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Advancing Tin Halide Perovskites: Strategies Toward ASnX_3 Paradigm for Efficient and Durable Optoelectronics

Yajie Yan[†], Tõnu Pullerits[⊥], Kaibo Zheng^{‡,⊥*}, and Ziqi Liang^{†*}

[†]Department of Materials Science, Fudan University, Shanghai 200433, China

Email: zqliang@fudan.edu.cn

[‡]Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

Email: kzheng@kemi.dtu.dk

[⊥]Department of Chemical Physics and NanoLund, Lund University, 22100 Lund, Sweden

ABSTRACT: Various less-toxic substitutes for the Pb^{2+} -based perovskites have been proposed wherein Sn^{2+} -based metal halide perovskites (namely, Sn-PVSKs) hold the best prospect due to their comparable optoelectronic properties to Pb analogues. Nevertheless, the intrinsic instability and unfavorable crystallization of Sn-PVSKs place restrictions on both the device performance/durability and the fabrication reproducibility/large-scale manufacturing, respectively. Therefore, numerous attempts have been directed at exploring the underlying mechanisms of Sn-PVSKs and acquiring high-quality, ambient-stable thin films. In this review, a retrospect is firstly given on the milestones and general properties of paradigm ABX_3 structured Sn-PVSKs. Then, their electronic structure evolution, photo-physics process and degradation pathways are thoroughly interpreted. The gained understanding triggers various strategies exploited in the categories of synthetic conditions, compositions, phase components as well as device architecture for diverse optoelectronic applications. The final section summarizes key advances in Sn-PVSKs and meanwhile offers the guidance for future improvements that depends critically on these methodologies.

Ever since the initial establishment in 2009,¹ perovskites solar cells (PSCs) have made unprecedented progress. The device performance is skyrocketing with the power conversion efficiency (PCE) exceeding 25% and the ambient device durability already over 10,000 hours.² This demonstrates its maturity of technology for the next generation optoelectronics.^{3–5} The nominal chemical formula of metal halide perovskites (PVSks) is ABX_3 . Based on the Goldschmidt tolerance factor⁶ and octahedral factor,⁷ the selection of A-sites fall within the range of organic/inorganic cations such as typically used $CH_3NH_3^+$ ($= MA^+$), $CH(NH_2)_2^+$ ($= FA^+$), Cs^+ and so on, the B-site candidates include group 14 metal cations such as Pb^{2+} , Sn^{2+} and Ge^{2+} , and the X represent halide or pseudo-halide monovalent anions such as Cl^- , Br^- , I^- and SCN^- . By rationally tailoring the composition and stoichiometry of PVSks, the optimal PCE of lead (Pb)-based PSCs (Pb-PSCs) has reached 25.2%.⁸

The crucial challenge towards commercialized applications is the toxicity of Pb, which necessitates its viable replacement while maintaining decent performance and stability of devices. Attentions have been directed at exploring either novel lead-free substructures or Pb substitutions in ABX_3 type PVSks. In the former efforts, three main categories of derivatives generated from aliovalent replacement of Pb^{2+} have been proposed with enhanced air and moisture tolerance as shown in Figure 1.^{9–14} Nevertheless, these structures exhibited inferior photovoltaic performance to their parent ABX_3 structure, which is attributed to the difficulties in synthesis or undesirable

electronic structures including wide and indirect optical bandgaps (E_g s).

On the other hand, the isovalent congeners of Pb^{2+} with less toxicity have been investigated both experimentally and theoretically, among which Sn^{2+} based PVSKs (denoted as Sn-PVSKs) manifest the best alternative with high charge-carrier mobilities and narrow E_g .¹⁵ In 2014, as an experimental proof, the $\text{MASnI}_{3-x}\text{Br}_x$ and MASnI_3 based PSCs demonstrated promising PCEs of 5.73%¹⁶ and 6.4%,¹⁷ respectively. However, the oxygen sensitive nature and uncontrollable film formation emerge as hurdles for Sn^{2+} based optoelectronics to fulfill the potential. From the perspective of valence electron configuration, the $6s^2$ electrons of Pb atoms are difficult to lose as a result of inert electron pair effect induced by Lanthanide shrinkage, which does not exist in the fifth period and thus the $5s^2$ electrons of Sn is unstable confronting strong electronegative matters such as oxygen. Therefore, Sn^{2+} is thermodynamically less stable than Sn^{4+} , which results in the Sn^{2+} vacancies in Sn-PVSKs upon oxidation and induces the undesirable self-doping effect. In order to maintain this metastable state under ambient atmosphere for reproducible film preparation and normal device operation, increasing attempts have been concentrated on optimizing the synthetic conditions (i.e., additive, solvent or preparation methods), elemental compositions, device architecture as well as phase composition to kinetically stabilize Sn-PVSKs, which have successfully boosted the PCE up to 13.24%¹⁸ and over 20%,^{19,20} respectively, for neat Sn and binary Sn/Pb systems, with the former demonstrating an outstanding stability of 3,800 h in inert atmosphere.²¹

Motivated by recent intensive efforts and great success in lead-free PVSKs, to the best of our knowledge, approximately 13 review articles haven been published on the topic. These reviews have focused on the designing rules,^{22,23} preparation methods,^{24–27} structural diversities,^{28–32} and the resulting optoelectronic properties,^{33,34} mostly based on lead-free derivatives of ABX_3 typed

PVSKs. However, few reviews unraveled the intimate correlations among thin-film forming kinetics, interface engineering and device performance of the mostly studied Sn-PVSKs, which is indeed critical to further improving both stability and efficiency. To fill this gap, this article seeks to offer a comprehensive yet critical review of Sn-based optoelectronics. Firstly, we will retrospect on the milestones and general properties of Sn-PVSKs based on dimensionalities and A-site cations. Next, the deterministic mechanisms in Sn-based optoelectronic devices such as electronic structure evolution, photophysics process, and degradation pathways will be discussed. Based on an understanding of the above underlying processes in Sn-PVSKs, various strategies will be presented to prepare high-quality and oxidation-resistant Sn-PVSKs thin films for diverse optoelectronic applications in PSCs, light-emitting diodes (LEDs) and photodetectors (PDs) with an emphasis on their relations to device performance and stability, which leads us to the conclusion and outlooks for the guidance of future optimization that depends critically on the strategies employed.

Figure 1. Schematic illustrations of ABX_3 typed PVSKs and derivatives generated from heterovalent substitution of B site divalent cation. The substructures feature a general composition of i) A_2BX_6 (i.e., vacancy-ordered double perovskites, $B = \text{Sn}^{4+}$, Te^{4+} , etc.), ii) $A_3B_2X_9$ (i.e., two-dimensional layered perovskites, $B = \text{Bi}^{3+}$, Sb^{3+}), or iii) $A_2B'B''X_6$ (i.e., elpasolites, $B' = \text{Bi}^{3+}$, Sb^{3+} ; $B'' = \text{Au}^+$, Ag^+ , Cu^+ , K^+ , etc.).

3D Sn-PVSKs. Given the comparable ion radius between Pb^{2+} (119 pm) and Sn^{2+} (112 pm), the ASnX_3 adopted similar crystal structure as Pb analogue. Typically, the inorganic framework of metal-halide ABX_3 perovskites consisted of divalent cations with six-fold coordination of halide monovalent anions. The corner-sharing $[\text{BX}_6]^{4-}$ octahedra constructed inorganic 3D networks with twelve-coordinated A-site cations centering in the cages formed by eight neighboring octahedra. Empirically, the crystallographic symmetry and the lattice stability of this structure are evaluated by Goldschmidt tolerance factor⁶ as expressed by $t = (r_A + r_X) / [2^{1/2}(r_B + r_X)]$, in which r_A , r_B and r_X represent the radius of A, B and X site ions, respectively. The ABX_3 structure, if exists, possesses a reduction of symmetry from cubic to orthorhombic lattice when t declines from unity and 0.813.⁷ When the A/B site cation becomes smaller/larger, the ABX_3 structure is more distorted as t decreases and finally collapse into non-perovskites. In the case of Sn-PVSKs, the A-site cation should range from ~140 to ~220 pm to preserve phase stability,³⁵ which is compatible with MA^+ (217 pm) and Cs^+ (167 pm).³⁶ The larger FA^+ (253 pm)³⁶ can also applicable except for slight distortions within the inorganic framework. Note that the tolerance factor itself is not a sufficient condition to predict the formation of perovskites. Another factor, namely, the octahedral factor, is also necessary for probing the formation of ABX_3 structure, which is determined to range between 0.414 and 0.895 for stabilization of the $[\text{BX}_6]^-$ units.³⁷ Based on the above criteria, the A-site cations play an important role in phase stability of perovskites, exhibiting different optical absorption from their Pb counterparts (Figure 2A). Moreover, it can be seen from Figure 2B and C that the E_g s of both Sn and Pb-PVSKs fall between 1.2–1.6 eV, whereas the absorption onset of Sn-PVSKs shows a strong dependence on the preparation method, which in part explains poor reproducibility of Sn-based devices. In this section, we will give a brief overview on basic

properties and summarize the development history based on the selection of A-site cation.

MA-Sn-X PVSKs: In the first attempts, both Kanatzidis¹⁶ and Snaith¹⁷ teams demonstrated the fabrication of solution-processed MASnI_3 based photovoltaic devices with impressive PCEs around 6% in a typical n-i-p architecture. Then, the comparable carrier diffusion length to Pb-PVSKs and the slow hot carrier cooling process in MASnI_3 were confirmed, implying the promising potential in lead-free PSCs.³⁸ However, the Sn-based optoelectronic devices were found extremely sensitive to oxygen, leading to inferior performance to that of Pb analogues. Therefore, extensive attentions have been paid upon the stability issues of MA-Sn-X PVSKs. By using density functional theory (DFT) calculation, Hu and coworkers revealed that the degradation of MASnI_3 is attributed to the reaction of Sn-I bond with ambient gas molecules to form new H-I and Sn-O bonds. Moreover, they found that the (011) surface was the most stable facet in MASnI_3 against moisture and oxygen.³⁹ Based on this work, Jiang and coworkers developed a novel two-step cation exchange method to enhance the (011) orientation, which remarkably suppressed the oxidation of Sn^{2+} and improved the fabrication reproducibility of MASnI_3 devices.⁴⁰ The resultant devices delivered an outstanding PCE of 7.13%, which is hitherto the highest among MASnX_3 based PSCs.

FA-Sn-X PVSKs: Despite the successful and wide exploitation of MA^+ in Sn-PSCs, the phase transition from tetragonal to cubic phase at 57 °C, which readily occurs in practical operation conditions, appears to restrict its further development.⁴¹ The replacement of MA^+ with FA^+ was reported as one effective means to improve phase stability up to 200 °C, which arises from the enhanced hydrogen bonding between FA^+ and the inorganic matrix.⁴² Moreover, Zhang and coworkers verified theoretically the weaker antibonding coupling between Sn-5s and I-5p in FASnI_3 than MASnI_3 due to the larger ionic size of FA^+ , which resulted in higher formation

energies of Sn vacancies and thus better stability of FASnI_3 .⁴³ In addition to phase stability, the FA-based Sn-PVSKs possess broader optical absorption, which indicates better photovoltaic performance than MA counterparts owing to a notable increase of photocurrent. However, the initial trial of FA^+ based Pb-free PSCs showed a limited PCE of 2.1%,⁴⁴ which is attributed to the poor film morphology because of uneven crystallization process. Such dilemma was resolved by Yan and coworkers who introduced diethyl ether anti-solvent to trigger simultaneous nucleation and prepared smooth film morphology as shown from the scanning electron microscope (SEM) imaging in [Figure 2D–I](#),⁴⁵ resulting in an optimal PCE of 6.22%. Recently, a newly discovered additive, ethylene diammonium diiodide (EDAI_2), was employed by the Diau team, to form an adduct of FASnI_3 – $y\text{EDAI}_2$ and passivate grain boundaries (GBs, [Figure 2J](#)).⁴⁶ The as-fabricated PSCs exhibited a continuous passivation process with the PCE increasing from 6.25% when prepared freshly to 8.9% after storage for over 1,400 h, which can be ascribed to the crystal strain relaxation upon the gradual effect of EDAI_2 . Aside from solar cell applications, the unique properties of FASnI_3 render it as promising materials for other optoelectronic devices such as lasers⁴⁷ and PDs^{48,49}, which will be discussed in the later sections.

Figure 2. Absorption spectra of (A) solution-processed Sn and Pb based 3D PVSKs, as well as various (B) MAPbI_3 and (C) MASnI_3 perovskites depending on the synthetic methods. (A–C) Reprinted with permission from Ref. 112. Copyright 2020, American Chemical Society. SEM images of FASnI_3 PVSK films on PEDOT:PSS with varying concentration of SnF_2 : (D) 0 mol%, (E) 5 mol%, (F) 10 mol%, (G) 15 mol%, (H) 20 mol%, (I) 30 mol%. The inset shows corresponding magnification with a scale bar of 1 μm . (D–I) Reprinted with permission from Ref. 45. Copyright 2019, Wiley-VCH. (J) Schematic representation of Sn-PVSK crystals in the presence of BAI and EDA_2 additives. Reproduced from Ref. 46 with permission from The Royal Society of Chemistry.

Cs-Sn-X PVSKs: The low thermal compositional stability of the above-mentioned organic cations— FA^+ and MA^+ —under high temperature remains to be a bottleneck for the applications in device. This is expected to be solved by establishing all-inorganic Cs-Sn-X type PVSKs with good thermal stability of Cs^+ .⁵⁰ Typically, the Cs-Sn-X based PVSKs have many polymorphs depending on the oxidation state of Cs^+ and temperature.

When the Sn adopt the valence state of +2, that is, in the chemical formula of CsSnX_3 , there exists various crystalline symmetries including cubic ($\text{X} = \text{Cl}$, Br and I), tetragonal ($\text{X} = \text{Br}$ and I),

orthorhombic ($X = \text{I}$) and monoclinic ($X = \text{Cl}$) phases, which undergo thermally reversible phase transitions owing to the rotation of the $[\text{SnX}_6]^{4-}$ octahedral as shown in Figure 3A and B.^{51,52} During device operation, the Cs-Sn-X PVSKs suffer from unfavorable phase transition to the photo-inactive orthorhombic yellow (Y) phase, which significantly deteriorates device performance.^{51,53–55} Such issue was first investigated by Seshadri et al. who confirmed the competing effect of off-centering instability of CsSnX_3 families caused by the $5s^2$ lone pair and an emerging asymmetry in the Sn–X correlations upon heating (Figure 3C and 3D),⁵⁶ which may be exacerbated by increasing the electronegativity of the X-site anions.⁵⁷ Both works revealed the correlation between the temperature-dependent phase transitions and properties of B/X site component. In another case, Soon and coworkers studied the impact of A-site Rb^+ substitution on the structural, thermodynamic and electronic nature of CsSnI_3 via first-principle calculation and attributed the enhanced phase stability to the decreased free energy that was caused by increased configurational entropy. Moreover, they claimed the importance of surface termination for stabilizing Sn-based halide PVSKs,⁵⁸ which was also stressed by Cai et al.⁵⁹ Such theoretical assumption was experimentally confirmed by Malavasi and coworkers, corroborating the local octahedral distortion caused by increasing Rb^+ content, which remarkably improved the phase stability of CsSnBr_3 .⁶⁰

In practical applications, though the intrinsic properties of CsSnX_3 such as electronic structures,⁵⁹ excitonic properties⁵² and dielectric constant⁶¹ was extensively investigated with a predicted PCE of $\sim 23\%$,⁶² the first attempt of CsSnX_3 was not used as active layer, yet for hole conduction use in all-solid-state dye-sensitized solar cells, which implies its potential as hole transporting layer (HTL) in Sn-PSCs.⁶³ Subsequently, Mi and colleagues revealed that CsSnBr_3 exhibited not only superior intrinsic properties as a free carrier semiconductor to their organic MA^+

and FA^+ based counterparts, but also remarkably high resistance towards heat induced decomposition.⁶¹ Impressively, an outstanding PCE of 7.11% in $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$ based PSCs were reported by Padture and coworkers,⁶⁴ which further demonstrated the prospect of the CsSnX_3 .

