nature portfolio

Peer Review File

All-site alloyed perovskite for efficient and bright blue light-emitting diodes

Corresponding Author: Professor Jianpu Wang

Parts of this Peer Review File have been redacted as indicated to remove third-party material.

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The fast and disordered crystallization of multicomponent perovskites has limited the efficiency of blue perovskite LEDs. Chen et al. developed a novel all-site alloy method to control the growth process of multiple-component perovskite films. Based on this approach, they achieved low-trap density blue perovskite films and high-efficiency perovskite LEDs. This work is important for the fabrication of high-performance blue perovskite LEDs. I recommend it for publication after the following concerns have been fully addressed.

1. The authors demonstrate that the interaction between SrBr2 and CsBr can impede the initial growth of FA/Cs alloyed perovskite, leading to the growth of FA-rich perovskite followed by gradual Cs+ migration. Could the authors comment on whether this interaction can hinder the phase homogenization of FA-based and Cs-based perovskites.
2. In order to shift the emission of perovskite LEDs to the deep-blue region, the authors used an IPA solution for post-treating perovskite films. Typically, IPA solvent may induce degradation of perovskite films. Have the authors observed any deterioration of perovskite films when using the IPA solution for treatment?
3. The B-site Sr2+ doping strategy has significantly improved the efficiency of blue perovskite LEDs. Typically, this method should also enhance device stability. Have the authors measured the stability of devices prepared with Sr2+ doping?
4. A recently published paper has achieved a high EQE of 23.6% for blue quasi-2D perovskite LEDs (Nature Communications, 2024, 15, 10621). It would be beneficial to include this work in Extended Data Table 1.

Reviewer #2

(Remarks to the Author)
In this manuscript, the authors present an innovative all-site alloy strategy to achieve efficient and bright blue perovskite LEDs. This approach effectively controls the growth of A- and X-site alloyed perovskites, leading to a significant reduction in trap density in 3D blue perovskite materials. The devices demonstrate an impressive EQE of 23.3% and a luminance of 5,700 cd m-2, representing the highest efficiency of blue perovskite LEDs with a luminance exceeding 5,000 cd m-2. The utilization of the all-site alloy method for growing high-quality multicomponent perovskite films holds significant promise for the advancement of perovskite optoelectronics. The manuscript could be considered if the following issues are addressed.
1. As reducing trap density is expected to enhance the stability of perovskite LEDs, I suggest the authors include the results of stability measurement for samples with and without SrBr2.
2. The authors have demonstrated that the incorporation of SrBr2 can significantly improve the performance of perovskite films. It would be insightful to explore whether Sr2+ can integrate into the perovskite lattice.
3. Since SrBr2 can impede the initial growth of FA/Cs alloyed perovskite due to the chemical interaction between SrBr2 and CsBr, the authors could investigate if SrBr2 directly inhibits the growth of Cs-based perovskite in samples without FABr.
4. While Figure 3e,f shows in-situ PL spectra of perovskites during the annealing process, the data is limited to a duration of 15 s. It would be beneficial to analyze how the spectra evolve with extended annealing times.
5. I suggest the authors add more experimental details, such as the annealing temperature of the (FA/Cs/Rb)(Pb/Sr)Br3 perovskite.
6. The 'mud bank-like' areas should be highlighted in Extended Data Fig. 3.

7. The author mentioned that the competitive crystallization process of the multiple A-site perovskite phases can lead to the formation of defects, could the author show the distribution of the A-site of the sample with SrBr2?
8. The author mentioned that the strategy can work in the deep blue regions, the performance of the sample without SrBr2 in the deep blue region should be provided.

Reviewer #3

(Remarks to the Author)
The authors describe a method for achieving high EQE perovskite LEDs using a 3D perovskite crystal structure. Since 3D perovskites with high efficiency are generally difficult to achieve (compared with quasi-2D or quantum dot), this is a significant breakthrough in the field of perovskite LEDs and will find a ready audience. The main conclusions about alloying and crystallization are believable and mostly well supported. However, while I feel this work is certainly impactful enough for Nature Communications, several issues must be addressed before it can be published.

1. Is the material truly a 3D crystal? I cannot find the UV-vis in the figures and the PL can be similar in spectrum and lifetimes, especially if the crystallites are small. The authors use in situ solution-based halide exchange to alloy Cl into the crystal structure but the counter ions (especially phenylbutylammonium) could, conceivably intercalate into the crystallites and cause the crystal to change to a quasi-2D structure.

2. Line 146: The authors describe the “chemical interaction” between SrBr2 and CsBr as being “stronger”, but this description is very vague. What precisely is meant here? Sr2+ and Cs+ are likely ions in solution during crystallization and are ions in an ionic solid after crystallizing. Since the binding energy is measured in the solid, the XPS data is measuring properties of Sr2+ in the perovskite lattice. Some more extensive explanation of their interpretation of the XPS is warranted. Although it is clear the 3d orbital energy is lower (more negative) in Cs than FA perovskites (by their measurement), there are a few possible reasons for these changes and not all of them are because the crystal itself is more tightly bound (and thus resistant to FA infiltration during crystallization, as the authors assert). In any case the authors should explain since this is a critical link in the paper. If the ionic bonds between the ions in the crystal are indeed “stronger” then is this observable as changes in bond distance in the XRD as well?

3. Line 77: some explanation of what cathodoluminescence is capable of observing is probably warranted since this technique is not ubiquitous among LED papers. This will bolster the conclusion on Line 81. A longer explanation of the experiment (including parameters such as beam current) and complete data should be added to the SI.
In mixed halide films, it is common to see ion migration affect the electroluminescence spectrum over time. Was this observed in the films here and what was the difference between the Pb and Pb/Sr films? If it was not observed, why not?

4. Lifetime is a critical aspect of blue LEDs so some lifetime data should be provided. It is not necessary for this to beat all other reports, at this stage of research, but the impact of the EQE is somewhat lessened if the lifetime is very short (e.g. minutes). Additionally, the device lifetimes might bolster the author’s argument that stability is improved by adding alloying/doping with Sr.
The results show very high EQE at 487 nm (sky-blue) but much lower EQE at true blue <470 nm (sometimes called deep blue). What is the reason for this drop-off if the trap density is still very low?
How does the EQE at Rec. 2020 blue (~463 nm here) compare with nanocrystal and quasi-2D blue perovskite LEDs, and what does this say about the future prospects for 3D perovskite LEDs? Some commentary in the conclusions section is appropriate.

5. How does the charge mobility change in these devices with Sr doping?

6. Some additional comparison to literature is needed in this work. Sr doped Pb perovskites have been used previously to make LEDs, although the results are not nearly as good. Similarly, the list of high EQE and high luminescence LEDs in the supplementary information is not entirely complete. Doping with Mn and Zn have also been reported to improve PLQY, EQE, ion migration etc. Why do these not work as well here?

7. This is a Nature journal, so the methods used to measure luminance, EQE, luminous efficacy including the type of setup, the equipment used and any equations must all be stated in the supplemental information. Since the EQE values are the main feature of these devices, it is imperative to establish they were measured accurately and this is a standard feature of LED papers in this field.

