

Preparation of inorganic chalcogenide solar cells by vapor phase deposition and performance study

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Abstract

Focusing on the poor stability of CsPbI₃ perovskite phase in traditional co-vapor deposition, based on the regulation strategy of anion component, the precise doping of halogen-level anions was realized by co-vapor doping process. Compared with the traditional co-evaporation CsPbI₃, prepared CsPbI₂Br mixed-halogen perovskite optimized the structural tolerance factor of perovskite, inhibited the torsion of lattice structure at room temperature, and thus improved the phase stability of the material. Based on this, the Br- doping amount in mixed-halogen perovskite was graded by high-throughput experiments. Combined with the X-ray diffraction phase analysis and scanning electron microscopy morphology analysis of the film, it was found that the Br-content had a significant indigenous effect on the formation and distribution of the non-conductive zero-dimensional phase Cs₄PbI_{6-x}Br_x in the film. Further, the phase stability and photovoltaic performance of the material were balanced by optimizing the Br-doping amount.

Keywords

Vapor deposition, Perovskite solar cells, Photoelectric conversion efficiency, Phase stability.

1. Introduction

At present, CsPbI₃ has gradually attracted wide attention of researchers due to its high thermal stability and suitability as the top battery of laminated solar cells. However, because the radius of Cs⁺ is smaller than that of FA⁺ or MA⁺ commonly used in halide perovskite, CsPbI₃ perovskite has a structural tolerance factor of 0.8 (τ). It is well known that the Goldschmidt structural tolerance factor derived from the empirical formula can be used to measure the structural stability of ABX₃ perovskite. In general, when it is close to 1, perovskite exhibits a highly symmetrical cubic phase at room temperature, and in the process of octahedral rotation, perovskite will transform to quadrilateral or orthogonal phase due to the rotation of octahedral. The results show that CsPbI₃ perovskite has three-dimensional perovskite phase, but its structural stability is poor due to its relatively low temperature. Previous studies have found four phase structures of CsPbI₃: 'black phase' (cubic Pm3m) with photovoltaic effect; β phase (tetragonal P4 / mbm); γ phase (orthogonal Pbnm) and 'yellow phase' δ phase (orthogonal Pnma) without photovoltaic effect. In addition, the structural stability of CsPbI₃ is greatly related to temperature. At high temperature, the CsPbI₃ phase with high symmetry is stable, and the structural stability of CsPbI₃ will change at low temperature^[1]. The traditional co-evaporative vapor deposition due to the characteristics of inorganic component purification, resulting in the poor stability of the resulting CsPbI₃ calcium titanite phase at room temperature, which seriously hinders its preparation and performance testing at room temperature and low temperature conditions, which becomes one of the important reasons for the lagging

development of the photovoltaic performance of traditional co-evaporative CsPbI₃ devices. In this paper, CsPbI₂Br inorganic perovskite was prepared by co-evaporation doping process by introducing some Br⁻ to replace I⁻ in halogen anions, which improved the phase stability of traditional co-evaporation CsPbI₃. Compared with the CsPbI₃ prepared by traditional co-evaporation, the structural tolerance factor was optimized to improve the phase stability of the material at room temperature.

2. Inorganic chalcogenide solar cells with vapor phase deposition

2.1. Overview of inorganic perovskite solar cells

The most rapidly developing type of inorganic chalcogenide solar cells (IPSCs) is Cs-based IPSCs: CsPbI_{3-x}Br_x (0 ≤ x ≤ 3), which consists of replacing all A-site cations in organic inorganic hybrid calcium titanite solar cells with inorganic ions Cs⁺. According to the different halide species of Cs-based IPSCs can be divided into four mainstream inorganic chalcogenides, CsPbI₃, CsPbI₂Br, CsPbIBr₂, and CsPbBr₃, which have optical band gaps around 1.71 eV, 1.92 eV, 2.10 eV, and 2.32 eV, respectively, which also indicates that by changing the Cs-based IPSCs: CsPbI_{3-x}Br_x (0 ≤ x ≤ 3) in the value of x can effectively regulate the band gap^[2]. After the stability of chalcogenides became an important research direction, a "tolerance factor "r was introduced as the main parameter to quantify the stability of the structure, which is described by the equation (1.1):

