The development of low toxic and high efficient solar cells

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Abstract: Since the perovskite battery was put forward in 2009 for the first time, it is widely believed that it may bring huge influence on the reform of the next generation of solar cells. However, the lead element that are widely used in perovskite battery has strong toxicity which determines that it cannot be widely used in industrial production. Therefore, scientific researchers are trying to replace the lead element with some nontoxic elements or the elements with low toxicity like tin, germanium, bismuth and antimony and so on. Although the photoelectric conversion efficiency of these lead-free perovskite is greatly lower than that of lead-base perovskite, researchers already pay great attention on lead free materials and they have achieved remarkable results. The paper mainly introduces the research situation and development prospect of lead-free perovskite material and related devices.

1. Introduction

Energy is the material foundation of human society and economic development, and energy, material and information are the three pillars of the 21st century. However, the main energies in the world like oil, natural gas and coal are faced with serious shortage problem. Therefore, improving the energy structure, guaranteeing the sustainable energy supply and exploring and applying new energies and resources have become a pressing challenge. Among various energies, solar energy is regarded as one of the most ideal energies. It is not only convenient and safe but also has the benefits of wide distribution and long durance. However, how to solve the dispersion and efficiency problem of solar energy is the main challenge that needs to be solved in solar energy application. Solar battery is a way to use solar energy and traditional solar energy is silicon solar energy, mainly in monocrystalline silicon form. But the monocrystalline silicon has high cost and it is very difficult to reduce this cost, which inhibits its further application. Fortunately, the photoelectric conversion efficiency of perovskite solar cells has reached 25.2% after 10-year development, which is comparable to that of crystalline silicon solar cells. This indicates that perovskite solar cells have great development space and high application potential[1].
Figure 1: The development process diagram of the photoelectric conversion efficiency of perovskite solar cells

Perovskite is the general term of a kind of material and its general formula is ABX₃. It can be seen from the figure that in ABX₃ crystal, BX₆ forms a regular octahedron and the BX₆ is connected by vertex X to form a 3D framework. Then, A is embedded in the octahedron gap to stabilize the crystal structure. A-site ion is normally the large inorganic cation or organic ammonium ion. B-site ion is normally lead or tin ion. C-site ion is usually halogen ion. In the actual crystal, the crystal structure may distort or the symmetry may decrease because of ion replacement or other reasons and the crystal can even convert into the non-perovskite structure. Therefore, normally the tolerance factor is used to speculate whether a crystal still has perovskite structure after a ion is replaced[2]. The tolerance factor can be calculated by the formula:

\[ t = \frac{r_A + r_X}{2(r_B + r_X)} \]  
(In the formula, rA, rB, rX are the radius of corresponding ions)

The research shows that the tolerance factor of the perovskite type compounds with stable structure is generally between 0.78 and 1.05. So far, t is still guiding to synthesize the stable perovskite material. This special structure ensures that perovskite has various excellent optical properties, like rational and adjustable band gap, high absorption coefficient, low exciton binding energy, bipolar transmission, low defect tolerance[3-7].

The perovskite solar cell that takes perovskite as photoactive layer is usually composed of five parts, which are anode, cathode, electron, hole transport layer and perovskite absorption layer. After the perovskite absorption layer absorbs the sunlight, it will generate electron hole pair. Then, the electron will be injected into the ETM layer (anode) and the hole will be injected into HTM (cathode). Finally, the current can be formed by the external circuit circulation.

Figure 2: (a) The general structure diagram of ABX₃ perovskite material, (b) The tolerance factor diagram of common perovskite iodide material (The blue mark represents perovskite material. The red mark means none perovskite material. The orange color means AGeI₃ with perovskite similar structure or non-perovskite structure)[8]

Although perovskite solar cells have incomparable advantages when compared with other solar cells,
the absorption material of current perovskite solar cells commonly uses Pb-base perovskite. But Pb is greatly harmful to human body and the environment and related experiments find that the volatility of lead ions can reach up to 0.15μg L⁻¹ and 15μg L⁻¹ in air and water. Thus, the wide application of Pb-base perovskite will inevitably cause serious pollution and damage. So researchers transfer their attention on the lead-free perovskite that does not have toxicity or has low toxicity. For example, the research experiment of Sn-base perovskite, Ge-base perovskite and Bi-base perovskite materials are already started.

