cation with a second metal divalent cation and hybridising the  
15 monovalent halide anion with a pseudohalide compound are fractional hybridisation processes.

4. The method of any one of the preceding claims wherein the first monovalent organic cation is an A-site Formamidinium ion ( $\text{FA}^+$ ).

20 5. The method of any one of the preceding claims wherein the second metal divalent cation is alkali ions.

6. The method of any one of the preceding claims wherein the second metal divalent cation is a Caesium ion or/and Rubidium ions.

25 7. The method of any one of the preceding claims wherein the halide anion is an X-site  $\text{I}^-$ ,  $\text{Br}^-$  or  $\text{Cl}^-$  ion.

8. The method of any one of the preceding claims wherein the pseudohalide compound is a thiocyanate compound.

- 25 -

9. The method of any one of the preceding claims wherein the pseudohalide compound is  $\text{SCN}^-$ ,  $\text{SeCN}^-$  or  $\text{OCN}^-$ .

10. The method of any one of the preceding claims wherein the stability of the material that has a perovskite structure is improved at least 30 times when compared to the stability of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ .

11. The method of any one of the preceding claims wherein the method further comprises the step of forming a charge selective interlayer adjacent the photon absorbing layer to further improve stability of the material that has a perovskite structure.

12. The method of claim 11 wherein the charge selective interlayer comprises  $\text{SnO}_2$  or Spiro-OMeTAD.

13. A photovoltaic device manufactured in accordance with the method of any one of claims 1 to 12.

14. A composition for an absorber material of a solar cell, the composition comprising a perovskite material of formula (I):



wherein

A is a hybridised monovalent cation comprising a Formamidinium ion ( $\text{FA}^+$ ) and a Caesium ion ( $\text{Cs}^+$ );

B is a divalent metal cation selected from the group consisting of  $\text{Ge}^{2+}$ ,  $\text{Sn}^{2+}$ , or  $\text{Pb}^{2+}$ , and

X is a hybridised ion comprising a monovalent halide selected from the group consisting of  $\text{I}^-$ ,  $\text{Br}^-$  or  $\text{Cl}^-$

- 26 -

and a pseudohalide compound selected from the group consisting of  $\text{SCN}^-$ ,  $\text{SeCN}^-$  or  $\text{OCN}$ .

15. A photovoltaic device comprising:

a substrate;

5 an electron transport layer;

a light-absorbing layer comprising a perovskite material based on the composition of claim 14; and

a hole transport layer;

a contact arrangement;

10 wherein photons absorbed in the light-absorbing layer induce generation of charge carriers that are extractable via the contact arrangement.