$$r = \frac{(R_A + R_B)}{\sqrt{2}(R_B + R_X)} \quad (0.1)$$

R_A, R_B and R_X represent the atomic radius of A, B and X sites, respectively. It is generally believed that perovskite has stable phase structure when 0.78 ≤ r ≤ 1.05.

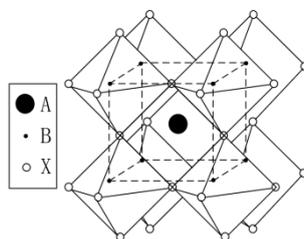


Fig.1 Crystal structure of ideal perovskite ABX₃

In general, for CsPbI_{3-x}Br_x (0 ≤ x ≤ 3), the tolerance factor of the chalcogenide phase structure decreases with increasing x value. In summary, the inconsistent ratio of halogens in CsPbI_{3-x}Br_x (0 ≤ x ≤ 3) has a large impact on the overall band gap and stability of Cs-based halide inorganic chalcogenide, so the photovoltaic performance of Cs-based halide inorganic chalcogenide solar cells can be tuned by adjusting the magnitude of x value.

2.2. Principle and Classification of Vapor Deposition

The gas phase deposition method is mainly through the heating sublimation of perovskite powder, and then the gas molecules are slowly deposited on the substrate. Therefore, in the whole deposition process, including evaporation rate, pressure, deposition thickness, substrate temperature and other factors will affect the formation and growth of perovskite crystals.

According to the different evaporation process of precursor, vapor deposition process can be divided into single source vapor deposition, sequential vapor deposition and co-evaporation phase deposition. Among them, co-vapor deposition is the most commonly used method for vapor deposition of perovskite thin films. In this method, the components of each precursor are put into a separate crucible, and the substances in a variety of evaporation sources are deposited on the substrate at the same time to form a continuous perovskite thin film. If the final deposition amount of substances in each evaporation source maintains a balanced

proportion in stoichiometry, the obtained perovskite film needs no subsequent annealing treatment.

2.3. Development of Inorganic Perovskite Solar Cells Prepared by Vapor Deposition

In 2017, in order to improve the phase stability of inorganic perovskite, the mixed halide doping strategy was developed. The inorganic CsPbI₂Br perovskite was prepared by partially replacing I with Br, and the influence of the component chemical dosage on the stability and photoelectric properties of perovskite was explored^[3]. In 2018, CsPbBr₃ perovskite with stable perovskite structure at room temperature was prepared by sequential deposition using Br to replace I completely. The best PCE of 8.34 % was obtained, and the good device stability of 80 % initial efficiency was still maintained after the device was stored for 1000 h at 45 % air humidity^[4]. Then, as the PCE of IPSCs deposited by vapor deposition is still in a backward state, Thomas et al. pioneered a high-throughput co-vapor deposition method in 2019, and studied the specific effect of the relative distance between different regions of the sample and the evaporation source on the final deposition of CsPbI₃ phase structure. It is concluded that an appropriate excess of cesium iodide can help to obtain CsPbI₃ perovskite orthorhombic black phase and obtain 12.5 % PCE^[5]. Then in 2020, Huang et al. optimized the PCE of CsPbI₃ solar cells to 16.3 % by using the high-throughput co-vapor deposition combined with the two-step mixed annealing process of 'air + nitrogen'^[6].

In summary, in order to overcome the research obstacles caused by the disadvantages of electrodeless perovskite materials and the characteristics of vapor deposition process, and to achieve the preparation of IPSCs with high phase stability and high PCE, new vapor deposition process and new inorganic material modification strategy need to be created.

