



The Doping of Alkali Metal for Halide Perovskites

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Doping, introducing impurities in the materials, plays a critical role for junction formation in semiconductor. It directs the flow of charge carriers and improves their transport properties in the thin-film electronic devices including halide perovskite materials based optical-electric devices. Dopants can strongly modify electronic, optical and other properties of materials. Due to the relative smaller size, alkali metals play an important role for halide perovskite materials. In this review, recent research work on the doping of halide perovskite materials by alkali metals, especially the electrochemical doping, have been studied from the view of chemistry and physics.

Keywords: Halide perovskite; Doping; Electrochemical; Alkali metal

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1. Introduction

Amazing progresses have been made in the storage of electrical energy,¹⁻⁴ the conversion of light energy,^{5,6} and the conversion of light energy into chemical energy.^{7,8} The halide perovskite materials have excellent prospects as materials to achieve all the above-mentioned properties.

Halide perovskite materials have the general formula ABX_3 . A is organic cation, such as $CH_3NH_3^+$ (MA), $CH(NH_2)_2^+$ (FA), $C_6H_5(CH_2)_2NH_3^+$ (PEA); or A can be inorganic cation, such as Cs^+ . B is metal, such as Pb^{2+} or Sn^{2+} . X is halide or pseudohalide, such as I^- , Br^- , Cl^- and SCN^- . Halide perovskites materials have attracted strong attention due to its excellent optical and electrical properties, such as a long free carrier diffusion length, high charge carrier mobility, tuneable band gap, high photoluminescence quantum yield (PLQY) and solution processability.⁹⁻¹⁴ The first application of halide perovskite materials in the field of optoelectronics was a perovskite-sensitized solar cell developed by the Miyasaka group in 2009.¹⁵ After a decade of development, the highest power conversion efficiency (PCE) for perovskite solar cells has reached over 25%. This PCE

value is already close to the highest value of polycrystalline silicon solar cells.¹⁶ In addition to the successful application of halide perovskite materials in solar cells,¹⁷ various other applications have been developed, such as LED,¹⁸⁻²⁰ photodetectors,²¹⁻³² field effect transistors,³³⁻³⁵ gas sensors,³⁶ resistance switching memory devices,³⁷⁻⁴¹ and others.⁴² Among them, light-emitting devices exhibit unprecedented performance with external quantum efficiencies (EQEs) exceeding 28.2%.⁴³ More interestingly, light of all visible wavelengths can be made by simply changing the halide anion. The high performance of perovskite LEDs can be attributed to the inherent properties of perovskite materials such as low defect density, high crystallinity, high absorption, high PLQY and efficient charge transport.

However, there are still limitations for the pristine halide perovskite materials and the photoelectric performance still needs to be improved. Doping can effectively adjust the photoelectric performance of the halide perovskite crystal without changing the structure and basic properties of the crystal.⁴⁴ Doping requires only a small amount of impurities to be into the matrix. Doping level is related to the final materials'

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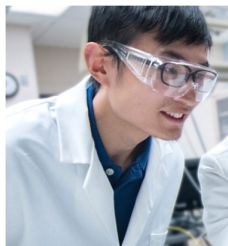
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properties. Therefore, the percentage of the impurities in the perovskite can be changed to change the relevant properties of halide perovskites in a targeted level. Continuous attempts with alternative materials have been studied in the past few years, including Li^+ , Bi^{3+} , Rb^+ , K^+ , Mn^{2+} , Fe^{2+} , Co^{2+} and many lanthanide metal ions such as Ce^{3+} , Tb^{3+} , Yb^{3+} . These dopants into halide perovskites have shown various optical and electrical properties changes.⁴⁵⁻⁵³ The dopants in halide perovskites usually can control over the optoelectronic properties of the material, such as crystal growth, structural stability and light emitting and light absorption. And the same element doping may cause changes in more than one property. For alkali metals, the doping of alkali metals can affect lots of properties, such as the photoelectric properties and stability of halide perovskites.⁵⁴

