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Study on instability factors and improvement methods of perovskite materials

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Abstract: *In recent years, due to the instability of perovskite, the road of commercialization is very difficult. First of all, this paper summarizes the two important factors affecting the stability, namely intrinsic and chemical instability, which can be specifically water, oxygen, temperature, light and so on. Secondly, the main methods to improve the stability of perovskite materials are summarized, including internal optimization and external optimization, such as crystallization regulation, doping control, additive addition and so on. Finally, the summary and Prospect of practical application in this field are given.*

Keywords: *perovskite, Crystal structure, Stability, Solar cell, Photodetector*

1. Introduction

In recent years, perovskite is widely worked in the fields of high-efficiency solar converters, and lasers, and have received extremely attention. It is considered by researchers to be one of the most valuable photovoltaic cells. As a member of optoelectronic devices, semiconductor photodetectors made of perovskite materials can convert incident light into electrical signals, it plays an important role in the fields of optical communication, imaging, environment and biochemical sensing [1-4].

This paper mainly tells the stability of perovskite, and lists the intrinsic and the effects of oxygen, water, temperature and light on the perovskite's stability. The methods of improving the stability of perovskite are writed. Finally, the paper shows the prospect of perovskite.

2. Factors affecting the stability of perovskite

Wan [6] used the first principle to study the thermodynamic stability of 138 possible perovskite cube structures, and introduced octahedral factor μ for comprehensive evaluation, in which $\mu = r_A / r_x$, r_A and r_x represent the ion radii corresponding to A-site element and x-site element respectively. The octahedral factor can be used to describe the octahedral stability of B-site element and X_6doped structure.

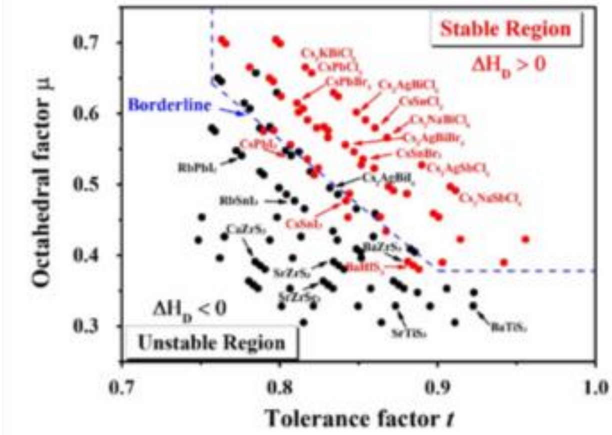

Figure 1: The relationship between tolerance and octahedral [6]

Figure 1 Used tolerance factor t as abscissa, octahedron factor μ for the ordinate, got the μ-t dimensional image. When the decomposition energy is > 0, perovskite is considered to be in a stable state, otherwise it is in an unstable state. There is an clear boundary between the stability and instability of perovskite. For example, $MAPbI_3$, as one of the most popular studies, also has intrinsic instability. He found that $MAPbI_3$ is easy to decompose into products without external stimulation[6].

When perovskite used in water vapor, temperature and light, there are a series of chemical phenomena. This is chemical instability of perovskite materials.

Liu [7] found that water can extremely change the formation energy of the defect surface. In aqueous solution, there may form hydrogen bonds with polar molecules around vacancy defects, which result in dislocation of surface atoms near defects. So the defect of halogen vacancy of perovskite conducts the decomposition of perovskite. For example, under high humidity environment, $MAPbI_3$ perovskite film will undergo chemical reaction, and with the volatilization of intermediate products CH_3NH_3 and HI, the final perovskite film will degenerate into PbI_2, H_2 and I_2 [8]. The reaction equation is as follows:

$$\mathrm{CH_3NH_3PbI_3} \longrightarrow \mathrm{CH_3NH_3I(aq)} + \mathrm{PbI_2\ (s)}$$

$$\mathrm{CH_3NH_3I(aq)} \longrightarrow \mathrm{CH_3NH_2(aq)} + \mathrm{HI(aq)}$$

$$\mathrm{4HI(aq)} + \mathrm{O_2} \longrightarrow \mathrm{2I_2(s)} + \mathrm{2H_2O}$$

$$\mathrm{2HI(aq)} \longrightarrow \mathrm{H_2} \uparrow + \mathrm{I_2\ (s)}$$

Similarly, the operating temperature will also affect the performance of the perovskite. The phase transition of perovskite at high temperature is one of the important reasons for the low stability of $CsPbX_3$ (X = I, Br, Cl) perovskite. For example, at high temperatures, $CsPbI_3$ will change from a cubic phase to an orthogonal phase, and finally to a non-perovskite phase. Figure 2 (a) shows the orthogonal, tetragonal, and cubic phase $CsPbX_3$. At the same time, another main reason for low stability is the decomposition of perovskite at high temperature. Liao [9] studied the low-temperature and high-temperature spectra of $CsPbX_3$ and analyzed the decomposition process of perovskite.

