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Zn²⁺ ion doping for structural modulation of lead-free Sn-based perovskite solar cells†

Hyungsu Jang,^{‡a} Hyeong Yong Lim,^{‡a} Chan Beom Park,^a Jongdeuk Seo,^a Jung Geon Son,^a Taehee Song,^a Jaehwi Lee,^a Yun Seop Shin,^a Jina Roe,^a Sang Kyu Kwak,^{‡*c} Dong Suk Kim^{*b} and Jin Young Kim^{‡*ab}

Sn-based perovskites have intrinsic defects, such as Sn vacancies, oxidised components (Sn⁴⁺), and local lattice strain in the perovskite crystalline structure. In this study, Zn metal powder (Zn⁰) was introduced to reduce Sn oxidation in the solution step based on the redox potential difference. Additionally, Zn²⁺ was introduced in the perovskite precursor, which decreased the intrinsic defects and lattice strain of the perovskite films. The diffusion length, particularly that of the hole, increased with a reduction in the lattice strain, and Zn doping led to interfacial energy-level alignment of the perovskite and hole-transporting layers. The reduced lattice strain decreased the defect density and charge carrier recombination of perovskite devices. The power conversion efficiency of the Zn-doped Sn-based perovskite solar cell was improved to 11.39% compared to the 8.56% of the reference device.

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Introduction

Organic–inorganic metal halide perovskite solar cells (PSCs) are considered promising photovoltaic devices because of their unique optoelectronic properties such as an easily tuneable bandgap, a long carrier diffusion length, and a high absorption coefficient.^{1–8} These properties can be easily controlled by including various A-, B-, and X-sites in the typical perovskite structure.^{9–15} Numerous studies of Sn-based and Pb-based PSCs have been reported in recent years, which have shown that the PSCs have outstanding optoelectronic properties, including a small exciton binding energy and high carrier mobility.^{16–23} Despite the advantageous properties of Sn-based PSCs, many concerns remain regarding their performance enhancement because Sn can be easily oxidized to Sn⁴⁺, leading to the formation of defect states. Sn⁴⁺ defects are the main factor limiting the performance of highly efficient Sn-based PSCs. The oxidation process generates Sn vacancies that undergo self-p-doping, which elevate the defect concentration and exacerbate carrier recombination in PSCs.

Recently, the local lattice strain affecting the optoelectronic properties of perovskite films has attracted attention.^{24–31} Local lattice strain is caused by lattice distortion of the octahedron in a perovskite film^{24–26} or mismatched thermal expansion coefficients of perovskite and its substrates.^{28,31} Saidaminov *et al.* reported that the local lattice strain in a single cation/halide perovskite facilitates the formation of vacancies.²⁶ They also reported that the mixed cation and halide can suppress defect formation *via* strain relaxation. Therefore, mixed-cation perovskites are more stable against decomposition. Zhu *et al.* investigated the evolution of in-plane residual strain with the film thickness in a mixed perovskite.²⁵ They found that the strain induced energy band bending, thus affecting the carrier dynamics across the interfaces over the device. Zhao *et al.* analysed another type of film strain and showed that the strain is caused by mismatched thermal expansion of perovskite films and substrates during thermal annealing.³¹ Perovskite films exhibit compressive strain in the out-of-plane direction and tensile strain in the in-plane direction. Sn-based perovskite based on formamidinium Sn triiodide also exhibits lattice strain due to a mismatch among the A, B, and X components,²⁴ which prevents the performance enhancement of Sn-based PSCs.