In the doped halide perovskites, the role of alkali metals is often used to passivate the surface and grain boundaries, which can only enhance the stability of the crystal. However, in this case, the alkali metal can only play the role as an additive, not the same as the case of a semiconductor doping. By definition, semiconductor doping refers to the doping of dopant atoms into the host lattice in substitution or interstitial sites. Doping requires certain methods (such as electrochemical^{47, 48}) to embed atoms into the crystal lattice. It is only by embedding atoms in the perovskite lattice that it can affect the photoelectric properties of the perovskite. In here, we will analyse the doping of alkali metal ions caused effect on halide perovskites, such as carrier lifetime, lower interface defect density, charge transfer, hysteresis, stability, power conversion efficiency and so on.

2. Doping of alkali metals as grain boundaries for halide perovskites

In the in-situ doping of halide perovskites, doped ions can easily replace cation A in halide perovskites. The cation A plays an important role in regulating the photoelectric properties of the halide perovskite materials. Theoretically, the use of cations with a larger ionic radius will expand the perovskite crystal lattice, resulting in a narrower forbidden band width and red shift of the absorption spectrum, while the opposite is true with cations with a smaller ionic radius. This type of doping is very helpful for the grain boundary optimization of halide perovskites and solving the problem of hysteresis.

It was found that doping with alkali metals can improve the halide perovskite interface and the study found that only a few simple alkali metal halide salts and their cations and anions were used. Several different types of ionic defects can be passivated simultaneously.^{55, 56} Boopathi⁵⁷ introduced an alkali metal halide as an additive into the perovskite to improve the coverage and crystallinity of the perovskite film on the PEDOT: PSS layer. This study indicates that alkali metal

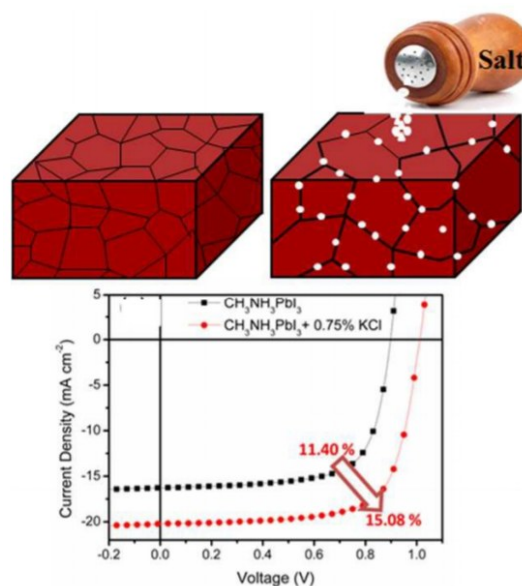


Fig. 1 Schematic diagram of passivation of the grain boundaries of alkali halides. Reproduced from Ref. [57], copyright 2016 Royal Society of Chemistry.

halides can chelate with Pb^{2+} to enhance the crystal growth of PbI_2 film, which promotes uniform nucleation and larger crystallite size. Thereby the morphology and crystallinity of the perovskite film have been enhanced. And alkali metal halides can recrystallize small grains and passivate grain boundaries and interface states (Fig. 1). Wang⁵⁸ used an alkali metal halide salt as an interfacial layer additive to make the interfacial layer have excess halide ions. These halide ions can fill vacancies well during deposition and annealing. And Wang also found that the doped devices have smaller hysteresis. However, Wang didn't mention in detail the reasons for reducing the hysteresis of perovskite solar cells. Son⁵⁹ performed a series of experiments using alkali metal iodides of LiI , NaI , KI , RbI , and CsI . Experimental results and theoretical studies show that the origin of lagging perovskite solar cells is not the migration of iodine vacancies, but the result of the formation of Frenkel defects of iodine. Potassium can prevent the formation of Frenkel defects because K^+ can fill more gaps, which in turn reduce the hysteresis of the device.

