Composition effects on structure and optical properties in double perovskite derivatives semiconductors Cs$_2$SnI$_{6-x}$Br$_x$ (x = 0–6)

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I. INTRODUCTION

Studies on perovskite materials have undergone rapid expansion over the past few years due to their applications in photovoltaic devices.\cite{1}–\cite{4} Perovskites with an ABX$_3$ structure [A = Cs, methylammonium (MA), formamidinium (FA); B = Pb, Sn; X = Cl, Br, I] have been the hot topic materials in recent years with power conversion efficiencies (PCEs) > 25%.\cite{5} However, it is noted that these perovskite halides suffer from several issues that currently preclude their use in widespread commercial applications, including lead toxicity, air and moisture sensitivity, and crystalline phase stability.\cite{6,7} To avoid toxic Pb, another group IV element tin (Sn) has become one of the potential candidates.\cite{8}–\cite{11} Therefore, tin based materials are also studied widely, such as CsSnI$_3$,\cite{12,13} FASnI$_3$,\cite{14} and Cs$_2$SnI$_6$.\cite{15}

It is well known that the lead-free Cs$_2$SnI$_6$ has excellent air and thermal stability, and a bandgap of 1.26 eV, which is ideal for photovoltaic applications. The Cs$_2$SnI$_6$ structure belongs to the A$_2$BX$_6$ form, which is the derivative structure of the double perovskite structure.\cite{16} At this time, the B$^+$ position is vacant and only the polyhedron [BX$_6$] is left. The B position changes from 2+ to 4+ due to the requirement of chemical valence state equilibrium. Fortunately, Sn$^{4+}$ is far more stable than Sn$^{2+}$.\cite{17} As shown in Fig. 1(a), Cs$_2$SnI$_{6-x}$Br$_x$ (x = 0–6) is composed of an isolated SnX$_6$ polyhedron structure, forming a zero-dimensional structure.

Lee et al. proposed that the stable tin-deficient perovskite structure (Cs$_2$Sn$_x$I$_{6-x}$) may be applied to all solid-state dye sensitized solar cells (DSSCs) as hole-transporting materials (HTMs).\cite{18} Soon after, Lee et al.\cite{19} and Yuan et al.\cite{20} discussed the optical properties and thermal stability of Cs$_2$SnI$_6$. Volonakis et al. proved that Cs$_2$Sn$_3$I$_7$Br$_3$ is a very good hole transport material.\cite{21} Currently, the general structure, the optic properties, the mechanic properties, etc., for the similar elements doping in Cs$_2$SnI$_6$ are still elusive. These lacking data are very important for the long-term application of photovoltaic devices, which is the motivation in our research.

Presently, we synthesize highly pure and air-stabilized polycrystalline Cs$_2$SnI$_{6-x}$Br$_x$ (x = 0–6) and discuss their structural evolution caused by halogen doping using the x-ray diffraction (XRD) techniques. The molecular vibration spectrum of [SnI$_{6-x}$Br$_x$] (x = 0–6) polyhedron is determined by Raman spectroscopy. The strain and grain size of the mixed halogen materials are investigated by structural refinement and Hall-plot analysis, which show that the
strain increases due to small amounts of doping, while the strain is relatively stable when the mixture concentration approaches 50%. Absorption spectra and theoretical calculations show that the introduction of Br increases the bandgap of the material from 1.26 eV to 2.93 eV, realizing the adjustment of visible light range of the bandgap of the material.

II. EXPERIMENTAL SECTION

The single phase of air-stabilized Cs$_{2}$SnI$_{6}$-xBr$_{x}$ (x = 0–6) eutectic materials are prepared by the liquid phase reaction and solid-state reaction. At the initial liquid phase reaction, SnI$_{4}$/SnBr$_{4}$ and CsI/CsBr with high purity are fully dissolved in hot alcohol solution, respectively, by the stoichiometric ratio of the products. Then, the precipitates are obtained by mixing the foregoing solutions with agitation until the reaction is complete. This liquid-phase reaction has an advantage because the raw material is dissolved in alcohol, while the product is insoluble in alcohol, so the single phase can be obtained easily. The second part of the solid phase reaction is to improve the crystallization of the material. The powder products produced in the first step are loaded into a quartz tube, encapsulated in vacuum, and annealed at 400 °C for 5 h. The scanning electron microscopy (SEM) images of Cs$_{2}$SnI$_{6}$-xBr$_{x}$ at same magnification showed that all of them are composed of dense particles with a particle size of 100–2000 nm as show in Fig. 1(c). The component information of Cs$_{2}$SnI$_{6}$-xBr$_{x}$ samples obtained by energy dispersive spectrometer (EDS) is shown in Table I.

