Accurate Adjusting the Lattice Strain of Triple-Cation and Mixed-Halide Perovskites for High-Performance Photodetector

Wenchi Kong, Chen Zhao, Tao Huang, Xiuyun Li, Jun Xing, Zhi Yu, Peng Yang, Wei Li,* and Weili Yu*



ABSTRACT: The instability of perovskite optoelectronic devices remains a big barrier to their commercialization. The instability caused by external stimuli has been addressed by encapsulation, such as humidity, oxygen, heat, and ultraviolet light. However, the intrinsic instability of perovskite materials due to the lattice strain has not been fully addressed, which affects the physical properties and device performance to a great extent. Tuning the lattice strain by controlling the perovskite composition and ratio is an effective way to further develop efficient and stable devices. Herein, we prepare a series of triple-cation and mixed-halide $(FAPbI_3)_x(MAPbBr_3)_y(CsPbI_3)_{1-x-y}$ perovskite single-crystal thin films and study the effect of lattice strain on the perovskite optoelectronic properties. Especially, the perovskite photodetector with a horizontal structure based on $(FAP-bI_3)_{0.79}(MAPbBr_3)_{0.13}(CsPbI_3)_{0.08}$ single-crystal thin films exhibits excellent performance with an enhanced responsivity of 40 A/W, high detectivity of 1.9×10^{13} Jones, external quantum efficiency of 9100%, and superior stability. This can be explained by the fact that the optimal coordination between each element leads to the release of lattice strain and further produces low defect density and long carrier lifetime in $(FAPbI_3)_{0.79}(MAPbBr_3)_{0.13}(CsPbI_3)_{0.08}$ a promising candidate for the next generation of optoelectronic devices. KEYWORDS: strain, perovskites, single crystal, photodetector, stability

■ INTRODUCTION

With the attractive features including tunable absorption wavelength, large light absorption coefficient, long carrier lifetime, high carrier mobility, and long diffusion length, organic-inorganic hybrid perovskites ABX₃ (A = MA, FA, Cs, etc. B = Sn, Pb, etc. X = Cl, Br, I) have attracted a great deal of interest from a variety of optoelectronic fields, such as solar cells, light-emitting diodes, high-sensitivity photodetectors, and efficient lasers.¹⁻⁹ Based on perovskite polycrystalline thin films (PCTFs), the solar cell power conversion efficiency (PCE) exceeds 25.5%.¹⁰ However, PCTFs have massive grain boundaries, which not only reduce the thermal decomposition temperature of the materials but also provide a pathway for ion aggregation, resulting in poor stability and low current-voltage (I-V).¹¹ Compared with PCTFs, perovskite single crystals exhibit outstanding properties due to the absence of grain boundaries and associated defects that negatively affect device performance.^{12,13} Therefore, it is more attractive to fabricate stable and efficient optoelectronic devices utilizing perovskite single-crystal thin films (SCTFs). The promising thirdgeneration perovskite materials (FAP bI_3)_x(MAPbBr₃)_y(CsPbI₃)_{1-x-y} have not only better water and oxygen stability than MAPbI₃ and better phase stability than FAPbI₃ in the first generation perovskite materials but also better light stability than (FAPbI₃)_x(MAPbBr₃)_{1-x} in the second-generation perovskite materials.¹⁴ However, different composition ratios of triple-cation and mixed-halide perovskite reported by some research groups have different influences on the performance of optoelectronic devices, and the underlying

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Figure 1. Schematic diagram of lattice strain relief in $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ perovskite. (a) Schematic diagram of the black α -FAPbI₃ on the (111) plane. (b) Schematic diagram of the lattice strain relief through the formation of vacancy defects. (c) Schematic diagram of the lattice strain relief by incorporating small ions MA⁺ and Br⁻ into the α -FAPbI₃. (d) Schematic diagram of the lattice strain further relief by adding smaller ions Cs⁺ based on (c).

reason is not well understood. Therefore, investigating the effect of ion content with different radii on perovskite optoelectronic properties and device performance is imperative.^{15,16}

