Title: Origins of p-Doping and Nonradiative Recombination in CsSnI3

Authors: Jiajia Zhang and Yu Zhong

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 2022, e202212002

Link to VoR: https://doi.org/10.1002/anie.202212002
Origins of p-Doping and Nonradiative Recombination in CsSnI$_3$

Jiajia Zhang,*,a Yu Zhong$^a$

[a] Dr. J. J. Zhang, Prof. Y. Zhong
Anhui Provincial Laboratory of Biomimetic Sensor and Detecting Technology, College of Materials and Chemical Engineering, West Anhui University, Lu'an 237012, China
E-mail: jjzh@wxc.edu.cn

Abstract: It is commonly believed that the spontaneous p-doping in Sn-based perovskites is caused by Sn vacancies. By performing rigorous first-principles calculations for a prototypical Sn-based perovskite CsSnI$_3$, we reveal that, in fact, the defects dominating p-doping are Cs vacancies. The reason that adding extra Sn$^{2+}$ could reduce p-doping is that Cs and Sn present the same changing trend in terms of chemical potentials, and thus inhibiting the formation of Sn vacancies will also limit the formation of Cs vacancies. Moreover, we show that I vacancies are the dominant nonradiative recombination centers, and can result in sizable nonradiative losses, which explains why the experimentally measured carrier lifetime is only a few nanoseconds even if p-doping is suppressed. This work provides new insights into the origins of p-doping and nonradiative recombination in CsSnI$_3$, and suggests that minimizing the formation of Cs and I vacancies is critical to realizing the best device performance.

Keywords: CsSnI$_3$ • first-principles calculations • nonradiative recombination • p-doping • vacancies

Introduction
Sn-based perovskites are regarded as promising alternatives to Pb-based perovksites for solar cell applications because of their low environmental toxicity and ideal band gaps for single-junction...
However, the highest power conversion efficiency reported so far for Sn-based pervoskite solar cells (PSCs) is only 14.8%, which is considerably lower than that achieved by Pb-based PSCs (25.7%). The unexpected low efficiencies have been proposed as a direct consequence of the huge carrier losses resulting from radiative recombination boosted by the heavy p-type self-doping and defect-assisted nonradiative recombination. Identifying the origins of p-doping and nonradiative recombination is crucial for further improving the efficiencies of Sn-based PSCs.

There is a common belief that the undesirable p-doping in Sn-based perovskites is caused by Sn vacancies (V\text{Sn}). This belief comes from the early first-principles studies, which show that V\text{Sn}, acting as a shallow acceptor, has an extremely low formation energy and is thus the major hole source. However, these theoretical works partially or even completely employ local or semilocal functionals, which yield some unreasonable predictions, e.g. severely underestimated band gap and negative formation energy for V\text{Sn}. Also, recent studies specifically indicate the deficiency of local or semilocal functionals in predicting defect configuration, energetic, and electronic structure of halide perovskites, and highlight the importance of higher levels of calculations using hybrid functionals such as Heyd-Scuseria-Ernzerhof (HSE) and including spin-orbit coupling (SOC) for accurately describing defect properties. Hence, it is quite necessary to reexamine the defect formation energies using the HSE + SOC approach.

Besides, previous studies in general treat the deep-level defects as the strong nonradiative recombination centers based on the conventional wisdom that the deeper the charge-state transition level the faster the nonradiative recombination. However, as suggested by the recent studies, this rule may break down for some defects with large, anharmonic structural relaxation following carrier capture, and explicit calculations of the nonradiative capture coefficients are essential for identifying the actual nonradiative recombination centers. To the best of our knowledge, such calculations have not yet been performed for Sn-based perovskites.

