

Structural parameters and development trend analysis of perovskite solar cells

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Abstract. Calcium titanite solar cells have been one of the hot spots of scientific research in recent years due to their excellent photovoltaic properties. This article talks about calcium titanite solar cells from three aspects: material structure, solar cell internal structure and photovoltaic properties. This paper describes the internal structure of perovskite cell and analyzes its photoelectric conversion principle. At the same time for open circuit voltage, short circuit current, conversion efficiency and other important indicators made a detailed introduction. In view of the current development of solar energy, we hope to make several optimization enhancements, one is to improve the stability of solar panels, the second is to reduce the toxicity of the raw material itself, and the last point is how to prepare the method of large area. It is hoped that the research and improvement in this paper can promote the industrialization and industrial preparation of calcium titanite solar cells, which has positive significance for the development of solar cells.

Keywords: solar cell, photovoltaic, internal structure, properties.

1. Introduction

Solar energy has always been considered inexhaustible and easily accessible, so humans have been using it for a long time. Of course, previous generations only used solar energy directly. In modern times, with the rise of scientific research, it has been discovered that solar energy can be converted into a variety of energy sources, and this interconversion of energy has opened up the prospect of solar energy applications. After years of development and research, there have been many applications of solar energy, such as solar collectors, solar cells, and solar wireless monitoring. Among them, solar cells have been a hot spot for research due to their wide variety and wide range of use.

There are many types of solar cells, and a common way to classify them is by the different light-absorbing layers (silicon-based, organic, dye-sensitized, polymer film, and chalcogenide). After more than ten years of research, the PCE of chalcogenide solar cells has grown from 3.8 % in 2009 to 25.5 % in 2021[1], and the highest efficiency has been certified at 25.2 % [2]. There are various processes for the preparation of chalcogenide solar cells and they have many advantages such as high photoelectric conversion efficiency and adjustable band gap, and many people are working on this direction today.

2. Internal Structure Of Calcium Titanite Solar Cell

2.1. Structure of Chalcogenide Material

Calcium titanite materials have a long history, and the calcium titanite solar cell is a recent direction, which was first proposed and introduced by Miyasaka, a Japanese scholar.

In the 19th century, the Russian geologist Perovski discovered the oxide CaTiO_3 (calcium titanate), so the ABX_3 structure has been collectively referred to as calcium titanite, and its English name is Perovskite after its discoverer. The structure of chalcocite is an octahedral structure, where the A-site ion is at the apex (usually cations such as MA^+ , FA^+ , Cs^+ , etc.), the B-site ion is at the center (usually

cations such as Pb^{2+} , Sn^{2+} , etc.), and the X-site ion is at the center (usually halogen ions such as I^- , Br^- , Cl^- , etc.). The octahedral shape of chalcogenide material is shown in Figure.

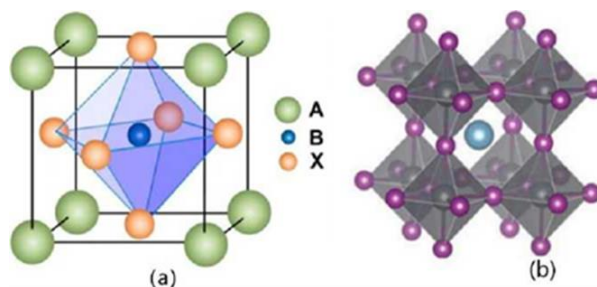


Figure 1. Structure of perovskite ABX_3

2.2. Structure of Chalcogenide Solar Cells

As in conventional cells, various materials with different functions are deposited on the substrate by spin coating and vapor deposition to form a chalcogenide solar cell. A chalcogenide cell is composed of a substrate, a transparent anode, an electron transport layer (ETL), a chalcogenide active layer, a hole transport layer (HTL), and a back electrode. The electron and hole transport layers are often collectively referred to as the charge transport layer. Depending on the charge transport layer and the order, the calcium titanate solar cells are generally divided into four structures: planar/mesoporous p-i-n structure, planar/mesoporous n-i-p structure.