The lattice strain plays a key role in determining the perovskite optoelectronic device performance and long-term stability. Huang group report that lattice strain is related to the methods of preparing perovskite PCTFs, and the lattice strain can be released by raising the temperature or making the perovskite PCTFs more compatible with the substrate.¹⁷ Dauskardt group demonstrate that reducing the stress of thin film can be accomplished by lowering the perovskite formation temperature, utilizing substrates with suitable thermal expansion coefficients for the perovskite, or applying external compressive stress after fabrication.¹⁸ Chen group spin-coat octylammonium iodide (OAI) and phenylethylammonium iodide (PEAI) on the surface of the perovskite PCTFs for relaxing the interfacial residual stress, improving the PCE of the solar cell from 20.02 to 21.48%, and greatly enhancing the stability.¹⁹ Snaith and co-workers introduce *n*-butylammonium (BA) into the $FA_{0.83}Cs_{0.17}Pb(I_{\nu}Br_{1-\nu})_3$ perovskite to release strain, resulting in improved efficiency and stability.²⁰ $(FAPbI_3)_x(MAPbBr_3)_y(CsPbI_3)_{1-x-y}$ has a natural advantage over other perovskite materials in terms of stability, although there is no agreement on the ion ratios.^{9,21} Fortunately, the approximate range of the Cs content about (FAP $bI_3)_x(MAPbBr_3)_y(CsPbI_3)_{1-x-y}$ is recently given in Tian's work, which demonstrates that the perovskite single crystal is unstable when the Cs content is 0 or greater than 0.1 and stable when the Cs content is 0.05. The reason for this is not well understood, and how to push this finding forward is still not clear. In view of this, we further study the physical properties of perovskite and device performance in detail when the Cs content is in a narrow range between 0 and 0.1 and try to clarify the underlying reason from the lattice strain perspective.¹⁴

Here, we precisely adjust the lattice strain by changing the Cs content from 0 to 0.1 at intervals of 0.02 in $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ to obtain the highestquality SCTFs. We obtain the relationship between lattice strain and the Cs content. Further, the result shows that the performance and stability of the $(FAP-bI_3)_{0.79}(MAPbBr_3)_{0.13}(CsPbI_3)_{0.08}$ photodetector are optimal due to the lattice strain relief. The systematic study of the lattice strain in the perovskite materials can not only obtain the perovskite structure with the best inherent performance, which is conducive to the development of high-performance perovskite optoelectronic devices, but also open a new way for designing better photovoltaic materials.

EXPERIMENTAL SECTION

Materials. We bought formamidinium acetate powder (99%), methylamine solution (40% aqueous solution), and lead bromide (PbBr₂, 99%) from Aladdin company. We bought lead iodide (PbI₂, \geq 99.99%) and cesium iodide (CsI, \geq 99.99%) from Xi'an Polymer Light Technology Corp. γ -Butyrolactone (GBL, 99.8%), hydrogen iodide solution (HI, 40% aqueous solution), and hydrogen bromide solution (HBr, 40% aqueous solution) were bought from Sigma-Aldrich.

Synthesis of Formamidinium lodide (FAI). Formamidinium acetate powder is first added to the HI solution in a molar ratio of 100%, which is stirred for 6 h at 0 °C. We then evaporate the fully dissolved solution by rotary evaporation for 3 h at 60 °C to get the white powder of FAI. After that, we rinse with anhydrous ethanol and recrystallize with anhydrous ether on FAI three times respectively. Finally, we obtain FAI through filtration, and store it in a vacuum drying oven for 12 h.

Synthesis of Methylammonium Bromide (MABr). Methylamine solution and HBr solution are mixed in a molar ratio of 100% and stirred for 2 h at 0 °C. Then, we evaporate the fully mixed solution by rotary evaporation at 60 °C until a white powder of MABr is obtained. After rinsing with anhydrous ethanol and recrystallization with anhydrous ether on MABr three times, we obtain MABr by filtration, and store it in a vacuum drying oven for 12 h.