X-ray diffraction (XRD) data are collected in the angular range 10° < 2θ < 90° with the step-size of 0.02° using a laboratory x-ray diffractometer (Rigaku D/max-RB diffractometer), operating with Cu Kα radiation. All diffraction patterns are analyzed by Rietveld refinement using the General Structure Analysis System (GSAS) computer code based on JCPDS files No. 51-0466. Raman spectra measurements are carried out using a micro-Raman spectrometer LabRAM HR800 with an excitation laser source of 785 nm. The scanning electron microscope (SEM) observation is carried out using S-3400N II (Hitachi Limited). Chemical component analysis is performed with the energy dispersive spectrometer (EDS) using EX-250 (HORIBA). The x-ray photoelectron spectroscopy (XPS) valence band spectrum is obtained by PHI 5000 VersaProbe (UVAC-PHI). The absorption spectra are measured with a Varian Cary 5000 UV-Visible (UV-Vis)-near-infrared (NIR) spectrometer with the range from 200 nm to 1200 nm. First-principle calculations are performed based on the screened hybrid Heyd-Scuseria-Ernzerhof (HSE) functionals, using the Vienna ab initio simulation computer code.

| Doping content x | Composition (at. %) |
|------------------|---------------------|
|                  | Cs         | Sn         | I          | Br         |
| 0                | 22.17      | 11.2       | 66.63      | 0          |
| 0.5              | 20.53      | 11.34      | 63.82      | 4.31       |
| 1                | 21.33      | 11.12      | 57.6       | 9.95       |
| 2                | 20.99      | 11.25      | 44.33      | 23.43      |
| 3                | 22.18      | 11.61      | 30.98      | 35.24      |
| 4                | 21.02      | 11.1       | 24.64      | 43.23      |
| 5                | 23.47      | 11.48      | 8.44       | 56.61      |
| 5.5              | 22.2       | 10.78      | 4.69       | 62.33      |
| 6                | 23.47      | 11.62      | 0          | 64.9       |
The primitive cell and a Γ-centered $6 \times 6 \times 6$ k-mesh are employed.

III. RESULTS AND DISCUSSIONS

A. Structural evolutions

The color of material appearance presents obvious gradual change from black to milky white in Cs$_2$Sn$_{6-x}$Br$_x$ with increasing the Br content as shown in Fig. 1(c) (above). The component information of Cs$_2$Sn$_{6-x}$Br$_x$ samples obtained by EDS is shown in Table I, which is consistent with expectations. Figure 2(a) shows the full XRD patterns of Cs$_2$Sn$_6$Br$_x$ with x = 0–6 in the angular range of 10°–90°. The data show that all samples are in single phase. The lattice constant decreases with an increase in the Br content. Reflection (111) shifts from 26.4° to 28.9°, as shown in Fig. 2(b). Rietveld refinements are adopted to obtain the detailed atomic parameters in the unit cell for all compositions. Some refined structural parameters are as shown in Fig. 3. For all refinements, the refined criteria Rwp and CHI$^2$ factors are, respectively, less than 15% and 3%. The structure of the Cs$_2$Sn$_{6-x}$Br$_x$ system (PDF No. 51-0466) is isostructural to the two end phases, i.e., Cs$_2$SnI$_6$ and Cs$_2$SnBr$_6$. They all belong to the cubic phase with the symmetry of Fm$\overline{3}$m. The lattice constant decreases from 11.67 Å to 10.83 Å. The bond length of Sn–X in the polyhedron decreases with the increase in the Br content, and the polyhedron shrinks accordingly. The contraction of the lattice constant of a is in good linear relationship with doping concentration x, that is, $a = -0.85x + 11.69$. The spacing between the nearest atoms of Cs–Cs is equal to $a/2$, the spacing between the

FIG. 2. XRD patterns range (a) and the shift of (111) reflection (b) for Cs$_2$Sn$_{6-x}$Br$_x$.