Minor issues:
Line 35: “…considered as promising…” should be “…considered to be promising…”
Line 46: what is complex about A-site cations like Cs and Rb? They are very simple.
Line 64: what is the effect, even if minor this sentence implies it is not zero. Perhaps the authors meant “minimal effect” meaning effectively none?
Line 92: although it is somewhat implied, I think it is the most efficient blue LED “to date” or “reported thus far”. Without that phrase at the end it could be misinterpreted as being the most possible. It is likely that the future will bring even more efficient LEDs.
Line 96: "phenylbutanammonium" is probably meant to be "phenylbutylammonium".
Line 100: There ought to be a space between “Rec.” and “2020”, I believe. The authors should state the Rec. 2020 coordinates for blue e.g. the (x,y) values required. Some sources state that the x-value should be 0.131 (or lower) so the

source used for comparison here should be referenced.
Line 129: I think “a slower, stepwise crystallization” is more fashionable phrasing.
Line 186: The authors names should have a space between the first and last name. Usually using initials is fine in contributions; it’s unclear how a human could make this error so I suggest more robust checking of errors in the draft, especially in any part where automation (find/replace or citation apps etc.) has been used (e.g. the references).

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have adequately addressed the reviewers' comments, and the quality of the manuscript has been highly improved. It is now recommended for publication as is.

Reviewer #2

(Remarks to the Author)
After carefully review the response from the authors, I believe they have answered all the questions raised by the reviewers. Thus, I suggest the manuscript can be accepted.

Reviewer #3

(Remarks to the Author)
The authors describe a method of producing high EQE perovskite LEDs using Sr doping in order to induce superior ordering of crystallite grains for better charge transport and recombination. The Sr treatment also improves the stability and lifetime. This work is interesting and of high impact. Having previously reviewed the work, I now believe it is ready for publication. The authors have addressed all the questions from reviewers, in my opinion, and performed additional calculations to prove their points. I believe this manuscript is ready for publication at this time.

Point-by-Point Response to Referees

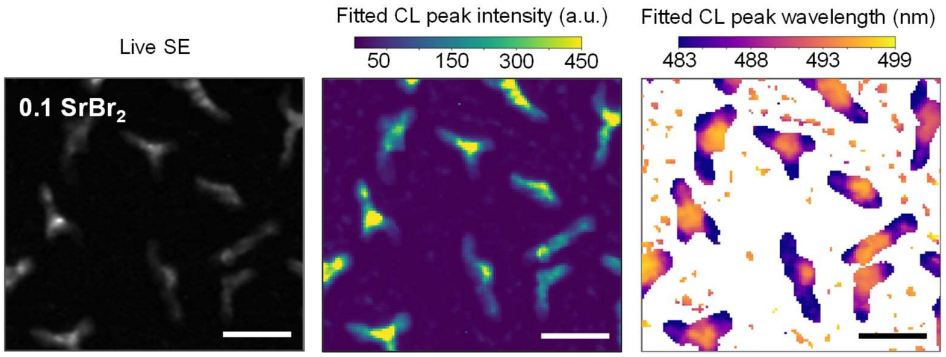
Reviewer #1:

Comment #1: The fast and disordered crystallization of multicomponent perovskites has limited the efficiency of blue perovskite LEDs. Chen et al. developed a novel all-site alloy method to control the growth process of multiple-component perovskite films. Based on this approach, they achieved low-trap density blue perovskite films and high-efficiency perovskite LEDs. This work is important for the fabrication of high-performance blue perovskite LEDs. I recommend it for publication after the following concerns have been fully addressed.

***Response*:** We thank the reviewer for recognizing the importance of our work and for the helpful comments.

Comment #2: The authors demonstrate that the interaction between $SrBr_2$ and CsBr can impede the initial growth of FA/Cs alloyed perovskite, leading to the growth of FA-rich perovskite followed by gradual Cs^+ migration. Could the authors comment on whether this interaction can hinder the phase homogenization of FA-based and Cs-based perovskites.

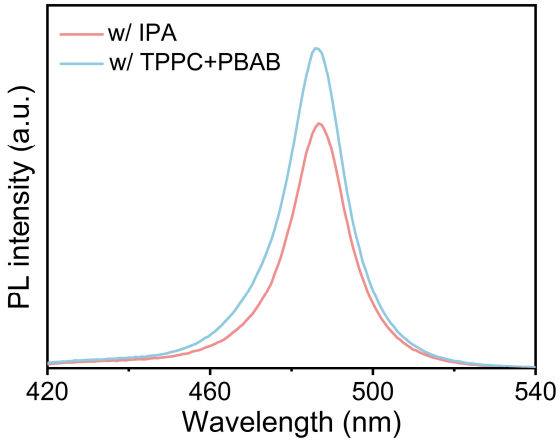
***Response*:** We thank the reviewer for this insightful suggestion. Our CL measurements indicate that the inclusion of 0.05 $SrBr_2$ can enhance the emission uniformity of the perovskite grains by facilitating a slow, stepwise crystallization process (Fig. 2). However, when the $SrBr_2$ ratio is further increased to 0.1, the perovskite grains exhibit heterogeneous emissions, wherein the perovskite grain edges exhibit a blue-shifted emission peak compared to the grain centers (Extended Data Fig. 8g). This observation can be attributed to the higher Sr^{2+} ratio, which impedes the migration of Cs^+ into the FA-rich perovskite framework. We have added this in the revised manuscript (Extended Data Fig. 8g and Line 184 and 188, Page 7).



Extended Data Fig. 8 g, Cathodoluminescence characterizations of perovskite film with a 0.1 ratio of $SrBr_2$. Scale bar, 700 nm.

Comment #3: In order to shift the emission of perovskite LEDs to the deep-blue region, the authors used an IPA solution for post-treating perovskite films. Typically, IPA solvent may induce degradation of perovskite films. Have the authors observed any deterioration of perovskite films when using the IPA solution for treatment?

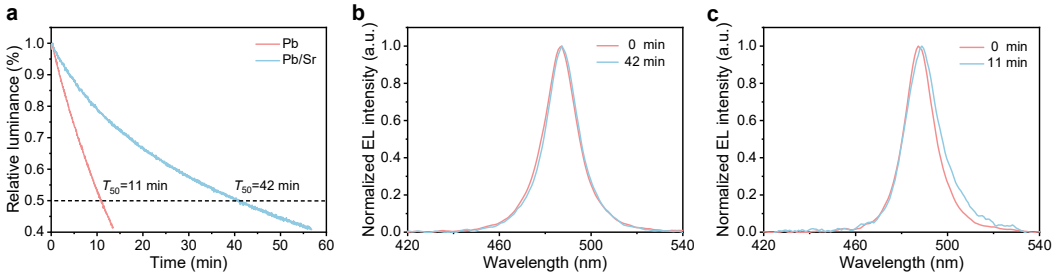
***Response*:** We thank the reviewer for this comment. We agree that the IPA solvent can induce damage to blue perovskite films. However, our previous work has demonstrated that the TPP^+ and PBA^+ in the post-treatment solution can effectively mitigate defects in the perovskite films (Adv. Mater. 35, 2207111 (2023)). Additionally, the below figure shows that post-treating the perovskite film with TPPC and PBAB in IPA solution can enhance the PL intensity compared to the sample treated with IPA, which can be attributed to the passivation effect of TPP^+ and PBA^+.



PL spectra of perovskite films treated by IPA or TPPC+PBAB in IPA.

Comment #4: The B-site Sr^{2+} doping strategy has significantly improved the efficiency of blue perovskite LEDs. Typically, this method should also enhance device stability. Have the authors measured the stability of devices prepared with Sr^{2+} doping?