In this study, we introduced Zn metal powder (Zn⁰) into perovskite precursor solution to suppress Sn oxidation during the solution step. In the precursor solution, Zn⁰ acts as a reducing agent to reduce Sn⁴⁺. Zn²⁺ was doped into the precursor based on the redox potential difference between Sn and Zn. Owing to the small radius of Zn²⁺, doped Zn²⁺ reduced not only oxidised Sn through redox reactions but also local lattice strain by forming a compressive octahedral structure. We

^aSchool of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea. E-mail: kimds@unist.ac.kr; jykim@unist.ac.kr

^bGraduate School of Carbon Neutrality, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea

^cDepartment of Chemical and Biological Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea. E-mail: skkwak@korea.ac.kr

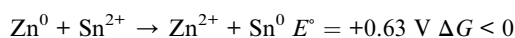
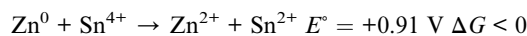
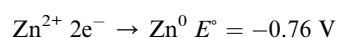
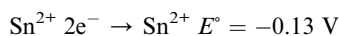
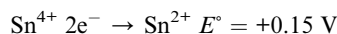
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‡ These authors contributed equally to this work.

investigated the residual local lattice strain using Williamson–Hall plots and grazing incident X-ray diffraction measurements. Incorporation of Zn can reduce the lattice constant of Pb-based perovskite and enhance optoelectronic properties.³² Similarly, in the Sn-based perovskite, Zn^{2+} doping reduced the lattice strain of perovskite films, resulting in increased diffusion of charge carriers and alterations in the energy band levels. Furthermore, the Zn-doped devices exhibited reduced trap-assisted recombination and trap density in the films, and the enhanced hole diffusion length of over 300 nm was well-balanced with the electron diffusion length. Consequently, the strain-engineered Zn-doped Sn-based PSCs showed a higher power conversion efficiency (PCE) of 11.39% and better reproducibility than those of the reference devices.

Result and discussion

To deposit Zn-doped Sn-based perovskite films, the reference solution (hereafter referred to as control) was prepared by mixing formamidinium iodide, ethylenediammonium iodide, SnI_2 , and SnF_2 at 0.98:0.01:1:0.1 molar ratios in a dimethylformamide and dimethyl sulfoxide co-solvent (4:1 v/v%). To evaluate the effect of the doping concentration on perovskite, we added varying concentrations (from 2 to 10 mol%) of Zn metal powder (denoted as Zn-2, -5, and -10) to the as-prepared reference solution and stirred the solutions for 8 h. Zn^0 can react with ionised Sn (both of Sn^{2+} and Sn^{4+}), we set the reaction time for Zn-doped Sn-based perovskite precursor because of its standard redox potential.



The pristine solution changed from yellow to red after 5 min of exposure to ambient air. In contrast, the solution containing Zn maintained a yellow colour despite exposure to air. The colour change of the precursor solution was due to Sn^{4+} and is shown in the UV-vis absorption spectrum of the solution (Fig. 1b and c). Sn^{4+} shifted the absorption spectra to a longer wavelength,³³ and Zn^0 suppressed oxidation of the precursor solution under ambient air. Following perovskite thin-film fabrication using these precursor solutions, X-ray photoelectron spectroscopy (XPS) was performed to analyse the replacement of Sn^{2+} by Zn^{2+} and its distribution. Fig. 1d and f show the XPS spectra of Zn and Sn with different Zn powder ratios. The $\text{Zn} \ 2\text{p}_{3/2}$ peak was located at 1022.5 eV, and the intensity of the peaks increased with increasing Zn ratios, indicating that Zn was successfully doped into the perovskite lattice. Energy-dispersive X-ray spectroscopy was performed to verify the Zn elements doped into the perovskite films. The quantitative