Figure 2. Characterizations of a series of SCTFs with different CsI contents. (a) XRD patterns of $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ SCTFs. Briefly, it is simplified as $FA_{0.79}MA_yCs_{1-y}$ and $FA_{0.79}$ represents $(FAPbI_3)_{0.79}$ and MA_y and Cs_{1-y} represent $(MAPbBr_3)_y$ and $(CsPbI_3)_{1-y}$, respectively. (b) Enlarged (110) plane of XRD for the SCTFs. (c) Ultraviolet–visible (UV–vis) absorption spectra for the SCTFs. The corresponding Tauc plots is given in the inset. The band gaps of $FA_{0.79}MA_{0.19}Cs_{0.02}$, $FA_{0.79}MA_{0.17}Cs_{0.04}$, $FA_{0.79}MA_{0.15}Cs_{0.06}$, $FA_{0.79}MA_{0.13}Cs_{0.08}$, and $FA_{0.79}MA_{0.11}Cs_{0.11}$ are 1.655, 1.635, 1.614, 1.589, and 1.568 eV, respectively. (d) The steady-state photoluminescence spectra for the SCTFs. These SCTFs are illuminated under 532 nm.



Figure 3. Characterizations of lattice strain in $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ SCTFs with different CsI contents. (a) Peak intensity versus interplanar spacing of the (110) plane, there is a regular red-shift and the lattice strain gradually decreases from 1.16, 0.84, 0.59, 0.50, to 0.45% as the CsI content increases. (b) Raman spectra for the $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ SCTFs. (c) Time-resolved photoluminescence spectra and average carrier lifetimes of a series of SCTFs excited at 532 nm. (d) Lattice strain and average carrier lifetimes as a function of different CsI contents for a series of SCTFs.

Fabrication of a Photodetector with Horizontal Structure. The substrate glasses and the covering glasses with a thickness of 1.1 mm are washed sequentially with ethanol, acetone, isopropanol, and deionized water. We dry the substrate glasses and the covering glasses in a drying oven at 70 °C for 12 h. To make the glass surface hydrophilic, we place it in a plasma cleaning machine for 3 min. We soak the covering glasses in the mixed solution of (3-aminopropyl)-triethoxysilane and hexane solution (v/v = 1/500) for 30 min. After

that, the covering glasses were rinsed with acetone for 30 s and blowdried with nitrogen to get a hydrophobic surface. To obtain the photodetector, $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ (y = 0.02, 0.04, 0.06, 0.08, or 0.1) is first stirred in GBL overnight at 60 °C. We then drop 5 μ L of the $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ solution onto the substrate glasses and put the covering glasses on top. Afterward, we transfer the sandwich structure sheet onto a hotplate. The temperature is gradually increased from 60 to 100 °C till

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Figure 4. Performance of photodetectors with different CsI contents. (a) Schematic diagram of a photodetector with a lateral structure. (b–d) Plots of *R*, D^* , and EQE of a series of photodetectors as a function of light intensity at 532 nm laser illumination under 3 V. (e) *R*, D^* , and EQE as functions of the lattice strain at 532 nm laser illumination (27.94 mW/cm²) under 3 V. (f) Photocurrent as a function of light intensity for the FA_{0.79}MA_{0.13}Cs_{0.08} photodetector and the curve can be fitted according to the power law. The inset shows the *I–V* curve for a hole FA_{0.79}MA_{0.13}Cs_{0.08} SCTFs device. We get the solid lines by fitting the data.

Table 1. Summary of Horizontal Photodetectors Based on Mixed-Cation Perovskites Containing Cs

year	material	modify	light power/wavelength	R (A/W)	D^* (Jones)	EQE (gain)	references
2019	FACsPbIBr	asymmetric nanogap	1.67 mW cm ⁻² /525 nm	33	1×10^{11}	7976%	Adv. Funct. Mater. 2019, 29, 1901371
2020	FAMACsPbIBr	BNA arrays	10.17 mW cm ⁻² /785 nm	0.12	1.5×10^{12}	118.8%	Small 2020, 16, 2001417
2020	DMACsPbI	no	$2.3 \text{ mW cm}^{-2}/532 \text{ nm}$	0.38	1×10^{13}	86%	Nano Energy 2020, 71, 104611
2021	FAMACsPbIBr	2% FAH + integrated/no	$0.52 \text{ nW cm}^{-2}/460 \text{ nm}$	600/420	$6 \times 10^{14}/9 \times 10^{13}$	(1700/1200)	Sci. Adv. 2021, 7, eabc8844
2022	FAMACsPbIBr	no	$1.5 \text{ mW cm}^{-2}/532 \text{ nm}$	40	1.9×10^{13}	9100%	this work

 $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ SCTFs are formed. After that, the covering glasses and the substrate glasses are gently separated u s i n g a b l a d e , w h i c h r e t a i n s t h e (FAP - bI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y} SCTFs on the substrate glasses due to the hydrophobic surface of the covering glasses. The photodetector with a horizontal structure is completed by thermal evaporation in a vacuum (<5 \times 10⁻⁴ Pa) of 80 nm Au as the electrode deposited on the (FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y} SCTFs.