***Response*:** We thank the reviewer for this valuable suggestion. The Pb/Sr perovskite LED reaches a longer half-lifetime of 42 min compared to the 11 min of the Pb perovskite device (Extended Data Fig. 2a). Moreover, the Pb/Sr perovskite LED exhibits better color stability, as evidenced by the consistent shapes of the EL spectra after aging (Extended Data Fig. 2b,c). We have added this in the revised manuscript (Extended Data Fig. 2, Line 99 to 104, Page 5, highlighted).



Extended Data Fig. 2 Stability characterization of Pb and Pb/Sr perovskite LEDs. a, Stability data of blue devices measured at an initial luminance of 50 cd m^{-2} (near the peak EQE position). **b,c**, EL spectra of blue Pb/Sr device (**b**) and Pb device (**c**) during stability measurement. The Pb/Sr perovskite LED remains unchanged EL spectra after aging for 42 min, while the Pb perovskite LED exhibits a significant red-shifted and broadening spectrum after aging for 11 min.

Comment #5: A recently published paper has achieved a high EQE of 23.6% for blue quasi-2D perovskite LEDs (Nature Communications, 2024, 15, 10621). It would be beneficial to include this work in Extended Data Table 1.

***Response*:** We thank the reviewer for this comment. We have updated the latest work in the Extended Data Table 1.

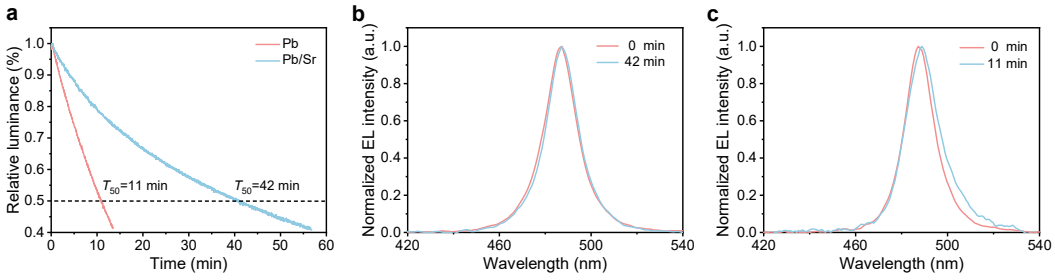
Reviewer #2:

Comment #1: In this manuscript, the authors present an innovative all-site alloy strategy to achieve efficient and bright blue perovskite LEDs. This approach effectively controls the growth of A- and X-site alloyed perovskites, leading to a significant reduction in trap density in 3D blue perovskite materials. The devices demonstrate an impressive EQE of 23.3% and a luminance of 5,700 cd m^{-2}, representing the highest efficiency of blue perovskite LEDs with a luminance exceeding 5,000 cd m^{-2}. The utilization of the all-site alloy method for growing high-quality multicomponent perovskite films holds significant promise for the advancement of perovskite optoelectronics. The manuscript could be considered if the following issues are addressed.

***Response*:** We thank the reviewer for recognizing the importance of our work and for the constructive comments.

Comment #2: As reducing trap density is expected to enhance the stability of perovskite LEDs, I suggest the authors include the results of stability measurement for samples with and without $SrBr_2$.

***Response*:** We thank the reviewer for this valuable suggestion. The Pb/Sr perovskite LED reaches a longer half-lifetime of 42 min compared to the 11 min of the Pb perovskite device (Extended Data Fig. 2a). Moreover, the Pb/Sr perovskite LED exhibits better color stability, as evidenced by the consistent shapes of the EL spectra after aging (Extended Data Fig. 2b,c). We have added this in the revised manuscript (Extended Data Fig. 2, Line 99 to 104, Page 5, highlighted).

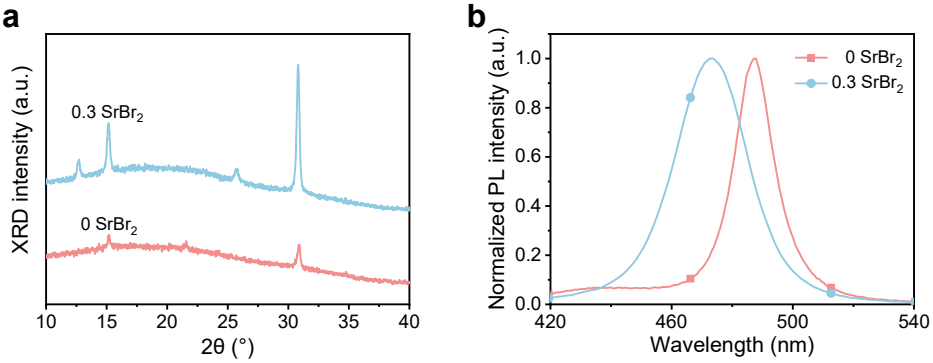


Extended Data Fig. 2 Stability characterization of Pb and Pb/Sr perovskite LEDs. a, Stability data of blue devices measured at an initial luminance of 50 cd m^{-2} (near the peak EQE position).

b,c, EL spectra of blue Pb/Sr device (**b**) and Pb device (**c**) during stability measurement. The Pb/Sr perovskite LED remains unchanged EL spectra after aging for 42 min, while the Pb perovskite LED exhibits a significant red-shifted and broadening spectrum after aging for 11 min.

Comment #3: The authors have demonstrated that the incorporation of $SrBr_2$ can significantly improve the performance of perovskite films. It would be insightful to explore whether Sr^{2+} can integrate into the perovskite lattice.

***Response*:** We thank the reviewer for this suggestion. In our optimized device, the molar ratio of Sr:Pb is only 0.05:0.95, making it difficult to directly characterize whether Sr^{2+} can integrate into the lattice. To verify the Sr doping, we increased the ratio of Sr:Pb to 0.3:0.7. XRD data shows that the 0.3 $SrBr_2$ induces two additional diffraction peaks at 12.7° and 25.7°, corresponding to $SrBr_2 \cdot H_2O$ and Pb/Sr perovskites (Adv. Opt. Mater. 8, 2001073 (2020)). Furthermore, the 0.3 $SrBr_2$ perovskite exhibits a blue shift in PL emission, in agreement with the literature (Adv. Opt. Mater. 8, 2001073 (2020)), suggesting the incorporation of Sr^{2+} into the perovskite lattice. Therefore, we conclude that Sr^{2+} can integrate into the perovskite lattice and we have added this in the revised manuscript (Line 67 to 68, Page 4, highlighted).

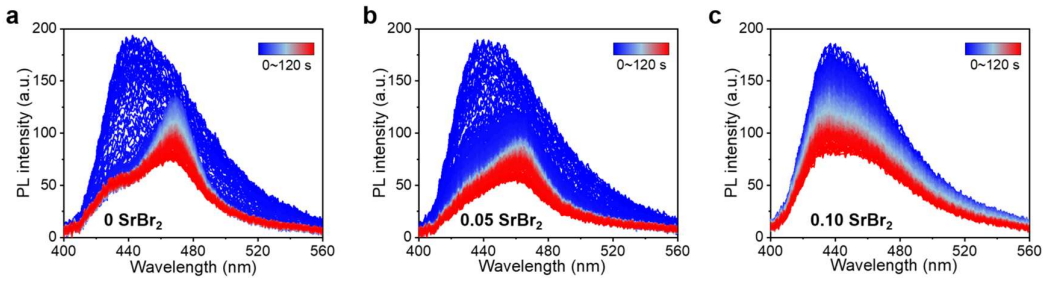


a, XRD patterns of perovskite films. b, Normalized PL spectra of perovskite films.