Figure 3. Structural characteristics of all-inorganic perovskites. **(A)** Illustration of phase transition among the four CsSnI_3 polymorphs with varied synthesis conditions and conversion temperatures obtained by in situ temperature-dependent synchrotron powder XRD studies. Crystal structures of the respective polymorph are shown: (i) black cubic (B- α) at 500 K, (ii) tetragonal (B- β) at 380 K, (iii) orthorhombic (B- γ) at 300 K and (iv) yellow (Y) phase at 300 K. Cs atoms, blue; Sn atoms, yellow; I atoms, violet. Green dashed lines represent a unit cell. **(B)** In-situ temperature-dependent synchrotron XRD patterns of black CsSnI_3 on heating. **(A, B)** Reprinted with permission from Ref. 51. Copyright 2019, American Chemical Society. **(C)** Increasing Sn^{2+} displacement from the center of the $[\text{SnBr}_6]^{4-}$ octahedron as temperature rises, determined from fitting the X-ray PDF over a range from 2 to 5 Å against the rhombohedral R3m model. **(D)** Evolution of the crystallographic structures of CsSnBr_3 upon heating from orthorhombic Pnma at 100 K, tetragonal P4/mbm at 270 K, to cubic Pm3m at 300 K. **(C, D)** Reprinted with permission from Ref. 56. Copyright 2019, American Chemical Society.

Other A-Site Based Sn-PVSKs: Since the Sn based PVSKs is less constrained by the tolerance factors compared to its Pb analogues,^{65,66} various organic molecules beyond the tolerance factor^{67–74} have also been demonstrated accommodable in forming 3D PVSK networks with

possibility of deriving novel AMX_3 -like structures. For instance, the Kanatzidis group reported the formation of '3D hollow' structures by substituting Sn–I units with moderate-sized diammonium cations such as ethylene diammonium ($\{\text{en}\}$),^{71,72} propylene diammonium (PN) and trimethylene diammonium (TN),⁷³ which was also demonstrated by Diau et al. with incorporation of hydroxyethylammonium into FASnI_3 .⁷⁴ As a result, such 3D-hollow structure exhibits both flexible E_g tunability and low trap densities. Importantly, the versatile ASnX_3 PVSKs provide systematic material platforms for in-depth studies on the relationship between structural tailoring and semiconductor properties.

Low-Dimensional Sn-PVSKs. As the alkyl chain of cations becomes extremely large ($t \gg 1$), the PVSK lattices finally fail to maintain the ABX_3 structure. However, some large molecules with certain groups such as amino-unit may serve as spacing ligands to afford low-dimensional PVSKs (LD-PVSKs).^{75–78} Generally, the LD-PVSKs are classified into 2D, 1D and 0D structures according to the electronically confined dimensionality. 2D PVSKs consist of one or several layers of octahedra sandwiched between ligands with 1D quantum confinement. In 1D PVSKs, the metal halide units are surrounded by ligands with different interconnection types—corner-sharing, edge-sharing or face-sharing with electrically 2D confined configuration. As for 0D cases, the small clusters of metal halide octahedra are completely isolated with 3D exciton confinement. It is worth noting that Sn-based LD-PVSKs discussed here with dimensionality-dependent confinement effect are distinct from the nanomaterials with only nanoscale morphology such as nanosheets, nanowires and nanoparticles wherein the $[\text{SnX}_6]^-$ units are interconnected in the manner of 3D PVSKs without electrical isolation. The long chain ligands effectively protect the lattices from external erosion, providing additional pathways to resolve the oxidation issue in Sn-PVSKs.

Various methods have been developed to prepare high-quality and ambient-stable Sn-based LD-PVSKs with different dimensionalities from 2D to 0D, including solvent engineering,⁷⁹ antioxidant addition,^{80,81} epitaxial growth,⁸² hot-injection,^{83–85} and ion-exchange.⁸⁶ Owing to the unique excitonic properties and enhanced stability, LD-PVSKs have been widely applied in LEDs^{80,87} and PSCs.^{88,89} For instance, Wang et al. employed an aqueous acid-based synthetic route to prepare highly emissive and air-stable octylammonium (OCTAm) 2D based Sn-PVSKs (Figure 4A), which showed a high PL emission centered at 600 nm and zero overlap between their absorption and emission spectra as shown in Figure 4B.⁸⁰ In another study, the Ma group prepared a novel organic metal halide hybrid with seesaw-shaped SnBr_4^{2-} co-crystalized with $\text{C}_9\text{NH}_{20}^+$, forming 0D structured $(\text{C}_9\text{NH}_{20})_2\text{SnBr}_4$.⁸⁷ The bulk crystals exhibit a broadband deep-red emission at 696 nm with a large Stokes shift of 332 nm upon photoexcitation as shown in Figure 4C and D. Note that the broadband photoluminescence (PL) with large Stokes shift in PVSKs exhibits a strong dimensional dependence in both Pb and Sn based systems, which is closely correlated to the radiative emissions from the self-trapping excitons (STEs). Upon photo-excitation, the hot carriers quickly relax into free excitons (FEs), which are stabilized as STEs through electron-phonon coupling that induces localized lattice distortion. In 3D PVSKs, the FE-to-STE process is negligible due to the large potential barrier for trapping process,⁹⁰ which gradually diminishes with the decreasing dimensionality. In 2D PVSKs, the STE induced broadband emissions only exist in certain structural configurations such as corrugated (*N*-MEDA)[PbBr_4] (*N*-MEDA = *N*¹-methylethane-1,2-diammonium)⁹¹ and (EDBE)[PbBr_4] (EDBE = 2,2'-(ethylenedioxy)bis-(ethylammonium))³ and such emissions may be attributed to their different dispersion relations in the vicinity of the band bottom.⁹² Similarly, the barrier separating the FE and STE states almost disappears in 1D PVSKs, which leads to room-temperature observation of

red-shifted broad emissions. The case is a bit different for 0D PVSKs in which the electronic band degenerates into discrete energy levels and hence their broadened PL can be interpreted by the molecular orbit theory whereby the photon-excited structural re-organization assists in relaxing the high energy excited states into lower ones.⁷⁷ By comparison between Pb and Sn based LD-PVSKs, both of them share similar dimensionality-dependent STE formation processes, however, the structural flexibility induced by smaller radius of Sn^{2+} may facilitate the STE generation, which renders Sn based LD-PVSKs promising candidates for broadband white-light emission.⁹³

Figure 4. (A) The crystal structure of $\text{OCTAm}_2\text{SnBr}_4$ and (B) corresponding UV-vis absorption and PL excitation (dashed line) along with PL emission spectra (blue solid line). (A, B) Reproduced from Ref. 80 with permission from The Royal Society of Chemistry. (C) Illustration of $(\text{C}_9\text{NH}_{20})_2\text{SnBr}_4$ crystal structure, where red: Sn, blue: Br, orange: N, gray: C, red polyhedral: SnBr_4^{2-} . Inset: molecular structure of $\text{C}_9\text{NH}_{20}^+$. (D) Excitation and emission spectra of $(\text{C}_9\text{NH}_{20})_2\text{SnBr}_4$ bulk crystals excited at 360 nm. Inset in (D) images of $(\text{C}_9\text{NH}_{20})_2\text{SnBr}_4$ bulk

crystals under ambient light (left) and UV irradiation (right). (C, D) Reprinted with permission from Ref. 87. Copyright 2019, Wiley-VCH.

Deterministic Mechanisms. The previous section presents a general view of state-of-the-art development in the Sn-based optoelectronics. In order to deepen the understanding of basic characteristics and optoelectronic properties in Sn-PVSKs and sparkle a rich variety of optimizing strategies as discussed in later sections, in this part we will concentrate on three main microscopic processes, beginning from the electronic band formation, and the subsequent photoexcitation dynamics, finally to critical issues of the degradation pathways.

Electronic Structures: Although the congener of Pb^{2+} and Sn^{2+} shared similar coordination environment, the Sn-PVSKs display notable differences in electronic structures. For instance, it was found that the ion size would significantly affect the lattice distortion and result in different E_g evolution trends.⁹⁴ In general, the ionization energy and electronegativity of Pb-PVSKs are larger than Sn PVSKs. As a result, the atomic levels elevate when replacing Pb with Sn in the PVSKs with an up-shift of VBM. In addition, the splitting between s and p orbits in a Sn atom is smaller than in a Pb atom, which leads to the larger variation of VBM and CBM in Sn-PVSKs. The schematic energy level diagram of various Sn-based metal halide PVSKs are summarized in Figure 5A.⁹⁵ Note the large Lewis acidity of Sn^{2+} is also the origin of fast and uncontrollable crystallization in Sn-PVSKs.⁹⁶

When the Pb atoms are partially replaced with Sn in the PVSKs, the nonlinear correlation also known as the bowing relationship between Sn/Pb ratio and the E_g s can be observed.^{97–99} Early studies by Freeman and coworkers on $\text{MASn}_{1-x}\text{Pb}_x\text{I}_3$ attributed it to the competition between the linear E_g reduction with spin-orbit coupling (SOC) and non-linear bandwidth increase caused by the lattice distortion as shown in Figure 5B.⁹⁹ Since the off-centering of Sn^{2+} in Sn-rich phases are more pronounced than in Pb-rich phases, the ferroelectric polarization diminishes the tilting of Sn-

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3 I-Sn, resulting in negligible rise of E_g s compared to the SOC induced decrease. Upon entering Pb-
4 rich regions, the non-SOC effect dominates. The widening of E_g s caused by intense octahedral
5 tilting and valence bandwidth reduction collectively compensates and/or outstrips the impact of
6 SOC and leads to a rapid and non-linear increase of E_g s. On the contrary, later DFT research by
7 Stevanović et al. excluded the impact of phase transition and stressed the main role of energy
8 mismatch between s and p atomic orbitals of Pb and Sn on the nonlinearity.¹⁰⁰ The bowing effect
9 can also be observed in FA-based PVSKs. However, large FA cation would lead to the maintained
10 band gap of 1.85 eV till 85% Sn in $\text{FAPb}_{1-x}\text{Sn}_x\text{Br}_3$ with decoupled SnBr_3 units.¹⁰¹ In addition,
11 whereas the phase transition temperature is dominated by the Sn fraction in Sn-Pb alloy PVSKs,
12 their anomalous E_g evolution is temperature independent for regions in which all compositions do
13 not exhibit structural disparities.¹⁰² Interestingly, when Sn is integrated with other element to form
14 alloyed PVSKs, such anomalous E_g s evolution may disappear. Nagane and colleagues reported the
15 monotonic increased band gap with the Ge content in $\text{CH}_3\text{NH}_3\text{Sn}_{1-x}\text{Ge}_x\text{I}_3$ PVSK, where the major
16 contributing orbitals to the conduction band change from Sn 5p orbitals to Ge 4p orbitals.¹⁰³ In
17 fact, the E_g s bowing in Sn-Pb alloyed PVSKs is not surprising among materials such as the
18 prototypical ABO_3 oxide PVSKs¹⁰⁴ and lead chalcogenides¹⁰⁵, which may provide model reference.
19 In the former compounds, it was demonstrated that high-temperature phase equilibrium,
20 compositional/structural defects and miscibility gap exhibited a remarkable influence on the
21 bowing behavior.¹⁰⁴ While the nonlinearity in lead chalcogenides depended largely on the
22 solubility variation and electronegativity differences among S, Se and Te.¹⁰⁵ Given the complete
23 solution and phase transition across the entire Sn-Pb ratio range. Herein we attempt to assign
24 $\text{ASn}_{1-x}\text{Pb}_x\text{X}_3$ to the similar case of BaTiO_3 – BaZrO_3 in which the bowing effect is predominately
25 affected by the different reactivity of B-site component in the end-members as expressed.¹⁰⁴
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$$E_g(\text{excess}) \approx W_{\text{ASnX}_3}y^2(1-y) + W_{\text{APbX}_3}y(1-y)^2$$

where W_{ASnX_3} and W_{APbX_3} represents the weighting parameters for each end-member. Mathematically, if both parameters are negative, the E_g evolution will exhibit a concave parabolic trend. Though further investigations between them remain to be explored, we suppose SOC contributes more to the W_{ASnX_3} for its greater influence on Sn-rich phases while the non-SOC may determine W_{APbX_3} because the steric effect takes control in Pb-rich region based on the discussions above.

Among Sn-PVSKs, the composition of A-site cations also affects the electronic structures. In the system of $\text{FA}_{1-x}\text{MA}_x\text{SnBr}_3$, the E_g value exhibited a much larger variation for A cation replacement (i.e., 0.5 eV) than Pb based counterparts (e.g., 0.1 eV in $\text{FA}_{1-x}\text{MA}_x\text{PbI}_3$ PVSKs). One possible origin of this new phenomenon is the contribution of MA and/or FA, especially the p -electrons of N and C atoms, to the density of states and in turn to the valence band characteristics.¹⁰⁶ Besides, the influence of A cations in the spin-orbit coupling via the variation on the octahedron distortion was reported in $\text{Rb}_x\text{Cs}_{1-x}\text{SnI}_3$ system.⁵⁸ Surface termination of Sn-PVSKs is as another factor modulating the electronic structures as both the ionization potentials and electron affinity are highly dependent on it.⁵⁸

In particular, Yu and coworkers revealed the flatter band in the CB edge of CsSnI_3 with SnI_2 termination than CsI -terminations resulting in much larger electron effective masses as shown in [Figure 5C](#). On the other hand, the E_g itself is independent of the surface termination.⁵⁹ Such a conclusion also establishes the structural difference of boundary and volume of the grains in Sn-PVSKs where various terminations are exposed at the GBs. Due to the homogenous E_g s, the energy band bending at the interface among grains could be negligible; however, the differences in electron effective masses would introduce a spatial gradient in charge carrier mobilities from the

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3 inside to the GBs. Besides engineering surface termination, applying an external pressure would
4 also drastically modify the electronic structures of Sn-PVSKs.^{107,108} Wang and coworkers reported
5 that the pressure induced $[\text{SnCl}_6]^{4-}$ octahedra in MASnCl_3 PVSKs results in the decreasing E_g as
6 well as strengthened interaction between A cations $[\text{SnCl}_6]^{4-}$ octahedra.¹⁰⁸ Such pressure-induced
7 lattice distortion can trigger in situ high-pressure photoluminescence in one-dimensional Sb-based
8 PVSK $\text{C}_4\text{N}_2\text{H}_{14}\text{SnBr}_4$, which is facilitated by the lifting the activation energy of de-trapping from
9 self-trapped states as shown in Figure 5D.¹⁰⁹ We also noticed that some intrinsic electronic
10 structures of 2D Sn-PVSKs have been reported.^{110,111} Similar to the 3D samples, Sn substitution
11 induces a smaller bandgap and more dispersed band structure in 2D structures.¹¹¹ However,
12 whether stabilized 2D framework can diminish the oxidation of Sn^{2+} to Sn^{4+} for Sn-PVSK has yet
13 to be rationalized.
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Figure 5. (A) Schematic energy level diagram of the 18 metal halide PVSKs. Reprinted with permission from Ref. 95. Copyright 2019, Springer Nature. (B) Experimental and calculated band gap evolution of MASn_{1-x}Pb_xI₃ solid solution as a function of composition x . Reprinted with permission from Ref. 99. Copyright 2019, American Chemical Society. (C) The band structure of two different surfaces calculated by GGA-PBE. Reprinted with permission from Ref. 59. Copyright 2019, American Chemical Society. (D) Pressure-dependence of PL spectra of 2D C₄N₂H₁₄SnBr₄. Reprinted with permission from Ref. 109. Copyright 2019, American Chemical Society.