The perovskite polycrystalline thin film formed during the battery preparation process often has many grain boundaries. The coordinated unsaturated halide ions and metal ions in the grain boundaries can induce the formation of defect states, thereby greatly increasing the carrier recombination. The introduction of alkali metal halides can play a good role in passivation, improve the stability and efficiency of perovskite solar cells, and can reduce the hysteresis of the device. In general, the developed method of doping alkali metal on the crystal plane can be universally applicable to the development of non-hysteretic perovskite.

3. In-situ doping

In the in-situ doping of halide perovskites, doped ions can easily replace cation A in halide perovskite. The cation A plays an important role in regulating the photoelectric properties of the perovskite materials. Theoretically, the use of cations with a larger ionic radius will expand the perovskite crystal lattice, resulting in a narrower forbidden band width and red shift of the absorption spectrum, while the opposite is true with cations with a smaller ionic radius. When the solution is doped in situ, the optoelectronic properties of the crystal can be changed when the doped ions occupy the A site. However, for example, K^+ doping will cause lattice shrinkage, so K^+ should occupy the A site. However, according to the law of tolerance parameters measuring tolerance parameters of perovskite lattices, the ionic radius of K^+ is too small to form a stable perovskite structure, and K^+ is difficult to occupy the A site.

Cao⁶⁰ added alkali cations to the precursor solution, and incorporated alkali cations (Rb^+ , K^+ , Na^+ and Li^+) into $FAPbI_3$. It was found through experiments and DFT calculations (Fig. 2) the basic cations can eliminate the gap position, thereby increasing the ion migration barrier and achieving the effect of suppressing the migration of iodine ions. Some literatures mentioned that Li can act as an n-type dopant and introduce energy levels in the band gap. It has been reported that lithium-doped perovskite can improve the conductivity of perovskite.^{47, 48, 61} And lithium doping can affect the crystal's light absorption and magnetic properties.^{47, 48} However, the mechanism in the carrier recombination process of lithium-doped perovskite has not been fully explained, while, it is very important to understand the photophysical properties in doped perovskite. Fang⁶² used the solution method to add lithium ions to the precursor solution to prepare lithium-doped halide perovskites and they were characterized by analyzing the thermal quenching of photoluminescence (PL). The results

show that the non-radiative recombination ratio is significantly reduced after lithium doping. Based on the research results, a model based on carrier trap passivation filling passivation was proposed to explain the mechanism of the carrier recombination process of lithium-doped perovskite. The role played by metals is not surface passivation, and the weakened electron-phonon coupling after lithium doping also proves that lithium has entered the perovskite lattice.

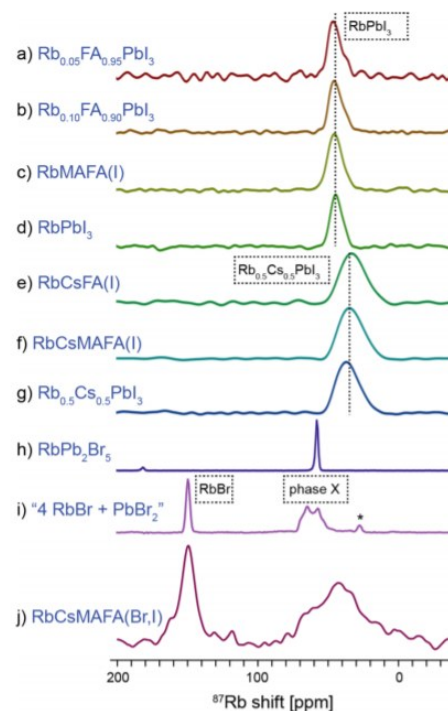


Fig. 3 11.7 T Solid-state ^{87}Rb echo-detected MAS (20 kHz, 298 K) spectra of various $(\text{Cs/Rb/MA/FA})\text{Pb}(\text{Br/I})_3$ systems. The corresponding 100 K ^{13}C CP MAS spectra of a – c, e, f, and j show only one FA signal corresponding to it being in a 3D perovskite environment. Reproduced from Ref. [71], copyright 2017 ACS Publications.