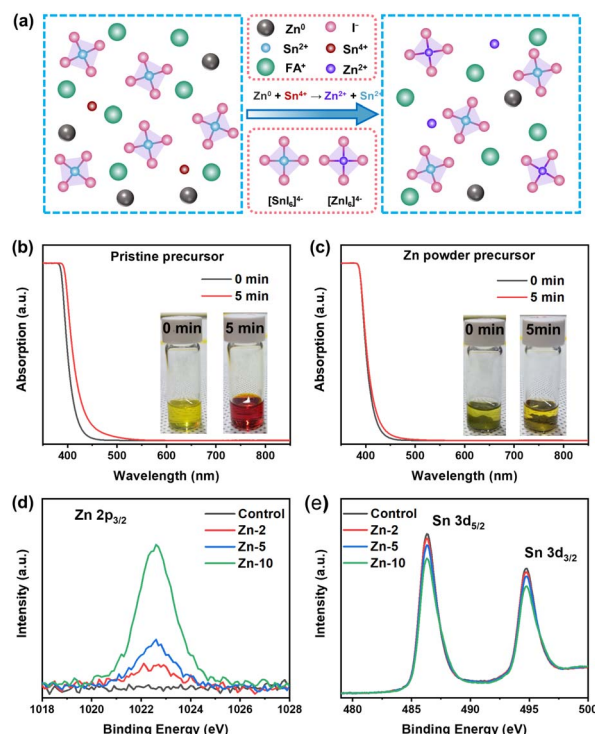


Fig. 1 (a) Schematic illustration of local strain reduced by incorporation of Zn^{2+} , pink: I^- , sky blue: Sn^{2+} , green: formamidinium (FA^+), and purple: Zn^{2+} . The UV-vis absorption spectra and photographs of (b) pristine (without Zn^0 powder) and (c) Zn^0 powder precursor solution. (d) $\text{Zn} \ 2\text{p}_{3/2}$ and (e) $\text{Sn} \ 3\text{d}$ XPS spectra in perovskite films with different concentrations of Zn^0 powder.

results of energy-dispersive X-ray spectroscopy and relative atomic ratios from the top view of the perovskite films are shown in Fig. S1†. The tables summarising the energy spectra show the measured weights and atomic percentages of the main elements (Zn, Sn, and I) in the perovskite films. The atomic percentage of Zn element increased with increasing Zn^0 concentrations. This result indicates that Zn^0 was ionised in the perovskite precursor due to the difference in the redox potentials of Zn and Sn, and the Zn-doped Sn-based perovskite film was thus successfully fabricated. Zn-doped perovskites can successfully reduce the lattice strain of crystals. Lattice strain originates due to ionic size mismatch, and the relaxation mechanism of strain generates vacancies and defects.²⁶ Incorporation of small ions can decrease defect formation and lattice strain.²⁶ The ionic radius of Zn^{2+} (74 pm) is smaller than that of Sn^{2+} (115 pm),^{16,34} which was sufficiently replaced by the B-site of Sn-based perovskite. The X-ray diffraction (XRD) patterns of the perovskite thin films confirmed the replacement of elements. Replacement of smaller ions reduced the d -spacing of the perovskite lattice (Fig. 2a and Table S1†), and the enlarged (100) peaks of the XRD patterns up to a 5% ratio of Zn were shifted to a higher degree (Fig. 2b). However, at a 10% ratio, the peak was downshifted. Because the Zn^{2+} concentration was saturated, the ions could enter the interstitial sites of the crystal lattice and thus expand the d -spacing of the lattice.³⁵ To investigate the effect of Zn doping on the reduction in lattice strain of

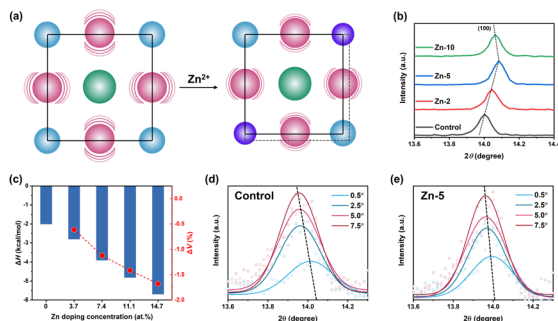


Fig. 2 (a) Schematic illustration of precursor solution with ionizing Zn^{2+} via a redox reaction. (b) (100) plane X-ray diffraction patterns of perovskite thin films to show shift in the Zn ratio. (c) Calculated enthalpies of formation (ΔH) and volume change of perovskite with different concentrations of Zn. (d and e) Grazing incident X-ray diffraction pattern of perovskite films.