Photophysics: In general, Sn based PVSKs exhibit high intrinsic charge carrier mobilities than Pb PVSKs due to larger bandwidth for both the CB and VB of the Sn-PVSK leading to the lower effective masses.^{38,112,113} Such an argument has been applied to different forms of Sn based PVSKs including single crystals, micro-crystals as well as bulk films.¹¹³ However, the low formation energy of Sn vacancies would inevitably result in excessive p-doping. Such a phenomenon results

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3 in strong monomolecular charge-carrier decay components from electron recombination with the
4 large background hole density, which may limit the carrier diffusion and extraction as shown in
5 [Figure 6A](#).¹¹⁴ The short carrier lifetime is problematic for planar device architectures requiring a
6 long diffusion length for carrier extraction.
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12 The Herz team systematically investigated the influence of p-doping on the photophysics of
13 Sn based PVSKs.¹¹⁵ Apart from enhanced monomolecular charge carrier recombination, a strong
14 Burstein–Moss effect would increase absorption onset energies beyond the bandgap energy at high
15 doping densities. In addition, the effective charge-carrier mobility would also be suppressed
16 through scattering with ionized dopants. The large background hole density can be diminished
17 either by engineering the A cation or employing additives specially SnF₂ in the PVSKs as shown
18 in [Figure 6B–D](#). The SnF₂ addition would increase the Sn chemical potential and consequently
19 increases the formation energy of Sn vacancy.³⁸ In addition, SnF₂ addition leads to less detrimental
20 band alignment at interfaces and increase stability.¹¹⁶ Replacing MA⁺ cations with FA⁺ would
21 reduce the antibonding coupling between Sn-5s and I-5p due to the larger ionic size of FA⁺, which
22 is also an effective approach to the formation energies of Sn vacancies.⁴³ The addition of Ge into
23 the FA_{0.75}MA_{0.25}Sn_{1-x}Ge_xI₃ framework was further reported by Hayase and coworkers to strikingly
24 suppresses the trap density by order of magnitudes.¹¹⁷
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42 Another critical photo-physical process determining the final performance of the PSCs is the
43 charge transfer at the interface between PVSKs and electron transporting layer (ETL) or hole
44 transporting layer (HTL). Earlier DFT calculation by the Zeng group revealed the potential wells
45 between PVSK and TiO₂ that could be introduced by the Sn addition. Such potential well is
46 induced by the enhanced charge accumulation in TiO₂ side for Sn rich samples due to more polar
47 surface confirmed from the calculation as shown in [Figure 6E](#).¹¹⁸ Despite the interfacial potential
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well, ultrafast spectroscopic characterization still verifies the rapid interfacial charge transfer between Sn-PVSKs and conventional ETL such as TiO_2 (1ps).¹¹⁹ More importantly, a drastic deterred interfacial backwards charge carrier recombination can be observed ($\sim 880 \mu\text{s}$), which ensured the efficient interfacial charge carrier separation in Sn-PSCs.

Sn-PVSKs also exhibit unique hot carrier dynamics which is the crucial processes for the application of hot carrier solar cells. In general, the relaxation of photoexcited high energy charge carriers above the bandgap of a semiconductor downhill to the band-edge (i.e., hot carrier cooling) includes three stages, that is, i) carrier-carrier scattering leading to a quasi-equilibrium distribution of hot carrier, ii) carrier-optical phonon scattering to relax the hot carrier to the band extrema by dissipating their excess energy as heat to the lattice via phonon emission, and iii) decay of an optical phonon into acoustic phonons. The slow hot carrier cooling dynamics has long been observed in lead halides PVSKs attributed to the hot-phonon bottleneck as well as the effect of Auger re-heating effect.^{120,121} Very early study reveal the similarly slow hot carrier decay in lead free MASnI_3 PVSKs at a timescale of 0.5 ps.³⁸ Extremely long-lived hot carriers (up to a few ns) with the possibility for hot PL emission has been observed in FASnI_3 later by the Loi group as demonstrated in Figure 6F.¹²² Such slow hot carrier cooling in Sn based PVSKs has been rationalized as i) smaller valence electronic density of states compared with Pb based counterparts leading to a reduction of the relaxation paths and ii) pronounced Rashba–Dresselhaus effect that reinforce the hot-phonon bottleneck. In the Pb-Sn alloyed PVSKs, a slower cooling process can be observed with the increasing of the Sn content revealed by Verma and coworkers.¹²³ The believed the Sn addition would influence all the three stages of the cooling process. First, increasing Sn content would increase carrier density along with stronger carrier-carrier scattering. Second, Sn addition should also lead to an increased effective dielectric constant, giving rise to

stronger screening, resulting in a suppressed rate of LO phonon emission. Finally, Sn addition should also lead to the phonon band gap opening and consequent a suppressed Klemens decay mechanism for the conversion from LO phonons to acoustic photons.^{123,124}

There are other photo-physical behaviors in Sn-PVSKs due to the deviation in electronic structures. For example, spin-dependent photocurrent becomes more prominent upon replacing the Pb with Sn in the PVSKs when the spin states are optically operated by switching the photoexcitation from linear to circular polarization due to the weakened spin-orbital coupling in Sn-PVSKs.¹²⁵ Clear ferroelectricity can be visualized in FA-based Sn-PVSKs which is strongly debated to occur in traditional MAPbI₃ PVSKs. It exists, and as postulated by many authors, ferroelectric charge discontinuities can affect the domain walls and GBs.¹²⁶

Photophysics of nanostructured Sn based PVSKs such as nanoplates or nanoparticles have been investigated in the literature mostly focused on all inorganic CsSnX₃.^{83,86} The strong quantum confinement of those nanostructure induced clear increased optical band gap analogous to other semiconductors.⁸³ However, the dominant intrinsic defects in CsSnX₃ tended to form shallow trap states which serves as radiative recombination centers instead of quenchers for the photoluminescence.

Figure 6. (A) TRPL kinetics of MASnI₃ film at various temperature. Reprinted with permission from Ref. 114. <https://pubs.acs.org/doi/10.1021/acs.jpclett.6b00322>. Copyright 2019, American Chemical Society. (B) Diminished dark conductivity with SnF₂ addition in FASnI₃ film extracted from time-resolved THz (THz-TDS) spectroscopy, (C) Optical pump THz probe spectroscopy (OPTPS) measurements of the charge-carrier recombination dynamics of FASnI₃ films with different concentrations of added SnF₂. (D) Relationship between doping density extracted from dark conductivity spectra shown in (B), and the monomolecular charge-carrier recombination rate, k_1 . The red markers are experimental data, and the solid black line is a linear fit. The dashed line indicates the y-intercept, and the shaded region marks the slope of the line. (E) Schematics to show the accumulation of charges at the polar interface between PVSKs and TiO₂. Reprinted with permission from Ref. 118. Copyright 2019, American Chemical Society. (F) ultra-slow hot carrier cooling dynamics with slow carrier temperature decay in FASnI₃ films.

Among the applications of emitters such as LEDs or lasing devices, the basic photophysical requirements for Sn-PVSKs is identical to those of Pb-PVSKs where the non-radiative

recombination and the trapping process should be minimized. Nonetheless, in order to obtain the high emission quantum yield, a localization of the photo-generated charge carriers in the active layer is highly preferable. Therefore, low-dimensional quantum confined systems—e.g., 2D Ruddlesden-Popper (RP) structures or quantum dots—seem to be more popular than conventional 3D PVSKs for Sn based LEDs.^{80,127–129} In those structures, the excitonic recombination should be dominated after charge carrier injection which is different than solar cell devices. As a result, the radiative recombination time is much shorter than in 3D Sn-PSVKs.¹²⁷ Moreover, the Sn addition in the PVSK lattice was reported to enhance the above-mentioned STE formation. Such STE formation is initiated by the hole trapping at the Sn sites followed by the electron localization by Columbic interaction. This would induce ultra-board band PL emission for white-light LED application.¹²⁸ Furthermore, the enhanced radiative monomolecular charge recombination pathway deriving from the doping can drastically facilitate the amplified spontaneous emission (ASE), and thus opening up a path for ultralow light-emission thresholds.⁴⁷ The ASE charge-carrier density threshold can be found as low as $8 \times 10^{17} \text{ cm}^{-3}$ in the benchmark FASnI₃.⁴⁷ Besides, Sn-PVSKs exhibited 1–2 orders of magnitude larger free-electron-hole bimolecular recombination rates compared with conventional MAPbI₃ after trap passivation by SnF₂. This renders it promising optical gain in the laser device applications.¹²⁸ However, the origins of the above superior charge carrier dynamics parameters in Sn-PVSKs have yet to be explored when comparing with Pb counterparts.

Atmospheric Degradation: The atmospheric instability of Sn based PVSKs has long been considered as one fatal obstacle restricting their commercialized application. Given the analogous structures between Pb and Sn based PVSKs, the degradation pathways of Pb-PVSKs such as water and oxygen-light induced decomposition may also exist in Sn-PVSKs. In addition, Sn-PVSKs

suffer from unwanted oxidation of Sn^{2+} , which causes severe self-doping and destroys their semi-conducting nature. For water ingress, it was demonstrated that the vacancy-type defects at the GBs played a critical role in the degradation circle of MAPbI_3 ¹³⁰ while the PbI_2 -terminated interface shows a stronger resistance to moisture thanks to the higher activation energy of water diffusion compared to MAI termination.¹³¹ It was further revealed that the Pb vacancies at the GBs accelerated this process.¹³² In addition, the light-oxygen induced decomposition is also a major degradation path in MAPbI_3 by following the procedures as shown below:¹³³

Such photolysis is originated from the deprotonation (3) between the superoxide (O_2^-) generated upon photoexcitation ((1) and (2)) and the excited MAPbI_3^* , of which the reaction rate exhibits strong correlation with I vacancies at surfaces and GBs. When it comes to Sn PVSKs, the interfacial passivation of B and X sites related defects with tin halide additives has demonstrated effective in improving long-term ambient stability Sn-based devices,^{134–136} which corroborates the similar degradation processes as Pb. For the oxidation sensitivity of Sn^{2+} , it is an inevitable process in Sn-PVSKs regardless of light/dark conditions for the thermodynamically inferior stability of Sn^{2+} to Sn^{4+} as discussed above. Analogous to Pb-PVSKs, such a process has also been found to correlate with Sn–I bonding. Recently, both the Hu and Nakamura groups theoretically simulated the detailed degradation processes of Sn based PVSKs and confirmed the critical role of surface Sn–I bonding on the degradation process, which would be significantly weakened by H_2O or O_2 invasion along with the depletion of a $\text{CH}_3\text{—NH}_3^+$ cation in the surface region.^{39,137} Such instability

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3 originating from the fragile surface Sn-I bonding can be well visualize from the ab initio molecular
4 dynamics calculation as shown in [Figure 7A](#).¹³⁷ More detailed Sn²⁺ oxidation pathways associated
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6 with the Sn-I bond breaking in full ASnI₃ PVSKs is later clarified by McGehee et al. using in-situ
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8 thermogravimetric analysis (TGA) as follows:¹³⁸
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15 Similar degradation by-products in various Sn-PVSK systems were also validated by Stranks
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17 et al. by using the ¹¹⁹Sn solid-state NMR spectra.¹³⁹ Nishikubo and coworkers revealed the
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19 influence of such degradation on the electronic structures and charge carrier dynamics of the
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21 MASnI₃ and FASnI₃ PVSKs.¹⁴⁰ The degradation process down-shifted the VBM of the samples
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23 as well as declined the photoconductivity of the samples observed from time-resolved microwave
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25 conductivity measurement (TRMC) as depicted in [Figure 7B](#).¹⁴⁰ They also confirmed the
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27 degradation process accompany with the formation of ASnI₆ low dimensional PVSKs. Integrating
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29 Pb element in Sn based PVSK or shrinking the cubic lattice by incorporation of smaller A-site
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31 cations such as Cs has been proved to effectively diminish the Sn²⁺ oxidation.¹³⁸ In the former
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33 case, the SnI₄ formation is apparently prevented by alloying Sn and Pb, forcing the oxidation
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35 reaction to proceed through the less favorable pathway, requiring more Sn-I and Pb-I bonds to
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37 break to form I₂. In addition, either SnF₄ or SnCl₄ doping is another widely-accepted method to
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39 enhance the stability of Sn based PVSKs.¹⁴⁰ Finally, the stability of the Sn-PVSKs is strongly
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41 related to the charge transport layer utilized in the device configuration as the oxidation process
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43 has been proved to be modulated by the density of microscopic pinholes and GBs among the
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45 crystallites.²⁴² A judicious selection of hole transport layers would therefore greatly influence the
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47 overall stability of the devices.
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Figure 7. (A) Results of ab initio molecular dynamics calculation of $\text{CH}_3\text{NH}_3\text{SnI}_3$ showing the breaking of surface Sn-I bonding. Reprinted with permission from Ref. 137. Copyright 2019, American Chemical Society. (B) TRMC transients of FASnI_3 over air exposure illustrating the decreased photoconductivity with degradation. Reprinted with permission from Ref. 140. Copyright 2019, American Chemical Society.