3. Experiment part

3.1. Experimental reagents and instruments

Experimental materials and reagents : lead iodide (PbI₂, 99%+, Adamas) ; cesium iodide (CsI, 99% +, Adamas) ; cesium bromide (BrCs, 99.9%, Adamas) ; diethanolamine (C₄H₁₁NO₂, 99%, Adamas) ; acetone (C₃H₆O, 99.5%, Adamas) ; 4 - tert-butylpyridine (C₉H₁₃N, 97% +, Adamas) ; acetonitrile (CH₃CN, 99.9%, Adamas) ; chlorobenzene (C₆H₅Cl, 99%+, Adamas) ; bis (trifluoromethane) sulfonamide lithium salt (CF₃SO₂NLiSO₂CF₃, 99.95%, Sigm aAlarich) ; anhydrous ethanol (CH₃CH₂OH, 99.5 %, Adamas).

Experimental instruments: six-source resistive coating equipment (ZD-400, Shenyang Kecheng Co., Ltd.); metal vaporizer (Beijing Taikono Co., Ltd.); membrane thickness controller (INFICON); spin coating instrument (EZ-4); ultrasonic cleaning instrument (UP-400, Shanghai Shanghai Co., Ltd.); magnetic stirrer (myPlate, IKA); plasma cleaning instrument; program Control Heater (STUART); electronic balance; nitrogen glove box (Wegg Instrument Co., Ltd.).

3.2. Preparation and performance characterization of devices

The solar cell devices in this paper adopt the n-i-p flat-panel device structure (as shown in Fig.2 - 1). The basic process of preparation is : preparation of fluorine doped tin oxide (FTO) conductive glass - preparation of electron transport layer (TiO₂) - preparation of inorganic perovskite absorption layer - preparation of hole transport layer (Spiro-OMeTAD) - preparation of metal electrode (Au).

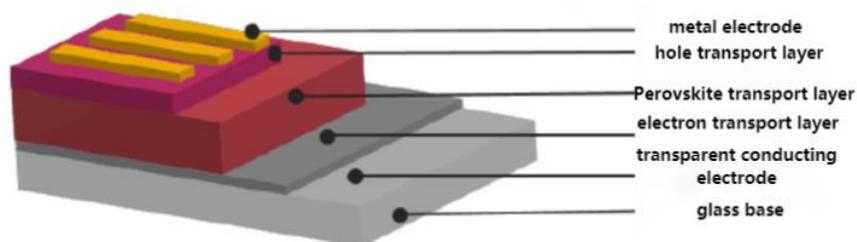


Fig.2 Structure of Perovskite Solar Cells

The specific operation process of preparing solar devices is:

(1) Preparation of FTO conductive glass : Characteristic parameters : square resistance 7Ω , size $19.5 \times 19.5\text{mm}$. First, clean the FTO conductive glass obtained by laser splitting, and then dry it with a nitrogen gun. Then stick high temperature tape on one side of the conductive surface of the FTO conductive glass and reserve the position of the FTO electrode.

(2) Preparation of electron transport layer (TiO_2) : Firstly, 6 mL deionized water, 1.25 mL diethanolamine and 12.5 mL anhydrous ethanol were used to prepare solution 1 ; subsequently, 12.5 mL tetrabutyl titanate was dropped into 94 mL absolute ethanol to prepare solution 2; Then solution 1 was added drop by drop into solution 2 and stirred evenly with IKA magnetic stirrer to obtain dense TiO_2 precursor solution. The precursor solution was coated on the conductive surface of clean FTO conductive glass obtained in Step 1 of plasma treatment by using EZ-4 spin coating instrument. The spin coating process parameters were as follows : the speed was 3000 rad / min and the spin coating time was 30 s. Finally, the coated substrate sample was placed in a hot stage for annealing (constant temperature of 500°C , 30 min).