Table 1. Structure of Chalcogenide Solar Cells

Planar p-i-n structure	Planar n-i-p structure	Mesoporous p-i-n structure	Mesoporous n-i-p structure
Metal Cathode	Metal Cathode	Metal Cathode	Metal Cathode
electronic transport layer	cavity transport layer	electronic transport layer	cavity transport layer
Calcium titanium oxide absorber layer	Calcium titanium oxide absorber layer	Calcium titanium oxide absorber layer	Calcium titanium oxide absorber layer
cavity transport layer	electronic transport layer	cavity transport layer	electronic transport layer
ITO/FTO Anode	ITO/FTO Anode	ITO/FTO	ITO/FTO

The difference between the mesoporous structure and the planar structure is that the mesoporous structure has an additional porous skeleton layer. This special mesoporous layer can assist the crystallization and growth of chalcogenide, and has an important role in regulating the morphology of chalcogenide. The common materials used for mesoporous layers are TiO_2 , ZnO , Al_2O_3 , ZrO_2 , etc [3]. Anode substrates are mainly conductive glasses (ITO and FTO), but many flexible devices use PET, PEN, and other bendable and foldable substrates.

bend and fold substrates [4]. The charge transfer layer should have a good ability to transfer charge in order to improve the photovoltaic performance of the device. The commonly used electron transport layer materials are mainly SnO_2 , TiO_2 , PCBM, O_{60} , etc. Commonly used hole transport layer materials include Spiro-OMeTAD [5], PEDOT: PSS [6], PTAA [7], small molecule cavities, etc. The commonly used metal cathodes are AIK Ag, Al, etc. These metal electrodes have high work function and can match well with the chalcogenide layer, but they also have problems such as high cost and poor environmental stability. In addition, there are some studies using carbon electrodes to replace metal electrodes, and good efficiency has been achieved.

2.3. Theory of Calcium Titanite Solar Cells

Sunlight shines from the glass side, and due to the good light transmission of the conductive glass and charge transport layer, photons reach the active layer of chalcogenide and are absorbed by

it. Because of the low exciton binding energy of chalcogenide at room temperature, the excitons are dispersed into freely moving electrons and holes. The electrons reach the anode through the electron transport layer and the holes reach the metal cathode through the hole transport layer, and finally a closed circuit is formed by external wiring to generate current.

In order to improve the performance parameters of the chalcogenide cell, according to the previously mentioned principles, we should choose a substrate with good transmittance in the visible range, a charge transport layer material with efficient carrier extraction and transport, a chalcogenide active layer with high absorption of visible light, or add some additional materials to improve the charge transport capability.

J_{sc} , V_{oc} , FF, and PCE together form the photovoltaic parameters of a chalcogenide solar cell. J_{sc} refers to the maximum current flowing through the circuit when the voltage is zero in the short-circuit condition; V_{oc} refers to the voltage across the p-n junction in the open-circuit condition; and the fill factor FF refers to the maximum output power? "The larger the FF, the smaller the chance of carrier compounding inside the cell and the higher the photoelectric conversion efficiency.

3. Photoelectric Properties

3.1. Open-Circuit Voltage

Under the same temperature and radiation conditions, the voltage in the no-load state of the battery is called the open circuit voltage, which is expressed by V_{oc} . Specifically, it can be interpreted as the voltage output of the ideal solar cell when the series resistance is 0 and the parallel resistance is infinity and the external circuit is open.

$$V_{OC} = \frac{AKT}{q} \ln\left(\frac{I_L}{I_0} + 1\right) \approx \frac{AKT}{q} \ln \frac{I_L}{I_0} \quad (1)$$

Where I_L is the light generated current inside the solar cell.

The open-circuit voltage V_{oc} of solar cells is not related to the size of the cell coverage. Under normal conditions, the voltage of a chalcogenide solar cell at no-load condition is about 877-891mV and can reach up to about 1260mV.

3.2. Short-Circuit Current

Under certain temperature and irradiance conditions, the output current of the solar cell when the terminal voltage is 0 is the short-circuit current. At the intersection of the IV curve and the ordinate, the store is the short-circuit current, usually represented by I_{sc} .

$$I = I_L - I_0(e^{qU/AKT} - 1) \quad (2)$$

The size of the solar cell coverage generally determines the size of the short circuit current of the solar cell. In general, the I_{sc} value of a $1cm^2$ Calcium Titanite Solar Cell ranges from 22 to 36 mA.

3.3. Fill Factor

Fill factor is an important parameter to judge the performance of solar cells. The fill factor is defined as the ratio of the maximum power of the solar cell to the product of the open-circuit voltage and the short-circuit current. Usually represented by FF.

$$FF = \frac{I_m V_m}{I_{sc} V_{oc}} = 1 - \frac{AKT}{qV_{oc}} \ln\left(1 + \frac{qV_m}{AKT}\right) - \frac{AKT}{qV_{oc}} \quad (3)$$

In this equation, I_{sc} and V_{oc} is the output power when the circuit is in the limit state, I_m and V_m is the maximum output power.