Sn-based perovskite, we performed density functional theory calculations. The enthalpy of formation (ΔH) provides valuable information on the thermodynamic stability of a structure. Fig. 2c shows that ΔH for the control and Zn-doped perovskite were negative, indicating that formation of the perovskite structures was thermodynamically favourable. Compared with that of the control, the Zn-doped perovskite systems showed more exothermicity with increasing atomic percentages (at%) of Zn. Because of the shorter bond length of Zn–I compared to that of Sn–I (Fig. S2†), continuous contraction of the lattice was also observed when the Zn doping concentration was increased (Table S2†). Because the differences in ΔH and volume change (ΔV) for each Zn doping concentration simultaneously decreased, we predicted that contraction would eventually reach a saturated point. This prediction was made using calculation model systems by replacing Sn with Zn.

The calculated lattice strain of perovskite films with different Zn ratios is shown in Fig. S4† in a Williamson–Hall plot drawn from the full XRD patterns (Fig. S5, S6, and Table S1†).³⁶ The strain decreased as the Zn ratio increased to 5% and then increased again to 10%. To verify the strain in the lattice between pristine and 5% Zn, grazing incidence XRD was performed.^{25,28,31} We selected grazing incidence angles of 0.5°, 2.5°, 5.0°, and 7.5° and showed the (100) planes of the control and Zn-5. As shown in Fig. 2d and e, Zn-5 perovskite film was obtained without conspicuous shifts at different incidence angles. According to Bragg's law and Hooke's law, residual strain is proportional to the slope of the $2\theta - \sin^2\psi$ line (Fig. S7†).²⁵ The absolute value of the slope at Zn-5 perovskite film was slightly lower than that of the control perovskite film. A negative value for the slope indicates the presence of tensile strain. The Zn-5 perovskite film exhibited reduced lattice strain. The tolerance factor was determined based on the Zn doping ratio in the Sn-based perovskite film (Fig. S8 and Table S3†). At 5% Zn (Zn-5), the lowest lattice strain and tolerance factor value closest to 1 was investigated. The surface morphology of perovskite film was also characterized using scanning electron microscopy of both the control and Zn^{2+} -doped films, as shown in Fig. S9.† When Zn^0 powder is added to the perovskite precursor solution, the

number of pinholes in the perovskite film decreased from 44 pinholes/ $120 \mu\text{m}^2$ (control) to 16 pinholes/ $120 \mu\text{m}^2$ (Zn-5), and the total pinhole area ratio decreased from 6.46% (control) to 1.64% (Zn-5); the mean grain size increased (Fig. S10†). Zn^{2+} doping in perovskite retards the crystallisation rate of perovskite films³⁷ because of the high chemical activity of Zn during binding with other elements in perovskite.^{38,39} The grain size of the Zn-5 film was larger than that of the control film, indicating that the film morphology and coverage were improved.⁴⁰

The perovskite energy level can be affected not only by B-site doping, such as with Zn ions, but also by changes in the valence and conduction bands of the perovskite due to lattice strain. Energy-level matching between the perovskite and charge-transport layers is important for charge extraction and suppressed recombination. Fig. 3a shows a schematic energy-band diagram of perovskite devices doped with different ratios of Zn. The valence band maximum (VBM) was measured using the secondary electron cut-off energy and onset energy of UV photoelectron spectroscopy (Fig. 3b), and the conduction band was estimated by adding the value of the bandgap energy determined from the UV-vis absorption spectra (Fig. S11†) and corresponding Tauc plots (Fig. S12†). The Fermi levels for the perovskite films were -4.94 , -4.70 , -4.74 , and -4.74 eV for the control, Zn-2, Zn-5, and Zn-10, respectively, shown in the secondary electron cut-off energy region of the UV photoelectron spectra (Left panel of Fig. 3b). The VBM was calculated as the electron onset energy of UV photoelectron spectroscopy (Fig. 3b, right panel), showing values of -0.56 , -0.40 , -0.38 , and -0.41 eV, respectively. The VBM difference between poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and perovskite was reduced following Zn doping, indicating that the energy loss of hole transfer from the perovskite to PEDOT:PSS was reduced. Long *et al.* reported that the shift in the energy level of the perovskite film to vacuum is mainly related to contraction of the lattice caused by doping