(3) Preparation of CsPbI_2Br perovskite thin films by co-evaporation : appropriate amount of cesium bromide and lead iodide powder were put into two evaporation sources in the evaporation chamber of ZD-400 six-source resistive coating equipment, in which cesium bromide was put into the tungsten boat and lead iodide was put into the quartz crucible. The prepared substrate was placed on the sample holder in the vacuum chamber, the chamber door was closed, and the vacuum was extracted. When the vacuum reached the order of 10^{-4} Pa, the substrate temperature was set to 150°C , and the evaporation rate of lead iodide was adjusted to $1.56 \text{ \AA} / \text{s}$, and the rate of cesium bromide was $0.8 \text{ \AA} / \text{s}$. When the evaporation rate was stable, the substrate baffle was opened to deposit the thin film, and the thickness of the deposition was 400 nm. The substrate was always rotated during the deposition process. After the deposition, the thin film was placed in the air environment, and the first annealing was carried out at 260°C for 40 s. The CsPbI_2Br thin film was initially obtained. After the first annealing reaction, the substrate was placed in the oxygen atmosphere for the second annealing. After annealing at 260°C for 60 s, the required CsPbI_2Br inorganic perovskite thin film was obtained.

(4) Preparation of CsPbI_3 perovskite thin films by co-evaporation: appropriate amount of cesium iodide and lead iodide powder were put into two evaporation sources in the evaporation chamber of ZD-400 six-source resistive coating equipment, in which cesium iodide was put into the tungsten boat and lead iodide was put into the quartz crucible. The substrate was placed on the sample frame in the vacuum chamber, the door was closed, and the vacuum was extracted. When the vacuum degree reached 10^{-4} Pa, the substrate temperature was set to 150°C , and the evaporation rate of lead iodide was adjusted to $160 \text{ \AA} / \text{s}$, and the rate of cesium iodide was $1.4 \text{ \AA} / \text{s}$. When the evaporation source rate is stable, the substrate baffle is opened to deposit the film, and the thickness of the deposition is 400 nm. The substrate rotation is always maintained during the deposition process. After the deposition, the film is placed in the air environment, and the first annealing is carried out at 350°C for 40 s. The CsPbI_3 film is initially obtained. After the first annealing reaction, the substrate was placed in nitrogen

atmosphere for the second annealing. After annealing at 350 °C for 60 s, the required CsPbI₃ inorganic perovskite film can be obtained.

(5) Preparation of cavity transport layer (Spiro-OMeTAD): 73.4 mg of Spiro-OMeTAD powder was dissolved in 1 mL of chlorobenzene and stirred well. Subsequently, 28.8 μL of tBP solution, 17.5 μL of Li-TFSI solution and 16 μL of Co-TFSI solution were added to 1 mL of Spiro-OMeTAD solution successively and stirred well with an IKA magnetic mixer. Finally, the solution was applied to the produced chalcogenide absorber layer using EZ-4 spin coater with the following parameters: speed of 4000 rad/min and spin coating time of 30 s.

(6) Preparation of metal electrode (Au): metal electrode Au was prepared by vapor deposition process using vapor deposition apparatus with the following deposition parameters: vapor pressure of 10⁻⁴ Pa; thickness of 120 nm; deposition rate of 1 Å/s.

4. Study on Co-vapor Deposition of CsPbI₂Br with High Phase Stability Based on Component Control

4.1. Study on Co-vapor Doping Optimization of Perovskite Structure Tolerance Factor

The existing strategies to improve the stability of CsPbI₃ perovskite phase are widely used by adjusting its crystal structure or composition. Therefore, we adopted the component control strategy to prepare CsPbI₂Br perovskite by using the co-vapor deposition process to achieve halogen anion doping. By replacing I with Br with smaller ionic radius, the structural tolerance factor of inorganic perovskite was optimized, and the phase stability of CsPbI₃ deposited in traditional co-vapor phase was improved. To investigate the specific improvement of the CsPbI₂Br chalcogenide phase in comparison, CsPbI₃ chalcogenide was also prepared using the conventional co-evaporation process. Specifically, CsPbI₂Br chalcogenide was first prepared by dual-source co-evaporation using CsBr and PbI₂, and CsPbI₃ chalcogenide was prepared by dual-source co-evaporation using CsI and PbI₂, as described in Section 2.2 of this thesis.