Comment #4: Since $SrBr_2$ can impede the initial growth of FA/Cs alloyed perovskite due to the chemical interaction between $SrBr_2$ and CsBr, the authors could investigate if $SrBr_2$ directly inhibits the growth of Cs-based perovskite in samples without FABr.

***Response*:** We thank the reviewer for this valuable comment. We compared the in-situ PL spectra of Cs-based samples with various ratios of $SrBr_2$ during the thermal

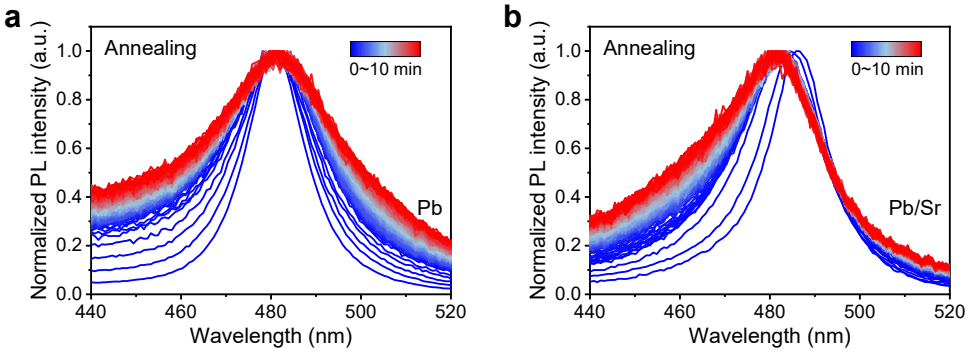
annealing process (see the below figure). It was observed that as the Sr^{2+} doping ratio increased to 0.1, the PL peak at ~468 nm associated with perovskite disappeared during the 120 s annealing process. This result suggests that the chemical interaction between $SrBr_2$ and CsBr can impede the growth of Cs-based perovskite, which is consistent with the results observed in the FA/Cs alloyed perovskite (Fig. 4).



In situ PL spectra of Cs-based perovskites with various ratios of $SrBr_2$ during the thermal annealing process. a, 0 $SrBr_2$. b, 0.05 $SrBr_2$. c, 0.1 $SrBr_2$.

Comment #5: While Figure 3e,f shows in-situ PL spectra of perovskites during the annealing process, the data is limited to a duration of 15 s. It would be beneficial to analyze how the spectra evolve with extended annealing times.

***Response*:** We thank the reviewer for this comment. When further increasing the annealing time, the PL peak wavelengths of both the Pb and Pb/Sr perovskites remain unchanged (see the below figure). We have added this description in the revised manuscript (Line 244 and 246, Page 13, highlighted).



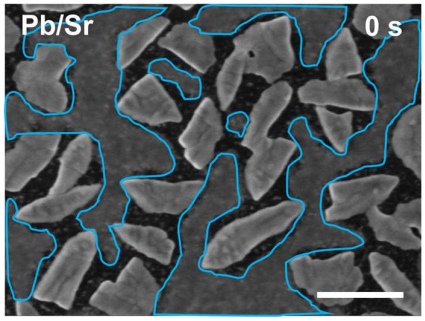
Normalized PL spectra of Pb and Pb/Sr perovskites during the annealing process. a, Pb perovskite. b, Pb/Sr perovskite.

Comment #6: I suggest the authors add more experimental details, such as the annealing temperature of the (FA/Cs/Rb)(Pb/Sr)Br_3 perovskite.

***Response*:** We thank the reviewer for this comment. The (FA/Cs/Rb)(Pb/Sr)Br_3 perovskites were annealed at 90 °C for 10 min. We have added this in the revised manuscript (Line 267 and 268, Page 14, highlighted).

Comment #7: The 'mud bank-like' areas should be highlighted in Extended Data Fig. 3.

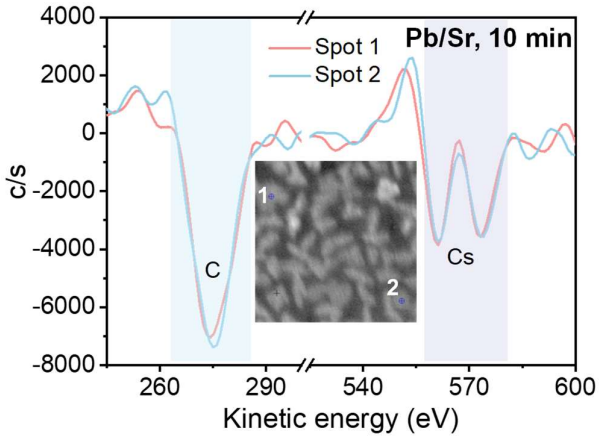
***Response*:** We thank the reviewer for this suggestion. We have highlighted the 'mud bank-like' areas (Extended Data Fig. 5a).



Extended Data Fig. 5 a, SEM image of Pb/Sr perovskite. The 'mud bank-like' areas in the 0 s Pb/Sr perovskite film are circled by blue lines. Scale bar, 500 nm.

Comment #8: The author mentioned that the competitive crystallization process of the multiple A-site perovskite phases can lead to the formation of defects, could the author show the distribution of the A-site of the sample with $SrBr_2$?

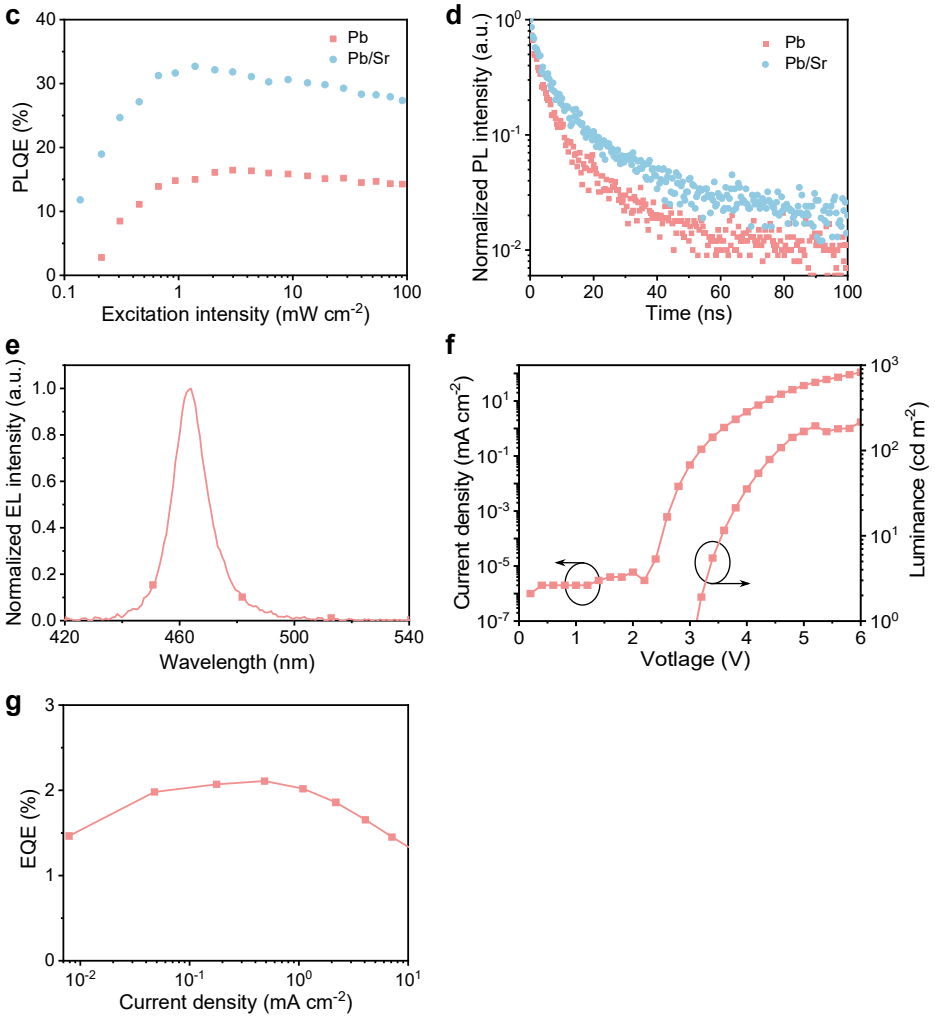
***Response*:** We thank the reviewer for this suggestion. Firstly, based on the CL measurements, we observed that the Pb/Sr perovskite exhibits a narrower distribution of CL peak wavelength compared to the Pb sample (Fig. 2c). Secondly, Auger electron spectroscopy measurement revealed that the grains of the Pb/Sr perovskite annealed for 10 min exhibit similar C and Cs signals. These results suggest a uniform distribution of perovskites. We have added this in the revised manuscript (Extended Data Fig. 5f, Line 149 and 150, Page 6, highlighted).