FIG. 3. Component dependence on the lattice constant (a) and selected bond lengths (b).
The nearest Sn–Sn is equal to $a/\sqrt{2}$, and the spacing between Cs–X is equal to $a/\sqrt{2}$. Although Cs5SnI$_{6-x}$Br$_x$ may be the eutectic in the whole range, the different lengths of the Sn–I bond from the Sn–Br bond may generate stress in polyhedral structures, even in the overall lattice inevitably. Therefore, it is very important to understand the strain caused by the halogen change for the application of materials. Here, the size-strain relationship of Cs$_2$SnI$_6$ is analyzed by the Hall-plot method.

As is well known, the breadth of the Bragg peak results from the instrument and the physical effects, i.e., the grain size and the strain. To decouple these contributions, it is necessary to collect a diffraction pattern from the line broadening of a standard material such as silicon to determine the instrumental broadening. The full width at half maximum (FWHM) to the diffraction peaks of Cs$_2$SnI$_6$ was estimated using the following:

$$\text{FWHM}(S)^2 = \text{FWHM(Measures)}^2 - \text{FWHM(instrumental)}^2,$$

(1)

$$\text{Size} = K \times \lambda/\text{FW}(S) \times \cos(\theta),$$

(2)

$$\text{FWHM}(S) \times \cos(\theta) = K \times \lambda/\text{Size} + 4 \times \text{Strain} \times \sin(\theta).$$

(3)

It is well known that the grain size may comply with the Scherrer equation, Eq. (2). However, in Cs$_2$SnI$_{6-x}$Br$_x$, the effect of stress is inevitable because of the existence of difference between Sn–I and Sn–Br bonds. After optimization, the lattice strain and grain size may be obtained semi-quantitatively by the Hall-plot method, referring to Eq. (3), where SIZE is the particle size, $\lambda$ is the wavelength of the radiation, $K$ is a constant, FW is the peak width at half-maximum intensity, and $\theta$ is the peak position.

In Fig. 4(a), similarly to the Williamson–Hall (W–H) methods, the term $\text{FW}(S) \times \cos(\theta)$ is plotted with respect to $\sin(\theta)$ for all orientation peaks of Cs$_2$SnI$_{6-x}$Br$_x$ from $2\theta = 10^\circ$ to $2\theta = 90^\circ$. The strain is determined from the slope of the linearly fitted data and the root of the y-intercept gives the particle size. The average crystallite size obtained from the W-H analysis [Fig. 4(b)] decreases with the increase in the X content, which is similar to SEM results. The composition effects on strain showed an interesting phenomenon: the strain increases gradually after a small amount of doping and flattens out as the amount of doping continues to increase. It can be understood that the coexistence of halogens at different atomic radii results in an increase in stress when doping is present. At the same time, the polyhedra and lattice will release some of the stress by shrinking or stretching the lattice size.

When a small amount of Br is doped into Cs$_2$SnI$_6$, the strain increases due to the smaller atomic radius of Br and flattens when there is a large amount of Br. The same thing happens with I doping into Cs$_2$SnBr$_6$. The strain increases due to the appearance of a small amount of I. The strain flattens out along with the iodine when more is doped because the stretching of the lattice relaxes some of the strain. It is noteworthy that the strain varies sharply in the high Br region from $x = 4$ to $x = 5$. It can be inferred that the sharp change of strain is strongly related to the composition. In the process of analyzing the composition of the sample, it was found that when the halogen composition changes from $x = 4$ to $x = 5$, the content of cesium changes in a small, stepped way. Data analysis shows that $(1-x)$SnI$_x$/Sn) was 5.66 in Cs$_2$SnBr$_5$, far less than the expected 6. It can be speculated that the deviations in these components resulted in the abnormal high strain of sample $x = 5$. The effects of the strain on the band structure will be discussed later.

The A$_2$BX$_6$ perovskites have been systematically studied for their vibrational properties at the early spectroscopic analyses.

In this phase, the B$^{1+}$ ions which form a fcc lattice are surrounded by an X$_6$ octahedral with the B–X bonds along the cubic axes. The A$^+$ ions are surrounded by [BX$_6$]$^{2-}$ octahedral in a tetrahedral coordination. The highest frequency mode, $\nu(A_{1g})$, is the Sn–X symmetric stretching, and $\nu(E_g)$ is due to Sn–X asymmetric stretching. The intermediate frequency mode, $\delta(F_{2g})$, is the symmetric bending X–Sn–X deformation. The lowest frequency mode, $\nu^\prime$ $(F_{3g})$, is a lattice mode that involves the vibrations of the [BX$_6$]$^{2-}$ octahedra as a rigid body against the Cs $^+$ cations.