2. The current research situation of lead free perovskite

2.1 The research progress of Sn-base perovskite
Among various lead-free perovskites, tin-base perovskite is the ideal replacement of lead-base perovskite because tin and lead belongs to the same group and has similar electronic structure. The common tin-base perovskite material includes cesium tin iodine (CsSnI₃), methylamine tin iodine (MASnI₃) and methamiprid iodine (FASnI₃), etc. These materials have excellent photoelectric properties. For example, their direct band gaps are 1.2-1.4eV, which is more suitable than the traditional lead-base perovskite. Meanwhile, they also have relatively small exciton binding energy and higher carrier mobility⁹. Theoretically, the tin-base perovskite material can obtain the photovoltaic performance that is no poorer than that of lead-base perovskite material. However, the performance of current tin-base perovskite battery is still greatly poorer than that of the same type of lead-base battery. This is mainly caused by two reasons. One is that the divalent tin (Sn²⁺) that constitutes the perovskite structure has chemical instability, which seriously affects the photoelectric properties and the stability of the tin-base perovskite material. The other one is that the crystallization of the tin-base perovskite film is too fast so it is difficult to control the film-forming process¹⁰.

During the exploration process, researchers find that tin-base perovskite material cannot form the film by two steps like other lead-base materials. This is because the dissolution of tin-base perovskite in isopropyl alcohol is greatly higher than that of lead-base perovskite. So the perovskite film cannot be produced by two-step method. Thus, by far, the Sn-base perovskite usually uses the one-step antisolvent method. In 2012, Chen and other researchers produced perovskite solar cell by using CSSnI₃ as the absorption layer of perovskite for the first time and the solar cell realized 0.9% photoelectric conversion efficiency, which paved a new road for the tin-base photoelectric solar cell development¹². In 2014, Kanatzidis and Snaith separately reported the MASnX₃ solar cell with the 6% efficiency, which greatly inspired the interest of scientific researchers. By far, the work efficiency of tin-base perovskite solar cell has exceeded 10%, which makes it possible to replace lead-base perovskite and to widely apply and produce tin-base perovskite¹³,¹⁴. Based on the careful observation of photovoltaic parameters of the Sn-base perovskite, it can be found that it has rational optical band gap and the short-circuit current density
can reach 20 to 25 mA cm\(^{-2}\). However, its average start voltage is only about 0.5V, which is greatly lower than 1.1V of lead-base photovoltaic solar cell. The open-voltage loss of tin-base photovoltaic solar cell is mainly caused by the reason that Sn\(^{2+}\) can be oxidized into Sn\(^{4+}\) easily, which will cause serious p doping and the excessive high background carrier. Then the photogenerated carrier will compound easily and then the start voltage will be decreased.

![Figure 4: The diagram of {en}MASnI\(_3\) type hollow perovskite and corresponding solar cells](image)

The recent studies show that the new 3D hollow perovskite created by introducing diamine ions with long alkyl chain (such as ethylenediamine) into Sn-base perovskite can effectively improve the start voltage of Sn-based perovskite solar cell. Ke and other researchers introduced 10\% ethylenediamine into MASnI\(_3\) to prepare lead free and tin-base perovskite solar cells that took {en}MASnI\(_3\) type perovskite as absorption layer, which increased the start voltage from 0.15V to 0.58V and increased the photoelectric conversion efficiency to 7.14\%[15]. This is because the introduction of diamine cation not only can improve the morphology of the film but also can effectively decrease trap density state so as to improve the service life of current carriers and to improve the property of tin-based perovskite. Based on this situation, Jokar and other researchers added guanidine group into ethylenediamine system and then successfully produced the Sn-base perovskite solar cell with the high photoelectric conversion efficiency up to 9.6. This was the lead free perovskite solar cells that had the highest efficiency at that time[16].

![Figure 5: The diagram of 2D-standard 2D-3D perovskite film and corresponding J-V curve line](image)

In addition, introducing in long-chain organic cations (phenylethylamine) to form low-dimensional structure can also improve the start voltage. Gao and other researchers prepare the (BA)\(_2\)(MA)\(_{n-1}\)Sn\(_n\)I\(_{3n+1}\) type low dimensional perovskite for the first time and realized the photoelectric conversion efficiency of 2.5\%. Later, the low dimensional perovskite steps into the fast development stage[18]. However, as the low dimensional perovskite film has oriented growth direction and conductivity problems, it is difficult to use it to produce the solar cells with high efficiency as well as high stability. To solve this problem, Wang and others use pseudohalide regulator NH\(_4\)SCN to regulate the crystallization process of the perovskite films containing phenylethylamine. They successfully produce the perovskite films with 2D-standard 2D-3D gradient structures. The perovskite with gradient structure can improve the oxidation resistance of the film, can reduce the defect concentration of the film and can improve the carrier.
transport performance. The tin-base perovskite solar cells produced based on this gradient structure can realize the photoelectric conversion efficiency of 9.41%. In the solar cell stability test process, this solar cell can still maintain 90% of the initial efficiency after it works for almost 600 hours[17]. Wu and others introduce 3-phenyl-2-propene-1-amine (PPA) into ammonium stannate iodide (FASnI3) perovskite. The conjugated structure of PPA can not only improve the conductivity of low dimensional perovskite, but also reduce the surface energy of perovskite, which grants it with certain self-repair function. After a series of regulation, the photoelectric conversion efficiency of the battery can reach 9.6% and 92% of the initial standard can be maintained after the battery works for 1140h[19].