On the IV curve, the Y axis represents the voltage in the no-load state, and the X axis represents the current when it is not normally connected, so the interval contained in X and Y is the limit output power of the battery. We consider the maximum output power value of the battery to be the

rectangular area formed by the line drawn parallel to the XY axis at the point of maximum power and its horizontal and vertical coordinates. The fill factor of the battery is defined as the ratio of the limit output power value to the maximum output power value.

The smaller the series resistance of the solar cell and the larger the shunt resistance, the larger the fill factor and the larger the area enclosed on the IV image, which means the IV curve is closer to a square. This represents that the maximum output power of the solar cell is about close to the limit output power that can be achieved, so the performance is better.

3.4. Efficiency

When we need to know the output power of a circuit, we draw a horizontal line at a point on the IV characteristic curve, and the point that passes through the vertical axis we identify as I. We then draw a line that is horizontal to the Y axis, and the point that passes through the horizontal axis is V. The area of the rectangle enclosed by these two lines and the horizontal axis is the product of the voltage V and the current I, which is the power we want. Each point on the IV characteristic curve represents a different product of voltage and current, and therefore a different output power. Different points have different output power, but there is always a point with the largest enclosed rectangular area, when the output power is suitable for the maximum power point we need. The output power curve is obtained by multiplying the I and V values of each point and drawing the curve, as shown in the figure below.

$$P_{MAX} = V_{OC} [I_L - I_0 (e^{qV/AKT} - 1)] \tag{4}$$

It also can be transformed to:

$$P_{MAX} = V_{OC} I_{SC} FF \tag{5}$$

The conversion efficiency of a solar cell is defined as the percentage of the maximum power of the solar cell in a given situation to the total radiated power to which the cell is exposed at that time.

$$\eta = \frac{V_{OC} I_{SC} FF}{P_{in}} \tag{6}$$

where P_{in} is the incident light power absorbed by the incident light when it hits the cell surface.

Another important parameter for investigating the performance of chalcogenide cells is the external quantum efficiency (IPCE), which refers to the ability of incident photons to convert into carriers.

3.5. Photovoltaic Properties of chalcogenide materials

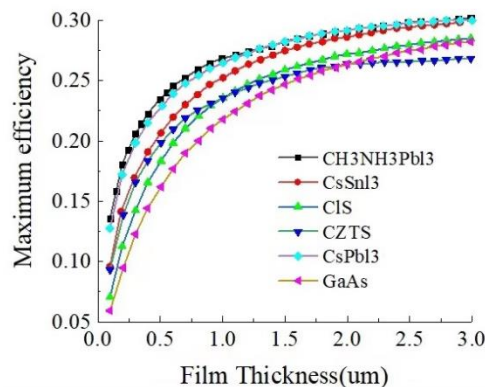


Figure 2. Efficiency of chalcogenide materials

Chalcogenide materials have very excellent optoelectronic properties. Firstly, the exciton binding energy of chalcogenide is very low, about 55 ± 20 meV[8], so it can be separated into free carriers rapidly at room temperature. At the same time, its dielectric constant is high, which can ensure efficient charge separation and inhibit carrier compounding, and the carrier diffusion rate is fast, with

electron mobility of $7.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ and hole mobility of $12.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ or more. the diffusion length of both electrons and holes of MAPbI₃ exceeds 100 nm [9], which ensures the effective transport of electrons and holes.

The absorption coefficient of photovoltaic materials directly determines their ability to absorb and utilize light. The absorption coefficient of GaAs, the absorbing layer material of conventional thin-film solar cells, is about 10 cm^{-1} in the visible region, which is significantly lower than that of MAPbI₃ (10^5 cm^{-1}) [10]. Figure 2-3 shows the common light-absorbing materials.

Compared with conventional CIS, CZTS and GaAs photovoltaic materials, CsSnI₃, CsPbI₃ and MAPbI₃ chalcogenide solar cells have higher theoretical photoelectric conversion efficiencies, making chalcogenide materials a very desirable new photovoltaic material.

Table 2. Energy band structure of different types of chalcogenide materials.