When delving into the fundamentals of electronic structure, photophysics, and degradation pathways as elucidated above, the intrinsic issues in Sn-PVSKs emerge as 1) easy oxidation of Sn^{2+} , which impairs long-term structural stability; 2) oxidation induced p-doping, which causes severe monomolecular recombination and E_g widening; 3) mismatched band alignment between the active layer and the transporting layers, which hinders the collection of free carriers; 4) rapid and uncontrollable crystallization, which present a critical technical challenge towards high-quality preparation of Sn-PVSK thin films. However, the anomalous band bowing effect upon Sn–Pb alloying, tunable band structure with A/B/X site ions and similar degradation pathways as Pb analogues may inspire enormous strategies for further enhancement in Sn-PVSKs based optoelectronics. In the next section, we will dive into detailed optimizing strategies for different Sn-PVSKs based optoelectronic devices from the aspects of additives/solvent selection, preparation improvement, compositional modulation, interfacial engineering and phase regulation.

Photovoltaic Cells. Additives: The commonly applied additives were focused on tailoring thin-film forming process, stabilizing the Sn-PVSK structure and suppressing the oxidation of Sn²⁺. Based on separate functions, we divide the commonly-used additives into four categories: i) tin halide (e.g., SnF₂), ii) Lewis base with active lone pair electrons such as thionyl or thiocyanate group), iii) antioxidant and iv) other additives. The detailed device performance and stability parameters are summarized in Table 1.

Table 1. Summary of device performance and stability of Sn-PSCs by the **additive strategy**

Active layer	Strategy	<i>V</i> _{OC} (V)	<i>J</i> _{SC} (mA/cm ²)	FF (%)	PCE (%)	Stability test (r.t.)	Ref.
FASnI ₃	SnF ₂	0.24	24.4	36	2.1	N/A	44
CsSnBr ₃	SnF ₂	0.41	9.1	57	2.2	MPPT, 65% RH, 15 min (0%)	116
CsSnI ₃	SnCl ₂	0.50	9.9	68	3.6	Continuous operation, 25% RH, 16 h (70%)	134
CsSnI ₃	SnBr ₂	0.44	18.5	53	4.3	Shelf life, N ₂ , 100 h	135
CsSnI ₃	SnF ₂	0.24	22.7	37	2.0	Shelf life, N ₂ , 250 h (100%)	142
CsSnI ₃	SnI ₂	0.43	12.3	40	2.8	Shelf life, N ₂ , 100 d (60%)	213
FASnI ₃	EDAI ₂	0.58	21.3	72	8.9	Shelf life, N ₂ , 1500–2000 h (100%)	46
CsSnI ₃	Piperazine & SnCl ₂	0.34	20.6	54	3.8	Continuous operation, 40–50% RH, 5 min (80%)	143
FASnI ₃	Pyrazine	0.32	23.7	63	4.8	Shelf life, encapsulated, 100 d (98%)	147
FA _{0.7} Cs _{0.3} Pb _{0.7} Sn _{0.3} I ₃	FACl & SnF ₂	0.74	25.9	81	15.8	Shelf life, 20% RH, 288 h (90%)	149

FASnI ₃	KHQSA & SnCl ₂	0.55	17.6	69	6.8	Shelf life, 20% RH, 500 h (80%)	150
CsSnI ₃ QDs	TPPi	0.42	23.8	41	4.1	Shelf life, N ₂ , 30 d (72%)	89
CsSnI ₃	HZ vapor & SnI ₂	0.38	25.7	49	4.8	N/A	136
CsSnBr ₃	HZ vapor	0.38	19.9	52	3.9	Shelf life, 40% RH, 70 min (80%)	158
FASnI ₃	N ₂ H ₅ Cl	0.46	17.6	67	5.4	Shelf life, N ₂ , 1000 h (65%)	165
MA _{0.3} FA _{0.7} Pb _{0.5} Sn _{0.5} I ₃	Metallic Sn	0.79	31.3	79	19.5	MPPT, N ₂ , 463 h (90%, tandem cells)	163
MA _{0.5} FA _{0.5} Pb _{0.5} Sn _{0.5} I ₃	AA	0.78	25.7	70	14.0	Shelf life, N ₂ , 1 month (99%)	164
MAPb _{0.75} Sn _{0.25} I ₃	C ₆₀	0.74	23.5	79	13.7	Shelf life, 30–50% RH, 7 d (80%)	166
FASnI ₃	5-AVAI	0.59	18.9	62	7.0	MPPT, encapsulated, 100 h (100%)	167

Note: a) Abbreviation: MPPT = max power point tracking, r.t. = room temperature, RH = relative humidity, Ref. = reference, KHQSA = hydroquinone sulfonic acid, EDAl₂ = ethylene diammonium diiodide, TPPi = triphenyl phosphite, HZ = hydrazine, AA = ascorbic acid, 5-AVAI = 5-ammonium valeric acid iodide; b) Terms for stability test, ‘Test condition, Storage condition, Duration (Remnant PCE percentage)’, for instance, the ‘MPPT, 65% RH, 15 min (0%)’ means the device was measured under air ambient with 65% RH under room temperature. The test condition is MPPT and the device kept 0% of the initial PCE after 15 min of measurements.

For tin halide additives, SnF₂ was first introduced by the Mathew group into CsSnI₃ system, which rendered it lower intrinsic conductivity owing to the increase in the formation energy of Sn vacancy as shown in Figure 8A and resulted in higher carrier densities as shown in Figure 8B.¹⁴² The same effect can be found for FASnI₃ with an encouraging PCE of 2.10% in a normal device structure, triggering the subsequent enormous development of tin halide PVSKs assisted by SnX₂ (X = F, Cl, Br, I), which is now regarded as paradigm additives for synthesis of lead-free halide

PVSKs for optoelectronics.^{44,45,116,134–136,143–146} Intriguingly, SnX_2 additives were reported to take into effect in different ways depending on the halogen atoms. For example, slightly excessive SnI_2 addition was reported to stabilize the PVSKs lattices by compensating the Sn^{2+} loss upon oxidation as displayed in Figure 8C.¹⁴⁶ While SnCl_2 was found to serve as desiccants and slow down the oxidation process.^{134,143} Additionally, Im et al. demonstrated SnBr_2 as both effective surface passivator and stabilizer of the B- γ black phase of CsSnI_3 because of its lowest adsorption energy and strongest binding on the surface among the three kinds of tin halide additives.¹³⁵ In short, SnX_2 is believed to not only ensure the Sn^{2+} -rich environment, increase the formation energy of Sn vacancies and thus suppresses the self-doping effect, but also improve its phase stability. Besides, SnX_2 may still be utilized to optimize the interfacial band alignment for separation of photoinduced excitons,^{116,134} which is of great significance in reducing the V_{OC} loss and improving the FF in device.

Second, some Lewis acids and bases theory can effectively stabilize the frame structure of Pb-PVSKs through the interaction between the lone pair electrons of Lewis base and Pb^{2+} . Likewise, the strategy of SnX_2 -additive Lewis-adduct had also proved valid for Sn-PVSKs.^{46,143,147–154} For example, the sulfonate group were reported to interact with Sn^{2+} in both Sn-PVSKs and the excessive SnCl_2 additives (Figure 8D), which not only regulate the crystallization of precursor solution, but also protect the polycrystals through in-situ encapsulation by SnCl-SO_3^- adducts at GBs.¹⁵⁰ Later, pseudo-halide additives have been confirmed to coordinate with Sn^{2+} and passivate the interfacial trap states.^{19,88,149–153} The Oh group initiated the application of the FASCN into FA based PVSKs, which was confirmed by XPS to interact with Sn^{2+} to prevent the oxidation during crystallization and enhance the crystallinity of the films.¹⁵¹ Such SCN based Lewis base was used by Ning's group to separate the nucleation and growth processes in 2D Sn-PVSKs with aid of the

removable NH_4SCN and delivered a record PCE of 9.41%.⁸⁸ Aside from direct addition to precursor, these additives were recently combined with anti-solvents by several research teams to modulate film formation through Lewis acid-base interaction,^{155–157} which holds promising prospects.

Figure 8. (A) Theoretical evolution between the Sn vacancy formation energy ($\Delta E(V_{\text{Sn}})$) and Sn chemical potential (μ_{Sn}). (B) Carrier concentration and mobility of CsSnI₃ PVSK films with

various SnF_2 addition. **(A, B)** Reprinted with permission from [Ref. 142](#). Copyright 2019, Wiley-VCH. **(C)** SEM images of the CsSnI_3 PVSK films grown with different CsI/SnI_2 molar ratios. Reprinted with permission from [Ref. 136](#). Copyright 2019, American Chemical Society. **(D)** Molecular structures of phenol sulfonic acid (PSA), 2-aminophenol-4-sulfonic acid (APSA) and hydroquinone sulfonic acid (KHQSA) and proposed interaction between the additive and Sn^{2+} . Reprinted with permission from [Ref. 150](#). Copyright 2019, Wiley-VCH.

Third, the antioxidant additives have been applied to hinder the oxidation in Sn-PVSKs.^{80,81,89, 136,158–165} Although we should emphasize the removability of additives, which may introduce impurities and defects in as-prepared Sn-PVSK thin films, the residual additives also ensure the long-time inhibition of oxidation. Generally, the difficulty of removing supplements increases from gas, liquid to solid state, depending on which we categorize the present antioxidants into three types. The gaseous antioxidants seem limited, in which the hydrazine vapor (HZ) was mostly exploited to create a reducing atmosphere during preparation of MASnI_3 as shown in [Figure 9A](#).¹⁵⁸ On the other hand, The solid-state antioxidants comprise both elemental substance.^{159,160,163} and compounds.^{164,165} The metal powder of Sn was employed to directly react with the Sn-PVSK precursor solution, thus maintaining Sn^{2+} -rich environment by comproportionating process between Sn and Sn^{4+} . [Figure 9B](#) shows the direct solid-liquid com-proportionation between Sn powder and MASnI_3 solution under continuous stirring. Using this method, Tan and coworkers achieved an impressive certified PCE of 19.5% and the resulting all-PVSK tandem solar cells delivered an outstanding stability of 463 h under maximum power point tracking (MPPT) in inert atmosphere. For the aqueous antioxidants, it was found that triphenyl phosphine (TPPi) addition effectively enhanced device durability of CsSnI_3 QD PSCs ([Figure 9C](#)), which resulted in stable operation for 25 days in an inert atmosphere.⁸⁹

Besides, other kinds of additives such as C_{60} ,^{166,169} 5-ammonium valeric acid iodide (5-AVAI)¹⁶⁷ and poly(vinyl alcohol) (PVA)¹⁶⁸ have manifested to interact with Sn-PVSK lattices via other forces such as hydrogen bonds, intermolecular forces and halide bonding. For example, the

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Islam group succeeded to passivate GBs of FASnI_3 by 5-AVAI, which formed hydrogen bonds with I^- with the carboxylic acid and the ammonium end-groups. Thus, the devices exhibited enhanced durability than pristine FASnI_3 based devices by maintaining 75% of the initial PCE after maximum power point tracking for 100 h in ambient atmosphere.¹⁶⁷ Moreover, the fullerene and its derivatives were reported to passivate GBs.¹⁶⁹ After spin-coating, C_{60} will disperse uniformly at the GBs and efficiently prevented the intrusion of oxygen and moisture into the lattices.¹⁶⁶

Figure 9. (A) Possible reaction mechanism between hydrazine vapor and Sn-PVSK lattices. Reprinted with permission from Ref. 158. Copyright 2019, American Chemical Society. (B) Preparation process of $\text{MAPb}_x\text{Sn}_{1-x}\text{I}_3$ solution via galvanic displacement reaction between MAPbI_3 solution and Sn powders. Reprinted with permission from Ref. 160. Copyright 2019, Wiley-VCH. (C) Schematic procedures of CsSnI_3 QDs prepared from TPPi aqueous solution. Reproduced from Ref. 89 with permission from The Royal Society of Chemistry.

Solvent: As the precursor solution of Sn-PVSK is spin-casted onto substrate, the uncontrollable film formation results in two main issues. Firstly, the randomly-oriented small

crystallites with high densities of GBs severely restrict the charge carriers transport and lower the tolerance for moisture and oxygen as discussed above. Second, the dynamics-dominated process gives rise to inhomogeneous nucleation/growth and discontinuity in thin films, which causes both electrical leakage and device failure. Since the solvent is direct medium of crystallization, the solvent engineering seems the most effective avenue to regulate the film formation by controlling the basic properties such as viscosity, solubility, boiling point, coordination and polarity. The adopted solvent can be classified into good solvents^{79,96,142,170–172} and anti-solvents^{173–175}. Generally, the former function to dissolve precursors and regulate the reaction rates among constituents, while the latter are added to lower the solubility during film preparation and aid in homogeneous nucleation and crystal growth. The detailed device performance and stability parameters are summarized in Table 2.

Table 2. Summary of device performance and stability of Sn-PSCs by the solvent strategy

Active layer	Solvent	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Stability test (r.t.)	Ref
BA ₂ MA ₃ Sn ₄ I ₁₃	DMSO & MAAc	0.38	21.9	48.3	4.0	Shelf life, N ₂ , 94 d (100%)	79
MASnI ₃	DMSO & DMF	0.32	21.4	46	3.2	N/A	96
MAPb _{0.75} Sn _{0.25} I ₃	DMSO & DMF	0.96	20.6	74	14.1	N/A	170
MASn _{0.25} Pb _{0.75} I ₃	DMSO & DMF	0.81	26.4	74	15.2	N/A	171
FASnI ₃	DE	0.46	22.1	60.7	6.2	Shelf life, N ₂ , 30 d (85%)	45
FA _{0.75} MA _{0.25} SnI ₃	Hot CB & DMSO vapor	0.55	19.4	67	7.2	Shelf life, N ₂ , 70 d (100%)	172
FA _{0.75} MA _{0.25} SnI ₃	CB	0.55	24.3	67	9.1	Shelf life, encapsulated, 30 d (75%)	173

Note: MAAC = methylammonium acetate, DE = diethyl ether, CB = chlorobenzene.