In order to determine the co-evaporation doping process, the halogen site in the lattice can be doped with Br, and the mixed halogen perovskite CsPbI₂Br with iodine and bromine content ratio of 2 : 1 can be formed. The XRD phase detection of the co-evaporation doped thin films was carried out, and the phase of the CsPbI₃ perovskite thin films prepared by traditional co-evaporation phase deposition was compared. It was found that the films prepared by co-evaporation doping had obvious sharp diffraction peaks at 14.71 °, 21.04 ° and 29.82 °, and the main peak of the traditional co-evaporation CsPbI₃ showed a shift to the direction of large diffraction angle, which was known by the Scherrer formula. When the XRD diffraction peak angle increases, the lattice size shrinks. Since the ionic radius of Br⁻ is smaller than that of I⁻, the shrinkage of lattice size indirectly proves that the co-evaporation doping process can realize the substitution of Br⁻ in the halogen site in the lattice. PL was used to detect the photoluminescence spectrum of the prepared film. The results are shown in Fig.3. Compared with the luminescence peak position of the traditional co-evaporated CsPbI₃ film, the film prepared by co-evaporated doping process had a blue shift at 645 nm, which was the same as the fluorescence emission peak position of CsPbI₂Br perovskite reported previously. It was proved that the film prepared by co-evaporated doping process was CsPbI₂Br perovskite.

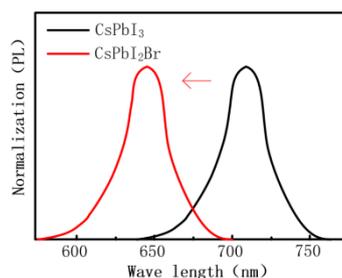


Fig.3 Normalized PL emission spectra of CsPbI₂Br and CsPbI₃ prepared by co-evaporation doping

Next, after halogen doping was realized by co-evaporation, CsPbI₂Br perovskite was prepared. In order to quantify the change of structural tolerance factor compared with traditional co-evaporation CsPbI₃, the tolerance factors of the two perovskites were calculated by using the formula (1-1) described in Section 1.1 of this paper. The atomic radii of Cs⁺, Pb²⁺, I⁻ and Br⁻ are 1.69 Å, 0.85 Å, 2.16 Å and 1.95 Å, respectively. The calculated structural tolerance factors of CsPbI₂Br and CsPbI₃ are 0.91 and 0.85, respectively. The results show that the structural tolerance factor of CsPbI₂Br prepared by co-evaporation doping is better than that of CsPbI₃, which can improve the stability of perovskite phase at room temperature.

4.2. Study on the effect of co-evaporative doping on the phase stability and photovoltaic performance of chalcogenide

First, to demonstrate the change in phase stability and photovoltaic performance, CsPbI₂Br chalcogenides prepared using co-doping need to be compared with CsPbI₃ chalcogenides prepared by conventional co-deposition in vapor phase. However, the existing studies show that the phase transformation of CsPbI₃ perovskite is easily affected by temperature. Therefore, in order to compare the referentiality and rationality, the microstructure of the films at different temperatures is compared and 350 °C is finally selected as the annealing temperature of traditional co-evaporated CsPbI₃ according to the crystal quality of perovskite phase. Thus, CsPbI₃ thin films with good crystalline quality can be obtained, which can improve the stability of CsPbI₃ and CsPbI₂Br phase and the rationality of device photovoltaic performance comparison in this work.

