Single crystals of mixed Br/Cl and Sn-doped formamidinium lead halide perovskites via inverse temperature crystallization†

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Hybrid organic–inorganic perovskite mixed halides of FAPbBr₃₋ₓClₓ and doped FAPb₁₋ₓSnₓBr₃ were synthesized using a generalized inverse temperature crystallization (ITC) method. With an appropriate choice of solvents and crystallization temperatures we show that large millimeter sized single crystals of these hybrid perovskites can be grown in a matter of hours to days using ITC. The structural and optical properties of these single crystals were characterized systematically. The mixed metal and mixed halide perovskites displayed a compositional bandgap tuneability in the region of 2.05 eV to 2.57 eV. The electrical properties of the perovskite single crystals were determined using a space-charge limited current (SCLC) method. The trap density determined from SCLC was between 10⁹ and 10¹¹ cm⁻³ for all perovskites which is exceptionally low. The mobility was found to increase by one order of magnitude on the addition of only 3% Sn for FAPb₁₋ₓSnₓBr₃ based perovskites which shows promise for enhancing the electrical properties. This demonstrates the generalizability of the ITC method to grow large high-quality perovskite single crystals with enhanced optical and electrical properties. In addition, it was observed for FAPbBr₃₋ₓClₓ based perovskites that initially degraded surfaces with suppressed PL emission could be repaired by using an anti-solvent treatment re-enabling the PL emission. Other perovskite compounds did not display any degraded surfaces and exhibited excellent stability in ambient conditions.

Introduction

In recent years, organic–inorganic halide perovskites (AMX₃) have been the focus of intense research due to their remarkable optical and electrical properties.¹–⁶ Recently, single crystal organic–inorganic halide perovskites have been shown to exhibit significantly longer diffusion lengths, higher mobilities and lower trap densities than polycrystalline thin films.⁷–⁹ These enhanced properties make single crystals attractive for further improving optoelectronic device performance. Typically single crystals have been grown using cooling induced precipitation (CIP),¹⁰,¹¹ seeded solution growth,⁹ or vapour-assisted crystallisation,⁹ however these methods typically take weeks to months to prepare high quality crystalline samples.

Inverse temperature crystallization (ITC) is method which takes advantage of the observed retrograde solubility of perovskites, allowing rapid growth of high-quality, millimetre-sized perovskites in a matter of days.⁷,¹²,¹³ Based on the ITC approach single crystal materials of MAPbX₃ (MA = methylammonium and X = halide),⁷,¹⁵,¹⁴ FAPbX₃ (FA = formamidinium),¹⁵,¹⁶ CsPbBr₃,¹⁷–¹⁹ MAPbBrₓ₋ₓClₓ,²⁰–²² MAPbBrₓ₋ₓIₓ,²¹,²²–²⁶ and heterovalent doped MAPbBr₃,²⁷ and MAPbCl₃,²⁸ have been reported. It has been shown that substitution of MA for FA can lead to improved stability in solar cells²⁹ and enhanced charge transport properties in thin films³⁰,³¹ and single crystals³² compared to their MAPbX₃ counterparts. However, formamidinium based mixed single crystals have yet to be reported. Here we report the successful synthesis of large, millimetre-sized, single crystal perovskites containing mixed halides of FAPbBr₃₋ₓClₓ and doped metals of FAPb₁₋ₓSnₓBr₃ with low trap densities using ITC. The incorporation of both mixed halides and doped metals into the single crystal perovskites permits tuning of the band gap across the visible spectrum and alters its electrical properties. While investigating air stability of these materials, FAPbBr₃₋ₓClₓ based single crystals were found to exhibit a degraded surface species that could be repaired using an anti-solvent treatment (see ESI†).

Experimental

Chemicals and reagents

Lead bromide (PbBr₂, ≥98%), lead chloride (PbCl₂, 98%), N,N-dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, ≥99.9%), tin(II) bromide (SnBr₂) and methylamine solution (33 wt% in absolute ethanol) were...
purchased from Sigma-Aldrich. Methylammonium bromide (MABr) and formamidinium bromide (FABr) were purchased from Dyessol Limited. γ-Butyrolactone (GBL, 99+%) was purchased from Acros Organics. All precursors were used as received without any further purification.

Synthesis

In general solutions were prepared by dissolving AX and MX₂ precursors in a suitable solvent (DMF/DMSO/GBL). After the precursors have dissolved the solution is filtered using a 0.22 μm PTFE hydrophilic filter. 2 mL of the solution is then placed into a glass vial with a 21G needle and heated in oil bath. Further details on specific temperatures, reaction conditions and initial precursor concentrations can be found in the ESI.†