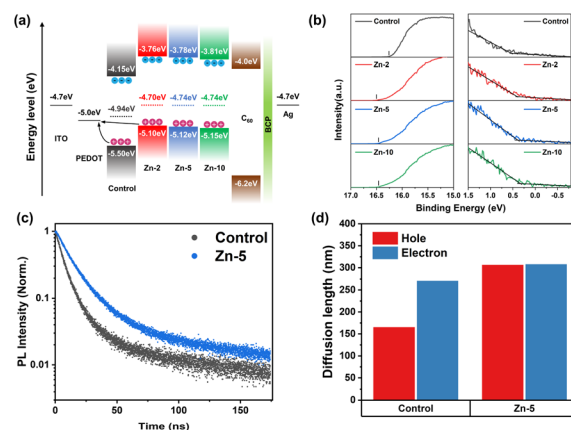


Fig. 3 (a) Energy level of Sn-based perovskite devices for various Zn-doped ratios. (b) Ultraviolet photoelectron spectra of secondary electron cut-off (left) and valence band (right) of perovskite films. (c) Time-resolved photoluminescence decay transient measured for glass/perovskite films with and without Zn. (d) Calculated hole and electron diffusion lengths for control and Zn-5 perovskite films.

with Zn^{2+} .³⁹ Moreover, the strain of the perovskite lattice affects the energy level, particularly the VBM. The VBM is predominantly composed of B-site *s* and iodine *p* orbitals in the octahedron of perovskite.⁴¹ Additionally, the tensile strain of the perovskite lattice causes downward bending of the valence band, hampering hole extraction and negatively affecting the mobility and diffusion length.²⁵ Therefore, the local lattice strain in Sn-based perovskite is important because of the band structure for transporting charge carriers in the device and the electrical properties of the perovskite layer.

Time-resolved photoluminescence was measured to investigate the nonradiative recombination of perovskite films and carrier diffusion length to be calculated from the quenched carrier lifetime (τ_{quench}) through charge transport/perovskite layer.^{42,43} The carrier lifetime (τ) of all films was obtained using the biexponential decay function:

$$Y = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) \quad (1)$$

$$\tau_{\text{ave}} = \frac{(A_1 \tau_1 + A_2 \tau_2)}{(A_1 + A_2)} \quad (2)$$

The average carrier lifetime (τ_{ave}) was calculated from the τ_i and A_i values of plotting the photoluminescence (PL) decay using the biexponential equation (eqn (1)), where τ_1 and τ_2 are related to the trap-assisted nonradiative and radiative recombination, respectively. The average carrier lifetimes of perovskite films with different Zn ratios were measured (Fig. 3c and Table S4†); the τ_{ave} of Zn-5 (16.26 ns) was much higher than that of the control film (8.173 ns). This increased carrier lifetime was consistent with the reduction in lattice strain, indicating that relaxation of the lattice strain suppressed nonradiative recombination by reducing the number of trap states.¹ Additionally, we measured the τ_{quench} of PEDOT:PSS/perovskite and perovskite/ C_{60} samples to calculate the diffusion length of the hole and electron using the 1D diffusion equation:^{42,43}

$$L_D \approx \frac{2d}{\pi} \sqrt{2\left(\frac{\tau}{\tau_{\text{quench}}} - 1\right)} \quad (3)$$