Here we carry out a systematic first-principles study of the native point defects in the
prototypical Sn-based perovskite CsSnI₃ using the above-recommended schemes. We find that $V_{\text{Sn}}$ is not the key defect inducing p-doping. Instead, the most favorable acceptor is Cs vacancy ($V_{\text{Cs}}$), which even pushes the native Fermi level into the valence band under I-rich conditions, leading to a strong p-doping. The experimental observation that adding extra Sn$^{2+}$ could reduce p-doping is due to the synchronized increase of the chemical potential of Cs with that of Sn. Even so, we propose adding extra Cs$^{+}$ rather than adding extra Sn$^{2+}$ to suppress p-doping because of the oxidative instability of Sn$^{2+}$. We also show that I vacancy ($V_{\text{I}}$) is the dominate nonradiative recombination center with a total carrier capture coefficient on the order of $10^{-8}$ cm$^3$ s$^{-1}$, which should be responsible for the short carrier lifetime under I-poor conditions. Our study uncovers the real causes of p-doping and nonradiative recombination in CsSnI₃, and points out direction for developing highly efficient Sn-based PSCs.

**Results and Discussion**

![Figure 1](#)

**Figure 1.** (a) The allowed chemical potential domain (yellow-shaded area) for CsSnI₃, shown in the ($\mu_{\text{Sn}}$, $\mu_{\text{I}}$) plane. $\mu_{\text{Sn}}$ and $\mu_{\text{I}}$ are the chemical potentials of Sn and I, respectively. $\mu_{\text{I}} = 0$ eV corresponds to the formation of an isolated I$_2$ molecule at 0 K while $\mu_{\text{I}} = -0.39$ eV corresponds to the formation of I$_2$ gas.
under the annealing condition of 340 K and 1 atm, as detailed in the section A in the Supporting Information. The inset depicts the crystal structure of the orthorhombic phase (γ phase) of CsSnI$_3$.[12] Points A and B mark the upper and lower bounds of the allowed domain for CsSnI$_3$. (b) Evolution of the chemical potentials of Sn, I and Cs ($\mu_{\text{Cs}}$) when ($\mu_{\text{Sn}}, \mu_{\text{I}}$) moves along the A-B line in panel a.

Figure 1a shows the allowed chemical potential domain for CsSnI$_3$. The domain is limited by the appearance of secondary phases such as CsI, SnI$_2$, SnI$_4$, Cs$_2$SnI$_6$, Sn and I$_2$ gas, and is very narrow, which means that the growth conditions of CsSnI$_3$ need to be controlled delicately in order to avoid creating secondary phases. The upper and lower bounds of the domain (points A and B in Figure 1a) correspond to I-rich (Sn-poor) and I-poor (Sn-rich) conditions, respectively.

![Figure 2](image)

**Figure 2.** Formation energies as a function of Fermi level for native points defects in CsSnI$_3$ under I-rich conditions.
(Sn-poor) and I-poor (Sn-rich) conditions. The vertical dashed line indicates the native Fermi level \( E_{\text{pin}}^F \) determined by donor and acceptor with the lowest formation energies.

Using the chemical potentials under I-rich and I-poor conditions, we calculate the formation energies of all possible native point defects, namely, three types of vacancies \( (V_{\text{Cs}}, V_{\text{Sn}}, V_{\text{I}}) \), three types of interstitials \( (\text{Cs}_i, \text{Sn}_i, \text{I}_i) \) and six types of antisite defects \( (\text{CsSn}, \text{SnCs}, \text{SnI}, \text{ISn}, \text{CsI}, \text{ICs}) \) in CsSnI\(_3\), as shown in Figure 2. It is clearly seen that the formation energies of electron acceptors such as \( V_{\text{Cs}} \) are lower than that of donors at each Fermi level in the band gap under I-rich conditions. As a consequence, the native Fermi level is pinned inside the valence band (i.e. \( E_{\text{pin}}^F < 0 \text{ eV} \)), which will give rise to an exceedingly high hole concentration and metallic behavior in CsSnI\(_3\). This is consistent with the experimental findings that the material behaves like a p-type metal.\(^{[12]}\) When the growth conditions change from I-rich to I-poor, the formation energy lines of acceptors move up while those of donors move down. Under I-poor conditions, \( V_{\text{Cs}} \) and \( \text{SnCs} \) pin the native Fermi level \( E_{\text{pin}}^F \) at 0.07 eV above the valence band maximum (VBM), as depicted by the gray dashed line in the right panel of Figure 2. Because of the higher native Fermi level, the hole concentration under I-poor conditions is lower than that under I-rich conditions. This suggests that it is feasible to reduce the hole concentration by optimizing growth conditions. Additionally, it is important to note that \( V_{\text{Cs}} \) is always the energetically most favorable species among all acceptors independently on the growth conditions, which implies that \( V_{\text{Cs}} \) has a higher concentration and can inject more holes into the material than other acceptors such as \( V_{\text{Sn}} \). Therefore, the intrinsic p-type conductivity in CsSnI\(_3\) is mainly induced by \( V_{\text{Cs}} \).