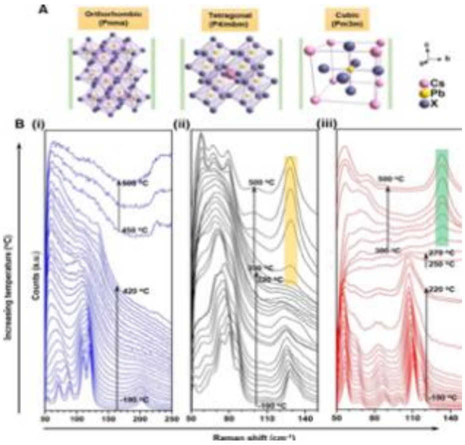

Figure 2: Raman spectra of $CsPbX_3$ B $CsPbCl_3$, $CsPbBr_3$, $CsPbI_3$ with different structures at different temperatures [9]

Above picture shows the variation of the Raman spectra of $CsPbCl_3$, $CsPbBr_3$ and $CsPbI_3$ with temperature. It is found that $CsPbX_3$ decomposes above 300 ℃. Although $CsPbBr_3$ does not decompose until 500 ℃, it is undeniable that $CsPbX_3$ decomposes at high temperature. When the temperature exceeds the bimodal merging temperature, $CsPbX_3$ will be in a highly disordered state, so it will be thermally decomposed at high temperatures. The decomposition equation is as follows:

$$\mathrm{CsPbX_3\ (s)} \rightarrow \mathrm{PbX_2\ (s)} + \mathrm{CsX\ (s)}\ (\text{or } \mathrm{CsX_3\ (s)})$$

The stability of perovskite will also be affected under light conditions. Related experiments have proved that the degradation process of mapbi3 is carried out under the combined action of light and oxygen, which is due to the deprotonation reaction of methylamine cation ($CH_3NH_3^{\ +}$) caused by oxygen.

Gaseous methylamine (CH_3NH_2) and superoxide ($O2^{\cdot-}$) are formed in the process of electron transfer from O_2 to $CH_3NH_3^{\ +}$, and by-products such as PbI_2, PbI_2, I_2 and water [10]. The reaction equation is as follows:

$$MAPbI_3 \xrightarrow{Light+O_2} MAPbI_3^* \xrightarrow{Electron\ transfer} MAPbI_3 + O_2^{\cdot -}$$

$$MAPbI_3 + O_2^{\cdot -} \xrightarrow{Deprotonation} CH_3NH_2 + PbI_2 + I_2 + H_2O.$$

Figure 3: Decomposition equation of mapbi$_3$ under the action of light and oxygen

Merdasa [11] found that due to the migration of methylamine ions (MA^+), the lattice structure was deformed, resulting in the deformation of Pb-I-Pb bond angle, and then changed the effective band gap. Finally, they proposed that the migrated MA^+ ions would lead to the structural collapse of $MAPbI_3$. The protonic acid property of methylammonium ions promoted the decomposition reaction, making the reaction completely decomposed into methylamine PbI_2 and I_2.

3. Method for improving stability of perovskite

The stability of perovskite greatly affects the photoelectric conversion performance and efficiency of the device. This is the biggest obstacle to the commercialization of perovskite optoelectronic devices. In this paper, we improve the stability of perovskite in two aspects: internal optimization and external optimization.

3.1 Internal optimization

3.1.1 Control film crystallization

Controlling the crystal growth of thin films has always been the most direct method to improve the stability of perovskite. It is not only simple to operate, but also can optimize the preparation of different types of perovskite films.

The result is that the solubility of CsBr and $PbBr_2$ in DMF solution makes the foundation, so the concentration of $CsPbX_3$ precursor cannot be increased, and the film prepared is thinner, which is easy to cause battery leakage and short circuit. DMSO can promote the transport and diffusion of substances, but excessive DMSO will increase the roughness of $CsPbX_3$ film, affect the contact between layers, cause charge loss, and finally reduce the performance of the battery [12]. Zai [13] optimized the one-step deposition process by adjusting the ratio of DMF and DMS. The residual DMSO can promote molecular transmission and improve the quality of the film. During the annealing process, DMSO gradually evaporates to obtain a dense $CsPbI_2Br$ film.

By improving the one-step deposition method, spin-coating with anti-solvent (chlorobenzene, etc.) to prepare high-quality perovskite film [14].

The antisolvent can wash away the residual DMSO in the spin coating process, eliminate the nucleation and aggregation phenomenon and solvent edge effect. The antisolvent can also "freeze" the precursor film, so as to form large perovskite grains [15], which is conducive to improving the stability of perovskite.

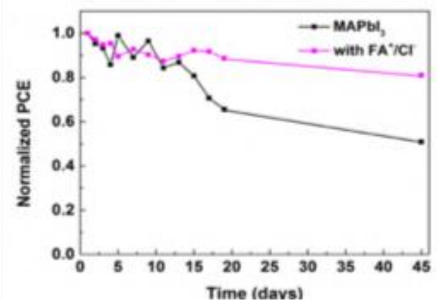

Figure 4: Dynamic mechanism of perovskite crystal [15]

3.1.2 Doping control

The method of doping with semiconductor impurities can indirectly improve the stability of the perovskite. The chemical formula of the perovskite material is ABX3.