Sulphur compounds	FASnCl ₃	MASnCl ₃	MAPbCl ₃	FAPbCl ₃	CsPbCl ₃
Ec(X/ev)	3.83	3.36	3.77	3.98	3.77
EV(X/ev)	7.33	6.85	6.92	6.94	6.80
Sulphur compounds	FAPbBr ₃	MASnBr ₃	CsSnBr ₃	CsPbI ₃	MAPbI ₃
Ec(X/ev)	4.51	3.42	4.07	4.47	4.36
EV(X/ev)	6.70	5.67	5.82	6.25	5.93
Sulphur compounds	CsPbCl ₃	CsSnCl ₃	FASnBr ₃	CsPbBr ₃	MAPbBr ₃
Ec(X/ev)	3.77	3.47	3.60	4.17	4.25
EV(X/ev)	6.80	6.44	6.23	6.53	6.60
Sulphur compounds	MAPbI ₃	FAPbI ₃	CsSnI ₃	MASnI ₃	FASnI ₃
Ec(X/ev)	4.36	4.74	4.38	4.07	4.12
EV(X/ev)	5.93	6.24	5.69	5.39	5.34

By adjusting the A, B and X contents, different components of chalcogenide materials can be obtained, and the band gap and energy level distribution of the corresponding chalcogenide materials are also different. The diagram shows the energy band structure of different types of chalcogenide materials, and the shift of the band gap and energy band structure of chalcogenide can be achieved by halogen occupation regulation [11]. For the A-site, the smaller the radius of the A-site cation, the larger the band gap of the corresponding chalcogenide, e.g., for the Cs, MA and FA ions, the ionic radii increase in order, and the band gaps of the corresponding CsPbI₃, MAPbI₃ and FAPbI₃ chalcogenides decrease in order, to 1.73eV, 1.57eV and 1.48eV, respectively. For the B-site, Sn is usually used instead of Pb as the B-site, and the band gap of chalcogenide decreases with the gradual increase of Sn content [12], e.g., 1.73eV for CsPbI₃, 1.48eV for FAPbI₃, 1.40eV for FASnI₃, and 1.30eV for CsSnI₃ [13]. For the X-site, the band gap of chalcogenide increases with the doping of Br ions. Therefore, the band gap can be continuously regulated by component modulation of chalcogenide, which determines that chalcogenide can be widely used in various fields such as luminescence, photovoltaics, and light detection.

In addition, according to Shockley-Queisser theory, the relationship between the band width and the ultimate short-circuit current, the open-circuit voltage, the filling factor and the photoelectric conversion efficiency of semiconductor materials can be obtained, as shown in the figure, for single-junction solar cells, when the band width of the absorbing material is 1.34eV, its theoretical photoelectric conversion efficiency can reach the highest 33.7%, and it is usually considered that The most commonly used chalcogenide materials, MAPbI₃ and FAPbI₃, have a forbidden band width of 1.5-1.6eV, and their theoretical maximum photovoltaic conversion efficiencies are above 30% [14].

4. Major Improvements

4.1. Improve stability

Perovskite solar cells are very sensitive to the change of the environmental conditions such as sunlight, temperature, and humidity. These factors could lead to the decomposition and hence reduce the stability. In order to achieve industrial application, lifetime is one of the most essential criteria. This is the reason why the goal of larger number of research is to ensure the stability. It is possible to improve the intrinsic stability of the material to eliminate the self-decomposition. Besides, finding a suitable transporting or packaging material is also useful to isolate the battery from the outer environment.

Dauskardt and his team analyzed the cohesive energy of perovskite which contains MA⁺, FA⁺, BA⁺, and 5-AVA⁺[15]. It determined the relationship between the mechanical stability and the efficiency of photoelectric conversion of the device. The reason why the high-efficiency devices have low cohesive energy is that the cations and PbI₂ additives could reduce the size of grain. Perovskite with multiple cations illustrates better stability than that of the perovskite which contains only single cation.

Transport layer additives can increase the carrier concentration and reduce the series resistance and impedance of transfer of interface charge. Further research also prove that the accumulation of charge caused by the ion migration in the perovskite is the main reason of the hysteresis. Therefore, developing several alternative transport layers could improve the stability of the solar cell. Among almost all kinds of the materials, SnO₂ has a better performance. The nanoparticles solution makes it possible to form a uniform and dense substrate. Compared with traditional TiO₂, SnO₂ have a better electron mobility and stability [16].