1/7

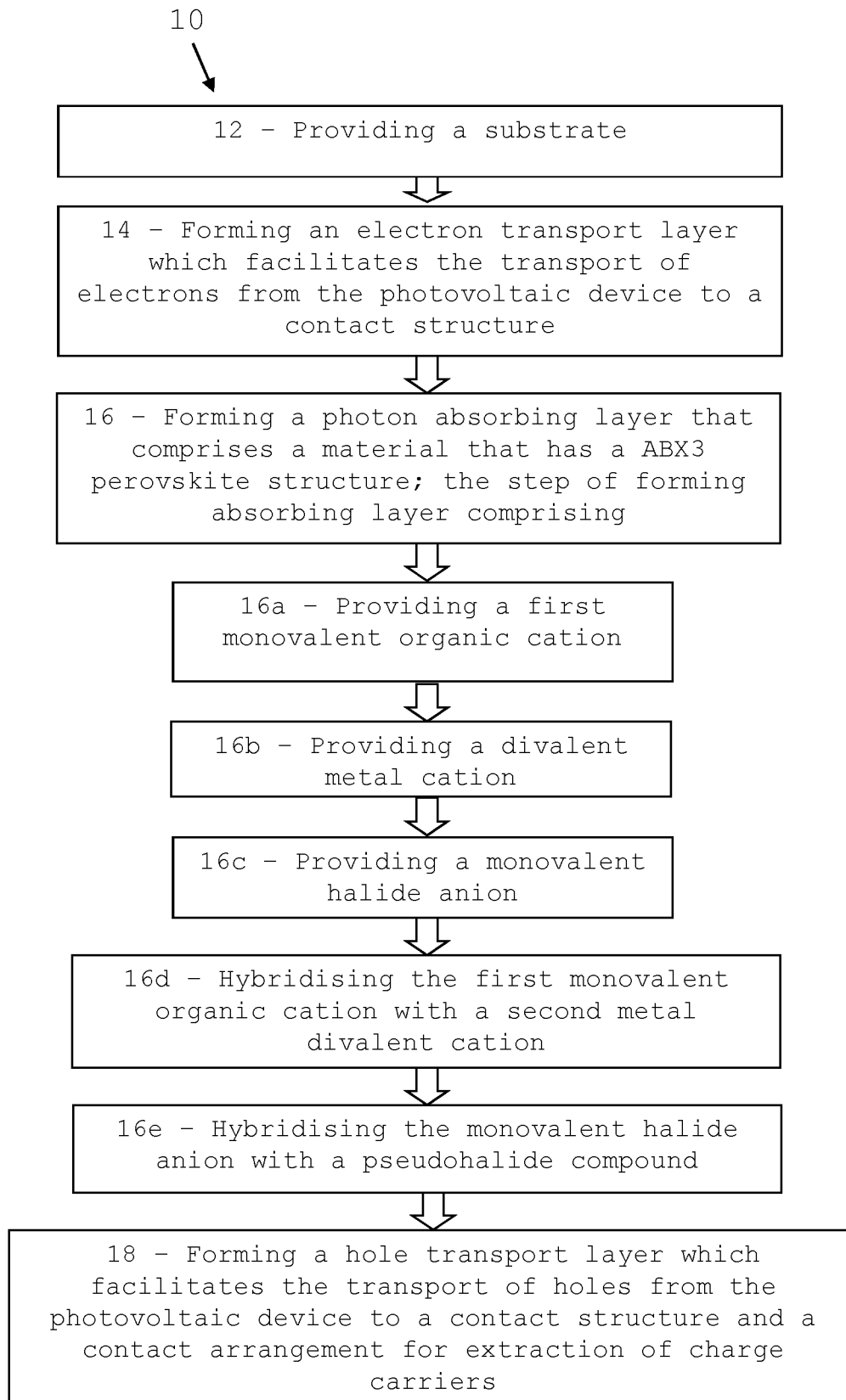


FIGURE 1

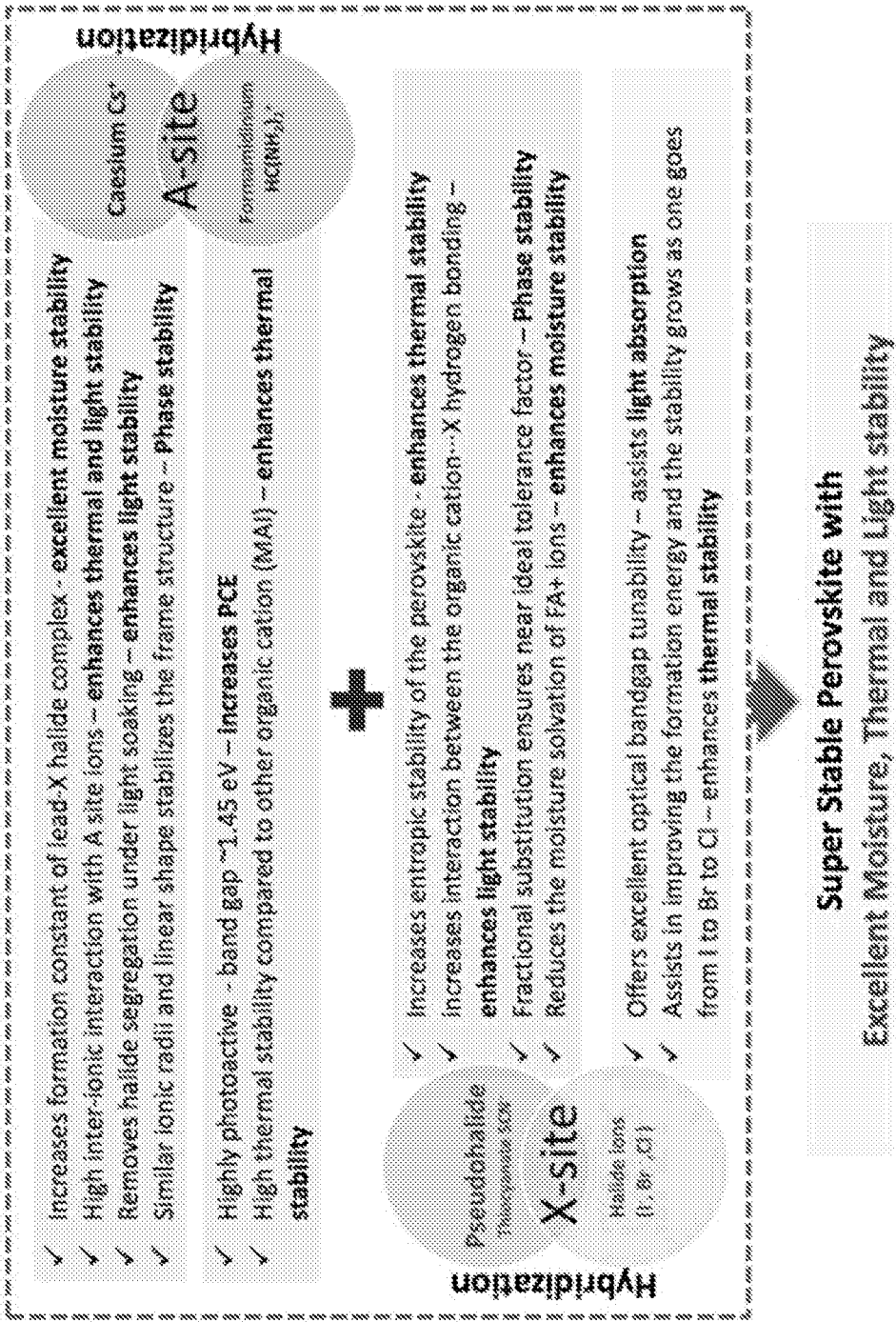


FIGURE 2