As for good solvents, the frequently used DMF in Pb-PVSKs is unfavorable in Sn-PVSKs because the greater Lewis acidity of Sn^{2+} than Pb^{2+} results in rapid and uncontrollable reaction between SnX_2 and AI units.⁹⁶ On the other hand, although DMSO with strong Sn^{2+} coordination affinity demonstrated effective in modulating the crystallization, its high boiling point and low saturated vapor pressure present a challenge on the complete removal of solvent. Furthermore, recent work by Sargent and coworkers found DMSO and Sn^{2+} underwent an irreversible redox reaction, thus forming dimethylsulfide and Sn^{4+} above 100°C even under inert atmosphere, which constrains the annealing temperature and makes more difficult to remove the residual DMSO.¹⁷⁶ The Mathew group reported an initial attempt to replace DMF with DMSO or 2-methoxyethanol as solvent for efficient light harvesting in CsSnI_3 based PSCs.¹⁴² Then the solvent effects on the crystallization was systematically investigated by the Kanatzidis team.⁹⁶ Their results unveiled that the self-assembled SnI_2 -3DMSO intermediates showed better coordination ability than their Pb analogues in form of PbI_2 -2DMSO, which explained the origin the uniform, pinhole-free morphology when DMSO were applied as displayed in Figure 10A and B. Impressively, the Choy group revealed the colloidal growth mechanism of precursors in the above mixed solvent, which established the state-of-art protocol of DMF:DMSO = 4:1 vol% in Sn-PVSK optoelectronics.¹⁷¹

In comparison to good solvents which serve as a growth rate regulator, anti-solvents such as diethyl ether (DE), toluene (TL), and chlorobenzene (CB) facilitate the homogeneous nucleation.^{45,172,173} It was claimed by Yan et al. that antisolvent dripping of DE is more desirable for synthesizing highly uniform and pinhole-free compact FASnI_3 films compared to CB and TL.⁴⁵ Conversely, Huang and coworkers also compared the morphological effect of these anti-solvents and found that CB dripping led to better film morphology in $\text{FA}_{0.75}\text{MA}_{0.25}\text{SnI}_3$ relative to DE and

TL. Despite that the XRD spectra of DE and CB treated samples exhibit similar crystallinity, the CB dripping films show higher PL intensity than those of TL and DE (Figure 10C), indicative of suppressed nonradiative recombination, which is further supported by the slightly longer lifetime extracted from TRPL profiles (Figure 10D). Furthermore, the remarkably larger recombination resistance (R_{rec}) in CB treated sample confirms the lower trap densities and recombination rates as revealed from the electrochemical impedance spectroscopy (EIS) in Figure 10E and F. The benevolent effect of CB was interpreted as its high boiling point and the penetration of CB into DMSO-perovskites intermediates during spin-coating.¹⁷³ Such seemingly controversial results may be attributed to either different response to the anti-solvent upon various composition of precursor or the different dripping times of antisolvent. With regards to the work of Yan et al., though no specific dripping time was found, a similar method was used by Park et al.¹⁷⁷ that DE was dropped slowly in 10 s before the film became hazy whereas Huang et al. applied CB at the 12th s of a spin-coating process at 4000 rpm for 60 s. Since CB possesses both much higher viscosity and boiling point than DE, CB tends to reside longer on substrate than DE during spin-coating, which may result in different film formation processes. The shorter residence time of DE also explains why DE necessitates slow and continuous dripping in both Yan and Park's work.

Figure 10. (A) XRD patterns of the $\text{CH}_3\text{NH}_3\text{SnI}_3$ layer with different solvents before (left) and after (right) thermal annealing process at 100 °C for 15 min. (B) Schematic film formation process starting from SnI_2 through the SnI_2 -3DMSO intermediate. (A, B) Reprinted with permission from Ref. 96. Copyright 2019, American Chemical Society. (C) Steady-state PL spectra and (D) TRPL spectra of the encapsulated $\text{FA}_{0.75}\text{MA}_{0.25}\text{SnI}_3$ films with different antisolvents on quartz substrates. (E) Nyquist plots of $\text{FA}_{0.75}\text{MA}_{0.25}\text{SnI}_3$ -based PSCs with different antisolvents dripping measured at 0.4 V under dark conditions. Inset: Zoomed-in patterns and the equivalent circuit model for fitting the plots. (F) Fitted R_{rec} at different applied voltages obtained from the EIS analysis. (C–F) Reprinted with permission from Ref. 173. Copyright 2019, American Chemical Society.

Preparation Methodology: In addition to the additive and solvent engineering, alternate methodologies have been developed to enrich the pathways of crystallization control and oxidation inhabitation for high-quality Sn-PVSK thin films. The conventional one-step spin-coating method fails to separate the nucleation and crystal growth processes, which lead to both random crystal orientation and poor film morphology in Sn-PVSKs if external intervention is not applied. In contrast, multi-step sequential deposition by either spin-coating,¹⁷⁴ thermal evaporation^{178–181} or post-ion exchange⁴⁰ artificially fixes the spatial location of reaction sites and manipulates the reaction steps among precursors. For instance, the Kanatzidis group proposed a multichannel inter-diffusion protocol by spin-coating of FAI/PEDOT:PSS polymer layer followed by thermal evaporation of SnI_2 to improve both the film coverage and crystallinity as shown in Figure 11A.¹⁷⁸ Most recently, Jiang et al. presented a novel two-step cation exchange method (Figure 11B) where reducing hydrazinium (HA^+) based PVSKs was firstly deposited to prevent the oxidation of Sn^{2+} .⁴⁰ Then, the film underwent cation exchange from HA^+ to MA^+ to generate highly uniform MASnI_3 thin films. The resulting devices delivered an excellent PCE of 7.13%. In compared to spin-coating, the vapor-phase sequential deposition features better stoichiometric accuracy and higher crystallinity. Fan and coworkers applied chemical vapor deposition to fabricate Sn-Pb alloyed PVSKs with large grain sizes up to 5 μm .¹⁸⁰ In another work, the Lunt group realized all thermal vapor-deposited CsSnBr_3 PSCs, which showed an outstanding stability against air and under light

illumination.¹⁷⁹ The improved durability of device prepared by a two-step vapor deposition method may arise from both decreased defects and GBs (enlarged crystals) owing to the thermodynamic dominated reaction among precursors. Most recently, Tao and coworkers employed a novel recrystallization process to prepare FASnI_3 single crystals, which showed an outstanding air-stability resulting from suppressed GBs. Such a strategy is helpful to improve both long-term storage stability and reproducibility.¹⁸²

Figure 11. Schematic illustration of (A) multichannel interdiffusion process (60 mg mL^{-1} FAI dissolved in 20% PEDOT:PSS aqueous solution). Reprinted with permission from Ref. 178. Copyright 2019, Wiley-VCH. Copyright 2019, Wiley-VCH. (B) Cation exchange process from MA^+ to HA^+ . Reprinted with permission from Ref. 40. Copyright 2019, Wiley-VCH.

Compositional Modulation: As aforementioned, the A/B/X site cations significantly affect the electronic structure, thermal and phase stability of a-prepared Sn-PVSKs. In this section, we will

discuss the compositional engineering on A, B and X site, respectively. The detailed device performance and stability parameters are summarized in Table 3.

Table 3. Summary of device performance and stability of Sn-PSCs by the **composition strategy**

Active layer	Strategy	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Stability test (r.t.)	Ref.
HA _{0.2} MA _{0.8} SnI ₃	Mixed A-Site	0.35	11.8	50	2.6	Shelf life, N ₂ , 5d (90%)	68
CS _{0.08} FA _{0.92} SnI ₃		0.44	20.7	67	6.1	Shelf life: N ₂ , 2000 h (90%)	186
FA _{0.75} MA _{0.25} SnI ₃		0.61	21.2	63	8.1	Shelf life, N ₂ , 400 h (80%)	190
CsSn _{0.5} Ge _{0.5} I ₃	Mixed B-Site	0.63	18.6	61	7.1	Continuous operation, N ₂ (45 °C), 500 h (92%)	64
MASn _{0.15} Pb _{0.85} I ₃		1.02	20.8	59	12.5	N/A	159
MAPb _{0.38} Sn _{0.62} I ₃		0.80	25.5	69	14.0	Continuous operation, encapsulate d, 100 h (90%)	180
MASn _{0.5} Pb _{0.5} I ₃		0.58	20.6	60	7.3	N/A	97
MASn _{0.5} Pb _{0.5} I ₃		0.42	20.0	50	4.2	N/A	191
FASn _{0.5} Pb _{0.5} I ₃		0.70	28.4	55	10.8	Shelf life, N ₂ , 100 h (85%)	195
MASnIBr ₂	Mixed X-Site	0.82	12.3	57	5.7	Continuous operation, encapsulate d, 12 h (80%)	16
CsSnI ₂ Br		0.29	15.1	38	1.7	N/A	201

						Shelf life, encapsulate d, maintain 2000 h (90%) Continuous operation, encapsulate d, 1000 h (83%)	
	MASnIBr _{1.8} Cl _{0.2}		0.38	14.0	57	3.1	200
	FASnI _{2.25} Br _{0.75}		0.41	19.8	67	5.5	202
	FA _{0.75} MA _{0.25} Sn _{0.95} Ge _{0.05} I ₃		0.45	21.9	70	6.0	52
	MA _{0.4} FA _{0.6} Pb _{0.4} Sn _{0.6} I ₃		0.80	26.9	71	15.1	187
	FA _{0.7} Cs _{0.3} Pb _{0.7} Sn _{0.3} I ₃	Mixed A/B-Site	0.77	26.4	72	14.6	188
	MA _{0.4} FA _{0.6} Sn _{0.6} Pb _{0.4} I ₃		0.83	27.3	80	17.8	189
	MA _{0.4} FA _{0.6} Pb _{0.4} Sn _{0.6} I ₃		0.85	28.5	73	17.6	198
	MAPb _{0.9} Sn _{0.05} Cu _{0.05} I _{2.9} Br _{0.1}		1.09	23.9	81	21.1	13
	MAPb _{0.5} Sn _{0.5} I _{2.4} Br _{0.6}		0.90	25.9	76	17.6	193
	CsPb _{0.9} Sn _{0.1} IBr ₂	Mixed B/X-Site	1.26	14.3	63	11.3	194
	MAPb _{0.75} Sn _{0.25} I _{1.2} Br _{1.8}		1.04	15.5	78	12.6	196
	MAPb _{0.85} Sn _{0.15} I _{1.3} Cl _{1.7}		0.76	19.1	66	10.1	197
	MA _{0.15} FA _{0.85} Pb _{0.6} Sn _{0.4} I _{2.55} Br _{0.45}	Mixed A/B/X-	0.87	26.4	79	18.2	160

Site	1000 (90%)
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A-Site: In comparison to B-site cation and X-site halide anion, which jointly determine the electronic structure, the A-site cation seems to impact less on the electronic structure of Sn-PVSKs⁹⁵ although A-site cations may affect E_g s to some extent because of their contribution to the density of states¹⁰⁶ or spin-orbit coupling via distorting octahedra.⁵⁸ Importantly, the ambient structural stabilities of PVSKs were found to strongly correlated with the A-site cations.^{41,42,58–60,183} As mentioned in Section 2, the incorporation of A-site cation with different ion radius results in variations of tolerance factor and remarkable changes in both crystal symmetry and phase stability of ABX_3 . Moreover, the practical applications in Sn-PSCs put forward various requirements for the intrinsic properties such as E_g and thermal stability, which cannot be fulfilled with single A-site cation. Therefore, the mixed A-site cation strategy emerges an effective method to combine the advantages with good miscibility of multicomponent precursors.^{21,184–190} For instance, Cs doping is adopted in $FASnI_3$ system to adjust the tolerance factor back to unity and improve phase stability along with structural symmetry.¹⁸⁶ Such doping process is energetically favorable since theoretical results showed decreased free energy upon Cs introduction. Moreover, McGehee et al. identified that the incorporation of Cs^+ will not change the cubic symmetry of $FASnI_3$ and investigated the influences of two competing A/B-site cations related mechanisms—octahedral tilting and lattice contraction—on the E_g of PVSKs as shown in Figure 12A–C, which widens and narrows the E_g , respectively, owing to the different orbital overlaps between Sn-5s and I-5p.¹⁸⁹ Besides Cs incorporation, FA^+ was also found to increase the thermal stability¹⁹⁰ and oxidation resistance⁴³ in MA-based Sn-PVSKs. Interestingly, the hydrazinium (HA), which was outlined above as either antioxidants¹⁶⁵ or intermediate components⁴⁰ in Sn-PVSK thin films, was also explored to partially substitute MA for better photo-stability in inert

atmosphere when compared to the reference MASnI_3 films.⁶⁸ To sum, the mixed cation strategy is a viable avenue to encompass all the merits of single A-site cation at one strike. Various functional groups such as reducing double bonds or coordinating endings may be worth to incorporate into their molecule structures to tailor the optoelectronic properties and stability of ASnX_3 provided that the tolerance factor is satisfied.

B-Site: One of the fundamental aspects towards higher performance of PSCs is to broaden the absorption range of the active layer to the near-infrared region. Since the conduction band minimum (CBM) and the valence band maximum (VBM) are determined by the anti-bonding states of B-p/X-s and B-s/X-p electrons, respectively, it is feasible to engineer the optical E_g by adjusting the B-site cation such as alloying Pb into Sn-PVSKs to make the full use of solar light absorption. Despite that the Sn-PVSKs exhibit significantly narrower E_g s than Pb analogues, it was found that that the E_g s of Pb/Sn alloys deviated from the Vegard's law with a minimum falling between the neat Sn and Pb phases as discussed in the previous section, which paves up a smooth way to the feasibility of high-Sn content or even pure Sn-PSCs. In this part, we seek to summarize recent advances in the Pb/Sn alloyed PVSKs,^{146,191–198} and then present the emerging Sn/Ge binary systems.^{64,117,199,}

The Hayase group firstly reported the preparation of $\text{MASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ PVSKs with an extended absorption edge up to 1060 nm, which red-shifted 260 nm than benchmark MAPbI_3 , verifying the beneficial influence of Sn addition on E_g s.¹⁹¹ Later, the Kanatzidis team unveiled the abnormal E_g evolution of alloyed Pb/Sn PVSKs, which was presumably attributed to a systematic change in the atomic orbital composition of the conduction and valence bands.⁹⁷ For detailed discussions on such anomalous E_g evolution trend, please refer to Section 3. Although the origin of the nonlinearity is still under debate, the experimental method to realize B-site alloying has been demonstrated by

both the Ginger¹⁴⁶ and Fan¹⁸⁰ via low-temperature ion exchange and chemical vapor deposition, respectively, which opens up a new means towards iso-valent and hetero-valent ion substitution in Sn-PVSKs. Since then, the device performance of Sn-PSCs began to surge by-tailoring the B-site composition.^{192–197} For instance, the Jen group gradually increased the Sn content in the Pb/Sn binary PVSKs and boosted the PCE from 10.1% (15 mol% Sn),¹⁹⁷ 12.59% (25 mol% Sn),¹⁹⁶ up to 17.63% (50 mol% Sn).¹⁹² The Yan group further increased the Sn ratio to 60 mol% and utilized the formed Pb/Sn alloyed PVSK as the bottom cell in all-PVSK tandem solar cells.¹⁹⁸ Consequently, the stacked 4-terminal-all-perovskite tandem solar cells show a steady-state efficiency of 21.0%.

Figure 12. (A) PVSK lattice illustration: undistorted cubic (middle), with lattice contraction (left) and with octahedral tilting (right) along with (B) corresponding energy level diagram. (C) 2D map of band gap across the FA–Cs and Sn–Pb compositional space. (A–C) Reprinted with permission from Ref. 189. Copyright 2019, American Chemical Society.