Characterizations and Measurements. The scanning electron microscopy image is conducted on Phenom ProX. The EDS mapping image is obtained using the Phenom Element Identification application attached to the Phenom ProX. The XRD measurement is conducted on BRUKER D8 focusing in the air. The absorption spectra and the photoluminescence spectra of perovskite SCTFs are obtained by Agilent Cary 5000 and a HORIBA Scientific Raman spectrometer at room temperature, respectively. The time-resolved photoluminescence spectra are acquired using a MicroTime 200 time-resolved fluorescence microscope (PicoQuant) in the air. The 3D pseudocolor plots are acquired using a KEYENCE VK-X200 3D laser scanning microscope. We obtain the *I*–*V* curves using a Keithley 4200A semiconductor parametric analyzer (Tektronix) and a 532 nm laser as a light source with adjustable light intensity from 1.5 to 67.52 mW cm⁻². We get the response stability of a series of photodetectors

under an on-off radiation in the air at room temperature. Particularly, we control the irradiation time of the photodetector through an optical shutter (VS2SS2TO, UNIBLITZ) with a radius of 1.25 mm.

RESULTS AND DISCUSSION

From the perspective of mechanical forces, when an object is deformed by an external force, an internal force is generated inside the object to resist the action of the external force;^{22,23} therefore, the whole system is in an unstable state, as shown in Figure S1 (Supporting Information). The situation is also true for lattices in perovskite materials, which are unstable under stress. The black-phase formamidinium lead iodide (α -FAPbI₃) with a wide light absorption range is a star material for efficient perovskite solar cells (Figure 1a); however, it is very unstable due to the lattice distortion caused by the large size of the FA^+ ion.^{24–29} One possible route to relieve the lattice strain is to construct vacancy point defects, as displayed in Figure 1b. Specifically, to reduce the lattice strain, FA⁺ and/ or I⁻ vacancies can be obtained in FAPbI₃ due to the low formation energy. These defects are detrimental to obtaining efficient and stable optoelectronic devices. Also, some other



Figure 5. Response stability of photodetectors with different CsI contents under on-off radiation. (a-e) On-off test period of $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ photodetectors is approximately 120 s. The left and right plots show the zoomed detail of the response at the beginning and at the end about 8 s in the middle plot, respectively. The response of a series of photodetectors at 532 nm laser illumination (27.94 mW/cm^2) under 3 V. (f) As the lattice strain decreases, the photocurrent is reduced by 22.8, 18.8, 7.7, 0.3, and 11.5%, respectively. A high activation energy of ion migration and low vacancy defects density lead to the excellent stability of the FA_{0.79}MA_{0.13}Cs_{0.08} device. (g) Response time of the FA_{0.79}MA_{0.13}Cs_{0.08} photodetector with a faster rise time (152 ms) than the rest of the devices due to the enhanced carrier dynamics.

routes have been developed to stabilize α -FAPbI₃. When FAPbI₃ is alloyed with ions of small radius like MA⁺ and Br⁻, the formation of vacancy defects is inhibited in FAPbI₃ as the lattice strain is relaxed to some extent (Figure 1c). Then, when we continue to incorporate ion Cs⁺ with a smaller radius, further relaxing the strain in the crystal (Figure 1d). In this work, we change the Cs content in (FAPbI₃)0.79-(MAPbBr₃)_y(CsPbI₃)_{0.21-y} to adjust the lattice strain and clarify the effect of lattice strain on the optoelectronic performance.

The $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ PCTFs with a triple cation as a light absorption layer have been reported to be a successful recipe to fabricate solar cells.³⁰ Based on this recipe, we prepare a series of $(FAP - bI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ SCTFs on a hotplate at 100 °C with the inverted temperature crystallization (ITC) method. With the increase in the Cs content, the FA_{0.79}MA_{0.12}Cs_{0.02}, FA_{0.79}MA_{0.17}Cs_{0.04}, and FA_{0.79}MA_{0.15}Cs_{0.06} solutions are clear and transparent at 1.4 M, whereas FA_{0.79}MA_{0.13}Cs_{0.08} and FA_{0.79}MA_{0.11}Cs_{0.1} solutions are murky.