Experimentally, it has been demonstrated that adding extra Sn\(^{2+}\) in the growth precursors could significantly reduce the background hole concentration of CsSnI\(_3\).\(^{[22,23]}\) This raises the question: since the major hole source is \( V_{\text{Cs}} \) instead of \( V_{\text{Sn}} \), why does the addition of extra Sn\(^{2+}\) reduce the spontaneous hole injection? To answer this question, we plot the evolution of the chemical
potentials of Sn, I and Cs ($\mu_{\text{Sn}}$, $\mu_I$ and $\mu_{\text{Cs}}$) when going from I-rich to I-poor conditions in Figure 1b. Interestingly, both $\mu_{\text{Cs}}$ and $\mu_{\text{Sn}}$ increase with the decrease of $\mu_I$. The same changing trend for $\mu_{\text{Cs}}$ and $\mu_{\text{Sn}}$ signifies that the addition of extra Sn$^{2+}$ would result in not only higher $\mu_{\text{Sn}}$ but also higher $\mu_{\text{Cs}}$; according to eq S6 (see the Supporting Information), higher $\mu_{\text{Cs}}$ indicates higher formation energy for $V_{\text{Cs}}$, and thereby lower concentration of these vacancies as well as lower hole injection level, which rationalizes the reduction of hole concentration after adding extra Sn$^{2+}$ in CsSnI$_3$.

It is noteworthy that adding extra Sn$^{2+}$ may increase the unintentional incorporation of Sn$^{4+}$ into the growth precursors owing to the facile oxidation of Sn$^{2+}$ to Sn$^{4+}$,[24,25] which has been shown to introduce additional recombination channel (see the section B of Supporting Information for detailed discussion).[26] By comparison, adding stable Cs$^+$ should be a safer, more effective approach for minimizing the formation of $V_{\text{Cs}}$ and its induced p-doping. Unfortunately, such attempt is still absent, but it deserves more attention due to the clear advantage.

We also calculate the formation energies of native point defects in FASnI$_3$ (FA = CH(NH$_2$)$_2$) and find that $V_{\text{FA}}$ is the main defect to cause p-doping behaviour. The chemical potential and defect formation energies for FASnI$_3$ as well as discussion about its p-doping are provided in the section C of Supporting Information.

We next turn our attention to the native point defects whose charge-state transition levels are in the band gap so as to identify the efficient nonradiative recombination centers in CsSnI$_3$. As shown in Figure 2, there are five defects presenting charge-state transition levels in the band gap: Cs$_{\text{i}}$, Sn$_{\text{i}}$, I$_{\text{Sn}}$, Sn$_{\text{r}}$, and $V_{\text{i}}$. Cs$_{\text{i}}$ has a (2+/+) transition level at 0.2 eV above the VBM. Sn$_{\text{i}}$ creates a (+/0) transition level at 0.4 eV below the conduction band minimum (CBM), while I$_{\text{Sn}}$ induces a deeper (−/2−) level at 0.62 eV below the CBM. Sn$_{\text{r}}$ has two levels in the band gap: a (+/0) transition at 0.54 eV above the VBM, and a (2+/+) transition at 0.29 eV above the VBM. It is noted that the (2+/0) transition of Sn$_{\text{r}}$ is ruled out as the simultaneous capture of two electrons or holes is highly unlikely.[27] For $V_{\text{i}}$, a (+/0) transition level is located at 0.62 eV above the VBM.
As mentioned in the Introduction section, explicit calculations of the capture coefficients is indispensable for correctly assessing defect-assisted nonradiative recombination, and we do so for the five defects of interest in the following part.