Recently, Sn-Ge alloyed PVSKs was found to possess an ideal E_g of 1.4–1.5 eV for photovoltaics.¹⁹⁹ With 5 mol% Ge-substitution, the inverted PSCs achieved a PCE of 4.48% and

further increased up to 6.90% after aging for 72 h, which outperformed the pure Sn-based reference device (3.31%). Afterwards, thermally stimulated current (TSC) was exploited by Hayase et al. to unravel that Ge addition efficiently reduced the trap states from 10^{15} – 10^{17} cm⁻³ to 10^8 – 10^{14} cm⁻³, thereby affording longer charge diffusion length (~ 1 μ m) and lifetime (5.04 ns) coupled with excellent charge mobility (98.27 cm² V⁻¹ s⁻¹).¹¹⁷ Besides E_g tuning and defects passivation, Padture and coworkers further demonstrated the in-situ encapsulation effect of Sn/Ge binary system.⁶⁴ It was found the Ge²⁺ may drift to the surface during operation and spontaneously generated native-oxide, i.e., Sn-doped GeO₂ layer, which protected the devices from oxygen incursion as indicated from the depth-dependent XPS and the ambient aging profile in [Figure 13A and B](#). Consequently, the optimal CsSn_{0.5}Ge_{0.5}I₃ film showed longer ambient stability than reference CsSnI₃ or even Pb-analogues ([Figure 13C](#)) and the resulting PSCs exhibited a promising PCE of 7.11% and outstanding stability which maintained 92% of the initial PCE after continuous operation in N₂ for 500 h.

X-Site: Since the np² electrons of halide anions contribute to the electronic structure of Sn-PVSKs, the E_g tuning may be realized by mixed X-site strategies. For instance, it was reported the E_g of MASnX₃ can be tailored over a large range of the visible spectrum with different Br/Cl/I-ratio.²⁰⁰ [Figure 13D and E](#) show the energy diagrams and absorption spectra of MA based Sn-PVSKs depending on various halide combinations. Similar phenomenon was also observed Br-doped CsSnI₃. However, structural evolution from orthorhombic to cubic lattices was observed as the Br⁻ content increased,²⁰¹ which may cause unexpected results during operation. Additionally, the octahedral factor is directly related to X-site halogen ions and hence a rational combination of different X-site halogen anion might significantly improve phase stability of Sn-PVSKs. The effect of mixing halides on the phase stability was investigated Diau team.²⁰⁰ The results showed that

large radius difference between Cl^- and I^- induced incomplete solid solutions in $\text{MASnI}_{3-x}\text{Cl}_x$, which could be mediated by incorporation of middle-sized Br to form stable tri-halide Sn-PVSKs.

Figure 13. (A) XPS characterization of Ge 3d XPS spectra of $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$ PVSK thin film at different incidence angles and (B) corresponding plot of the Ge^{2+} content vs. the incidence angle. (C) XRD patterns of PVSK thin films before and after exposure for 24, 48, and 72 h to light-soaking (1 sun) at approximately 45 °C and 80% RH. From left to right: $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$, CsSnI_3 , CsPbI_3 , and MAPbI_3 . (D) Energy diagrams of mixed-halide Sn-PVSK films with various MAI and

SnCl₂/SnBr₂ ratios. **(E)** The absorption spectra of mixed halide Sn based PVSKs on glass substrates. **(D, E)** Reprinted with permission from [Ref. 200](#). Copyright 2019, Wiley-VCH.

Interfacial Band Alignment: The afore-mentioned strategies focused on preparing ambient stable and high-quality Sn-PVSK. However, the larger variation of VBM and CBM in Sn-PVSK from those of Pb will cause band alignment mismatch between the charge-extraction and the active layers,⁶⁴ which results in severe V_{OC} loss in photovoltaic devices. Therefore, the optimization of band alignment is crucial to enhance device performance. In this section, we will summarize recent advances in this field in order to compare the pros/cons of different HTLs and ETLs. The detailed device performance and stability parameters are summarized in [Table 4](#).

Table 4. Summary of device performance and stability of Sn-PSCs by the **interlayer strategy**

Active Layer	Interfacial layer	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)	Stability Test (r.t.)	Ref.
FAPb _{0.75} Sn _{0.25} I ₃	NiO _x	0.81	28.2	75	17.3	Shelf life, N ₂ , 46 d (92%)	204
FASn _{0.5} Pb _{0.5} I ₃	PCP-Na	0.78	28.5	73	16.3	N/A	205
FASnI ₃	PEG-PEDOT:PSS	0.37	22.1	63	5.1	Shelf life, N ₂ , 30 d (95%)	208
FA _{0.6} Sn _{0.6} Pb _{0.4} I ₃	PBDB-T:ITIC/PEDOT:PSS	0.86	27.9	75	18.0	Shelf life, N ₂ , 600 h (80%)	209
FASnI ₃	LDP	0.45	24.9	63	7.0	N/A	210
PEA ₂ FA _{n-1} Sn _n I _{3n+1}	LiF	0.47	20.1	74	7.0	Shelf life, N ₂ , 5d (90%)	211
MASnI ₃	m-TiO ₂	0.88	16.8	42	6.4	N/A	17
PEA _{0.15} FA _{0.85} SnI ₃	indene-C ₆₀	0.94	17.4	75	12.4	Shelf life, N ₂ , 3800 h (90%)	21
FASnI ₂ Br	C ₆₀	0.47	6.8	54	1.7	Shelf life, N ₂ , Degraded in few hours	169

FASnI ₃	TiO ₂ –ZnS	0.38	23.1	60	5.3	N/A	201
MASn _{0.5} Pb _{0.5} I ₃	Fullerene Derivatives	0.69	22.8	65	10.2	N/A	212
FA _{0.5} MA _{0.5} Sn _{0.5} Pb _{0.5} I ₃	PC ₆₁ BM	0.75	30.6	76	17.6	N/A	214

Note: LDP = low dimensional perovskites, PEG = polyethylene glycol.

Hole-Transporting Layer (HTL): Despite the compatible band alignment of Spiro-OMeTAD with Sn-PVSKs, an additional oxidation step is needed to obtain high electrical conductivity, which place the underlying Sn-PVSK active layer at a risk of oxidation. Although alternate hole-transporting material such as poly[bis(4-phenyl) (2,4,6-trimethylphenyl)amine] (PTAA) was implemented,^{40,71,73,202} the normal device configuration may suffer electron-deficient environment at the utmost surface of devices under operation if the holes are not effectively extracted, which makes the Sn²⁺ adjacent to HTL easy to oxidize. Therefore, most of the highly-efficient Sn-PSCs were fabricated with the inverted structure. However, the commonly used PEDOT:PSS HTL exhibits problematic issues such as hygroscopic nature, strong acidity, irreversible reactivity and imperfect match with Sn-PVSKs, which lead to deteriorated device performance and stability in the devices.

To circumvent these issues, some research groups managed to find alternatives for the PEDOT:PSS layer.^{203–207} For instance, Sun and coworkers applied p-type NiO_x with a suitable energy level for efficient hole extraction from CsSnI₃, which delivered a promising PCE of 3.31% in the absence of any additive.²⁰³ In another work, PCP-Na (Figure 14A) was introduced between PEDOT:PSS and FASn_{0.5}Pb_{0.5}I₃ layers to facilitate hole extraction for its high HOMO energy level as shown in Figure 14B, leading to hysteresis-free *J–V* characteristics as shown in Figure 14C.²⁰⁵

Other groups sought to overcome the abovementioned issues in PEDOT:PSS by chemical modification^{208,209} or inserting buffer layer.^{210,211} For example, the Han's group intercalated

PEDOT:PSS with PEG molecule to minimize the mismatch of band alignment between FASnI_3 and HTL, which increased the PCE from 2.01% to 5.12% as shown in Figure 14D–F.²⁰⁸ The Li team improved the humidity tolerance of devices by blending PEDOT:PSS with hydrophobic PBDB-T:ITIC, which further passivated the trap states and dramatically decreased the device E_{loss} below 0.4 eV.²⁰⁹ As for buffer layer, both the Zhu and Wu groups introduced a thin 2D layer between the Sn-PVSKs and HTL, which reduced both crystal lattice and energy level mismatch and delivered outstanding PCEs of 7.05% and 6.98%, respectively.^{210,211}

Electron-Transporting Layer (ETL): Besides the endeavor to improve the compatibility between HTL and active layer, there were also many researches on tuning the properties of ETL, aiming at minimizing energy level mismatches and suppressing the ion diffusion.^{202,212–217}

Inherited directly from normal structure of Pb-PSCs, the utilization of c- TiO_2 /m- TiO_2 ETL was firstly used in MASnI_3 by the Snaith group and realized a promising PCE over 6% for PVSK solar cell.¹⁷ In order to minimize the energy level mismatch, the Kanatzidis group modified TiO_2 with ZnS to form a cascade energy level landscape, which suppressed interfacial recombination and promoted electron transfer. As a result, the devices exhibited a decent PCE of 5.27% with an improved V_{OC} of 0.380 V.²⁰² On the other hand, fullerene and its derivatives are commonly used in the inverted device configuration. Guo and coworkers systematically compared different kinds of fullerene derivatives as ETL for $\text{MASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ based PSCs (Figure 14G–I) and then found the lowest unoccupied molecular orbit (LUMO) energy level of ETL critically affect to acquire high V_{OC} .²¹² Consistently, Hatton et al. also reported that the V_{OC} loss in CsSnI_3 based PSCs decreased with increasing LUMO level, which reduced the electron energy loss upon its extraction into the ETL.²¹³ Inspired by highly efficient $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells, Kapil and coworkers introduced a thin buffer layer of PC_{61}BM between the C_{60} and active layer to realize a spike structure which

efficiently suppresses interfacial recombination and maximized the V_{OC} up to 0.5 V. Consequently, the champion devices achieved a superior PCE of 17.6%.²¹⁴

Figure 14. (A) Chemical structure of PCP-Na. (B) Schematic diagram of the energy levels of the various layers used in the device structure. (C) J-V curves of the champion device fabricated with PCP-Na as HEL tested with different sweep rates. (A–C) Reprinted with permission from Ref. 205. Copyright 2019, Wiley-VCH. (D) Molecular structures of PEDOT:PSS and PEG together with schematic illustration of a possible mechanism for VBM changes induced by intercalation of PEG into PEDOT:PSS. (E) energy diagram for devices with this configuration. (F) J-V curves and for FASnI₃ PSCs based on PEDOT:PSS and PEG-PEDOT:PSS. (D–F) Reprinted with permission from Ref. 208. Copyright 2019, American Chemical Society. (G) Chemical structures of the electron transport materials (C₆₀ and fullerene derivatives and (H) energy diagram in real device. (I) J-V curves of MASn_{0.5}Pb_{0.5}I₃ PSCs with the scan-rate of 50 mV s⁻¹. (G–I) Reprinted with permission from Ref. 212. Copyright 2019, Elsevier.

Phase/Structure Tailoring: In order to enhance structural stability along with charge transport

in Sn-PVSKs. Researchers sought to adopt strategies such as lattice structure tailoring (e.g., 3D hollow structure and LD-PVSKs) and phase component regulation (i.e., heterojunctions), both of which have demonstrated feasible to mitigate the controversy between device reliability and performance. In this part, we will focus on three approaches towards modulating the phase/structure of Sn-PVSKs. The detailed device performance and stability parameters are summarized in Table 5.

Table 5. Summary of device performance and stability of Sn-PSCs by the **phase and structure regulation strategies**

Active Layer	Strategy	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Stability Test (r.t.)	Ref.
{en}MASnI ₃	Hollow 3D PVSKs	0.43	24.3	63.7	6.6	Continuous operation, Air, 10 min (60%)	71
{en}FASnI ₃		0.48	22.5	66.0	7.1	Shelf life, encapsulated, 1000 h (96%)	72
PN-FASnI ₃		0.43	22.2	60.7	5.8	N/A	73
HEA _{0.4} FA _{0.6} SnI ₃		0.37	18.5	56.0	3.9	Shelf life, N ₂ , 1000 h (100%)	74
{en}FA _{0.5} MA _{0.5} Sn _{0.5} Pb _{0.5} I ₃		0.82	27.2	76.1	17.0	Shelf life, 10- 30% RH, 2 h (92%)	218
PEA _{0.15} FA _{0.85} SnI ₃	2D/3D heterojunc tions	0.61	22.0	70.1	9.4	Shelf life, N ₂ , 600 h (90%)	88
PEA ₂ FA _{n-1} Sn _n I _{3n+1}		0.52	24.1	71.0	9.0	Shelf life, 20% RH, 76 h (59%)	230
BA ₂ MA ₃ Sn ₄ I ₁₃	2D RP PVSKs	0.38	21.87	48.3	4.0	Shelf life, N ₂ , 94 d (100%)	79

BA ₂ MA ₃ Sn ₄ I ₁₃		0.23	24.1	45.7	2.5	Shelf life, encapsulated, 30 d (92%)	223
t-BA ₂ FA _{3,4} Cs _{0.6} Pb ₃ Sn ₂ I ₁₆		0.70	24.2	63.0	10.6	Shelf life, N ₂ , 2000 h (29%)	224
PEA ₂ FA ₈ Sn ₉ I ₂₉		0.59	14.4	69.0	5.9	Shelf life, N ₂ , 100 h (96%)	225
Bn ₂ FASn ₂ I ₇		0.40	10.6	55.1	2.4	N/A	220
4AMP-FA ₃ Sn ₄ I ₁₃	2D DJ PVSKs	0.64	14.9	44.3	4.2	Shelf life, N ₂ (45°C), 100 h (91%)	226
HAPbI ₄		0.91	2.6	46.7	1.1	N/A	94
CsSn _{0.6} Pb _{0.4} I ₃	0D NCs	0.63	10.1	46.0	2.9	N/A	221

Note: {en} = ethylene diammonium, PN = propylene diammonium, HEA = 2-hydroxyethylammonium, t-BA = tert-butylammonium, Bn = benzimidazolium, 4AMP = 4-(aminomethyl)piperidinium, HA = hydrazinium, NCs = nanocrystals, RP = Ruddlesden-Popper, DJ = Dion-Jacobson.

3D Hollow Structures: The 3D hollow-structured have demonstrated as promising light-absorbing materials because of their flexible E_g tunability as well as the improved ambient tolerance.⁷² Typically, the hollow 3D structure derives from conventional ABX₃ with neutral fragments of SnI₂ vacancies substituted by moderate sized organic cations. The interconnected 3D [BX₆]⁴⁻ framework can be partially replaced by moderate sized diamine cations such as ethylene diammonium ({en}, also referred as EDA as mentioned in previous sections),^{71,72,218} propylene diammonium (PN) and trimethylene diammonium (TN)⁷³ without disturbing the dimensionality as displayed in [Figure 15A](#). The resultant structure features massive B and X site vacancies accompanied by a blue-shift of E_g from 1.25 to 1.51 eV owing to adjustable orbital overlaps between Sn/I.²¹⁹ Besides, the air stability is dramatically enhanced in comparison to the FA and MA based reference devices, which originates from the downshift of VBM induced by SnI₂

vacancies.