Then, we dilute the solutions of $FA_{0.79}MA_{0.13}Cs_{0.08}$ and FA_{0.79}MA_{0.11}Cs_{0.1} to 0.7 and 0.35 M, respectively, and they become clear. The solution concentration decreases with increasing Cs content due to the low solubility of the inorganic perovskite component CsPbI₃.¹⁴ As shown in Figure S2 (Supporting Information), the FA_{0.79}MA_{0.21} SCTFs without Cs had already undergone phase separation and elemental precipitation of iodine at 85 °C during the crystal growth process, so the FA_{0.79}MA_{0.21} SCTFs is not discussed further. The cubic-phase $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ SCTFs have a smooth surface and a regular edge, as shown in the scanning electron microscopy (SEM) images of Figure S3 (Supporting Information). The powder X-ray diffraction (XRD) of a series of (FAPbI₃)_{0.79}(MAPbBr₃)_y(CsPbI₃)_{0.21-y} display Bragg peaks corresponding to the (100), (110), (111), (200), (210), (220), and (300) planes in Figure S4 (Supporting Information), respectively. To further assess the crystalline quality, we directly perform the XRD measurements on a series of (FAPbI₃)_{0.79}(MAPbBr₃)_v(CsPbI₃)_{0.21-v} SCTFs on glass substrates. As shown in Figure 2a, only the (110) and (220) diffraction peaks are presented through the X-ray scan on the maximal facet of typical (FAP $bI_3)_{0.79}$ (MAPbBr₃)_y (CsPbI₃)_{0.21-y} SCTFs, which indicates a well-structured single-crystal eminence except for FA_{0.79}MA_{0.11}Cs_{0.1} SCTFs. The FA_{0.79}MA_{0.11}Cs_{0.1} SCTFs show two additional Bragg peaks at 14.08 and 40.58° corresponding to the (100) and (200) planes, which indicates a disordered growth of FA0.79MA0.11Cs0.1 SCTFs. The disordered growth and the greatly decreased diffraction intensity imply the low crystallinity of FA_{0.79}MA_{0.11}Cs_{0.1} SCTFs. We zoom in on the (110) plane to extract more information from XRD in Figure 2b. The (110) peaks of $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ SCTFs regularly shift to a small diffraction angle as the CsI content increases and the absorption spectra show a red-shift after the alloying process (Figure 2c), indicating the successful incorporation of different CsI contents. Furthermore, the band gaps of the (FAPbI₃)_{0.79}(MAPbBr₃)_v(CsPbI₃)_{0.21-y} SCTFs are estimated according to the Tauc diagrams. As is shown in the inset of Figure 2c, the band gaps decrease from 1.655 to 1.568 eV as the CsI content increases. The photoluminescence (PL) spectra of the (FAPbI₃)_{0.79}(MAPbBr₃)_v(CsPbI₃)_{0.21-v} SCTFs also display a regular red-shift by 30 nm as the CsI content increases (Figure 2d), which matches well with the trend of change in the absorption spectra. These results provide evidence of the successful incorporation of different CsI contents in SCTFs. Then, we try to prove that each element is displayed in $(FAPbI_3)_{0.79}(MAPbBr_3)_{\nu}(CsPbI_3)_{0.21-\nu}$ SCTFs. The energy-dispersive spectrometry (EDS) mapping of FA_{0.79}MA_{0.13}Cs_{0.08} is presented in Figure S5 (Supporting Information) as an example, which shows a uniform elemental distribution of carbon, nitrogen, cesium, lead, iodine, and bromide. This result exhibits that each element is incorporated into FA0.79MA0.13Cs0.08 SCTFs successfully, which directly proves that each element is incorporated into the series of $(FAPbI_3)_{0.79}(MAPbBr_3)_{\nu}(CsPbI_3)_{0.21-\nu}$ SCTFs successfully, matching well with the above XRD, PL, and absorption spectra.