where L_D is the carrier diffusion length, d is the film thickness, and τ is the carrier lifetime. The film thickness was 210 nm for the control and 240 nm for Zn-5 perovskite (Fig. S13†). The carrier lifetimes related to radiative recombination from bulk film of the control and Zn-5 perovskite were 64.18 and 29.77 ns, respectively. The τ_{quench} of the electron and hole were 14.86 ns ($\tau_{\text{quench,e}^-}$, control), 31.64 ns ($\tau_{\text{quench,e}^-}$, Zn-5), 21.67 ns ($\tau_{\text{quench,h}^+}$, control), and 31.80 ns ($\tau_{\text{quench,h}^+}$, Zn-5) for the perovskite/buffer layer (PEDOT:PSS or C_{60}), respectively (Fig. S14†). Fig. 3d shows the calculated diffusion lengths of the hole and electron determined using eqn (3). The hole diffusion length increased from 165.2 (control) to 306.4 nm (Zn-5), which was much larger than the enhancement of the electron diffusion length from 270.8 (control) to 307.9 nm (Zn-5). The diffusion length of Sn-based perovskite is affected by the higher charge density related to $\text{Sn}^{2+}/\text{Sn}^{4+}$ self-p-type doping in films

because of oxidation.^{44,45} In this Zn-doped Sn-based perovskite film, Sn oxidation of the perovskite films was suppressed regardless of whether Zn was added (Fig. 1f). Additionally, the lattice strain affected the electrical properties of perovskite, particularly the diffusion length of the hole and VBM, because of relaxation caused by Zn ions doping in perovskite octahedrons composed of B and X sites.

The lattice strain relaxation pathway generates defect sites such as vacancies without the incorporation of small ions.²⁶ To validate whether charge carrier recombination was suppressed and calculate the defect density, light intensity-dependent $J-V$ and space charge-limited current measurements were performed. As shown in Fig. 4a and b, the light intensity *versus* J_{SC} and V_{OC} for the control and Zn-doped perovskite devices were investigated. Fig. 4a shows the linearly fitting plot of J_{SC} *versus* the logarithm of light intensity under short circuit conditions determined by a power law ($J_{\text{SC}} \propto I^\alpha$). The exponent α for the Zn-5 device is close to 1, indicating that bimolecular charge recombination was suppressed. Fig. 4b shows a semi-logarithmic plot of V_{OC} as a function of light intensity for the control and Zn-doped perovskite devices. The ideality factor (n) was calculated according to the equation:

$$V_{\text{OC}} = \frac{nk_B T}{q} \ln\left(\frac{I}{I_0} - 1\right) \quad (4)$$

where q is the elementary charge, k_B is the Boltzmann constant, and T is temperature. The ideality factor is determined from the slope of the semi-logarithmic plot; when the ideality factor value approaches 2, as the Shockley–Read–Hall type, trap-assisted recombination under open-circuit conditions dominates. The ideality factor values were 1.519, 1.483, 1.305, and 1.593 for the control, Zn-2, Zn-5, and Zn-10, respectively. The ideality factor was lowest for Zn-5 and showed a similar tendency for lattice strain. This indicates that trap-assisted Shockley–Read–Hall recombination was suppressed by reducing local lattice strain.²⁶ Additionally, steady-state PL measurements were performed to investigate nonradiative trap-

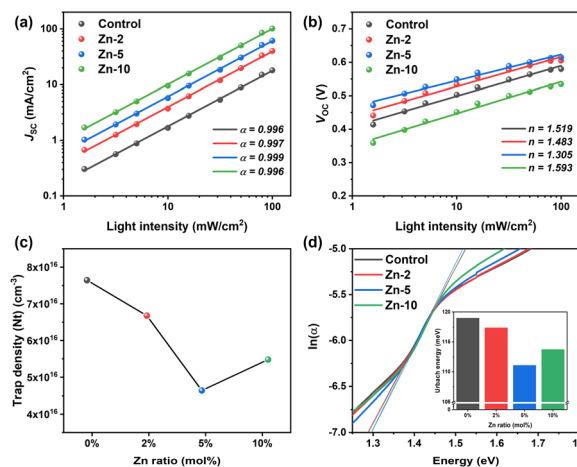


Fig. 4 Light intensity dependence of (a) J_{SC} and (b) V_{OC} of perovskite devices. (c) Trap density. (d) Logarithm of absorption coefficient *versus* photon energy and (inset) Urbach energy calculated in perovskites.