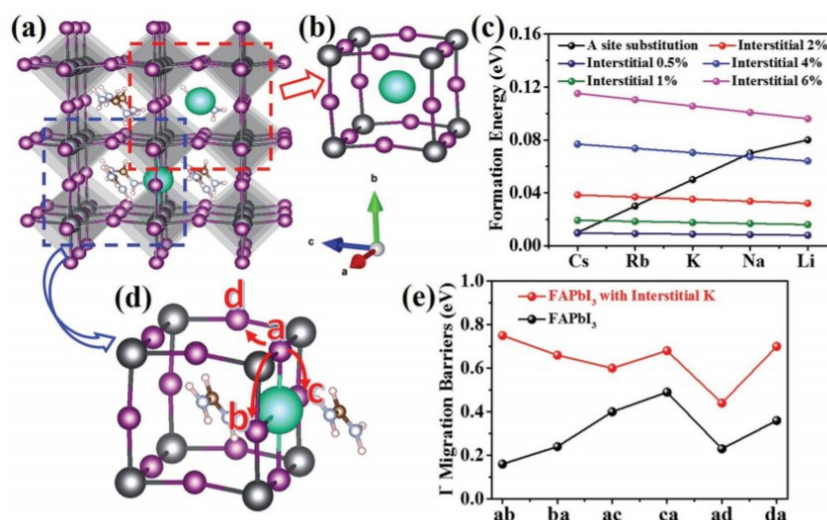


Fig. 2 DFT calculation chart of alkali metal. Reproduced from Ref. [60], copyright 2018 John Wiley & Sons, Inc.

In contrast, Cs ions and Rb ions often occupy the A position of the crystal lattice. In addition to changing the photoelectric properties of perovskite,⁶³⁻⁶⁷ the doping of these two ions can also make the crystal more stable.⁶⁸⁻⁷⁰ Ghosh⁷⁵ studied the local structure and kinetics of mixed A cations. It was found that as relatively small Rb cations are introduced into the organic perovskite crystal lattice, hydrogen bonding is enhanced, thereby acting as a stabilizer. However, when Kubicki⁷¹ analyzed Cs, Rb, and K-doped perovskites by solid-state NMR, there was no evidence that Rb or K was incorporated into the 3D perovskite lattice in these systems. As shown in Fig. 3, the spectra of $\text{Rb}_x\text{FA}_{1-x}$ and RbMAFA (I) exactly match the spectra of RbPbI_3 , indicating that the only form of Rb^+ in these systems is a separate RbPbI_3 phase, and Rb is not incorporated into the MAFA perovskite lattice.

The in-situ doping of the solution can simply and quickly dope the required dopant ions into the halide perovskite, and in addition to change the photoelectric properties of the perovskite. It can also enhance the stability of the halide perovskite. However, there is still a big debate about whether doped ions are in the A position in the crystal or in the lattice gap.

4. Electrochemical doping

Electrochemical doping uses electrodes as a medium to provide doping, thereby changing the state of charge for a substance and improving its properties. Comparing with chemical doping, it does not affect the chemical composition of the substance (Fig. 4), the doping method is simple and the doping process is easy to control. It is more noticeable that the electrochemical doping and de-doping processes are reversible. It is easy to control the doping state of the substance by changing the electrode potential and doping time.

Jiang⁴⁷ reported doping lithium ions into CsPbBr_3 in a lithium electrolyte. The doping of lithium ions is an n-type doping. It was found that the doping improves the conductivity of CsPbBr_3 and the light absorption in the wavelength range of 450 to 850 nm (Fig. 6). Like the phenothiazine derivative,⁷² it has an electrochromic effect. It was found that doped halide perovskite can be used as electron transport layer (ETL), which also have a strong emission light intensity at lower turn on voltage for light emitting and better electrical performance (Fig. 5). Then Jiang⁴⁸ also found that the electrochemically doped halide perovskite has the Burstein-Moss effect (Fig. 7), and the blue shift reaches 15 nm. The increase and decrease of the