We then quantitatively analyze the lattice strain of $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ SCTFs by XRD measurement. To the best of our knowledge, the observed diffraction peak width in each (*hkl*) plane is a convolution of instrumental broadening, nanoscale grain sizes, and lattice strain, as represented by the following equation³¹

$$\Delta d_{\rm obs}^2 = \Delta d_{\rm inst}^2 + \Delta d_{\rm size}^2 + \Delta d_{\varepsilon}^2 \tag{1}$$

where Δd_{obs} is the observed peak width at full width at halfmaximum (FWHM) in terms of the lattice interplanar spacing for a specific (*hkl*) plane, Δd_{inst} is the contribution of the test instrument, Δd_{size} is the contribution of the grain size, and Δd_{e} is the contribution of the lattice strain. Here, (FAPbI₃)_{0.79}(MAPbBr₃)_y(CsPbI₃)_{0.21-y} SCTFs have large grain sizes (more than hundreds of nanometers), so Δd_{size} value can be ignored. Therefore, eq 1 can be simplified as¹⁵

$$\Delta d_{\varepsilon} = \sqrt{\Delta d_{\rm obs}^2 - \Delta d_{\rm inst}^2} = d_{hkl} \tag{2}$$

where ε is the lattice strain (given by $\Delta d_{\varepsilon}/d_{hkl}$) and d_{hkl} is the interplanar spacing of the (hkl) planes, calculated from the Bragg equation $n_{\lambda} = 2d_{hkl} \sin \theta$. Δd_{inst} value is 0.003 Å, which can be gained by measuring an XRD pattern on a calibration standard (high-quality silicon) under the same setting as in the above samples. According to the XRD results in Figure 3a, the lattice strain d_{110} decreases gradually from 1.16, 0.84, 0.59, 0.5, to 0.45% as the CsI content increases. Next, the Raman spectra qualitatively provide another evidence of lattice strain release. In Figure 3b, these peaks at around 136 cm^{-1} in the Raman spectra are caused by the stretching of the lead-iodine bond, which becomes weaker in intensity and broader in width with the increase in the CsI content, indicating that the Raman activity decreases due to the reduction in lattice strain.³² The detectable signals are weakest and broadest in FA_{0.79}MA_{0.13}Cs_{0.08} and FA_{0.79}MA_{0.11}Cs_{0.1} SCTFs, indicating that they have the lowest Raman activity and the least lattice strain. This is consistent with the lattice strain value calculated above.

To explore the carrier recombination dynamics in $(FAPbI_3)_{0.79}(MAPbBr_3)_{\nu}(CsPbI_3)_{0.21-\nu}$ SCTFs, time-resolved photoluminescence (TRPL) measurements are conducted, as displayed in Figure 3c. We fit the average carrier lifetime by a triple exponential decay function.^{33,34} Especially, the average carrier lifetime of FA_{0.79}MA_{0.13}Cs_{0.08} SCTFs is up to 173 ns, which is much larger than those of others. This indicates that nonradiative recombination is inhibited due to the significantly reduced defect density. Further, the prolonged carrier lifetime also suggests that FA⁺ and I⁻ ion migration is alleviated at a smaller lattice strain in FA_{0.79}MA_{0.13}Cs_{0.08} SCTFs.¹⁴ Generally, the lattice strain is gradually reduced from FA_{0.79}MA_{0.19}Cs_{0.02} to FA_{0.79}MA_{0.11}Cs_{0.1} as the CsI content increases (Figure 3d). However, carrier lifetime is the largest for FA_{0.79}MA_{0.13}Cs_{0.08} SCTFs instead of FA0.79MA0.11Cs0.1 SCTFs with minimal lattice strain in Figure 3d, which may be caused by disordered and low-quality FA_{0.79}MA_{0.11}Cs_{0.1} SCTFs due to excessive CsI content.