assisted recombination of the perovskite film. As shown in Fig. S15,[†] addition of Zn led to an increase in the PL intensity. The Zn-5 film showed the strongest intensity, indicating fewer defects and nonradiative recombination in the film. The reduced Shockley–Read–Hall recombination can be attributed to the reduced trap density in the Zn-5 devices. To investigate the defect density of the perovskite films, space charge-limited current measurements were performed on ITO/PEDOT:PSS/perovskite/Poly(3-hexylthiophene)/Au devices, as shown in Fig. S16.[†] As the bias voltage increased, the J – V relationship transformed from a linear increase to a rapid nonlinear increase, which identified the trap-filled limit voltage (V_{TFL}). The trap density (N_t) (Fig. 4c) was calculated using V_{TFL} according to the following equation:

$$V_{\text{TFL}} = \frac{qN_t L^2}{2\epsilon\epsilon_0} \quad (5)$$

where ϵ (5.7)⁴⁶ and ϵ_0 are the dielectric constants of perovskite and the vacuum permittivity, and L is the thickness of the perovskite films. From the V_{TFL} of Zn-doped perovskite films, the calculated hole N_t was $5.03 \times 10^{16} \text{ cm}^{-3}$ for Zn-5, which was lower than that of the control ($7.64 \times 10^{16} \text{ cm}^{-3}$). The decreased trap density was attributed to the reduced local lattice strain and induced nonradiative recombination suppression in the perovskite films.²⁹

There were notable changes in the lattice strain and trap density but little change in the bandgap because of UV-vis absorption (Fig. S11[†]) and PL spectra (Fig. S15[†]). The Urbach energy was investigated to evaluate the localised energy states acting as trap states within the bandgap.²⁷ The Urbach energy (E_u) was determined from the UV-vis absorption spectra using the following equation:

$$\ln(\alpha) = \ln(\alpha_0) + h\nu/E_u \quad (6)$$

where α is the absorption coefficient and $h\nu$ is the photon energy, which was calculated as 119.0, 117.4, 111.1, and 113.7 meV for the control, Zn-2, Zn-5, and Zn-10, respectively (Fig. 4d). A lower value of E_u indicates a higher optoelectronic property of perovskite and lower voltage loss between V_{OC} and the bandgap voltage.¹ The tendency of lattice strain in perovskite films was similar to that of the E_u values as well as that of the ideality factor values and trap density. These results indicate the positive effect of adding a small amount of Zn ions to Sn-based perovskite films.

We compared the effects of different Zn ratios on the photovoltaic performance. The J – V characteristics in Fig. 5a show a PCE of 8.560% for the control, with a J_{SC} of 21.95 mA cm^{-2} , V_{OC} of 0.583 V, and fill factor (FF) of 66.92%. Although Zn-5 was the best condition for the device, it exhibited an improved PCE of 11.39%, with a J_{SC} of 24.72 mA cm^{-2} , V_{OC} of 0.649 V, and FF of 71.02%. Details on the performance of these devices at other concentrations are listed in Table S5.[†] In particular, the V_{OC} and FF were enhanced by addition of Zn until 5%, which agrees with the results of lattice strain, charge recombination, and defect density analyses. Fig. 5b shows the efficiency distribution with various concentrations of Zn showing acceptable