The Raman vibration spectrum for Cs$_2$SnI$_{6-x}$Br$_x$ is shown in Fig. 5 and Table II. Considering the Raman studies in several publications, the A$^+$ ions are surrounded by [BX$_6$]$^{2-}$ octahedral in a tetrahedral coordination. The highest frequency mode, $\nu(A_{1g})$, is the Sn–X symmetric stretching, and $\nu(E_g)$ is due to Sn–X asymmetric stretching. The intermediate frequency mode, $\delta(F_{2g})$, is the symmetric bending X–Sn–X deformation. The lowest frequency mode, $\nu^\prime$ $(F_{3g})$, is a lattice mode that involves the vibrations of the [BX$_6$]$^{2-}$ octahedra as a rigid body against the Cs $^+$ cations.

**FIG. 4.** The Williamson–Hall (W–H) analysis of Cs$_2$SnI$_{6-x}$Br$_x$ (a). The average grain size and strain obtained according to the fitting (b).
isostructural systems, we attribute the peaks as ν(A1g) = 123 cm⁻¹, ν(Eg) = 90 cm⁻¹, and δ(F2g) = 76 cm⁻¹ in the Raman spectrum of Cs₂SnI₆, the strongest being the ν(A1g) symmetric stretching. The Raman spectrum of Cs₂SnBr₆ reveals three main peaks at ν(A1g) = 185 cm⁻¹, ν(Eg) = 136 cm⁻¹, and δ(F2g) = 107 cm⁻¹. The frequency mode of the highest intensity is that of the Sn–I stretching vibration ν(A1g) at 123 cm⁻¹ for Cs₂SnI₆, which is corresponding to the results for Cs₂SnBr₆ at 185 cm⁻¹, following the change of the reduced atomic mass for the Sn–X harmonic oscillator. Above 200 cm⁻¹, second modes are observed due to the resonance Raman conditions. These results are close to the theoretical calculation and relevant experiments discussed before.

Our research focuses on the process of the component change. With the change of Br/I content ratio, the vibration modes of Sn–I and Sn–Br in the system are independent of each other, and the frequencies of their modes change slightly with the doping. The essentially constant frequency means that the Sn–I and Sn–Br bond lengths do not contract or stretch significantly because the vibrational energy is determined by the distance between the two atoms, according to the harmonic oscillator model.

More phenomena occur in the frequency range of 124 cm⁻¹ to 185 cm⁻¹, and there are several Raman vibrations peaks of 131 cm⁻¹, 138 cm⁻¹, 146 cm⁻¹, 160 cm⁻¹, and 170 cm⁻¹ in the interval. The frequency of their vibration modes is constant basically, but the relative strength of the peaks changes regularly. In the material of Cs₂SnIₓ₋ₓBrₓ system, these intermediate vibration modes become the strongest vibration mode of Raman spectrum alternately with the increase in the Br content. These vibration modes represent the vibration mode of Sn–X in [SnX₆] (X = Iₓ₋ₓBrₓ) the polyhedron, respectively. The occurrence ratio of polyhedra [SnI₆], [SnIₓBr₆₋ₓ], [SnI₄Br₂], [SnI₃Br₃], [SnI₂Br₄], [SnIBr₅], and [SnBr₆] is determined by the Br/I content. The more related the Sn–X modes appear, the stronger the peak in the Raman spectrum, which explains what happened in the Raman experiment above.

To sum up, the structural evolution process induced by Br doping has two key points. First, the Sn–Br bond and Sn–I bond

The frequencies of Raman active modes for Cs₂SnIₓ₋ₓBrₓ (x = 0–6) in cm⁻¹ and its related polyhedron structure. The boldface values indicate the frequency of the strongest vibration mode in Raman spectrum.

| x   | [SnI₆] | [SnI₅Br] | [SnI₄Br₂] | [SnI₃Br₃] | [SnI₂Br₄] | [SnIBr₅] | [SnBr₆] |
|-----|--------|----------|----------|----------|----------|----------|---------|
| 0   | 124.7  |          |          |          |          |          |         |
| 1   | 124.7  |          |          |          |          |          |         |
| 2   | 124.8  | 131.4    | 135.6    |          |          |          |         |
| 3   | 133.9  | 138.5    | 143.8    | 156.9    | 168.1    | 180.1    |         |
| 4   | 140.5  | 145.8    | 159.8    | 170.1    | 181.4    |          |         |
| 5   | 160.7  | 171.7    |          | 183.6    |          |          |         |
| 6   |        |          |          |          |          | 185.2    |         |