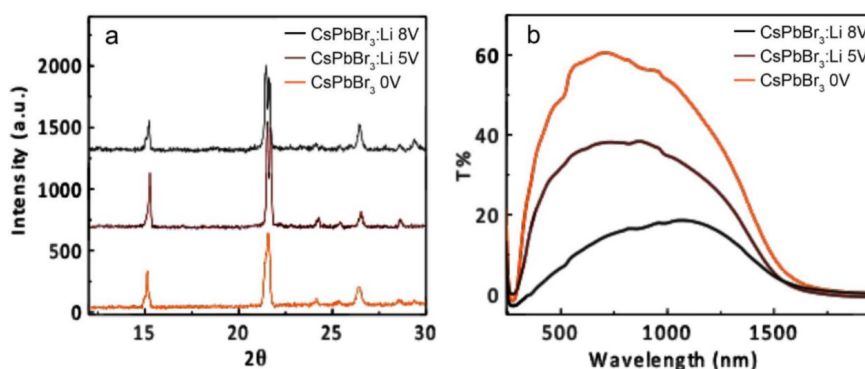


Fig. 4 a. XRD of original CsPbBr_3 and lithium doped crystal; b. electrical-optical change of CsPbBr_3 perovskite: UV-Vis-NIR spectra before and after lithium ion doping with LiClO_4 as electrolytes.

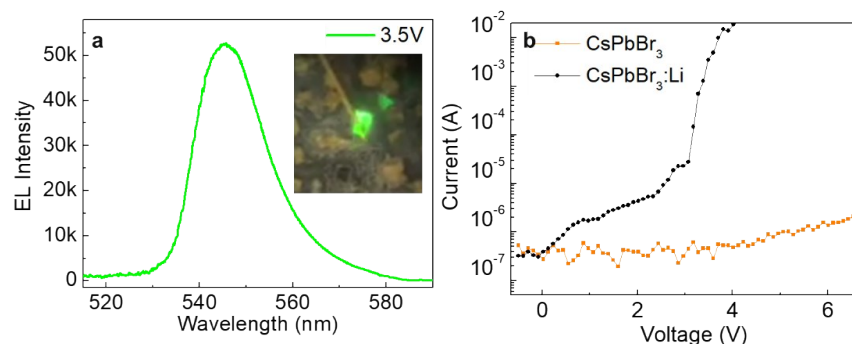


Fig. 5 a. Electroluminescence spectrum and a microscopic optical image from a lit LED with the doped perovskite ETL. Both were obtained at 3.5V; b. characteristics of light emitting with (black) and without (red) Li doped halide perovskite.

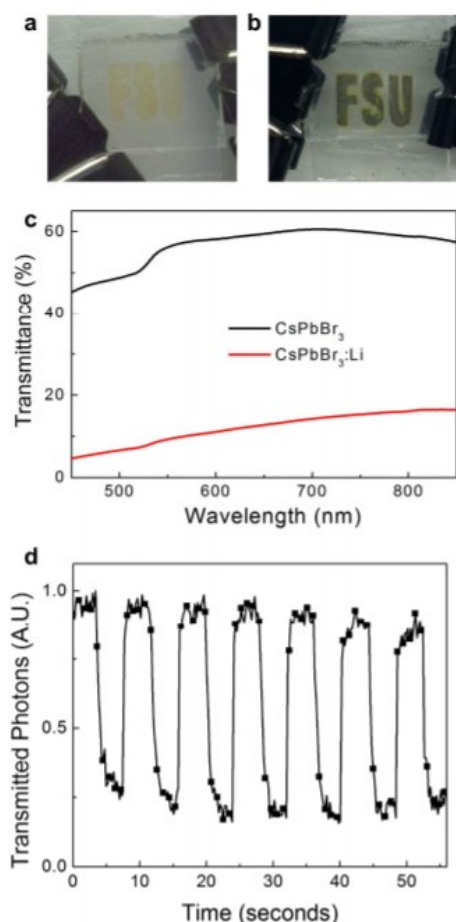


Fig. 6 a) and b) photos of CsPbBr₃ samples before (a) and after (b) lithium ion intercalation showing the electrochromism of the perovskite film; c) transmittance spectra for films before and after lithium ion intercalation; d) transient response and cyclic testing of CsPbBr₃ electrochromic devices with a square wave bias between -5 V and +5 V.