To further investigate their performance as optoelectronic devices, we fabricate a series of horizontal photodetectors based on perovskite $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ SCTFs, as shown in Figure 4a. We carefully study the *I*–*V* curves of these devices with different light intensities at 532 nm in Figures S6a–S10a (Supporting Information). With the increase in light intensity, the photocurrent gradually increases, which can be attributed to the increase in photogenerated carriers in the photodetector. The responsivity (*R*), detectivity (*D**), and external quantum efficiency (EQE) are used as the key figure-of-merit parameters to evaluate the performance of photodetectors, and the corresponding calculation formulas are shown in the Supporting Information). Figures S6c–S10b (Supporting Information), Figures S6c–S10c (Supporting

Information), and Figures S6d-S10d (Supporting Information) show the R, D^* , and EQE values as a function of the laser light intensity at 532 nm, which are summarized in Figure 4bd, respectively. First, it can be observed that R, D*, and EQE decrease as the light intensity increases. This can be attributed to more carrier recombination happening under high light intensity, which is highly consistent with the previous reports.³⁹ Second, the FA_{0.79}MA_{0.13}Cs_{0.08} photodetector not only shows the best R, D*, and EQE of 40 A/W, 1.9×10^{13} Jones, and 9100% in a series of (FAPbI₃)_{0.79}(MAPbBr₃)_v(CsPbI₃)_{0.21-v} photodetectors (Figure 4e) but also leads to better performance than those of many other horizontal photodetectors based on the Cs⁺ ions due to the suitable Cs content, as shown in Table 1. These results again show that the FA_{0.79}MA_{0.13}Cs_{0.08} SCTFs have high quality. The quality of FA_{0.79}MA_{0.13}Cs_{0.08} SCTFs needs to be further developed. We denote the effect of photocurrent on the light intensity by the power law $I_{\rm ph} \propto P^{\theta}$, where $I_{\rm ph}$ is the photocurrent, P is the light intensity, and θ is the index reflecting the response of the photocurrent to light intensity. The θ value for FA_{0.79}MA_{0.13}Cs_{0.08} in Figure 4f is 0.90, which is close to the value of low-defect-state junctions ($\theta \approx 1$), which means that there are fewer defect states between the Fermi level and the conduction band edge.^{40–42} This also confirms the longer carrier lifetime in FA_{0.79}MA_{0.13}Cs_{0.08} SCTFs by TRPL measurement. To further confirm the low hole defect density of FA_{0.79}MA_{0.13}Cs_{0.08}, a space charge limited current (SCLC) measurement is conducted. For the SCLC measurements of thin-film semiconductors, we fabricate a gap-type device using two 23 μ m gap Au electrodes.^{39,43} The current in the SCLC region is primarily driven by the charge carriers injected by the Au electrodes. According to the I-V curve, the defect density of the $FA_{0.79}MA_{0.13}Cs_{0.08}$ SCTFs with a gap-type geometry is deduced from the Geurst's SCLC model^{39,43}

$$V_{\rm t} = \frac{\pi \sigma_0 L}{4\varepsilon_0 \varepsilon_{\rm r}} \tag{3}$$

where $V_{\rm t}$ is the trap-filled limit voltage, σ_0 is the surface charge density per unit area, L is the gap between the two Au electrodes, ε_0 is the vacuum permittivity, and $\varepsilon_{\rm r}$ is the relative dielectric constant of perovskite, which is about 46.5.⁹ As shown in the inset of Figure 4f, the order of the hole trap density is 10^{10} cm⁻², which is close to the defect density of bulk single crystals.⁹

The stability of the devices is also crucial for practical operation. Here, we investigate the reliability of a series of unencapsulated photodetectors under working conditions (bias = 3 V, light intensity = 27.94 mW/cm^2 in the air. Figure 5a-e shows the response of a series of photodetectors under on-off laser radiation. The photocurrent of the $FA_{0.79}MA_{0.13}Cs_{0.08}$ photodetector has no significant attenuation throughout the whole test period of more than 120 s as displayed in the middle plot of Figure 5d, while the photocurrent decreases 22.8% for the FA_{0.79}MA_{0.19}Cs_{0.02} device (Figure 5a) and decreases 18.8% for the $FA_{0.79}MA_{0.17}Cs_{0.04}$ device (Figure 5b). The drop is 7.7% for the $FA_{0.79}MA_{0.15}Cs_{0.06}$ device (Figure 5c) and 11.5% for the $FA_{0.79}MA_{0.11}Cs_{0.1}$ device (Figure 5e). Further, we provide the on-off current of the $FA_{0.79}MA_{0.13}Cs_{0.08}$ photodetector after being stored in a glovebox for 6 months in Figure S11 (Supporting Information). The overall photocurrent of the $FA_{0.79}MA_{0.13}Cs_{0.08}$ photodetector decreases by about 3% compared to 6 months ago (Figure 5d), and there is no