Extended Data Fig. 5 f, Analysis of C and Cs elements for AES measurements of Pb/Sr perovskite annealed for 10 min. The perovskite grains exhibit similar C and Cs signals, suggesting a uniform distribution of perovskites.

Comment #9: The author mentioned that the strategy can work in the deep blue regions, the performance of the sample without $SrBr_2$ in the deep blue region should be provided.

***Response*:** We thank the reviewer for this important suggestion. We have compared the performance of deep-blue perovskite films and devices with and without $SrBr_2$. Our findings indicate that the deep-blue Pb/Sr perovskite exhibits a higher PLQE and longer PL lifetime compared to the deep-blue Pb perovskite (Extended Data Fig. 3c,d), indicating a lower trap density. Consequently, the deep-blue Pb perovskite LEDs with an EL peak at 464 nm achieve an EQE of 2.1% (Extended Data Fig. 3e-g), which is significantly lower than the 7.5% EQE of the Pb/Sr device (Fig. 3e). We have added these results in the revised manuscript (Extended Data Fig. 3c-g, Line 111 to 113, Page 5, highlighted).



Extended Data Fig. 3 Characteristics of deep-blue (464 nm) perovskite films and LEDs. c, Excitation-intensity-dependent PLQEs. **d**, Transient PL decays of Pb and Pb/Sr perovskites at a carrier density of 1.7×10^{15} cm^{-3}. **e**, EL spectrum of the device without $SrBr_2$. **f**, Current density and luminance versus voltage of the device without $SrBr_2$. **g**, Dependence of the EQE on the current density of the device without $SrBr_2$.

Reviewer #3:

Comment #1: The authors describe a method for achieving high EQE perovskite LEDs using a 3D perovskite crystal structure. Since 3D perovskites with high efficiency are generally difficult to achieve (compared with quasi-2D or quantum dot), this is a significant breakthrough in the field of perovskite LEDs and will find a ready audience. The main conclusions about alloying and crystallization are believable and mostly well supported. However, while I feel this work is certainly impactful enough for Nature Communications, several issues must be addressed before it can be published.

Response: We thank the reviewer for recognizing the importance of our work and very helpful comments.

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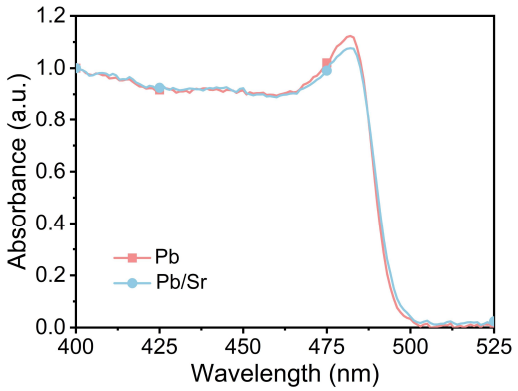
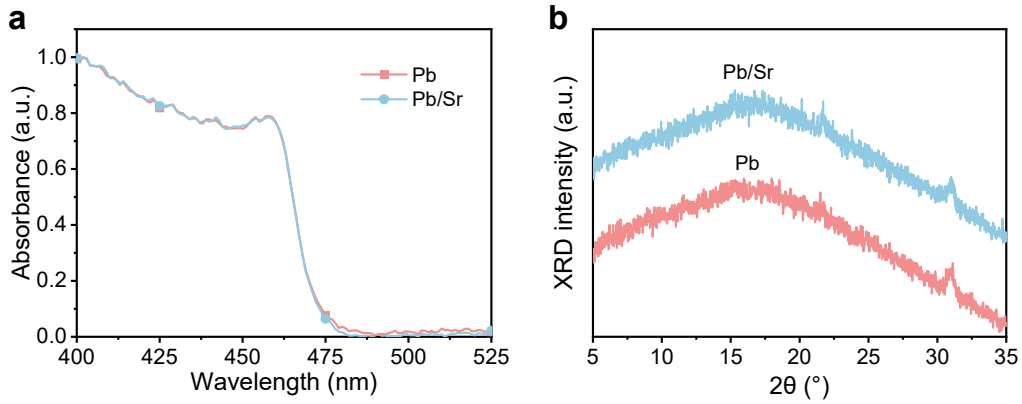
***Response*:** We thank the reviewer for this comment. Figure 1b,c shows that the majority of grains in both the Pb and Pb/Sr perovskites have sizes exceeding 100 nm. Additionally, these films exhibit similar absorption spectra of typical 3D perovskites (Extended Data Fig. 1b). Therefore, we can conclude that the blue perovskites are indeed 3D crystals. Furthermore, the absorption spectra and XRD patterns of the deep-blue perovskites obtained through PBAC ion exchange also show no signals of low-dimensional perovskites (Extended Data Fig. 3a,b). These findings collectively indicate that both our blue and deep-blue perovskites are 3D crystals. We have added these results in the revised manuscript (Extended Data Fig. 1b and Extended Data Fig. 3a,b, Line 63, Page 3, highlighted).



Extended Data Fig. 1 b, Absorption spectra of blue perovskite films.