Figure 3. (a) Local environments around Cs$_{i}$ in the 2+ and + charge states in CsSnI$_{3}$. Green, blue and orange spheres represent Cs, Sn and I atoms, respectively, and the sticks denote the bonds between these atoms. The defect, Cs$_{i}$ in this case, is ringed by a red dashed line. Gray dotted lines means that these is a special relationship between two atoms, and here it is the attractive coulombic interaction. Arrows and labels indicate the carrier capture processes associated with the charge-state transition. Similar representations are also used in Figure 4a, 5a, 6a and 7a. (b) Configuration coordinate diagram for the (2+/+) charge-state transitions of Cs$_{i}$. Solid lines depicting the potential energy surfaces are the spline fit to the calculated data points (solid circles). The same treatment is also employed for the potential energy surfaces in Figure 4b, 5b, 6b, 7b and 7c. (c) Nonradiative capture coefficients of Cs$_{i}$ as a function of temperature.

Figure 3a shows the local environments around Cs$_{i}$ in the 2+ and + charge states. Cs$_{i}^{2+}$ and Cs$_{i}^{+}$ assume similar configurations: the defect Cs$_{i}$, perhaps driven by coulomb forces, moves from the original substitutional site between two Sn atoms to a new site surrounded by five I atoms. There are two carrier capture processes accompanying the Cs$_{i}^{2+} \rightleftharpoons$ Cs$_{i}^{+}$ transitions:
electron capture by $\text{Cs}_1^{2+}$ and hole capture by $\text{Cs}_1^+$. The corresponding capture coefficients are labeled as $C_n^{2+}$ and $C_p^+$, with the superscript denoting the initial charge state of defect and the subscript specifying the carrier type ($n$ for electron and $h$ for hole).

Figure 3b exhibits the configuration coordinate diagram of the $\text{Cs}_1^{2+} \Leftrightarrow \text{Cs}_1^+$ transitions, which maps the potential energy surfaces of $\text{Cs}_1^{2+}$ and $\text{Cs}_1^+$ as a function of a generalized configuration coordinate $Q$. $Q$ is defined as $\sqrt{\sum_m m_i \Delta r_i^2}$, where $m_i$ is the mass of the $i$-th atom in the supercell and $\Delta r_i$ the displacement from a reference position. Here, the equilibrium configuration of $\text{Cs}_1^+$ is chosen as the reference. Thus $Q = 0$ corresponds to the equilibrium configuration of $\text{Cs}_1^+$, and $Q = \Delta Q$ is related to that of $\text{Cs}_1^{2+}$.

The configuration coordinate diagram in Figure 3b has several important functions. First, it contains information about one recombination cycle. Assuming the initial state corresponds to $\text{Cs}_1^{2+}$ with an electron at the CBM and a hole at the VBM (the orange curve), $\text{Cs}_1^{2+}$ can transition to $\text{Cs}_1^+$ (the blue curve) by capturing the electron, and then $\text{Cs}_1^+$ transitions back to $\text{Cs}_1^{2+}$ (the brown curve) after capturing the hole. Second, one can qualitatively assess the capture rate in a classical manner by examining the energy barrier of each capture process, namely, the intersection of potential energy surfaces. In the case of $\text{Cs}_1^{2+} \Leftrightarrow \text{Cs}_1^+$, the barrier of electron capture is very large but that of hole capture is very small (too large or too small to be shown in Figure 3b). This implies a slow electron capture and a fast hole capture. Third, one can solve the one-dimensional Schrödinger equation for each potential energy surface to obtain the vibrational wave functions which, in combination with the thermal occupation probability, yields the phonon overlap between potential energy surfaces at any temperature.$^{[28]}$ This is a requisite step in calculating nonradiative capture coefficients.