In 2017, the Kanatzidis group for the first time introduced {en} in replacement of MA⁺ or FA⁺ to generate the so-called 3D hollow structure for Pb-PSCs.^{71,72} As mentioned above, the {en} manifests an efficient crystallization regulator by forming an adduct with the Sn-PVSK lattices, which significantly improves film morphology. Besides, an incorporation of {en} partially replaces the neutral SnI₂ unit and generate vacancies in the 3D Sn-PVSK lattices, which reduces the average length of the remaining Sn–I bonds and lowers the position of CBM and VBM, leading to a larger E_g and oxidation-resistant lattices in Sn-PVSKs. Afterwards, Diau et al. realized the same structure by introducing bifunctional 2-hydroxyethylammonium (HEA) into FASnI₃. Such structural doping gradually increases the crystallographic symmetry from orthorhombic ($x = 0$), rhombohedral ($0.2 \leq x \leq 0.4$), tetragonal 3D-vacant structure ($0.6 \leq x < 1$) (Figure 15B) to the kinetically preferable HEASn_{0.67}I_{2.33} and thermodynamically preferable HEA₂SnI₄ with complete HEA⁺ replacement (Figure 15C).⁷⁴ Moreover, they stressed that this 3D-vacant perovskite bridged 2D and 3D perovskites, which indicates its potential to achieve both high ambient stability and device performance. Later, the Kanatzidis group continued to enrich the diversity of 3D hollow PVSKs by discovering two new kinds of diammonium—PN and TN, followed by their incorporation into FASnI₃, which exhibited reduced leakage current and lower trap-state density. As a result, a 10 mol% addition of PN and TN enabled highly efficient devices with promising PCEs of 5.85% and 5.53%, respectively.⁷³ Most recently, they extended the universality of hollow structure to Pb/Sn alloyed system by loading 5 mol% {en} into FA_{0.5}MA_{0.5}Sn_{0.5}Pb_{0.5}I₃, which obtained a better match between the HTL and the active layer and facilitated charge transport. The as-fabricated device exhibited enhanced ambient stability and an outstanding PCE of 17.04%, which holds good promise of 3D hollow structure in achieving ideal- E_g materials with better

chemical stability.²¹⁸

Low-Dimensional Structures: The hollowed 3D structure can be viewed as the transition state between 2D and 3D PVSKs, which will transform to lower dimensionality if larger ligands are introduced. As previously discussed, the LD-PVSKs are symbolic of layered $[BX_6]^{4-}$ octahedra sandwiched between or surrounded by hydrophobic organic spacers, which remarkably improve the ambient tolerance of PVSKs lattices.^{89,220–222} However, the increasing quantum confinement effect with a decreasing dimensionality results in larger binding energy (E_b) and E_g s, which makes difficult exciton splitting and limits the absorption range. Therefore, most photovoltaic applications regarding Sn-based LD-PVSKs are based on 2D layered structure with moderate E_b and E_g . On the other hand, the insulating nature of organic spacer significantly blocks charge transport in thin films. Therefore, various strategies of end-groups functionalization and structural tailoring in organic spacers were proposed and added great synthetic and structural versatility to the Sn-based 2D-PVSKs.^{89,220,223–229}

As the initial attempt, the Ning group demonstrated the first photovoltaic application of 2D $(PEA)_2(FA)_{n-1}Sn_nI_{3n+1}$ and found the crystal orientation of 2D domains varied with the PEA content, which exhibited the highest orientation vertical to the substrate with an optimal loading of 20 mol% PEA, thereby strikingly improving charge transport in device.²²⁵ As a result, the $(PEA)_2(FA)_8Sn_9I_{28}$ based devices achieved a PCE of 5.94% with an enhanced stability over 100 h in inert glovebox compared to the $FASnI_3$ reference device. In order to address the widened E_g s, the Nazeeruddin group presented the synthesis of benzimidazolium (Bn) and benzodiiimidazolium (Bdi) based 2D Sn-PVSKs with narrower E_g s than traditional amino groups, which resulted from the minor distortions caused by symmetrical hydrogen bonding of the imidazolium cations.²²⁰ As for the hindered charge transport, Padture and coworkers explored the probability of 2D Dion-

Jacobson (DJ) structured PVSKs by applying a newly discovered 4-(aminomethyl)piperidinium cation ($4AMP^+$) as an organic spacer. The resultant layered PVSKs exhibited improved charge transport as a result of the reduced organic content compared to its RP analogues, yielding the best-performing device ($n = 4$) with a PCE of 4.22%.²²⁶

Heterojunction Construction: In addition to structure tailoring, introduction of extra phases to form heterojunctions also proved to facilitate exciton separation and charge transport.^{88,211,230,231} The heterojunction provides additional driving force for exciton splitting owing to the energy level differences between and heterogeneous phases. Besides, some components may act as defect passivator or in-situ encapsulation, which improve the ambient stability of Sn-PVSK matrix. In an early attempt, the Loi group introduced a trace amount of PEA based 2D Sn-PVSKs into $FASnI_3$ to enable the homogeneous growth of 3D phases with high orientation at low temperature as indicated from the crystal structures and GIWAXS profiles in Figure 15D–F.²³⁰ The resulting 2D/3D bulk heterojunctions (BHJs) showed decreasing GBs along with Sn vacancies, which pushed the device performance from 6% to 9%. Then, Ning et al. demonstrated a gradient 2D-quasi-2D-3D structure in $PEA_{0.15}FA_{0.85}SnI_3$. The overlaying 2D PVSKs effectively protected the underlying 3D phases from oxidation. The hierarchical alignment of phases formed cascade energy landscapes for efficient charge transport. Consequently, the device yielded an outstanding PCE up to 9.41% along with excellent stability, which retained 90% of its initial performance for almost 600 h in inert atmosphere.⁸⁸ Besides, Chen and coworkers introduced PTN-Br into GBs of $FASnI_3$ to construct BHJs. The PTN-Br with compatible VBM not only facilitated hole transport from PVSK crystals to PTN-Br, but also passivated interfacial trap states via the formation of Lewis adduct between uncoordinated Sn atoms and the di-methylamino group of PTN-Br. As a result,

the best-performing devices achieved a PCE of 7.94% with better UV stability, which maintained ca. 66% of its initial PCE under continuous working operation for 5 h.²³¹

Figure 15. (A) Schematic illustration of the structure of the 3D pristine FASnI_3 PVSK and 3D hollow FASnI_3 with PN or TN. Reprinted with permission from Ref. 73. Copyright 2019,

American Chemical Society. **(B)** Kinetic preferred PVSK structures of single crystals with HEAI proportions 0, 40, and 80% represented from left to right. **(C)** Thermodynamically preferred crystal structures obtained from two HEAI 100% single crystals show the 2D structural features. **(B, C)** Reprinted with permission from [Ref. 74](#). Copyright 2019, American Chemical Society. Schematic crystal structure of **(D)** 3D reference FASnI_3 , **(E)** 2D/3D mixture and **(F)** 2D PEA_2SnI_4 . **(D–F)** Reprinted with permission from [Ref. 230](#). Copyright 2019, Wiley-VCH.

Light-Emitting Diodes. In contrast to a multitude of efforts in Sn-PSCs, the other two prime optoelectronic functions—LEDs and lasing seem to catch less attention, which might be ascribed to either the poor device stability or the unsatisfactory performance lagging behind the existing commercialized materials. However, the favorable optoelectronic properties of Sn-PVSKs such as narrow E_{gs} , red-broadband emissions with large stokes shift, suppressed non-radiative recombination rates along with room-temperature solution processability have shown brighter future than other semiconductor materials such as GaAs, InGaN, organic polymers and colloidal quantum dots (QDs). In addition to the common issues in photovoltaic applications, the optimizing strategy for LED may focus on reducing non-radiative recombination. In this part, we will dive into the highly efficient Sn-based LED applications and discuss about the commonly adopted strategies to improve the device performance as well as stability issues.

As for the additive, The Seok group added elemental sulfur to introduce S^{2-} into the host lattice alloyed $\text{MAPb}_{0.75}\text{Sn}_{0.25}\text{Br}_3$, which lowered the defect concentration by neutralizing the Sn^{4+} , and suppressed defect-assisted non-radiative recombination processes. The S-modified QDs remained phase-stable for more than a month in air conditions.²³² In another case, Stranks and coworkers employed ZnI_2 to promote homogeneous mixing of Sn and Pb precursor in the alloyed systems, which decreased the Sn-rich regions that act as oxygen-induced degradation sites and thus improved its resistance to oxygen.²³³ Similar to photovoltaics, SnF_2 was applied into CsSnX_3 ($\text{X} = \text{Br}$ or I) by Sum and coworker to reduce the full width half maximum (FWHM) as observed

from Figure 16A. Mover, they utilized the wing texture of the butterfly (Figure 16B) to form natural photonic crystals and provided the cavity resonance close to the emission peak of CsSnI₃, which realized a single-mode, low-threshold lasing ($\sim 15 \mu\text{J cm}^{-2}$).²³⁴

The B and X-site compositional engineering in Sn-PVSKs proved effective approaches to achieve flexible emission tunability.^{235–239} Liu and coworkers doped the CsPb_{1–x}Sn_xBr₃ system with air-stable Sn⁴⁺, which effectively suppressed the tr-ion generation and improved PLQY from 45% to 83%. The optimal CsPb_{0.67}Sn_{0.33}Br₃ QDs based LED exhibited bright emission at 517 nm, a luminance of 12,500 cd m^{–2}, a current efficiency of 11.63 cd A^{–1}, an external quantum efficiency (EQE) of 4.13%, a power efficiency of 6.76 lm w^{–1} and a low turn-on voltage of 3.6 V, all of which are the best values among reported Sn-PVSK QDs based LEDs.²³⁶ Besides B-site modulation, Tan and coworkers demonstrated tunable NIR electroluminescence in MASn(Br_{1–x}I_x)₃ by partial halide substitution,²³⁷ which led to continuous blue-shifted absorption with increasing Br content, which was also observed by the Haque group in 2D PEA₂SnI_{4–x}Br_x crystals.²³⁹

As discussed above, the lattice distortion related STE state may cause broadband emission in Sn based LD-PVSKs,^{80,84,87,239–241} which shows potential in white-lighting LEDs. For example, the Haque group reported the fabrication of highly luminescent 2D PVSK crystals by incorporating PEA cations (Figure 16C).²³⁹ The emissive excitons in trap states resulted in wide-band emission (Figure 16D), large stokes-shifted emission (Figure 16E) and increasing lifetime with increasing iodine content (Figure 16F). Similarly, Ma and coworkers presented a series of 0D structured (C₄N₂H₁₄X)₄SnX₆ (X = Br, I),²⁴⁰ (C₉NH₂₀)₂SbCl₅,²⁴⁰ and (C₉NH₂₀)₂SnBr₄,⁸⁷ where the individual metal halide octahedra (SnX₆^{4–}), quadrangular pyramids (SbX₅^{2–}) and seesaw-shaped (SnBr₄^{2–}) were completely isolated. Since such structure underwent pronounced excited state structural deformation and reorganization (similar to FE-to-STE conversion), the 0D structured PVSKs also

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2
3 feathered strong stokes-shifted broadband emissions. Although STE emission in Sn-based LD-
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5 PVSKs results in high photoluminescence quantum yield (PLQY), the broadband emission may
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7 not be desirable in those applications demanding high color purity. Based on the positive correlated
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9 PLQY and binding energy, Chiu and coworkers modulated quantum confinement in 2D layered
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11 PVSKs by varying the dielectric constant and managed to realize narrow band emission with a
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13 record-high PLQY of 21%.²⁴² Recently, the Kanatzidis group reported a new family of all-
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15 inorganic Sn-PVSKs and perovskitoids that can be stabilized by the heteroleptic coordination of
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17 Cl^- and I^- — $\text{Cs}_2\text{SnCl}_2\text{I}_2$ and $\text{Cs}_{2.38}\text{Rb}_{1.62}\text{Sn}_3\text{Cl}_8\text{I}_2$.²⁴³ Further replacement of A-site Cs^+ with
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19 smaller-sized Rb^+ led to drastic phase evolution into to a mixture of low-dimensional compounds.
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22 The as-prepared PVSKs possessed wide and direct E_g s and good oxidation resistivity, which paves
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24 a new path toward the realization of optoelectronic devices with heteroleptic-halide PVSKs.
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Figure 16. (A) Normalized emission at low pump fluence (open circles, $\approx 1 \mu\text{J cm}^{-2}$) and high pump fluence (solid lines, $\approx 70 \mu\text{J cm}^{-2}$) for CsSnI₃ with different molar concentrations of SnF₂ treatment. (B) Optical image of a butterfly scale from the white part of the wing. Inset is a photograph of the butterfly. The right panel shows the SEM image of vertical lamellae structure in the scale. (A, B) Reprinted with permission from Ref. 234. Copyright 2019, Wiley-VCH. (C) General crystal schematic of a (PEA)₂SnI_xBr_{4-x} PVSK (light gray balls: $-\text{NH}_3^+$ groups; red polyhedra: corner-sharing SnX_6^{4-} octahedra, where X represents a halide) with alternating organic-inorganic layers. (D) Electroluminescence spectrum of a (PEA)₂SnI₄ device at a bias of 4 V. Inset: the photograph of the LED under operation. (E) Normalized absorbance and PL spectra together with (F) TRPL kinetics (excited at 404 nm) of (PEA)₂SnI₄ (black), (PEA)₂SnI₃Br (red), (PEA)₂SnI₂Br₂ (orange), (PEA)₂SnIBr₃ (green) and (PEA)₂SnBr₄ (blue) PVSK thin films processed on glass. (C–F) Reprinted with permission from Ref. 239. Copyright 2019, American Chemical Society. Further permissions related to the material excerpted should be directed to the

ACS.

Photodetectors. Giving the promising optical and electrical properties of Sn-PVSKs, they are also potential building blocks for the application of photodetectors. However, the PD applications differ from photovoltaics in designing purpose and requirements. For example, solar cells are expected to absorb light as wide as possible whereas PDs require selective photo-sensitivity. On the other hand, a large active area is favored in photovoltaic cells while it is necessary to minimize the size of PDs to eliminate the junction capacitance. Nevertheless, the influences of charge carrier dynamics and photo-stability on both devices are similar, which provides analogous avenues for the optimization in PDs.

Recently, the Choy group realized low-temperature and solution-processed Sn-rich PVSK PDs by incorporation of Rb^+ into A-site cation, which enabled the tunable photodetection from UV to NIR range.²⁴⁴ The partial replacement of MA^+ with Rb^+ promoted the preferable growth of (110) plane with a lower surface energy, which remarkably ameliorated the film morphology. Consequently, the optimal $\text{Rb}_{0.1}\text{MA}_{0.9}\text{Sn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ -based PDs achieved both large photocurrent and low noise current along with an outstanding linear dynamic range of 110 and -3-dB cut-off frequency of 1 MHz. For the phase regulation strategies,^{245–249} the Fan group reported the first preparation of MASnI_3 PVSK nanowire arrays in nano-engineering templates as shown in Figure 17A–E.²⁴⁸ The alumina template successfully blocked the incursion of water and oxygen molecules, which efficiently suppressed the aggregation of nanowire. As a result, the phase stability of the embedded nanowires was dramatically enhanced by 840-fold in comparison to the reference films. To build up heterojunctions, Noh and coworkers coupled the 2D $(\text{PEA})_2\text{SnI}_4$ with conjugated polymer wrapped semi-CNTs to form BHJs as shown in Figure 17F–H, wherein the semi-CNTs provided extra pathways for efficient carrier transport.²⁴⁶ Consequently, the

(PEA)₂SnI₄/semi-CNTs hybrid phototransistors exhibited an ultrahigh photoresponsivity of 6.3×10^4 A/W with excellent operational stability compared to reference neat (PEA)₂SnI₄ based devices as shown in Figure 17I.