On the other hand, studies have shown that different environmental atmospheres are easy to affect the stability of halide perovskite. For example, when coupled with oxygen, oxygen molecules will adsorb and diffuse through iodine vacancies, forming a defect state close to the conduction band and capturing a photoexcited electron under light, forming charged superoxide, which will eventually lead to the degradation of the film. Therefore, in order to explore the poor phase stability of traditional co-evaporated CsPbI₃ in what kind of atmosphere environment, in order to determine the environmental atmosphere applied in the comparison of phase stability with CsPbI₂Br, the change of phase stability of co-evaporated CsPbI₃ in air environment and oxygen environment was monitored, and the phase transformation of the film was reflected by the change of the absorption band gap of the film in the UV-Vis detection spectrum. When yellow phase occurs, the absorption initiation band edge appears near the wavelength range of 400 nm. The results are shown in Fig.4, indicating that the traditional co-evaporation CsPbI₃ in the air environment has worse phase stability. Therefore, the air atmosphere was selected as the ambient atmosphere for the stability comparison of co-evaporated CsPbI₂Br and co-evaporated CsPbI₃.

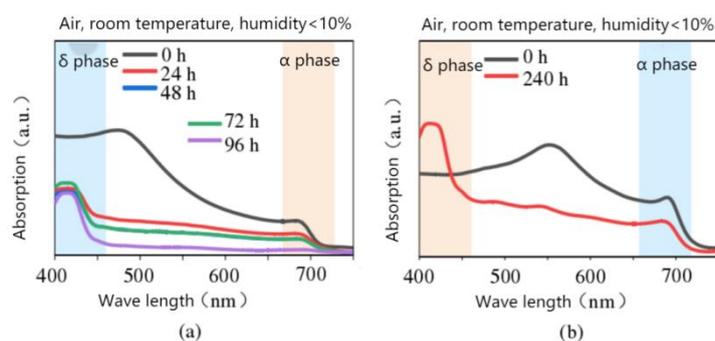


Fig.4 Phase stability monitoring of CsPbI₃ thin films prepared by conventional co-evaporation in air and nitrogen atmosphere.

(a) UV-Vis spectra of CsPbI₃ phase stability in dry air at room temperature ;

(b) Drying at room temperature UV-Vis spectra of CsPbI₃ phase stability under nitrogen environment

Then, the phase stability of CsPbI₂Br film prepared by co-evaporation doping was compared with that of CsPbI₃ prepared by traditional co-evaporation. We placed both films in air environment at the same time, and by observing the change of phase stability of the films, we can see that the partial replacement of I⁻ by Br⁻ can optimize the structural tolerance factor of chalcogenide and thus achieve the improvement of the phase stability of the material, which in turn indicates that the component modulation is an effective way to enhance the phase stability of conventional co-evaporated CsPbI₃.

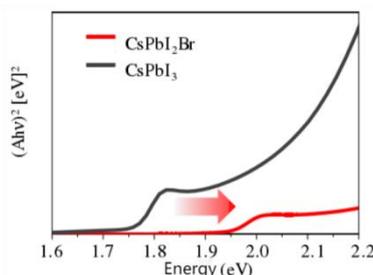


Fig.5 Tauc diagram from UV-Vis absorption spectra conversion of two perovskite films

In order to be able to further investigate the effect of component modulation on the photovoltaic performance of chalcogenide solar cell devices using a co-doping process, CsPbI₂Br films were paired with other functional layers to produce CsPbI₂Br PSCs. By comparing the photovoltaic performance of the two PSCs, it can be found that the PCE of CsPbI₂Br is lower. Then, UV-Vis was used to test the absorption layer films of the two devices, and the results are shown in Fig.5. It is found that the absorption band edge of CsPbI₂Br prepared by co-evaporation is blue shift compared with that of CsPbI₃ prepared by traditional co-evaporation, and the absorption range is also reduced.