Figure 3c presents the calculated nonradiative capture coefficients based on static coupling.
perturbation theory, which factors in phonon overlap, electron-phonon coupling matrix element, and Sommerfeld parameter for charged defect (see eq S7 in the Supporting Information). Clearly, $C_p^{+}$ is much higher than $C_n^{2+}$ (a difference of eight orders of magnitude), in line with the classical prediction. For a defect with only one charge-state transition level in the band gap, the total capture coefficient is given by\cite{29}

$$C_{\text{tot}} = \frac{C_n C_p}{C_n + C_p}. \quad (1)$$

Here, we omit the superscript in the notation of the capture coefficients for the sake of universality. Obviously, $C_{\text{tot}}$ is determined by the smaller one of $C_n$ and $C_p$. As shown in Figure 3c, the total capture coefficient of CsI is on the order of $10^{-18} \text{ cm}^3 \text{s}^{-1}$ at room temperature. The defect-assisted nonradiative recombination can be measured by the Shockley-Read-Hall (SRH) coefficient $A$,\cite{29} which is determined jointly by the total capture coefficient and the defect density ($N_{\text{def}}$), i.e. $A = N_{\text{def}} C_{\text{tot}}$. If $A$ coefficient reaches $10^7 \text{s}^{-1}$, the device performance would be badly affected. It can be estimated that the $N_{\text{def}}$ threshold of degrading device performance is $10^{25} \text{ cm}^{-3}$ for CsI. Such a high defect density is evidently impossible to achieve. Hence, CsI is not an efficient nonradiative recombination center.

Figure 4. (a) Local environments around SnI in the + and 0 charge states in CsSnI$_3$. Gray dotted lines indicate the broken Sn-I bonds. (b) Configuration coordinate diagram for the (+/0) charge-state transitions

This article is protected by copyright. All rights reserved.
of Sn\textsubscript{l}. (c) Nonradiative capture coefficients of Sn\textsubscript{l} as a function of temperature.

Figure 4a shows the local environments around Sn\textsubscript{l} in the + and 0 charge states. Sn\textsubscript{l}\textsuperscript{+} bonds to a host Sn atom and two neighboring I atoms, leading to the break of a Sn-I bond on the other side. Sn\textsubscript{l}\textsuperscript{+} also forms chemical bonds with the neighboring Sn and I atoms, but breaks two host Sn-I bonds. The Sn\textsubscript{l}\textsuperscript{+} ⇄ Sn\textsubscript{l}\textsuperscript{0} transitions involve two capture processes: electron capture by Sn\textsubscript{l}\textsuperscript{+} and hole capture by Sn\textsubscript{l}\textsuperscript{0}. The corresponding capture coefficients are labeled as \( C_{n}^{+} \) and \( C_{p}^{0} \).

Figure 4b displays the configuration coordinate diagram of the Sn\textsubscript{l}\textsuperscript{+} ⇄ Sn\textsubscript{l}\textsuperscript{0} transitions. Despite the deep transition level (0.9 eV above the VBM), both electron and hole capture need to overcome the relatively high barriers: \( \Delta E_{n}^{+} = 0.72 \text{ eV} \) and \( \Delta E_{p}^{0} = 0.77 \text{ eV} \). This implies a slow recombination. The high barriers can be attributed to the large structural relaxation (\( \Delta Q \approx 33 \text{ amu}^{1/2} \text{ Å} \)) following carrier capture, which causes a dramatic upshift of the intersection between potential energy surfaces.

In Figure 4c, we present the calculated nonradiative capture coefficients of Sn\textsubscript{l}. As expected, both \( C_{n}^{+} \) and \( C_{p}^{0} \) are relatively small. At room temperature, the total capture coefficient of Sn\textsubscript{l} is on the order of \( 10^{-20} \text{ cm}^{3} \text{ s}^{-1} \), which is even smaller than that of Cs\textsubscript{l}. Thus, Sn\textsubscript{l} is also not an efficient nonradiative recombination center. Moreover, it is observed that \( C_{n}^{+} \) and \( C_{p}^{0} \) increase rapidly with temperature. This is due to the fact that the nonradiative carrier capture is a thermally activated process and the high carrier capture barriers lead to a strong dependence of capture coefficients on temperature.
Figure 5. (a) Local environments around $I_{Sn}$ in the $-$ and $2-$ charge states in CsSnI$_3$. Gray dotted lines indicate the I octahedron. (b) Configuration coordinate diagram for the ($-/2-$) charge-state transitions of $I_{Sn}$. (c) Nonradiative capture coefficients of $I_{Sn}$ as a function of temperature.