In addition to improving the start voltage of tin-base perovskite, the stability of the battery also needs to be improved. To solve this problem, on the one hand, the perovskite that is easy to oxidize shall be coated. Yan and other researchers adopted the in-situ oxidation resistance technology to treat the tin-base perovskite crystals, which obviously improved the stability of tin-base perovskite film and devices in the air. The battery produced in this way can be used in the air stably for over 400 hours when it is not coated and this is the longest service life that the tin-base perovskite battery can realize in the air[20]. On the other hand, the tin-base material that cannot be oxidized can be adopted. Lee and other researchers used Cs2SnI6 as hollow hole transport material and used it to produce dye-sensitized solar cells. In tin-base perovskite material, the Sn of CsSnI3 and CH3NH3SnI3 is in 2+ oxidation status but the Sn in Cs2SnI6 molecular iodide compounds is in 4+ oxidation status, which ensures that it is very stable in the air. However, normally this kind of molecules are isolated octahedrons and they have defects in charge transferring aspect. If the carrier mobility of this material can be improved, it will become a strong competitor for the new perovskite batteries[21].

2.2 The research progress of none Sn-base perovskite
Germanium-base perovskite has the similar ns2np0 electronic structure with Pb2+, and many researchers explored and expected to replace lead-base perovskite with it. However, the band gap of germanium-base perovskite normally is very large and the direct band gap of MAGeI3 and FA GeI3 is about 1.9eV and 2.2eV. Only the band gap of CsGeI3 (1.6 eV) is suitable for the absorption layer of perovskite battery.

In 2015, Constantinos team started to explore the AGeI3 type germanium-base perovskite for the first time (A= MA, FA, CS, etc.)[22]. By adding rational amount of tin element into a kind of 2D germanium perovskite material compounded in the previous time, Han and other researchers formed a series of 2D germanium-tin mix perovskite materials, that are (PEA)2Ge1-xSnxI4. The related researches show that the added Sn element can effectively reduce the gap of 2D perovskite material. When the Sn and Ge ratio is 1:1 in the material, the 2D perovskite material will have the smallest band gap, which can furtherly strengthen the light absorption ability of the material and can improve the sunlight application efficiency[23]. Min and related researchers successfully prepared CsSn0.5Ge0.5I3 solid solution perovskite through sublimation method and its work efficiency can reach 7.11%. The most important thing is that this battery has very good stability and its work efficiency can decrease for less than 10% after it works in N2 air under the sunlight of a single day for 500 hours. These researches find a new development direction for germanium-base perovskite, that is to combine with tin-base perovskite[24].

In addition to germanium, the double-layer bismuth-base and antimony-base perovskite material also attracts the attention of researchers. However, as its gap is indirect gap and is very large and it has transmission inhibition problem, it cannot be applied in perovskite solar cells easily. Although other types of bismuth and antimony compounds like Cs3Sb2I9 and Cs3Bi2I9 do not completely have the excellent photoelectric property of 3D perovskite and they are very stable in the air, it is difficult to apply them in practice because of the gap problem. Therefore, this kind of perovskite is not very good light absorption material at present[25].

In the future, the research ideas shall not only be limited to the halide perovskite. Instead, the oxysulfide perovskite and some double perovskite materials can also be researched so as to obtain more composition change related information of the perovskite lattice. The final research aim is to produce the new type solar cells with higher efficiency, better stability, lower toxicity, lower cost and wide application possibility.
3. Conclusion
The new solar cells shall not only have high energy conversion efficiency, but also shall have the characteristics of none toxicity, low cost, large production possibility and good stability. Although the total Pb content in 500 nanometer perovskite film is very small and some production methods can be adopted to prevent the Pb diffusion, like collecting all the Pb-base perovskite, these will greatly increase the cost of perovskite. The research on lead free perovskite can fundamentally solve the toxic lead problem.

Based on the previous discussion, it seems that only tin-base perovskite and germanium-base perovskite has the possibility to realize high performance in the future. However, even if Sn-base perovskite is coated, its stability is still poorer than that of Pb-base perovskite. But, once the Sn4+ oxidation problem is solved and once the photocarrier recombination rate is inhibited to the same level of that of APbI3 material, the Voc of 0.8 to 1.00 V can be realized and the photoelectric conversion rate can be improved to 15%. In this way, perovskite will become a powerful competitor in the photovoltaic industry. Although the photoelectric conversion efficiency of germainium-base perovskite is relatively low at present, it has high stability. Combing the benefits of tin-base perovskite and germanium-base perovskite together, that means producing the Ge/Sn perovskite, is the hot point of current perovskite research. The research of perovskite solar cell technology is constantly developing and more researches and investments are conducted, which ensures that it will have a broad development prospect.

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