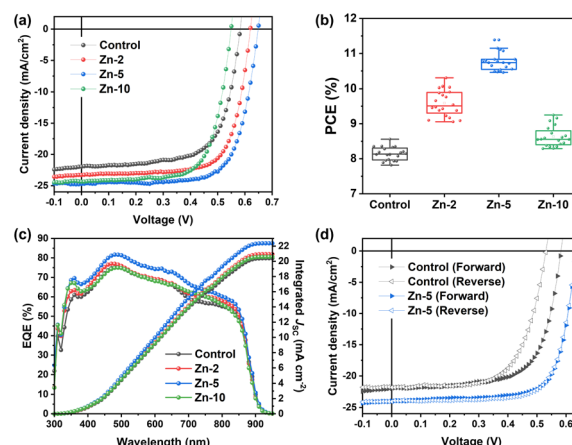


Fig. 5 (a) J – V curves of different molar ratios Zn-doped Sn-based perovskite solar cells. (b) Statistical PCE distribution of perovskite solar cells. (c) External quantum efficiency (EQE) curves of different Zn-doped Sn perovskite solar cells. (d) J – V curves of 0 and 5% Zn-doped perovskite solar cells under reverse and forward voltage scans.

reproducibility. The external quantum efficiency (EQE) spectra and integrated J_{SC} are shown in Fig. 5c. The solar cells exhibited almost identical EQE onsets at 920 nm. In contrast, the Zn-5 device increased the EQE over the entire wavelength range from 350 to 850 nm, corresponding to a higher J_{SC} for the Zn-5 perovskite solar cell. The calculated J_{SC} values of the control and Zn-5 devices from the perspective of the EQE were 20.66 and 22.65 mA cm^{-2} , respectively (Table S5[†]). The J – V hysteresis features of Sn-based PSCs are shown in Fig. 5d. The hysteresis of the Zn-5 device was suppressed; the hysteresis index ($\text{HI} = (\text{PCE}_{\text{reverse}} - \text{PCE}_{\text{forward}})/\text{PCE}_{\text{reverse}}$, $\text{HI}_{\text{Zn-5}} = 0.042\%$) of the device was lower than that of the control device ($\text{HI}_{\text{control}} = 13.98\%$), as shown in Table S6.[†] Relaxation of the lattice strain suppressed the formation of lattice vacancies, which can reduce ion migration causing hysteresis. Fig. S17[†] shows the PCE degradation of the control, Zn-5, and Zn-10 devices without encapsulation exposed to ambient air (25 °C, humidity 35%). The time of degradation to 90% of the initial PCE for the Zn-5 device was over 350 min, whereas those of the control and Zn-10 devices were 180 and 90 min, respectively. Thus, the device stability was improved by incorporating Zn^{2+} to relax the lattice strain.

Conclusions

In the present study, Zn^0 was introduced to prevent the oxidation of Sn based on their redox potential difference. According to the potential, Zn^{2+} was doped into the precursor solution. After coating the perovskite film, Zn^{2+} doping was confirmed through XPS and XRD measurements. Because the radius of Zn^{2+} is smaller than that of Sn^{2+} , the octahedron of the perovskite crystalline structure is compressive, and the lattice strain is reduced. The Williamson–Hall plot and grazing incidence XRD results validated the reduction in the lattice strain of the Zn-doped perovskite films. Zn^{2+} doping affects optoelectronic properties such as the diffusion length and energy level. The

hole diffusion length of the Zn-doped perovskite film was enhanced and matched the electron diffusion length. The trap-assisted charge carrier recombination and trap density perovskite devices were decreased with the reduction in lattice strain. The efficiency of Zn-doped Sn-based PSCs was achieved at 11.39% PCE. These results demonstrate that the Sn-based PSCs have high efficiency.

Author contributions

H. Jang conceived the experiments, data analysis, and interpretation. H. Jang performed the GIXRD measurement and the fabrication of devices, device performance measurement, and characterization. H. Y. Lim performed the theoretical calculation and analysed the results. C. B. Park performed the XPS and UPS measurements. J. Seo and J. G. Son performed the XRD measurement. T. Song, J. Lee, and J. Roe performed the UV-vis absorption and PL measurement. Y. S. Shin performed the TRPL measurement and analysed the results. The manuscript was written by H. Jang and H. Y. Lim. The project was planned, directed, and supervised by S. K. Kwak, D. S. Kim, and J. Y. Kim. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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