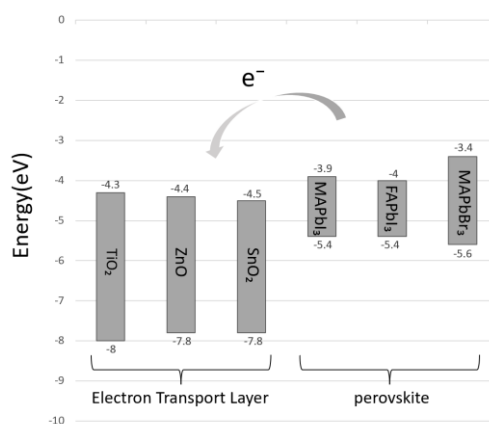


Figure 3. Electron mobility and stability

4.2. Diminish toxicity

Lead-containing materials are harmful to both environment and human health. Therefore, researchers are trying best to get rid of the Pb element. The most straightforward method is to replace it with its group elements such as Sn and Ge. Tin ion has similar radius as lead, while Tin halide perovskite has similar photoelectric characteristics to lead based perovskite. However, the efficiency of the photoelectric conversion of this kind of solar cell has several structural defects and is easy to be oxidized. Thus, it finally leads to the low efficiency and open circuit voltage. As high-quality perovskite films can inhibit the oxidation, Huang Wei team reported that the mixed solvent project achieved the regulation of the crystallization kinetics and improved the thermodynamic stability and hydrophobicity of Sn based devices [17]. Moreover, after being placed in the nitrogen atmosphere for 94 days, the efficiency of the device has hardly declined.

Another way to reduce toxicity is to partially replace lead in perovskite materials. A certain amount of Pb doped tin perovskite can improve the stability and performance, so that Sn-Pb mixed perovskite has adjustable band gap, which makes it an ideal light absorbing layer for perovskite laminated batteries. Nevertheless, the high defect density caused by Sn^{2+} oxidation reduces the carrier lifetime and limits the charge collection in tin-based perovskite. Tan Hairen's team found that the disproportionation reaction with metal tin powder could prevent the oxidation of Sn^{2+} in the solution to Sn^{4+} , and the photoelectric conversion efficiency of two-terminal full perovskite laminated battery was high to 24.8% [18].

4.3. Massive fabrication

Solution spin coating is one of the most communally used approaches to fabricate perovskite solar cells. Even though it has advantages of simple operations and reliable repeatability, the manufacturing requirements of large area and low cost for large-scale industrial production still cannot be fully met. Researchers have explored and tried a variety of methods to fabricate large-area perovskite films. At present, production processes mainly include scraping coating method, slit coating method, spray printing, vapor assisted deposition technology and so on.

In 2020, Lidzey team prepared ternary perovskite solar cells by full spraying method. After optimization, 19.4% photoelectric conversion efficiency was obtained in a small area. After Applying 25 mm * 75mm substrate by rapid spraying and dividing the substrate into devices with an area of 15.4 mm² of each, the maximum efficiency of photoelectric conversion is 16.3%, and the average efficiency is 10.3% [19]. Seven devices with an effective area of 1.08 cm² are obtained in parallel, and the efficiency of them is 12.7%.

Slit coating technology is a printing technology in which ink is pressed out and transferred to the substrate under certain pressure. It has the potential of stable controllability and high yield. Lin Weifang's team used environment-friendly materials with different solvents and coated the material solution into a wet film by the large-area slit coating method under atmospheric temperature [20]. Then they dried it with fast infrared light to form a uniform film, shown as figure x. The maximum efficiency of photoelectric conversion of 12 cm uniform large-area perovskite film can reach 14.30%.

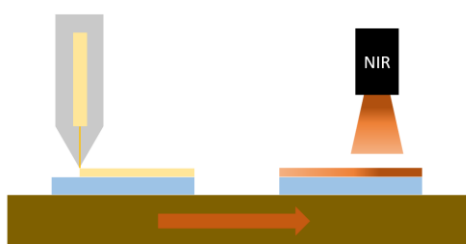


Figure 4. Slit coating technology

5. Conclusion

From the angle of the algorithm and existing problems of perovskite photovoltaic materials, it makes clear that there is significant breakthrough on method and technologies of improving efficiency and stability, reducing toxicity and large-area fabrication strategies of perovskite materials and perovskite photovoltaic devices. Perovskite solar cell is expected to take the leading position of the development of the next generation of eco-friendly and low-cost cell, as a sustainable battery with high photoelectric conversion efficiency. Therefore, the key challenges in the field of perovskite solar cells in the future will come from further improving the photoelectric conversion efficiency and stability of devices, low toxic components and processes, large-area fabrication methods, and the development and optimization of flexible devices.

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