Figure 5a shows the local environments around $I_{Sn}$ in the $-$ and $2-$ charge states. In the case of $I_{Sn}^-$, a I trimer is formed at the edge of I octahedron. But this I trimer dissociates when $I_{Sn}^-$ transitions to $I_{Sn}^{2-}$, which is also accompanied by the server distortion of I octahedron. For the $I_{Sn}^- \leftrightarrow I_{Sn}^{2-}$ transitions, the relevant carrier capture processes are electron capture by $I_{Sn}^-$ and hole capture by $I_{Sn}^{2-}$ with capture coefficients labeled as $C_n^-$ and $C_p^{2-}$.

Figure 5b exhibits the configuration coordinate diagram of the $I_{Sn}^- \leftrightarrow I_{Sn}^{2-}$ transitions. Because of the significant structural difference between $I_{Sn}^-$ and $I_{Sn}^{2-}$ (see Figure 5a), $\Delta Q$ is as high as 67 amu$^{1/2}$ Å, which brings about high electron and hole capture barriers ($\Delta E_n^e = 1.09$ eV and $\Delta E_p^{2-} = 1.48$ eV). It is thereby inferred that the carrier capture should be very slow.

Figure 5c presents the calculated nonradiative capture coefficients of $I_{Sn}$. Consistent with the above inference, both $C_n^-$ and $C_p^{2-}$ are very small ($< 10^{-22}$ cm$^3$ s$^{-1}$) even at a temperature of 400 K. This excludes the possibility of $I_{Sn}$ as a strong nonradiative recombination center.
Figure 6. (a) Local environments around Sn$_i$ in the 2+, + and 0 charge states in CsSnI$_3$. (b and c) Configuration coordinate diagrams for the (2+/+) (b) and (+/0) (c) charge-state transitions of Sn$_i$. (c) Nonradiative capture coefficients of Sn$_i$ as a function of temperature.

Sn$_i$ has two charge-state transition levels in the band gap, and the three charge states involved (2+, + and 0) ought to be considered. In Figure 6a, we show the local environments around Sn$_i$ in the 2+, + and 0 charge states. In the + and 0 charge states, Sn$_i$ is in the host Sn-I plane. In particular, Sn$_i^+$ sits close to the center of the Sn-I square. In the case of the 2+ charge state, Sn$_i$ is out the Sn-I plane and bonds to five neighboring I atoms. There are four capture processes associated with the transitions between the three charge states: electron capture by Sn$_i^{2+}$ and
Sn$_i^+$, and hole capture by Sn$_i^+$ and Sn$_i^0$. The corresponding capture coefficients are labeled as $C_{n}^{2+}$, $C_{n}^{+}$, $C_{p}^{+}$ and $C_{p}^{0}$.

Figure 6b and 6c display the configuration coordinate diagrams of the Sn$_i^{2+}$ ⇄ Sn$_i^{+}$ and Sn$_i^{+}$ ⇄ Sn$_i^0$ transitions. Among the four capture processes, the electron capture by Sn$_i^{2+}$ undergoes a very small barrier, while the other three have modest barriers ($\Delta E_p^{+} = 0.42$ eV, $\Delta E_n^{+} = 0.37$ eV and $\Delta E_p^{0} = 0.18$ eV) in spite of the large configurational differences between Sn$_i^{2+}$ and Sn$_i^{+}$ ($\Delta Q = 27$ amu$^{1/2}$ Å) and between Sn$_i^{+}$ and Sn$_i^0$ ($\Delta Q = 43$ amu$^{1/2}$ Å). The small or modest barriers stem from strong anharmonicity in the potential energy surfaces of Sn$_i^{+}$, as depicted by the blue curve in Figure 6b and the orange and brown curves in Figure 6c. Apparently, anharmonicity substantially decreases the curvature of the potential energy surfaces of Sn$_i^{+}$ within $0 \leq Q \leq \Delta Q$, leading to downshift of the intersection between potential energy surfaces and therefore reducing the carrier capture barriers.