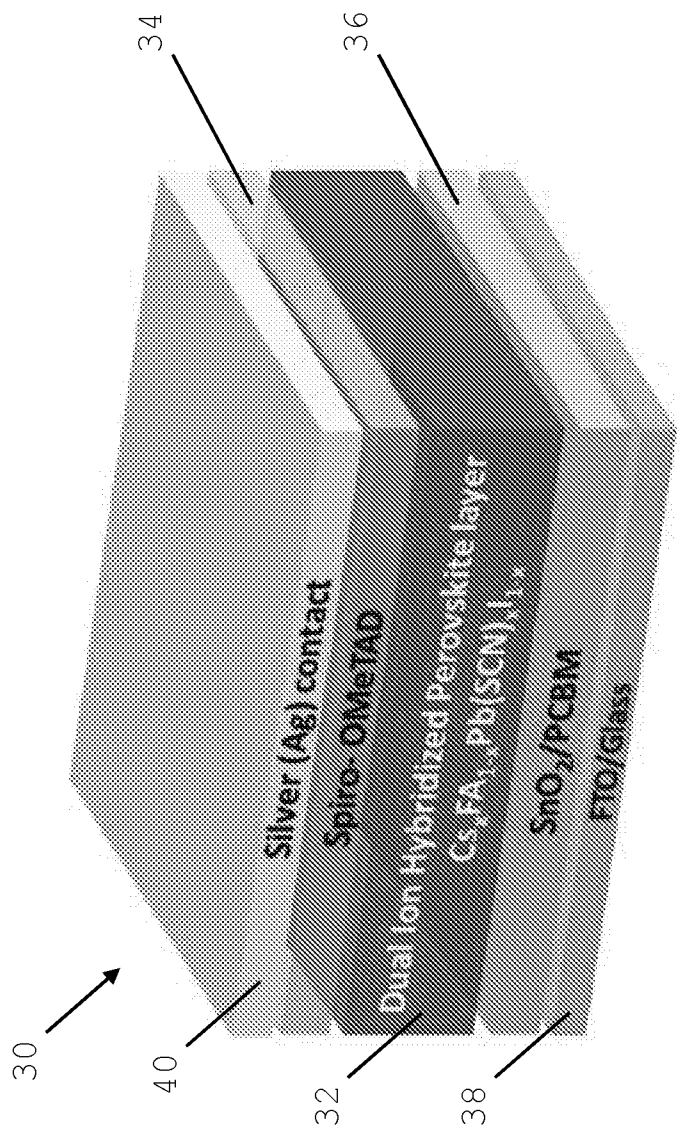


FIGURE 3

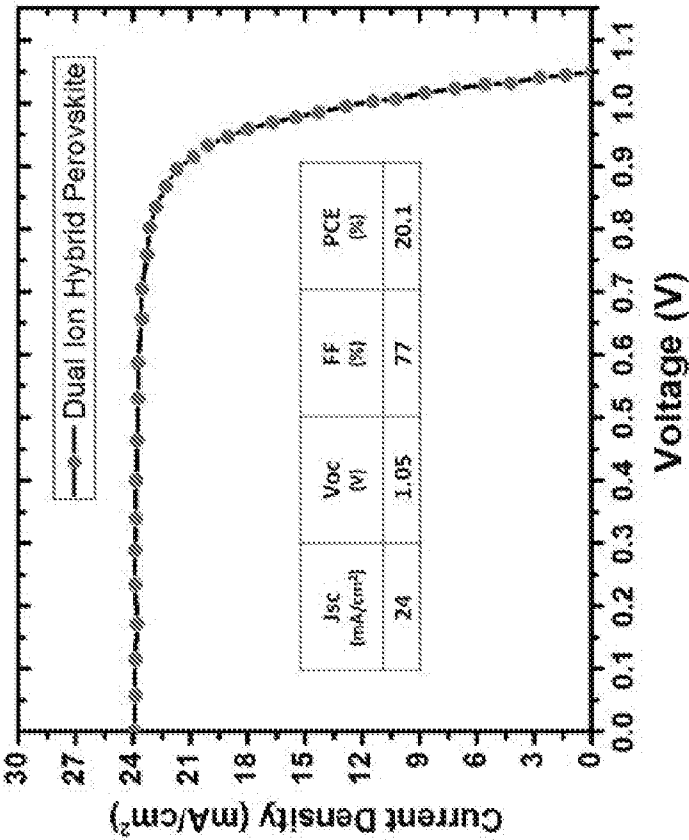


FIGURE 4

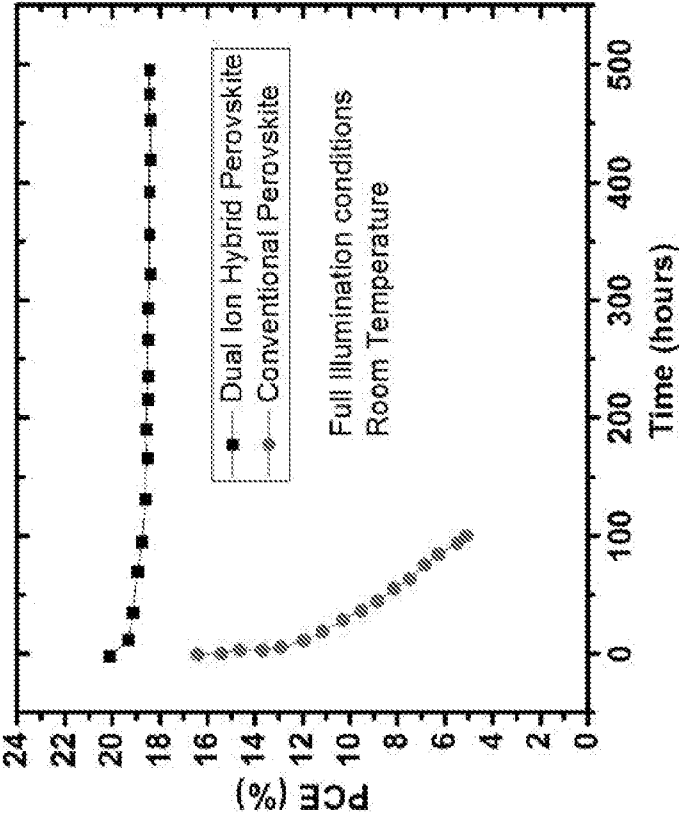