photocurrent of the lithium-doped perovskite have a certain delay compared with the undoped halide perovskite due to the doped lithium plays the role of defect centres and traps as lithium dopants will generate deep electron traps in the semiconductor, which will affect the carrier diffusion length and lifetime.⁷³ And the defect will increase the light response time of the semiconductor. Vicente⁷⁵ research showed that more than one lithium ion can be inserted into the unit cell of the halide perovskite CH₃NH₃PbBr₃. Therefore, Jiang speculated that due to the reduction of Pb²⁺, lithium was still at +1 valence to maintain the charge balance, and the reduced lead became a trap in CsPbBr₃. State transitions via indirect traps or direct conduction transitions. As a result, the transient and descent of the photocurrent are delayed (Fig. 7).

Electrochemical doping can dope without affecting the original lattice of perovskite and can greatly improve the optical and electrical properties of perovskite.

5. Conclusion

Halide perovskite materials have been greatly developed and can be widely used in various optoelectronic devices. The photoelectric properties of halide perovskites can be further adjusted through ion doping. For alkali metal ions (Li⁺, Na⁺, K⁺ and Rb⁺) doping, the doping of alkali metal ions can make halide perovskites-based devices have longer carrier lifetime and lower interface defect density. Faster charge transfer, hysteresis free, higher stability and higher power conversion efficiency. For the doping of alkali metal ions using different methods, the method of doping the alkali metal as a grain boundary can effectively passivate the halide perovskite and reduce the hysteresis, and the in-situ doping of the solution can precisely control the doping. The content of hetero ions, in

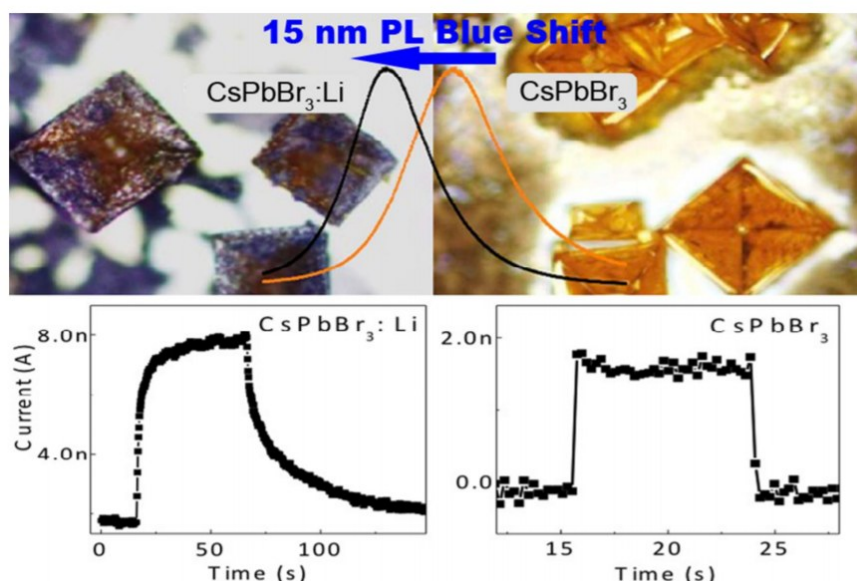


Fig. 7 15 nm Burstein-Moss effect and Current V. S. time of un-doped and lithium doped CsPbBr₃ crystal.

addition to improving the photoelectric performance of perovskite, also contributes to the stability of halide perovskites. Electrochemical doping can greatly improve the photoelectric performance of the crystal, and it has reversibility and greater operating space, however, issues such as the location of doped ions are still controversial and the mechanism of doped ions to improve the photoelectric properties of perovskite is still lacking.

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