Yan[16] studied the doping of $MAPbI_3$, namely FAyMA1-yPbI3-XClX. Based on $MAPbI_3$ perovskite material, Yan Measured the air stability of PSCs prepared based on undoped MAPbI$_3$ film and FAyMA1-yPbI$_3$-XCl$_X$ film under optimal doping conditions. The unencapsulated test equipment is stored in air at 20 ℃ and a relative humidity of 20%. The photoresponse characteristics of the device reflect the degree of hysteresis of the device. The test result is shown in Figure 5.

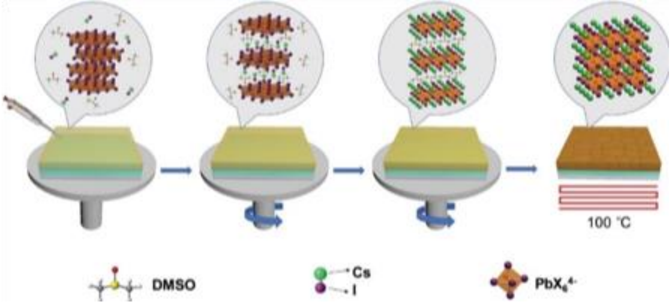

Figure 5: Stability of MAPbI$_3$ and FAyMA$_1$-yPbI$_3$-xCl$_X$ films in air

We can see that the device prepared by undoped mapbi3 film retains only 51% of the original efficiency after being stored in the atmospheric environment for 1000 h. In contrast, the PSCs prepared by f FAyMA1-yPbI3-XClX film under the optimal doping conditions show better stability, and the device still retains 80% efficiency under the same storage conditions and time. This is because the introduction of Cl$^-$ions inhibits the yellow δ$^-$, while the formation of the FA $^+$ phase promotes the black α$^-$, thereby improving the crystal quality. In addition, the FAyMA$_{1-y}$PbI$_{3-x}$Cl$_X$ film under the optimal doping conditions has larger particles and fewer pinholes, which also improves the long-term effectiveness of the device in the air.

3.2 External optimization

3.2.1 Introduction of additives

It is found that external additives can use macromolecular or long-chain compounds to improve the hydrophobicity of CsPbX$_3$ films, isolate water and effectively delay the degradation of perovskite.

Zhang [17] added a small amount of ethylenediamine cation (EDA$_2$ $^+$) to CsPbI$_3$ precursor. On the premise of not affecting carrier transport, cspbi3 perovskite crystal was crosslinked with the amino group of EDA$_2$ $^+$, so that α- CsPbI$_3$ is difficult to degrade into δ- CsPbI$_3$. In the stability test experiment, CsPbI3 xEDAPbI4 film can still be maintained after heating at 100 ℃ for 168h α Phase, showing excellent stability. In addition, the battery based on CsPbI3 0.025EDAPbI4 can still maintain more than 10% photoelectric conversion efficiency (initial efficiency 11.86%) when stored in an unpacked dry environment for one month.

3.2.2 The electron transport and hole transport layer

In the preparation of perovskite devices, the environmental stability of perovskite is improved by using electron transport layer (ETL) or hole transport layer with high stability.

C$_8$BTBT is a good semiconductor material because of ultra-high hole carrier mobility and good stability in air.

Because it can perfectly fill the gap between perovskite particles, and its inherent high mobility and matching with the energy level of CH$_3$NH$_3$PbI$_3$, holes can be transmitted to the electrode quickly. Tongs [18] obtained CH$_3$NH$_3$PbI$_3$ thin films on FTO glass. After that, a layer of C$_8$BTBT film is deposited on the top of the CH$_3$NH$_3$PbI$_3$ film to form an heterojunction. This process improves the efficiency of hole generation from the CH3NH3PbI3 layer to the C8BTBT layer, and effectively reduces the rapid recombination of hole-electron pairs.

The experimental data show that when the heterojunction photodetector is exposed to environmental conditions for 20 days, its photocurrent does not change significantly, only from 28 μ A down to 26 μ A. The C$_8$BTBT layer has excellent waterproof performance, which results in the photodetector with this structure having 90% performance after exposure for 20 days under environmental conditions. This process of improving the environmental stability of CH$_3$NH$_3$PbI$_3$ by preventing water diffusion greatly improves the environmental stability of perovskite due to the protection of the C$_8$BTBT layer.

4. Summary and Prospect

In a word, Intrinsic and chemical instability can affect the stability of perovskite materials. Water and oxygen are specific factors. This paper also gives some main methods to improve the stability of perovskite, such as crystal growth regulation, doping control and external interface protector optimization.

But getting out of the laboratory is still a huge challenge. Once the perovskite material containing lead decomposes, it will cause heavy metal pollution. Moreover, due to the influence of oxygen, water, light, temperature, light and other factors, the structure of perovskite will decompose, thus affecting the performance and service life, which also extremely hinders the progress of its application. At present, many studies on the stability of perovskite have achieved great success, but most of them stay at the laboratory level, and will encounter worse environment and longer use in the process of practical application, so more work needs to be done to improve perovskite stability.

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