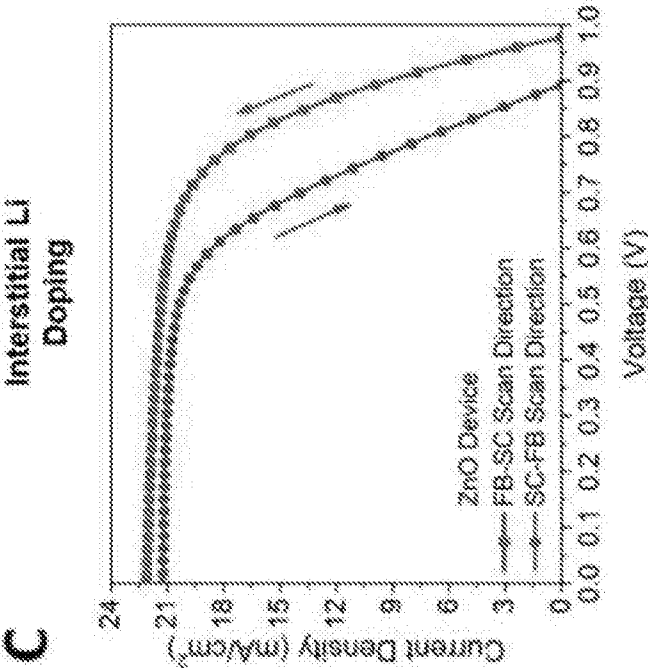
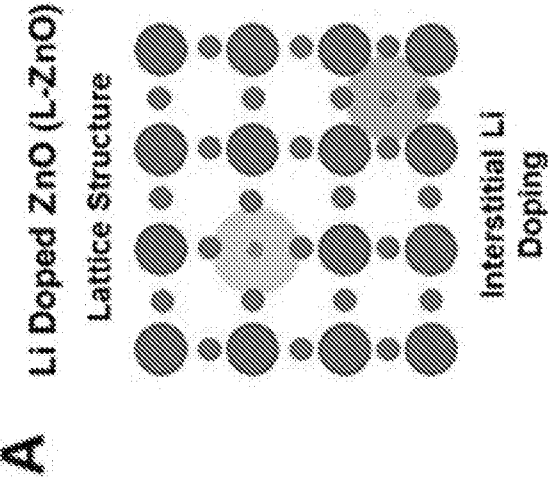
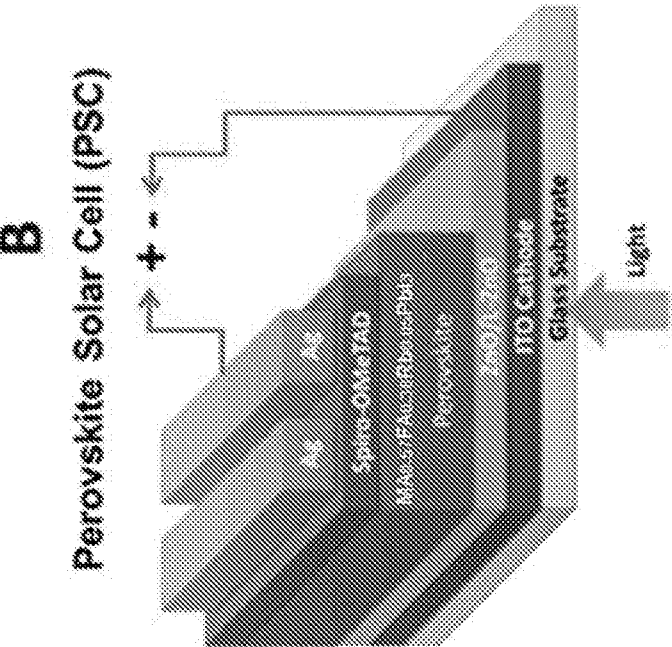