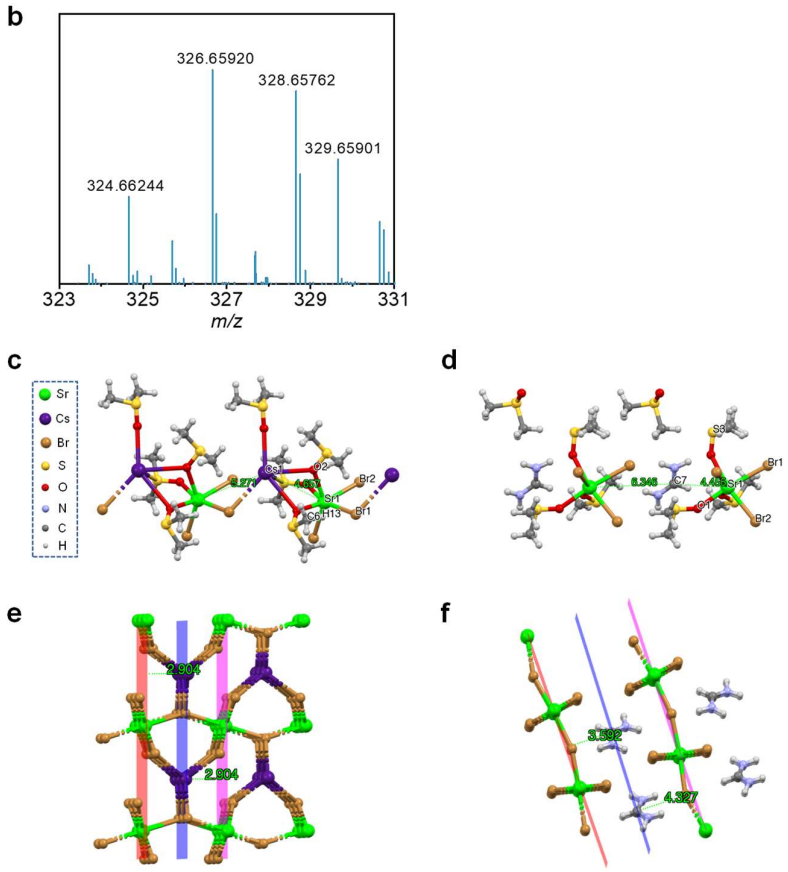


Extended Data Fig. 3 a, Absorption spectrum of deep-blue perovskite film, showing no absorption peaks from low-dimensional perovskites. **b**, XRD patterns of deep-blue perovskite film. There is no diffraction peaks from low-dimensional perovskites, suggesting the deep-blue perovskites are 3D crystals.

Comment #3: Line 146: The authors describe the "chemical interaction" between $SrBr_2$ and CsBr as being "stronger", but this description is very vague. What precisely is meant here? Sr^{2+} and Cs^{+} are likely ions in solution during crystallization and are ions in an ionic solid after crystallizing. Since the binding energy is measured in the solid, the XPS data is measuring properties of Sr^{2+} in the perovskite lattice. Some more extensive explanation of their interpretation of the XPS is warranted. Although it is clear the 3d orbital energy is lower (more negative) in Cs than FA perovskites (by their measurement), there are a few possible reasons for these changes and not all of them are because the crystal itself is more tightly bound (and thus resistant to FA infiltration

during crystallization, as the authors assert). In any case the authors should explain since this is a critical link in the paper. If the ionic bonds between the ions in the crystal are indeed "stronger" then is this observable as changes in bond distance in the XRD as well?

***Response*:** We thank the reviewer for this insightful suggestion. We first performed electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) measurement of $SrBr_2$, which reveals a main peak of $[SrBr_3]^-$ (Extended Data Fig. 7b). Additionally, we conducted first-principles calculations, which indicate that the average distance between Sr^{2+} and Cs^+ ions is 4.964 Å, while the distance between Sr^{2+} and FA^+ ions is 5.401 Å, with DMSO solvent molecules surrounding the cations (Extended Data Fig. 7c,d). This indicates that the interaction between $[SrBr_3]^-$ and Cs^+ is stronger than that between $[SrBr_3]^-$ and FA^+, which is consistent with the solid-state structures (average Cs-Sr distance: 2.904 Å and average FA-Sr distance: 3.960 Å) (Extended Data Fig. 7e,f). We have revised the XPS description and added these results in the revised manuscript (Extended Data Fig. 7b-f, Line 158 to 168, Page 7, highlighted).



Extended Data Fig. 7 b, ESI-TOF-MS spectrum of $SrBr_2$ solution in DMSO. The $SrBr_2$ solution shows typical $[SrBr_3]^-$ peaks. **c,d**, Schematic illustration of interactions between Sr^{2+}-based anions and Cs^+ (**c**) or FA^+ (**d**) cations in the solvent environment with $[SrBr_3]^-$. **e,f**, Schematic illustration of interactions between Sr^{2+}-based anions and Cs^+ (**e**) or FA^+ (**f**) cations in the solid-state structures.

Comment #4: Line 77: some explanation of what cathodoluminescence is capable of observing is probably warranted since this technique is not ubiquitous among LED papers. This will bolster the conclusion on Line 81. A longer explanation of the experiment (including parameters such as beam current) and complete data should be added to the SI.

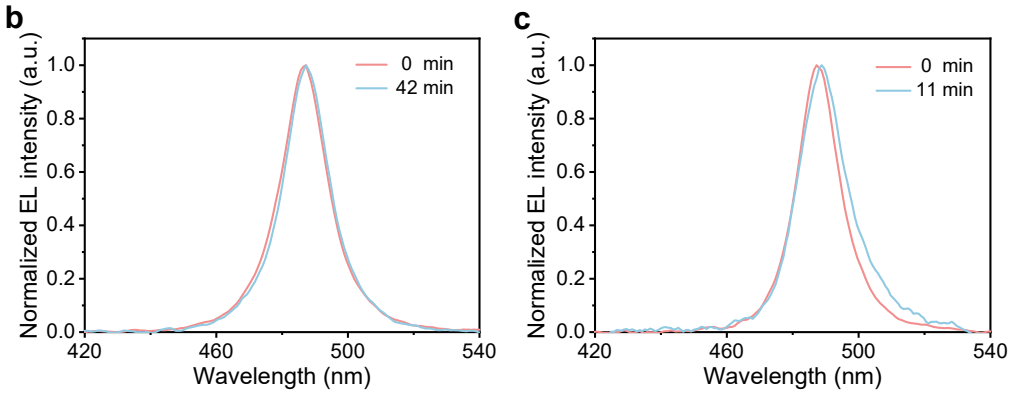
In mixed halide films, it is common to see ion migration affect the electroluminescence spectrum over time. Was this observed in the films here and what was the difference between the Pb and Pb/Sr films? If it was not observed, why not?

***Response*:** We thank the reviewer for this valuable suggestion.

The Cathodoluminescence Scanning Electron Microscope has been considered as a

powerful tool to investigate the local emission behaviour of perovskites, providing high resolution down to several tens of nanometers (Science 349, 1518−1521 (2015); Nat. Electron. 3, 704−710 (2020); Research 2020, 9017871 (2020)). We have added more explanations of CL measurements in the revised manuscript (Line 80 to 82, Page 4 and Line 293 to 298, Page 15, highlighted).

We agree that the ion migration-induced phase segregation of perovskites can affect the EL spectra stability of LEDs. In our work, the Pb/Sr perovskite device exhibits a significant improvement in the spectral stability of the device during stability measurements (Extended Data Fig. 2b,c). This enhanced color stability can be attributed to the reduced trap density in the Pb/Sr perovskite film, which can mitigate ion migration (Nano Lett. 24, 16443−16449 (2024)). We have added this in the revised manuscript (Extended Data Fig. 2b,c, Line 101 to 104, Page 5, highlighted).



Extended Data Fig. 2 b,c, EL spectra of blue Pb/Sr device (**b**) and Pb device (**c**) during stability measurement. The Pb/Sr perovskite LED remains unchanged EL spectra after aging for 42 min, while the Pb perovskite LED exhibits a significant red-shifted and broadening spectrum after aging for 11 min.