Figure 17. (A) The schematic illustration of the overall growth process for MASnI₃ NWs in a porous alumina template (PAT). (B, C) top and cross-sectional view of SEM image for Sn based PVSK NWs inside PAT. (D) TEM image of a single NW. Inset: SEM image of NWs grown out of nanopores of PAT. (E) Selective area electron diffraction (SAED) pattern for MASnI₃ NWs. (A–E) Reprinted with permission from Ref. 248. Copyright 2019, American Chemical Society.

(F) Structure of $(\text{PEA})_2\text{SnI}_4$ PVSK and preparation process of $(\text{PEA})_2\text{SnI}_4$ /semi-CNT mixture by bath sonication. The photographs below show the suspensions/solutions of bare CNTs, polymer wrapped semi-CNTs, PVSKs, PVSKs and semi-CNTs along with PVSK and bare CNTs, respectively (from left to right). (G) Absorption spectra of $(\text{PEA})_2\text{SnI}_4$ precursor w and w/o semi-CNTs. Inset: Enlarged scale suggesting the absorption of semi-CNTs. (H) Schematic fabrication process and (I) Stability test of $(\text{PEA})_2\text{SnI}_4$ based photo-transistor w/ and w/o semi-CNTs. (F–I) Reprinted with permission from Ref. 246. Copyright 2019, American Chemical Society.

Other Applications. The Sn-PVSKs have further fulfilled its potential in other fields such as lasering,²⁵⁰ neuromorphic computing,^{251,252} nanogenerator,^{253,254} hydrogen evolution reaction (HER),²⁵⁵ electronic logic gates²⁵⁶ and field effect transistor.²⁵⁷ For example, Ding and coworkers realized photoelectric synaptic plasticity on the basis of $(\text{PEA})_2\text{SnI}_4$, which was activated in response to a light stimulus in a neuron-like way. The device exhibited several essential synaptic functions such as short- or long-term plasticity and their mutual transmission based on spike frequency control.²⁵¹ As for laser application, Lee and colleagues proposed a low-cost solvothermal method to dope the cholesteric liquid crystal (CLC) with efficient optical gain medium of CsSnI_3 QDs, which combined the advantages of suppressed PL loss caused by the quantum confinement of QDs and amplified PL intensity originating from the band-edge effect of the cholesteric liquid crystal (CLC)-distributed feedback resonator.²⁵⁰ The resultant CLC lasing cavities doped with QDs presented low threshold (150 nJ/pulse) and narrow line width (0.20 nm) coupled with lasing-wavelength tunability and long-term durability under humid ambient atmosphere.

In nanogenerator applications, the Yoon group reported the room-temperature preparation of an air-stable MASnI_3 piezoelectric nanogenerator, which delivered an output voltage/current of ~ 3.8 V and $0.35 \mu\text{A cm}^{-2}$, respectively. Further incorporation with porous PVDF led to enhanced output voltage of ~ 12.0 V and current density of $\sim 4.0 \mu\text{A cm}^{-2}$.²⁵⁴ Similarly, Kabra and coworkers employed PVDF to prepare the FASnI_3 /PVDF nanocomposites, which boosted the ferroelectricity

of the compounds and ensured the environmental inertia of FASnI_3 .²⁵³ The improved piezoelectric response may also originate from the soft polar optic phonon modes as a consequence of the unique orthorhombic ferroelectric phases of FASnI_3 , which hinders efficient optic to acoustic phonon conversion and results in significant slow hot carrier cooling as revealed by Loi et al.¹²² Interestingly, Tao and coworkers observed DI water induced a self-heal process from black to yellow phase in DMASnI_3 ($\text{DMA} = \text{CH}_3\text{NH}_2\text{CH}_3^+$) PVSK single crystals,²⁵⁵ which suggested its potential in HER application. Consequently, the photo-catalysis devices with a HER rate of 0.64 mmol h^{-1} and good recycling properties. Such unique self-heal properties may be inspirable to address the stability issues in Sn-based optoelectronic applications.

This review has summarized recent advances in Sn-PVSK optoelectronics towards improving both device performance and durability. Based on the detailed discussion of the underlying mechanisms and various strategies, we argue that the development of highly efficient and stable Sn-PVSKs optoelectronics has evolved well along the following two paths. Firstly, the rationally tailored composition, crystal structure and phase composition guarantee the intrinsic stability of Sn-PVSKs structures. Second, the external factors such as additive, solvent, preparation methods as well as interfacial engineering significantly improve the reproducibility, charge transport and block degradation pathways from the aspect of device fabrication. These two means interact with each other and deserve prudential consideration when jointly employed. According to the classification used in Section 4, we present the following directions toward desirable device performance and durability in Sn-PVSKs based optoelectronics.

Additive: Whatever kind of additive is selected, it should not add to instability of Sn-PVSKs during film preparation. From this point-of-view, it would be better for additives to possess certain bonding affinity, for example, lone pair electrons with Sn^{2+} so as not to elevate the internal energy

of the whole system. Besides, the cohesive energy of additives and SnX_2 bonding need to be carefully considered. Strong interaction between them may restrict SnI_2 units from forming the ASnX_3 structure. Moreover, if the additive exhibits high electronegativity, the 5s electrons of Sn^{2+} may also be taken away, similar to the high-temperature oxidation of Sn^{2+} in DMSO.¹⁷⁶ In order to pinpoint appropriate additives, the Hard-Soft-Acid-Base theory may be useful. Since Sn^{2+} belongs to the borderline acid, it can coordinate with either hard or soft bases, which include a wide range of options, to name a few, SO_3^- (hard base) and SCN^- (soft base). Importantly, the shielding and un-shielding effects may provide additional inspirations. For multivalent ions, the lower valence state favors bonding with sulfur or nitrogen atoms containing groups while the higher favors oxygen. To exemplify it, the coordinated phenanthroline and Fe^{2+} complex is much more stable than that of Fe^{3+} , which is the opposite to that of citrate and ethylenediaminetetraacetic acid (EDTA).

Solvent: The core role of solvent in device engineering lies in the modulation of crystallization. Analogous to the additives, the Lewis base solvent such as DMSO effectively regulates the crystallization by forming intermediates with SnI_2 units. However, the high boiling point and low saturated vapor pressure of DMSO makes it difficult to dissipate upon thermal annealing. The mixed solvent strategy then proves viable to modulate the crystallization kinetics and maintain a fine balance of between precursor solubility, crystallization rates and removability. In order to trigger simultaneous nucleation and homogeneous growth, temporally and spatially sufficient contact with anti-solvent is the crux, which necessitates appropriate the residence time on the substrate during spin-coating. In this scenario, the basic properties of solvents such as miscibility with good solvent, viscosity and volatility all deserve careful considerations. The mixed anti-solvent strategy seems a viable approach. Moreover, if the additives (either crystallization

regulator or antioxidants) can be incorporated in to the antisolvent, undesirable film forming and oxidation during preparation may also be effectively modulated and suppressed.

Alternative Methodologies: Since an alternately effective method requires thermodynamically dominated and elegantly designed preparation, a precise control of the stoichiometry, crystallization process and morphological features should be focused on improve the reproducibility and quality of as-prepared thin films. As an exemplary case, the multi-step deposition process successfully separates the nucleation and growth stages, thus providing additional means to tune the crystallization, which complements the solvent and additive engineering strategies.

Composition Engineering: The approach of compositional engineering takes into effect mainly by structure/phase stabilization and E_g tuning. Therefore, the tolerance factor and octahedral factors need to be satisfied first to ensure the stable existence of PVSK structure. Because the A-site cations with different sizes significantly affect the tolerance factor and the structure diversity of Sn-PVSKs, the size control of A-sites may induce various lattice symmetries, thereby affording extra ways to tailor the optoelectronic properties of Sn-PVSKs. Furthermore, the mixed A-site strategy with Cs incorporation manifests as an effective method to enhance the tolerance of moisture, light and heat. Moreover, A-site cations with unique functions such as HA^+ antioxidant may endow the PVSK lattices with great ambient stability, which encourages one to perform functionalization on the A-site cations. As for the B-site cations, the anomalous E_g bowing effect upon Sn-Pb alloying extends the absorption range into the NIR region. However, the toxicity issue of Pb is not completely resolved and this method seems more like an optimization strategy for Pb-PVSKs rather than for Sn-PVSKs. The Ge incorporation might be a promising alternative to enhance both the device performance and durability despite its poor solubility and

high cost. The mixed X-site strategy is more helpful in LED and PD applications due to its wide-range tunability of E_g , while in PSCs, it is commonly used to suppress the unwanted phase transition during device operation. Moreover, the pseudo-halide anion may be applied to strengthen the crystallinity and orientation simultaneously, much as it functions in Pb-PVSKs.

Transporting Layer: Careful attention should be placed on the reducing energy level mismatch between transporting and active layers. Given the varied ion radius between Sn^{2+} and Pb^{2+} , both VBM and CBM of Sn- and Pb-PVSK vary from each other, which necessitates the engineering of extraction layer for optimal electron/hole collection. Based on the aforementioned works, the cascade structure with gradient energy level alignment is firstly suggested. Apart from successful demonstration of $\text{TiO}_2\text{-ZnS}$ and PEDOT:PSS-PCP-Na, there still remain a wide range of combination in both ETL (e.g., TiO_2 , PTAA, NiO_x , PC_{61}BM and C_{60}) and HTL (e.g., PEDOT:PSS, PCP-Na, PEG and PTAA) materials. Meanwhile, the cascade transporting layer efficiently encapsulate active layer, which improves the stability of devices. Second, chemical functionalization is also suggested to customize the existing transporting material to match the active layer. The high background hole density in Sn-PVSK results in intensive hole diffusion into the extraction layer driven by the Fermi level difference. After the equilibrium between carrier diffusion and drift processes is reached, the resulting built-in potential area will fall mainly onto the transporting layer. According to the depletion approximation, the main part of active layer will be electrically neutral, which lacks driving force for charge carrier separation and drift upon photo-excitation and aggravate geminate recombination because of the stagnant electron-hole pairs. Therefore, both the ETL and HTL may possess high background carrier concentrations with respective types of charge carriers to ensure the full coverage of built-in potential zone on the entire the active layer.

Phase Regulation: For LD-PVSKs, despite various organic spacers enhance the structural stability against ambient erosion, the concomitant quantum confinement along with insulating nature of organic components significantly increases E_B and deteriorates charge transport along the operational direction of devices. Attentions should be then directed towards introducing functional groups and atoms such as S, P, S=O, P=O and C=O, which not only ameliorates crystallization as discussed in the sections of solvent and additive, but also assists in constructing artificially designed heterojunctions that are advantageous to exciton separation and charge transport. Aside from small molecules, an incorporation of narrow- E_g conjugated polymers to form either BHJs or planar heterojunctions seems more beneficial to enhance both light absorption and stability of the active layer by side-chain decoration and self-encapsulation effect of polymer. On the other side, the construction of 3D hollow structure realizes the flexible tunability of E_g with the least perturbation to the overall 3D lattices, which ensures comparable charge transport to the parent PVSKs and circumvents the drawbacks of LD-PVSKs. Recently, an unprecedented 2D PVSKs with alternating cation in the interlayer (ACI) emerged as a potential candidate for Pb-PSCs. These ACI-type 2D compounds adopt structures with a high alternative ordering of GA^+ and MA^+ in the interlayer space, which integrate the favorable characteristics from both DJ and RP archetypes. Just as the 3D-hollow PVSKs, we consider the ACI structure an intermediate state from 2D to 3D PVSKs with a trade-off between charge transport and structural durability, which may exhibit a bright future in the territory of Sn-based optoelectronics.

Conflicts of interest

There are no conflicts to declare.

Author Biographies

Yajie Yan achieved his bachelor degree at Nanjing University of Science and Technology in 2017. Then, he pursued graduate study under the supervision of Prof. Ziqi Liang at Fudan University. He is now a Ph.D. candidate focusing mainly on developing highly efficient and ambient stable metal halide perovskite solar cells.

http://www.opv-te.fudan.edu.cn/yajie_yan_zh.html

Tõnu Pullerits obtained his Ph.D. at Tartu University in 1991 and pursued his postdoc work in Free University of Amsterdam, Umea University and Lund University. He is the head of the Chemical Physics Division at Lund University, concentrating on energy transport, charge dynamics, photophysics and coherence multidimensional spectroscopy.

<http://www.chemphys.lu.se/people/head-of-department/tonu-pullerits/>

Kaibo Zheng received his Ph.D. degree at Fudan University in 2010. Then, he joined Prof. Tõnu Pullerits's group in Lund University as postdoc fellow. Currently double affiliated by the Technical University of Denmark and Lund University, he is centered on photo-excitation and carrier dynamics of semiconductor quantum dots and perovskites.

<http://www.chemphys.lu.se/people/researchers/kaibo-zheng/>

https://www.dtu.dk/english/service/phonebook/person?id=130500&cpid=233304&tab=2&q=dtu_publicationquery

Ziqi Liang obtained his Ph.D. at Pennsylvania State University in 2006 and pursued postdoctoral work at the University of Cambridge. In 2008, he joined National Research Energy Laboratory and later became Scientist III. Since 2012, Prof. Liang's group has been focusing on organic/perovskite photovoltaics and thermoelectrics at Fudan University.

<https://mse.fudan.edu.cn/ab/14/c18341a174868/page.htm>

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Quotes

1. When delving into the fundamentals of electronic structure, photophysics, and degradation pathways as elucidated above, the intrinsic issues in Sn-PVSKs emerge as 1) easy oxidation of Sn^{2+} , which impairs long-term structural stability; 2) oxidation induced p-doping, which causes severe monomolecular recombination and E_g widening; 3) mismatched band alignment between the active layer and the transporting layers, which hinders the collection of free carriers; 4) rapid and uncontrollable crystallization, which present a critical technical challenge towards high-quality preparation of Sn-PVSK thin films. (Page 26)
2. To sum, the mixed cation strategy is a viable avenue to encompass all the merits of single A-site cation at one strike. Various functional groups such as reducing double bonds or coordinating endings may be worth to incorporate into their molecule structures to tailor the optoelectronic properties and stability of ASnX_3 provided that the tolerance factor is satisfied. (Page 44)
3. In order to pinpoint appropriate additives, the Hard-Soft-Acid-Base theory may be useful. Since Sn^{2+} belongs to the borderline acid, it can coordinate with either hard or soft bases, which include a wide range of options, to name a few, SO_3^- (hard base) and SCN^- (soft base). Importantly, the shielding and un-shielding effects may provide additional inspirations. (Page 68)
4. In this scenario, the basic properties of solvents such as miscibility with good solvent, viscosity and volatility all deserve careful considerations. The mixed anti-solvent strategy seems a viable approach. Moreover, if the additives (either crystallization regulator or antioxidants) can be incorporated in to the antisolvent, undesirable film forming and oxidation during preparation may also be effectively modulated and suppressed. (Page 69)