FIGURE 5



**FIGURE 6**

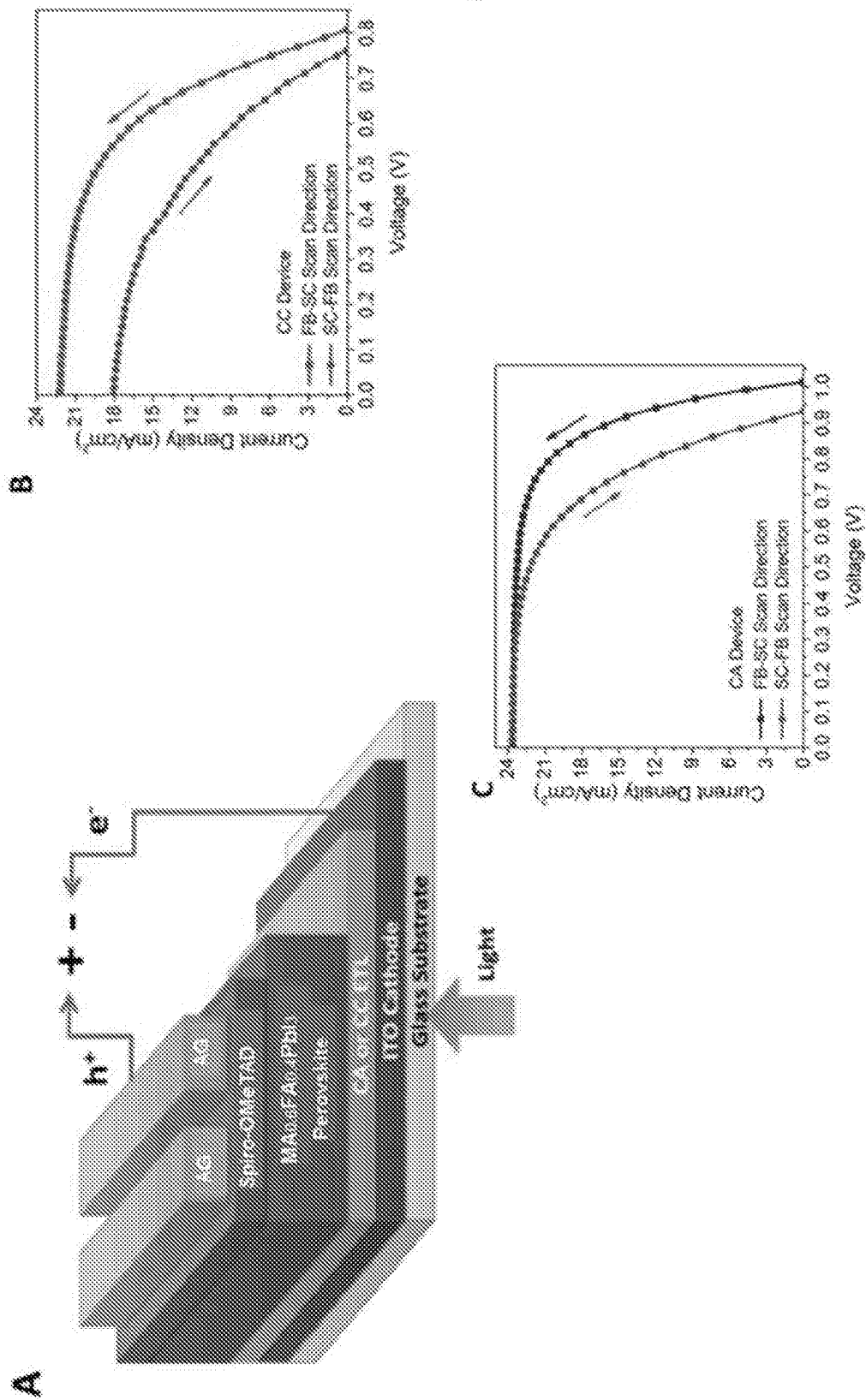


FIGURE 7

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2017/051114

## A. CLASSIFICATION OF SUBJECT MATTER

**H01L 31/0256 (2006.01) H01L 31/032 (2006.01) H01L 31/06 (2012.01) H01L 31/18 (2006.01)**

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)

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)

Database: PATENW (EPODOC, WPIAP and English full text databases). Search terms: H01L 31/-- (IPC and CPC), H01L 27/142 (and sub-marks in IPC and CPC), H01L 51/42 (and sub-marks in IPC and CPC), Y02E 10/50 (and sub-marks in CPC), H01G 9/20 (and sub-marks in IPC and CPC); photovoltaic, solar, H01L 31/04 (and sub-marks in IPC and CPC); H01G 9/2068 (and sub-marks in CPC); perovskite, CMX3, H01L 21/02197 (CPC); pseudohalide, thiocyanate, selenocyanate, cyanate, isocyanate; cation; organic; formamidineum; hole; electron; transport, conduction; layer, film, coating, material; ETL; HTL; AND LIKE TERMS. Database: INSPEC. Search terms: perovskite; Uddin (Author), Elumalai (Author); pseudohalide, thiocyanate, selenocyanate, cyanate, isocyanate; AND LIKE TERMS. Database: Espacenet. Search terms: Newsouth Innovations Pty Limited (Applicant); Ashraf Uddin (Inventor), Naveen Kumar Elumalai (Inventor); perovskite; pseudohalide; formamidineum; caesium; AND LIKE TERMS. Database: Auspat. Search terms: Newsouth Innovations Pty Limited (Applicant); Ashraf Uddin (Inventor), Naveen Kumar Elumalai (Inventor); perovskite; AND LIKE TERMS. Database: Google Scholar. Search terms: Uddin (Author), Elumalai (Author); perovskite; pseudohalide. Applicant and Inventor names searched in internal databases provided by IP Australia.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------|-----------------------|
|           | Documents are listed in the continuation of Box C                                  |                       |