Figure 6d presents the calculated nonradiative capture coefficients of Sn$_i$. $C_{n}^{2+}$ is relatively high due to the small electron capture barrier, while $C_{n}^{+}$, $C_{p}^{+}$ and $C_{p}^{0}$ are modest (on the order of $10^{-15} - 10^{-10}$ cm$^3$ s$^{-1}$ at room temperature) since the corresponding carrier capture processes have modest barriers. For a defect with two transition levels in the band gap, e.g. Sn$_i$, the total capture coefficient is given by\cite{29}

$$C_{\text{tot}} = \frac{C_{n}^{+} + C_{p}^{+}}{1 + \frac{C_{n}^{+}}{C_{n}^{0}} + \frac{C_{p}^{+}}{C_{p}^{0}} + \frac{C_{n}^{2+}}{C_{n}^{+}}}. \quad (2)$$

As shown in Figure 6d, $C_{\text{tot}}$ is dominated by $C_{n}^{+}$ rather than by $C_{p}^{+}$; that is to say, the total capture coefficient is not governed by the slowest capture process. This characteristic is different
from that of the defect with only one transition level, for which the total capture coefficient is
definitely limited by the slower one of the electron and hole capture processes. We can explain
the peculiar dependence of the total capture coefficient of Sn with eq 2. As $C_n^+$ and $C_p^+$ are
orders of magnitude lower than $C_p^0$ and $C_n^{2+}$, both $C_n^+/C_p^0$ and $C_p^+/C_n^{2+}$ are much less than
1. As a result, the denominator in eq 2 is approximately 1, and $C_{tot}$ is equal to $C_n^+ + C_p^+$. Since $C_n^+$ is much larger than $C_p^+$, $C_{tot}$ is almost identical to $C_n^+$.

At room temperature, the total capture coefficient of Sn is $5.3 \times 10^{-13}$ cm$^3$ s$^{-1}$. The threshold of
the defect density $N_{def}$ of impacting device performance is thus on the order of $10^{20}$ cm$^{-3}$. It is
unrealistic to achieve such a high defect density on account of the high formation energy of Sn (see Figure 2). Therefore, Sn is not a strong nonradiative recombination center.

![Figure 7](image)

**Figure 7.** (a) Local environments around V$_1$ in the + and 0 charge states in CsSnI$_3$. (b) Configuration
coordinate diagram for the (+/0) charge-state transitions of V$_1$. (c) Nonradiative capture coefficients of V$_1$
as a function of temperature.

The last of the defects of interest is V$_1$. Figure 7a shows the local environments around V$_1$ in the
+ and 0 charge states. For the 0 charge state, the removal of I atom causes a local contraction
with the distance between the two Sn atoms adjacent to V$_1$ decreasing from 6.158 Å in the
perfect system to 5.635 Å. Interestingly, this distance increases to 6.514 Å when the charge state
changes to +, indicating a local expansion. The capture processes involved in the \( V_i^+ \rightleftharpoons V_i^0 \) transitions are electron capture by \( V_i^+ \) and hole capture by \( V_i^0 \), with capture coefficients labeled as \( C_n^+ \) and \( C_p^0 \).

Figure 7b displays the configuration coordinate diagram of the \( V_i^+ \rightleftharpoons V_i^0 \) transitions. Both the electron and hole capture barriers are very small, signifying fast carrier capture.

The explicitly calculated capture coefficients of \( V_i \) are presented in Figure 7c. \( C_p^0 \) exceeds \( 10^{-8} \) cm\(^3\) s\(^{-1}\), and \( C_n^+ \) even reaches an order of \( 10^{-6} \) cm\(^3\) s\(^{-1}\). Both \( C_n^+ \) and \( C_p^0 \) are large, verifying the above qualitative prediction. There are two main reasons leading to the result that \( C_n^+ \) is two orders of magnitude higher than \( C_p^0 \) even though the two capture processes have similar barriers. First, the potential energy surfaces of \( V_i^+ \) (orange curve in Figure 7b) and \( V_i^0 \) (blue curve in Figure 7b) are very close at \( Q > 20 \) amu\(^{1/2}\) Å, which allows an effective phonon overlap for the electron capture process. Second, there is an attractive coulombic interaction between \( V_i^+ \) and electron, corresponding to a Sommerfeld parameter greater than 1, which enhances the electron capture rate. In contrast, the Sommerfeld parameter is 1 for hole capture by the neutral defect \( V_i^0 \).