4.3. Study on the effect of halogen doping on the phase stability and photovoltaic performance of chalcogenide

A high-throughput approach was used to investigate the effect of Br⁻ incorporation on the photovoltaic properties of chalcogenide, and five CsPbI_{3-x}Br_x (x approximately 1) chalcogenide films were prepared with the gradient of Br⁻ substitution with the relative position of the sample from the evaporation source. To observe the effect of different sample components on the chalcogenide films, XRD physical phase examination was performed, and the results are shown in Fig. 6, indicating that the content of zero-dimensional Cs₄PbI_{6-x}Br_x in chalcogenide increases with the increase of Br⁻ content, which also proves that the amount of Br⁻ incorporation has a modulating effect on the content of zero-dimensional Cs₄PbI_{6-x}Br_x in the material. Some studies have shown that the zero-dimensional Cs₄PbI_{6-x}Br_x in inorganic

perovskite can act as a $[\text{PbX}_6]^{4-}$ octahedral torsion around the grain boundaries of three-dimensional perovskite, so as to improve the phase stability. It can be seen that the substitution of halogen by co-evaporation doping Br^- can improve the structural tolerance factor of inorganic perovskite and produce more zero-dimensional $\text{Cs}_4\text{PbI}_{6-x}\text{Br}_x$ to achieve the significant enhancement of phase stability of materials.

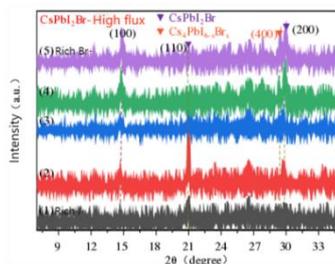


Fig.6 XRD patterns of CsPbI_2Br thin films prepared by high flux co-evaporation

The $\text{CsPbI}_{3-x}\text{Br}_x$ perovskite thin films with five different chemical components prepared by high throughput were further applied to the solar cell devices to prepare the flat-panel solar cells with FTO / TiO_2 / CsPbI_2Br / Spiro-OMeTAD / Au device structure. The PCE of five kinds of PSCs was detected, and it was found that the PCE of PSCs decreased when the Br-content in the thin film was too much, which was the result that too much non-conductive zero-dimensional $\text{Cs}_4\text{PbI}_{6-x}\text{Br}_x$ in the thin film hindered the effective transmission of photocurrent.

5. Conclusion

In this paper, based on component regulation, a co-evaporation doping method was adopted to achieve the preparation of mixed halogen CsPbI_2Br inorganic perovskite, and its phase stability and photovoltaic performance were studied by changing the Br^- doping amount. The results show that the inorganic lead iodide perovskite prepared by this process has higher phase stability than the traditional co-evaporation CsPbI_3 . Inorganic chalcogenide tolerance factor optimization based on co-evaporative doping. Component modulation strategy was adopted to solve the problem of CsPbI_3 phase stability and to achieve the optimization of tolerance factor of chalcogenide structure. Study on the effect of co-evaporative doping on the phase stability and photovoltaic performance of the material. The phase stability and photovoltaic performance of co-doped CsPbI_2Br were compared with conventional co-doped CsPbI_3 , and the change of halogen doping on the performance of chalcogenide was investigated. The optimization of halogen doping amount was investigated. High-throughput experiments were carried out to adjust the Br^- doping content gradiently and balance the phase stability and photovoltaic performance of the material. Firstly, through XRD phase analysis, it is determined that with the increase of Br^- doping content, the zero-dimensional $\text{Cs}_4\text{PbI}_{6-x}\text{Br}_x$ with low formation energy in the film will increase, thus helping to improve the phase stability of the material. Then the photovoltaic performance test of CsPbI_2Br PSCs with gradient Br^- content shows that excessive Br^- doping will lead to the excessive generation of non-conductive zero-dimensional $\text{Cs}_4\text{PbI}_{6-x}\text{Br}_x$ and the loss of photovoltaic performance. Finally, it is concluded that the appropriate amount of Br^- should be introduced when the phase stability and photovoltaic performance of the material are adjusted by co-evaporation doping balance.

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