Further documents are listed in the continuation of Box C



See patent family annex

|          |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |
|----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| *<br>"A" | Special categories of cited documents:<br>document defining the general state of the art which is not considered to be of particular relevance                      | "T" | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention                                              |
| "E"      | earlier application or patent but published on or after the international filing date                                                                               | "X" | document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone                                                                     |
| "L"      | document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "Y" | document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| "O"      | document referring to an oral disclosure, use, exhibition or other means                                                                                            | "&" | document member of the same patent family                                                                                                                                                                                                    |
| "P"      | document published prior to the international filing date but later than the priority date claimed                                                                  |     |                                                                                                                                                                                                                                              |

Date of the actual completion of the international search  
19 December 2017Date of mailing of the international search report  
19 December 2017

## Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE  
PO BOX 200, WODEN ACT 2606, AUSTRALIA  
Email address: pct@ipaustalia.gov.au

## Authorised officer

Richard Baker  
AUSTRALIAN PATENT OFFICE  
(ISO 9001 Quality Certified Service)  
Telephone No. +61262832583

| INTERNATIONAL SEARCH REPORT                           |                                                                                                                                                                                                                                                                                                                                                                    | International application No. |
|-------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------|
| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                                                                                                                                                                                                    | PCT/AU2017/051114             |
| Category*                                             | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                 | Relevant to claim No.         |
| X                                                     | WO 2016/038338 A1 (OXFORD PHOTOVOLTAICS LIMITED) 17 March 2016<br>Page 4 lines 17 to 24, page 5 lines 9 to 21, page 6 line 30 to page 7 line 4, page 7 line 13 to page 8 line 5, page 12 lines 28 to 36, page 16 line 27 to page 17 line 10, page 21 lines 31 to 32, page 22 lines 12 to 25, page 23 lines 6 to 21, page 24 lines 18 to 24, page 24 lines 28 to 33 | 1-15                          |
| X                                                     | US 2015/0318477 A1 (IRWIN, MICHAEL D., et al.) 05 November 2015<br>Paragraphs 0028, 0035, 0044, 0048, 0067, 0069, 0076, 0078, 0079, 0107 to 0109, 0112 to 0114 and 0120 to 0121, figures 4 and 10                                                                                                                                                                  | 1-15                          |
| X                                                     | WO 2016/110851 A1 (YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW UNIVERSITY OF JERUSALEM LTD) 14 July 2016<br>Pages 2, 9 to 10, 14 to 17 and 21 to 27, figure 5                                                                                                                                                                                                | 1-15                          |
|                                                       |                                                                                                                                                                                                                                                                                                                                                                    |                               |

Form PCT/ISA/210 (fifth sheet) (July 2009)