At room temperature, the total capture coefficient of \( V_i \) in CsSnI\(_3\) is \( 3.3 \times 10^{-8} \) cm\(^3\) s\(^{-1}\). To quantify the impact of \( V_i \) on nonradiative recombination, we need to compute the SRH coefficient (\( A \)), which is dependent on the defect density \( N_{def} \). However, the growth of perovskites is usually a nonequilibrium process, making it difficult to accurately compute the defect density. Instead, we can use the experimentally measured density, which is in the range of \( 3 \times 10^{15} - 4 \times 10^{15} \) cm\(^{-3}\).[30,31] Using the median density, i.e. \( 3.5 \times 10^{15} \) cm\(^{-3}\), we obtain a \( A \) coefficient of \( 1.2 \times 10^8 \) s\(^{-1}\), which corresponds to a carrier lifetime of 8 ns. This value is very close to the experimentally reported lifetimes (3 − 7 ns).[30−32] Note that the carrier lifetime is
influenced by both radiative recombination associated with background hole and defect-assisted
nonradiative recombination. Under I-rich conditions, the former may have a more pronounced
effect on carrier lifetime than the latter due to the high background hole concentration (≈ 10^{19}
cm^{-3}).[22,32] To exclusively reflect nonradiative recombination, we only list the carrier lifetimes
measured under the conditions that the background hole concentration is significantly reduced,
namely under I-poor conditions. Hence, we can conclude that V_I is the dominant nonradiative
recombination center in CsSnI_3 and should be responsible for the short carrier lifetime under
I-poor conditions.

It seems that I-rich conditions is beneficial for inhibiting the formation of V_I and its induced
nonradiative recombination. Nevertheless, this is not the case. As shown in Figure 2, the
formation energy line of V_I actually moves up when the conditions change from I-poor to I-rich,
but the native Fermi level $E_F^{\text{pin}}$ enters the valence band; as a result, the formation energy of V_I
does not increase dramatically and it is still low. This suggests that V_I is abundant and can cause
sizable nonradiative recombination even under I-rich conditions. It is imperative to propose new
strategies rather than optimize growth conditions for minimizing V_I-assisted nonradiative
recombination.

**Conclusion**

To summarize, we have uncovered the causes of the high p-doping and fast nonradiative
recombination in CsSnI_3 by performing a comprehensive study of the native point defects. V_{Cs}
instead of V_{Sn} is the most favorable acceptor, which gives rise to a high p-doping under I-rich
conditions. V_I is the dominant nonradiative recombination center and can cause sizable
nonradiative losses under both I-rich and I-poor conditions. Synthesizing CsSnI_3 under I-poor
conditions is optimal for suppressing radiative recombination promoted by p-doping. To achieve
I-poor conditions, adding extra Cs\(^+\) should be a superior approach compared to the widely
employed scheme that adding easily oxidized Sn\(^{2+}\). The primary mission of future research is to
develop new methods to minimize V_I-assisted nonradiative recombination.
Conflict of interest

The authors declare no conflict of interest.

Acknowledgements

The authors acknowledge the funding support from the National Natural Science Foundation of China (11804253), the Supporting Plan for Excellent Youth Talents of Colleges (gxyqZD2022074) and the Scientific Research Foundation for High-Level Talents of West Anhui University (WGKQ201702003), and the computational support from Hefei Advanced Computing Center.

References

1002.


Sn vacancies have long been thought to be the key defects inducing high p-type self-doping in Sn-based perovskites, such as CsSnI₃. However, by performing rigorous first-principles calculations, it is revealed that the defects dominating p-doping are Cs vacancies instead of Sn vacancies.