FIG. 6. UV-Visible absorption spectrum (a) and the XPS valence band spectrum (b) of Cs₂SnIₓ₋ₓBrₓ powder samples. The summary diagram of experimental bandgaps and calculated bandgap (c).
exist in Cs$_2$SnI$_{6-x}$Br$_x$ ($x = 0–6$), and the length of the two kind of bonds is basically unchanged. The more Sn–Br there is, the smaller the average bond length of Sn–X will be, resulting in a change in the crystal lattice, as shown in the XRD pattern. Because the Sn–Br bond length is different from the Sn–I bond length, there is a strain. The strain tends to level off when the doping concentration approaches 50%. Second, in the mixed halogen material, iodine is randomly replaced by bromine one after another so that the polyhedron [SnI$_6$] gradually becomes [SnBr$_6$]. Mixed polyhedra [SnI$_{6-x}$Br$_x$] ($x = 0–6$) all appear with a certain probability, and the distribution is determined by the ratio of I/Br elements.

B. Optical properties

Cs$_2$SnI$_6$ has been widely discussed as a typical photoelectric applied material,\cite{16, 18, 30} so the discussion on the material properties of Cs$_2$SnI$_{6-x}$Br$_x$ system mainly focuses on its optical properties, namely, the optical bandgap. One of the main purposes of Br doping experiments is to regulate the material bandgap by mixing halogens. In this part, the discussion of material bandgap is mainly composed of two parts, experimental and theoretical calculation, which are the ultraviolet visible absorption spectrum experiment and the first-principles calculation based on the XRD structure evolution model.

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**FIG. 7** The band structure, and the total and partial density of states for Cs$_2$SnI$_6$ (a), Cs$_2$SnI$_3$Br$_3$ (b), and Cs$_2$SnBr$_6$ (c).
The UV-Visible light absorption spectrum shows a typical shape as shown in Fig. 6(a). The bandgap is determined based on the Kubelka-Munk equation $F(R) = (1 - R^2) / 2R$ (where $R$ is reflectance) and the corresponding Tauc plot. The Tauc plot is used to estimate the energy gap of Cs$_2$SnI$_{6-x}$Br$_x$ ($x = 0–6$) powder. As a direct bandgap material, the variation of $(a h v)^2$ with photon energy hv is plotted. The bandgap of the material obtained by calculating the absorption edge is 1.24 eV, 1.32 eV, 1.34 eV, 1.46 eV, 1.5 eV, 1.75 eV, and 2.93 eV in the Cs$_2$SnI$_{6-x}$Br$_x$ system, corresponding to $x$ from 0 to 6, respectively. The nonlinearity in the material bandgap is conventionally expressed as

$$E_g(Cs_2SnI_{6-x}Br_x) = E_g(Cs_2SnI_6) + (1 - X)E_g(Cs_2SnBr_6) - bX(1 - X),$$  

where $b$ is the bowing parameter, and $X$ is the Br content, which is between 0 and 1. The change of the energy bandgap with component $x$ is expressed as $E_g(Cs_2SnI_{6-x}Br_x) = 2.3X^2 - 0.61X$, and the bowing parameter for the actual bandgap is $b = 2.3$ as shown in Fig. 6(c).

The valence band spectrum was analyzed by XPS, as shown in Fig. 6(b). The valence band maximum of Cs$_2$SnI$_{6-x}$Br$_x$ is 0.35 eV, 0.52 eV, 0.64 eV, 1.09 eV, 1.41 eV, 1.76 eV, and 2.15 eV corresponding to $x$ from 0 to 6, respectively. The valence band maximum of a material is sensitive to component changes, especially in the high Br region. In the high Br region, the substitution of I for Br by each one-sixth resulted in a valence band maximum shift of about 0.35 eV, which is about 0.13 eV in the high I region. Combined with the above experiments, it is found that the change trend of the bandgap obtained by absorption spectrum is consistent with that of the bandgap obtained by absorption spectrum. It is proved that changing the bandgap is realized by changing the Br concentration. In particular, in the high Br region, the component-dependent bandgap (and VBM) changes more dramatically, as shown in Fig. 6(c).