| INTERNATIONAL SEARCH REPORT                                                                                                                                                                                                                                           |                  | International application No. |                  |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|-------------------------------|------------------|
| Information on patent family members                                                                                                                                                                                                                                  |                  | PCT/AU2017/051114             |                  |
| This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information. |                  |                               |                  |
| Patent Document/s Cited in Search Report                                                                                                                                                                                                                              |                  | Patent Family Member/s        |                  |
| Publication Number                                                                                                                                                                                                                                                    | Publication Date | Publication Number            | Publication Date |
| WO 2016/038338 A1                                                                                                                                                                                                                                                     | 17 March 2016    | WO 2016038338 A1              | 17 Mar 2016      |
|                                                                                                                                                                                                                                                                       |                  | EP 3191408 A1                 | 19 Jul 2017      |
|                                                                                                                                                                                                                                                                       |                  | US 2017243699 A1              | 24 Aug 2017      |
| US 2015/0318477 A1                                                                                                                                                                                                                                                    | 05 November 2015 | US 2015318477 A1              | 05 Nov 2015      |
|                                                                                                                                                                                                                                                                       |                  | US 9425396 B2                 | 23 Aug 2016      |
|                                                                                                                                                                                                                                                                       |                  | AU 2005256138 A1              | 05 Jan 2006      |
|                                                                                                                                                                                                                                                                       |                  | AU 2005256138 B2              | 08 Mar 2012      |
|                                                                                                                                                                                                                                                                       |                  | AU 2014354911 A1              | 09 Jun 2016      |
|                                                                                                                                                                                                                                                                       |                  | AU 2014354911 B2              | 01 Dec 2016      |
|                                                                                                                                                                                                                                                                       |                  | AU 2015296288 A1              | 23 Feb 2017      |
|                                                                                                                                                                                                                                                                       |                  | AU 2015296288 B2              | 13 Apr 2017      |
|                                                                                                                                                                                                                                                                       |                  | AU 2015349902 A1              | 06 Jul 2017      |
|                                                                                                                                                                                                                                                                       |                  | AU 2015349902 B2              | 23 Nov 2017      |
|                                                                                                                                                                                                                                                                       |                  | AU 2016261906 A1              | 30 Nov 2017      |
|                                                                                                                                                                                                                                                                       |                  | AU 2017201243 A1              | 16 Mar 2017      |
|                                                                                                                                                                                                                                                                       |                  | AU 2017204662 A1              | 27 Jul 2017      |
|                                                                                                                                                                                                                                                                       |                  | CA 2931692 A1                 | 04 Jun 2015      |
|                                                                                                                                                                                                                                                                       |                  | CA 2956633 A1                 | 04 Feb 2016      |
|                                                                                                                                                                                                                                                                       |                  | CA 2968367 A1                 | 26 May 2016      |
|                                                                                                                                                                                                                                                                       |                  | CN 101065159 A                | 31 Oct 2007      |
|                                                                                                                                                                                                                                                                       |                  | CN 105934807 A                | 07 Sep 2016      |
|                                                                                                                                                                                                                                                                       |                  | CN 105934807 B                | 12 Sep 2017      |
|                                                                                                                                                                                                                                                                       |                  | CN 107078219 A                | 18 Aug 2017      |
|                                                                                                                                                                                                                                                                       |                  | CN 107210134 A                | 26 Sep 2017      |
|                                                                                                                                                                                                                                                                       |                  | CN 107437466 A                | 05 Dec 2017      |
|                                                                                                                                                                                                                                                                       |                  | EP 1768729 A1                 | 04 Apr 2007      |
|                                                                                                                                                                                                                                                                       |                  | EP 1768729 B1                 | 04 Jun 2014      |
|                                                                                                                                                                                                                                                                       |                  | EP 2774646 A1                 | 10 Sep 2014      |
|                                                                                                                                                                                                                                                                       |                  | EP 2774646 B1                 | 03 May 2017      |
|                                                                                                                                                                                                                                                                       |                  | EP 3075012 A1                 | 05 Oct 2016      |
|                                                                                                                                                                                                                                                                       |                  | EP 3195372 A1                 | 26 Jul 2017      |
|                                                                                                                                                                                                                                                                       |                  | EP 3221898 A1                 | 27 Sep 2017      |
|                                                                                                                                                                                                                                                                       |                  | JP 2008503278 A               | 07 Feb 2008      |
|                                                                                                                                                                                                                                                                       |                  | JP 5002453 B2                 | 15 Aug 2012      |
|                                                                                                                                                                                                                                                                       |                  | JP 2017504188 A               | 02 Feb 2017      |

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

Form PCT/ISA/210 (Family Annex)(July 2009)

| INTERNATIONAL SEARCH REPORT                                                                                                                                                                                                                                           |                  | International application No. |                  |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|-------------------------------|------------------|
| Information on patent family members                                                                                                                                                                                                                                  |                  | PCT/AU2017/051114             |                  |
| This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information. |                  |                               |                  |
| Patent Document/s Cited in Search Report                                                                                                                                                                                                                              |                  | Patent Family Member/s        |                  |
| Publication Number                                                                                                                                                                                                                                                    | Publication Date | Publication Number            | Publication Date |
|                                                                                                                                                                                                                                                                       |                  | JP 2017535047 A               | 24 Nov 2017      |
|                                                                                                                                                                                                                                                                       |                  | KR 20160078433 A              | 04 Jul 2016      |
|                                                                                                                                                                                                                                                                       |                  | KR 101740206 B1               | 25 May 2017      |
|                                                                                                                                                                                                                                                                       |                  | KR 20170054389 A              | 17 May 2017      |
|                                                                                                                                                                                                                                                                       |                  | KR 20170059487 A              | 30 May 2017      |
|                                                                                                                                                                                                                                                                       |                  | KR 20170093159 A              | 14 Aug 2017      |
|                                                                                                                                                                                                                                                                       |                  | MX 2016006714 A               | 16 Jan 2017      |
|                                                                                                                                                                                                                                                                       |                  | MX 2017001390 A               | 01 Sep 2017      |
|                                                                                                                                                                                                                                                                       |                  | MX 2017006646 A               | 01 Sep 2017      |
|                                                                                                                                                                                                                                                                       |                  | NZ 552297 A                   | 26 Nov 2010      |
|                                                                                                                                                                                                                                                                       |                  | NZ 588502 A                   | 12 Jan 2012      |
|                                                                                                                                                                                                                                                                       |                  | US 2008283060 A1              | 20 Nov 2008      |
|                                                                                                                                                                                                                                                                       |                  | US 8826906 B2                 | 09 Sep 2014      |
|                                                                                                                                                                                                                                                                       |                  | US 2014275552 A1              | 18 Sep 2014      |
|                                                                                                                                                                                                                                                                       |                  | US 8889909 B2                 | 18 Nov 2014      |
|                                                                                                                                                                                                                                                                       |                  | US 2014261692 A1              | 18 Sep 2014      |
|                                                                                                                                                                                                                                                                       |                  | US 9000294 B2                 | 07 Apr 2015      |
|                                                                                                                                                                                                                                                                       |                  | US 2015144195 A1              | 28 May 2015      |
|                                                                                                                                                                                                                                                                       |                  | US 9136408 B2                 | 15 Sep 2015      |
|                                                                                                                                                                                                                                                                       |                  | US 2016035496 A1              | 04 Feb 2016      |
|                                                                                                                                                                                                                                                                       |                  | US 9305715 B2                 | 05 Apr 2016      |
|                                                                                                                                                                                                                                                                       |                  | US 2015144196 A1              | 28 May 2015      |
|                                                                                                                                                                                                                                                                       |                  | US 9331292 B2                 | 03 May 2016      |
|                                                                                                                                                                                                                                                                       |                  | US 2015243444 A1              | 27 Aug 2015      |
|                                                                                                                                                                                                                                                                       |                  | US 9416279 B2                 | 16 Aug 2016      |
|                                                                                                                                                                                                                                                                       |                  | US 2014275602 A1              | 18 Sep 2014      |
|                                                                                                                                                                                                                                                                       |                  | US 9466798 B2                 | 11 Oct 2016      |
|                                                                                                                                                                                                                                                                       |                  | US 2015020808 A1              | 22 Jan 2015      |
|                                                                                                                                                                                                                                                                       |                  | US 9504795 B2                 | 29 Nov 2016      |
|                                                                                                                                                                                                                                                                       |                  | US 2015249172 A1              | 03 Sep 2015      |
|                                                                                                                                                                                                                                                                       |                  | US 9520512 B2                 | 13 Dec 2016      |
|                                                                                                                                                                                                                                                                       |                  | US 2016240796 A1              | 18 Aug 2016      |
|                                                                                                                                                                                                                                                                       |                  | US 9530972 B2                 | 27 Dec 2016      |
|                                                                                                                                                                                                                                                                       |                  | US 2016075881 A1              | 17 Mar 2016      |
|                                                                                                                                                                                                                                                                       |                  | US 9617431 B2                 | 11 Apr 2017      |
|                                                                                                                                                                                                                                                                       |                  | US 2015144198 A1              | 28 May 2015      |