significant attenuation during the whole test period, which indicates the device is very stable. There are three key reasons for the outstanding optoelectronic parameters of the $FA_{0.79}MA_{0.13}Cs_{0.08}$ photodetector. First, the long carrier lifetime and the low defect density of the $FA_{0.79}MA_{0.13}Cs_{0.08}$ SCTFs are due to the released lattice strain. Second, the better alignment of VBM of $FA_{0.79}MA_{0.13}Cs_{0.08}$ to the Fermi level of the gold electrode is achieved under appropriate lattice strain.⁴⁴ Third, the lowest current drop and the superior stability of the $FA_{0.79}MA_{0.13}Cs_{0.08}$ photodetector can be attributed to the inhibited ion migration due to the proper release of lattice strain, as shown in Figure $5f.^{21}$ The rise time of the $FA_{0.79}MA_{0.13}Cs_{0.08}$ device is 152 ms, which is the shortest among the series of photodetectors, indicating large carrier mobility, as depicted in Figure $5g.^{44}$

CONCLUSIONS

In summary, we study the physical properties and the device performance of a series of perovskite (FAPbI₃)_{0.79}(MAPbBr₃)_y(CsPbI₃)_{0.21-y} SCTFs by precisely regulating the content of small-radius ions. The ratio of these elements plays a vital role in controlling crystallization and device performance. We got an optimum perovskite composition FA_{0.79}MA_{0.13}Cs_{0.08} and prepared a high-performance photodetector based on FA_{0.79}MA_{0.13}Cs_{0.08} SCTFs. The greatly improved performance for this specific composition can be attributed to the long carrier lifetime induced by a small lattice strain and the low defect density of the FA_{0.79}MA_{0.13}Cs_{0.08} SCTFs. The alleviated lattice strain plays a key role in improving the device's performance. This research shows the significance of ion ratios in tuning the lattice strain and device efficiency and stability and demonstrates perovskite $(FAPbI_3)_{0.79}(MAPbBr_3)_{0.13}(CsPbI_3)_{0.08}$ as a promising candidate for the third generation of optoelectronic devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c02427.

Schematic diagram of mechanical analysis; three-dimensional height map of $(FAPbI_3)_{0.79}(MAPbBr_3)_{0.21}$ heated at 85 °C in the crystal growth; SEM images of a series of SCTFs; powder XRD patterns of $(FAP-bI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$; SEM image and EDS mapping of $FA_{0.79}MA_{0.13}Cs_{0.08}$ SCTFs; Raman spectra of $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ SCTFs; and characterization of parameters for the $(FAPbI_3)_{0.79}(MAPbBr_3)_y(CsPbI_3)_{0.21-y}$ photodetector under 532 nm (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Wei Li GPL Photonics Laboratory, State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P. R. China; Email: weili1@ ciomp.ac.cn
- Weili Yu GPL Photonics Laboratory, State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P. R. China; ⊙ orcid.org/0000-0001-5075-9638; Email: weili.yu@ciomp.ac.cn

Authors

- Wenchi Kong GPL Photonics Laboratory, State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P. R. China; University of Chinese Academy of Sciences, Beijing 100049, P. R. China
- Chen Zhao GPL Photonics Laboratory, State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P. R. China; University of Chinese Academy of Sciences, Beijing 100049, P. R. China
- Tao Huang GPL Photonics Laboratory, State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P. R. China; University of Chinese Academy of Sciences, Beijing 100049, P. R. China
- Xiuyun Li GPL Photonics Laboratory, State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P. R. China; University of Chinese Academy of Sciences, Beijing 100049, P. R. China
- Jun Xing Xinjiang Key Laboratory of Solid State Physics and Devices, School of Physics and Technology, Xinjiang University, Urumqi 830046, P. R. China
- Zhi Yu GPL Photonics Laboratory, State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P. R. China; The Key Laboratory of Bionic Engineering of Ministry of Education, Jilin University, Changchun 130012, P. R. China; © orcid.org/0000-0002-5139-0569
- **Peng Yang** The First Military Representative Office of the Army Military Representative Bureau of Shenyang Division in Changchun District, Changchun 130033, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.2c02427

Notes

The authors declare no competing financial interest.

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