In order to understand the materials further, or to design new materials, a large number of first-principles calculations have been made for material design with the perovskite structure in the past, including metal halide perovskite materials. In the present, the HSE framework using the VASP is used to estimate the energy band and the wave density of the material as shown in Fig. 7. The theoretical calculation of materials is carried out according to the structure evolution model obtained by XRD structure refinement. The most striking finding is that the bandgap is direct, with both valence and conduction band extrema at the center of the Brillouin zone (Γ point). The bandgap is very sensitive to the change of the Br/I content. The bandgap is rather sensitive to the structural evolution model and ranges from 1.2 eV to 2.9 eV. The bandgap calculated by Cs$_2$SnI$_6$ and Cs$_2$SnBr$_6$ is 1.28 eV and 2.90 eV, respectively, which is in good agreement with the experimental results of 1.24 eV and 2.93 eV. The contribution of each atomic orbital to the energy state density is examined by analyzing the density of wave states. The orbitals constituting the bandgap are I-4d$^{10}$/5s$^2$/5p$^3$; Br-3d$^{10}$/4s$^2$/4p$^3$; Sn-4d$^{10}$/5s$^2$/5p$^3$; Cs-6s$^1$. The conduction band bottom is mainly composed of I-5p/Br-4p and Sn-4d, and the valence band top is mainly composed of I-5p/Br-4p and Sn-4d, and the valence band top has no occupied Sn-s orbitals. More importantly, since the material structure is of the Br/I mixed type, I-5p/Br-4p will jointly contribute to the composition of the material bandgap. The main contribution of I-5p/Br-4p state directly depends on the Br/I content value of the material.

There is a deviation between the experimental results and theoretical calculations in mixed halogen compounds. The reason may be explained. The structural evolution model in mixed halogen materials is such that Br doping is random, and halogen mixed polyhedra will appear with certain probability, adjusted by the stoichiometric ratio, as shown by Raman. Moreover, valence band spectrum and absorption spectrum experiments show that the bandgap (and VBM) changes sharply in the high Br region due to the component change. However, the theoretical calculation is based on the structural evolution model obtained by XRD refinement. In the structure evolution model, Br doping is carried out uniformly, and the change of the bond length is steady. The structural evolution model of mixed halogen samples is different from the actual situation, and there are no other modifications to the model. Therefore, the theoretical calculated bandgaps will deviate from the actual ones in the mixed halogen region. In particular, the valence band spectrum shows that the changes of VBM in the high I region and high Br region are about 0.1 eV and 0.3 eV, respectively. These differences are not reflected in the XRD structure model. Therefore, the bandgaps deviate so much between the experimental and theoretical calculated ones in the high Br region.

IV. CONCLUSION

The pure phase Cs$_2$SnI$_{6-x}$Br$_x$ ($x = 0–6$) alloy materials are synthesized by means of liquid phase reaction together with solid phase annealing. XRD and Raman experiments are used to characterize the structural evolution of the material under Br doping. [SnI$_6$] polyhedron transfers gradually into the [SnI$_{6-x}$Br$_x$] ($x = 1–5$) polyhedron and finally into the [SnBr$_6$] polyhedron. When [SnI$_{6-x}$Br$_x$] ($x = 0–6$) polyhedrons coexisted, the chemical distribution is determined by the stoichiometric ratio. The bond lengths of Sn–I and Sn–Br are essentially constant. Because the Sn–Br bond length is different from the Sn–I bond length, there is a strain. The more Sn–Br there is, the smaller the average bond length of Sn–X will be, resulting in a change in the crystal lattice. The average effect is that the volume of the polyhedron shrinks and the lattice of the material decreases with Br doping. The strain increases due to small amounts of doping and the strain is relatively stable when the mixture concentration approaches 50%, because the changes in the lattice relax parts of the strain. The optical bandgap properties of the system materials are determined by the UV-Visible absorption spectrum, the valence band spectrum experiment, and the first-principles calculation. The results of the absorption spectrum show that the bandgap of the material is more sensitive to the halogen composition. With the increase in the bromine content, the bandgap increased from 1.26 eV to 2.93 eV. The calculation results show that the main energy band structure of the material changes from 1-5p state to Br-4p state with the change in the Br/I content.

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