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

Form PCT/ISA/210 (Family Annex)(July 2009)

| <b>INTERNATIONAL SEARCH REPORT</b><br>Information on patent family members                                                                                                                                                                                            |                         | International application No.<br><b>PCT/AU2017/051114</b> |                         |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------|-----------------------------------------------------------|-------------------------|
| This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information. |                         |                                                           |                         |
| <b>Patent Document/s Cited in Search Report</b>                                                                                                                                                                                                                       |                         | <b>Patent Family Member/s</b>                             |                         |
| <b>Publication Number</b>                                                                                                                                                                                                                                             | <b>Publication Date</b> | <b>Publication Number</b>                                 | <b>Publication Date</b> |
|                                                                                                                                                                                                                                                                       |                         | US 2016020038 A1                                          | 21 Jan 2016             |
|                                                                                                                                                                                                                                                                       |                         | US 2016240805 A1                                          | 18 Aug 2016             |
|                                                                                                                                                                                                                                                                       |                         | US 2016248027 A1                                          | 25 Aug 2016             |
|                                                                                                                                                                                                                                                                       |                         | US 2016268529 A1                                          | 15 Sep 2016             |
|                                                                                                                                                                                                                                                                       |                         | US 2016308154 A1                                          | 20 Oct 2016             |
|                                                                                                                                                                                                                                                                       |                         | US 2017028147 A1                                          | 02 Feb 2017             |
|                                                                                                                                                                                                                                                                       |                         | US 2017178822 A1                                          | 22 Jun 2017             |
|                                                                                                                                                                                                                                                                       |                         | US 2017186558 A1                                          | 29 Jun 2017             |
|                                                                                                                                                                                                                                                                       |                         | WO 2006000017 A1                                          | 05 Jan 2006             |
|                                                                                                                                                                                                                                                                       |                         | WO 2014151522 A1                                          | 25 Sep 2014             |
|                                                                                                                                                                                                                                                                       |                         | WO 2015080990 A1                                          | 04 Jun 2015             |
|                                                                                                                                                                                                                                                                       |                         | WO 2016019124 A1                                          | 04 Feb 2016             |
|                                                                                                                                                                                                                                                                       |                         | WO 2016081682 A1                                          | 26 May 2016             |
|                                                                                                                                                                                                                                                                       |                         | WO 2016183273 A1                                          | 17 Nov 2016             |
|                                                                                                                                                                                                                                                                       |                         | WO 2017011239 A1                                          | 19 Jan 2017             |
| WO 2016/110851 A1                                                                                                                                                                                                                                                     | 14 July 2016            | WO 2016110851 A1                                          | 14 Jul 2016             |
|                                                                                                                                                                                                                                                                       |                         | CN 107431127 A                                            | 01 Dec 2017             |
|                                                                                                                                                                                                                                                                       |                         | EP 3243225 A1                                             | 15 Nov 2017             |
| <b>End of Annex</b>                                                                                                                                                                                                                                                   |                         |                                                           |                         |
|                                                                                                                                                                                                                                                                       |                         |                                                           |                         |
| Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.<br>Form PCT/ISA/210 (Family Annex)(July 2009)                                                                                               |                         |                                                           |                         |