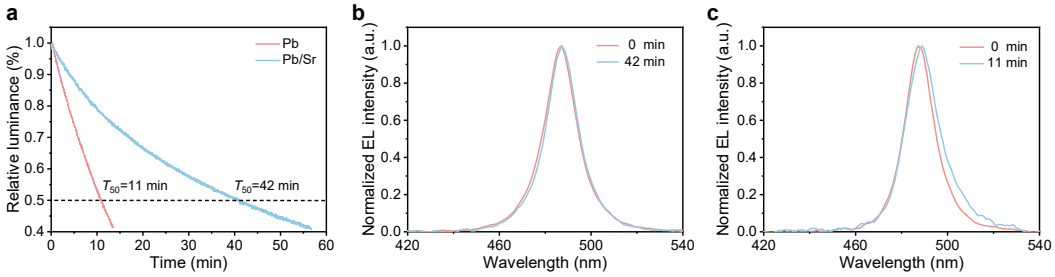
Comment #5: Lifetime is a critical aspect of blue LEDs so some lifetime data should be provided. It is not necessary for this to beat all other reports, at this stage of research, but the impact of the EQE is somewhat lessened if the lifetime is very short (e.g. minutes). Additionally, the device lifetimes might bolster the author's argument that stability is improved by adding alloying/doping with Sr.

The results show very high EQE at 487 nm (sky-blue) but much lower EQE at true blue <470 nm (sometimes called deep blue). What is the reason for this drop-off if the trap density is still very low?

How does the EQE at Rec. 2020 blue (~463 nm here) compare with nanocrystal and quasi-2D blue perovskite LEDs, and what does this say about the future prospects for 3D perovskite LEDs? Some commentary in the conclusions section is appropriate.

***Response*:** We thank the reviewer for these insightful suggestions.

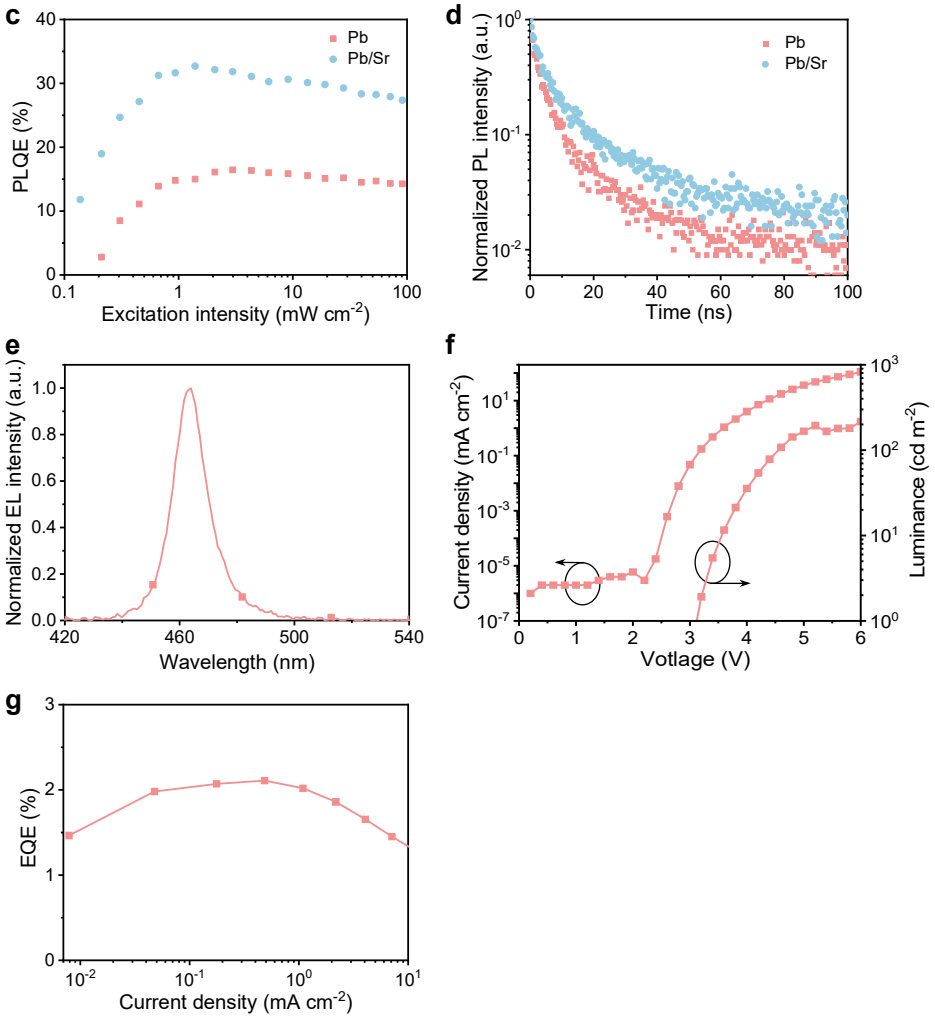
Firstly, the Pb/Sr perovskite LED reaches a longer half-lifetime of 42 min compared to the 11 min of the Pb perovskite device (Extended Data Fig. 2a). Moreover, as shown in the response to comment #4, the Pb/Sr perovskite LED exhibits better color stability, as evidenced by the consistent shapes of the EL spectra after aging (Extended Data Fig. 2b,c). We have added this in the revised manuscript (Extended Data Fig. 2, Line 99 to 104, Page 5, highlighted).



Extended Data Fig. 2 Stability characterization of Pb and Pb/Sr perovskite LEDs. a, Stability data of blue devices measured at an initial luminance of 50 cd m^{-2} (near the peak EQE position). **b,c**, EL spectra of blue Pb/Sr device (**b**) and Pb device (**c**) during stability measurement. The Pb/Sr perovskite LED remains unchanged EL spectra after aging for 42 min, while the Pb perovskite LED exhibits a significant red-shifted and broadening spectrum after aging for 11 min.

Secondly, PLQE and transient PL decay measurements indicate that the deep-blue Pb/Sr perovskite exhibits a lower PLQE and shorter PL lifetime than the blue perovskite (Extended Data Fig. 3c,d and Fig. 1d,f), indicating a higher trap density. Therefore, the drop-off in EQE of the deep-blue perovskite LEDs can be attributed to the increased trap density of the deep-blue perovskite compared to the blue perovskite. This increase in trap density is associated with the formation of defects related to the wider bandgap

(Phys. Chem. Chem. Phys., 18, 27143, (2016)). Nonetheless, the deep-blue Pb/Sr perovskite still exhibits a lower trap density compared to the deep-blue Pb perovskite (Extended Data Fig. 3c,d), resulting in a higher EQE of 7.3% compared to the 2.1% of the Pb perovskite device (Extended Data Fig. 3e-g and Fig. 3d,e). This highlights the advantage of the all-site alloy method employed in this work. We have added this result in the revised manuscript (Extended Data Fig. 3 and Line 111 to 113, Page 5, highlighted).

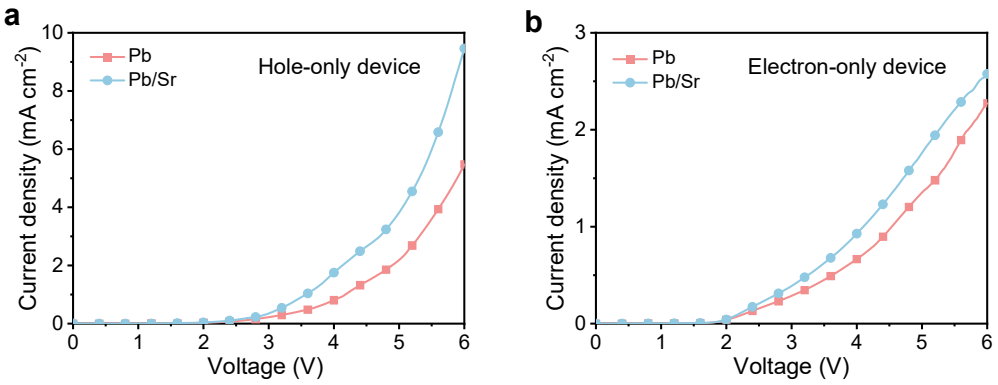


Extended Data Fig. 3 Characteristics of deep-blue (464 nm) perovskite films and LEDs. c, Excitation-intensity-dependent PLQEs. **d**, Transient PL decays of Pb and Pb/Sr perovskites at a carrier density of 1.7×10^{15} cm^{-3}. **e**, EL spectrum of the device without $SrBr_2$. **f**, Current density and luminance versus voltage of the device without $SrBr_2$. **g**, Dependence of the EQE on the current density of the device without $SrBr_2$.

Thirdly, the 464 nm device exhibits higher luminance compared to the nanocrystals and quasi-2D deep-blue perovskite LEDs (Extended Data Table 1), indicating the potential advantages of 3D perovskite LEDs. We have added this discussion in the revised manuscript (Line 197 to 198, Page 8, highlighted).

Comment #6: How does the charge mobility change in these devices with Sr doping?

Response**:** We thank the reviewer for this suggestion. Our films consist of discrete and island like perovskite crystallites with a very thin thickness (~50 nm), making it difficult to directly measure the mobilities. Nevertheless, we can try to compare the current density versus voltage characteristics of single-carrier devices. Hole-only and electron-only devices were fabricated with device structures of ITO/NiO_x/Meo-2PACz/TFB/PVK/perovskite/TAPC/MoO_3/Ag and ITO/ZnO/perovskite/TPBi/LiF/Al, which correspond to the LED structure. It is observed that the inclusion of $SrBr_2$ increases the hole and electron current densities compared to the devices without $SrBr_2$ (see the below figure). This indicates that $SrBr_2$ can slightly increase the motilities of the perovskite, which may be attributed to the reduced defect density.



Comparison of single-carrier devices. a, Current density versus voltage characteristics of hole-only device. b, Current density versus voltage characteristics of electron-only device.

Comment #7: Some additional comparison to literature is needed in this work. Sr doped Pb perovskites have been used previously to make LEDs, although the results are not nearly as good. Similarly, the list of high EQE and high luminescence LEDs in the supplementary information is not entirely complete. Doping with Mn and Zn have also been reported to improve PLQY, EQE, ion migration etc. Why do these not work as

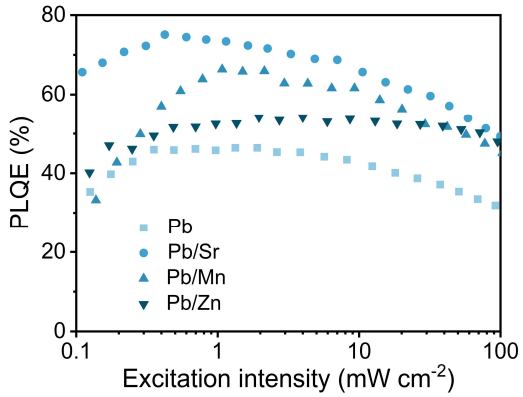
well here?

***Response*:** We thank the reviewer for this comment.

Firstly, we have added discussions about previously published Sr-doped Pb perovskites in the revised manuscript (Line 67 to 68, Page 4, highlighted).

Secondly, we have updated the high EQE and high luminance LED works in the Extended Data Table 1.

Thirdly, we agree that the Mn and Zn doping have enhanced the PLQE and suppressed ion migration in perovskites by stabilizing lattices, improving crystallinity, and reducing trap density, thereby enhancing device EQE. We compared the PLQEs of perovskites with the same $MnBr_2$ and $ZnBr_2$ ratio as $SrBr_2$ (see the below figure). It can be observed that the Mn- and Zn-doped perovskites exhibit enhanced PLQEs compared to the Pb sample. However, these values are lower than the Pb/Sr sample. We attribute the relatively lower PLQEs of the Mn- and Zn-doped perovskites to the lower formation energy of perovskites compared to Sr-doped perovskites (J. Am. Chem. Soc. 139, 11443 (2017)), which can impact the crystallization tuning of FA/Cs-based perovskites. We will further investigate this influencing factor in our future work.



Excitation-intensity-dependent PLQEs of Pb, Pb/Sr, Pb/Mn and Pb/Zn perovskites.

Comment #8: This is a Nature journal, so the methods used to measure luminance, EQE, luminous efficacy including the type of setup, the equipment used and any equations must all be stated in the supplemental information. Since the EQE values are the main feature of these devices, it is imperative to establish they were measured accurately and

this is a standard feature of LED papers in this field.

***Response*:** We thank the reviewer for this suggestion. Our devices were measured by using an integrating sphere method (see the below figure from our previous work for characterization setup, *Nat. Photonics* 10, 699 (2016)). This approach can directly collect all photons by using an integrating sphere and a spectrometer, which can avoid the potentially systematic errors introduced in the photodetector methods (*Nat. Photonics* 13, 818 (2019)).

[FIGURE REDACTED]

Figure from [Nat. Photonics 10, 699 (2016)]. Layout of our LED device characterization setup.

The EQEs were calculated using the following equation,

$$EQE = \frac{N_{\text{photon}}}{N_{\text{electron}}} = \frac{\int \frac{P(\lambda) \times \lambda d\lambda}{h \times c / t}}{I \times t / e} = \frac{e}{J \times S \times c \times h} \int P(\lambda) \times \lambda d\lambda$$

where N_{photon} is the number of the photons emitted from the LED during a time interval t, N_{electron} is the number of the electrons injected into the LED during t, $P(\lambda)$ is the radiant energy of EL for each given wavelength λ during t, h is the Planck constant, c is the speed of light, e is the elementary charge, I is the current injected into the LED during t, S is the area of the surface light source and J is the current density.

We have added more details about measurements in the revised manuscript (Line 273 to 276, Page 14, highlighted).

Comment #9: Minor issues:

Line 35: "…considered as promising…" should be "…considered to be promising…"

Line 46: what is complex about A-site cations like Cs and Rb? They are very simple.

Line 64: what is the effect, even if minor this sentence implies it is not zero. Perhaps the authors meant “minimal effect” meaning effectively none?

Line 92: although it is somewhat implied, I think it is the most efficient blue LED “to date” or “reported thus far”. Without that phrase at the end it could be misinterpreted as being the most possible. It is likely that the future will bring even more efficient LEDs.

Line 96: "phenylbutanammonium" is probably meant to be "phenylbutylammonium".

Line 100: There ought to be a space between “Rec.” and “2020”, I believe. The authors should state the Rec. 2020 coordinates for blue e.g. the (x,y) values required. Some sources state that the x-value should be 0.131 (or lower) so the source used for comparison here should be referenced.

Line 129: I think “a slower, stepwise crystallization” is more fashionable phrasing.

Line 186: The authors names should have a space between the first and last name. Usually using initials is fine in contributions; it’s unclear how a human could make this error so I suggest more robust checking of errors in the draft, especially in any part where automation (find/replace or citation apps etc.) has been used (e.g. the references).

***Response*:** We thank the reviewer for this suggestion. We have corrected all these issues.