Measurement and characterization

Powder X-ray diffraction was performed on a Panalytical X’Pert Pro diffractometer using a Cu-Kα radiation. The steady state absorption was carried out on a Varian Cary 50 UV–vis spectrophotometer. Photoluminescence emission and decay were carried out on a Horiba Jobin Yvon Fluorolog/Fluorohub setup, a xenon lamp was used as the source for PL emission and absorption was carried out on a Horiba Jobin Yvon Fluorolog/Fluorohub setup, and inert atmosphere to prevent Sn oxidation. Speciﬁc X-ray spectroscopy (EDS) was used to identify the actual composition of the mixed halides and mixed metals present in the single crystals. The elemental compositions are summarised in Table 1. We can see that the nominal Cl inclusion is close to that determined using EDS. This also resembles the observations for MAPbBr₃–ₓClₓ analogues grown using ITC (Table S2, ESI†), where no preferential incorporation of Br or Cl is observed. Single crystals of MAPb₁₋ₓSnₓBr₃ have been recently reported via the TSSG method,22 motivated by this report we also attempted to synthesize mixed Pb/Sn single crystals using ITC. Using DMF–GBL (1 : 1 v/v) as a solvent, perovskites of FAPb₁₋ₓSnₓBr₃ were successfully achieved by substituting an equal molar ratio of PbBr₂ for SnBr₂ and using inert atmosphere to prevent Sn oxidation. Specific reaction conditions can be found in the ESI.† Photographs of the FAPb₁₋ₓSnₓBr₃ perovskites are shown in Fig. 1C. We can see that with increasing Sn inclusion the crystals appear from orange for pure Pb, to dark red for mixed metals (1% and 3% of Sn). The powder XRD spectra are shown in Fig. 1D. The diffraction peaks for FAPb₁₋ₓSnₓBr₃ based perovskites are shifted to slightly higher angles with increasing Sn inclusion resulting in a smaller lattice constant as summarized in Table 1. The actual composition of Sn in the doped metal perovskites are shown in Table 1. We can see that the actual percentage of Sn incorporated into the perovskite is only between 1–3%. This shows a preferential incorporation of Pb relative to Sn in the FAPb₁₋ₓSnₓBr₃ based perovskites, only allowing dopant level...
incorporation of Sn to be achieved using ITC. Similar percent level dopants of Sn are also observed for MA analogues that we synthesized using ITC (Table S2, ESI†), and as such this method appears to be generally less useful than TSSG for preparing mixed metal single crystals.

Optical characterization

The absorption and PL spectra for FAPbBr3-xClx single crystals are shown in Fig. 2A. The absorption edges are blue-shifted with increasing Cl content and show a similar trend to the photographs. The absorption edge for perovskites with different synthesis times also appear blue shifted, suggesting that the observed differences in the photographs of the single crystals are indeed a surface effect which is discussed in more detail in the ESI†. Similar to MAPbBr3-xClx based perovskites the PL emissions are blue-shifted but otherwise show similar trends to the absorption spectra with increasing Cl content (Fig. S7, ESI†). The blue shifted (see ESI† for more detail) PL peak is similar to other perovskite single crystals grown using CIP.† With this in mind, Tauc plots (Fig. S8, ESI†) are used to extract an estimate of the band gaps. The estimated band gaps for mixed Br/Cl single crystals are shown in Fig. 2B. We can see a rough linear trend with increasing Cl content. In general, the FAPbBr3-xClx perovskites show a slight red shift compared to their MAPbBr3-xClx analogues.

UV-vis absorption spectra are shown in Fig. 2A for the tin-doped FAPb1-xSnxBr3 single crystals. We can see that the incorporation of only 1–3% Sn results in a much broader absorption edge which is red-shifted relative to pure FAPbBr3. We observe a similar trend for MA analogues as shown in Fig. 2C. No PL emission was observed for the doped Sn single crystals, ostensibly due to an increased number of trap states (relative to pure FAPbBr3, see Fig. 3) causing non-radiative recombination.

Electrical characterization

The current–voltage (I–V) properties were measured using a sandwich type device (Au/perovskite/Au) structure with two Au (100 nm) electrodes. Under an applied bias the dark current should follow the space charge limited current model (SCLC), which displays three distinct regimes. It should be noted that not all the single crystal perovskite materials exhibited all three distinct regions, as is shown in Fig. 3. Nevertheless the SCLC method has been consistently used to measure single crystal properties in the literature, despite some limitations.† This may be due to

| Samples               | Lattice constant (Å) | Nominal Cl or Sn inclusion (in solution) | Actual Cl or Sn inclusion (via EDS) |
|-----------------------|----------------------|-----------------------------------------|-----------------------------------|
| FAPbBr3               | 6.03                 | —                                       | —                                 |
| FAPbBr2.69Cl0.31a     | 5.99                 | 16.7% [Cl] 10.3% (Cl)                   |                                   |
| FAPbBr2.22Cl0.77a     | 5.90                 | 33.3% [Cl] 25.6% (Cl)                   |                                   |
| FAPbBr1.33Cl1.67b     | 5.86                 | 50.0% [Cl] 55.7% (Cl)                   |                                   |
| FAPb0.99Sn0.01Br3     | 6.02                 | 25.0% [Sn] 1.0% (Sn)                    |                                   |
| FAPb0.97Sn0.03Br3     | 5.98                 | 30.0% [Sn] 3.0% (Sn)                    |                                   |

† Perovskites placed in anti-solvent (dichloromethane) for 4 months to repair the crystal surface. b Perovskites placed in anti-solvent (chloroform) for 1 month to repair the crystal surface.
degradation of the perovskite surfaces upon exposure to humid conditions. The addition of 1–3% Sn in FAPb$_{1-x}$Sn$_x$Br$_3$ has resulted in up to a 2 order of magnitude increase in the conductivity, and this trend is also observed for MAPb$_{1-x}$Sn$_x$Br$_3$ analogues prepared by ITC (Fig. S10, ESI†). In general, the trap density of our single crystal perovskites is between $10^9$–$10^{11}$ cm$^{-3}$ which is significantly lower than their thin film counterparts and comparable to previous reports on perovskite single crystals [Fig. S11 and Table S4, ESI†]. For FAPb$_1$–$_x$Sn$_x$Br$_3$ based perovskites the inclusion of only several percent of Sn has resulted in an increase in trap density by 1 order of magnitude and MAPb$_1$–$_x$Sn$_x$Br$_3$ perovskites also exhibit similar trends (Fig. S10, ESI†). The hole mobilities for FAPbBr$_3$ were found to be 0.12 cm$^2$ V$^{-1}$ s$^{-1}$ which appears to be lower than that determined previously, in part related to the observed degradation at the surface of these FA based perovskites. In the case of FAPbBr$_{1.23}$Cl$_{0.77}$ the mobility is 12 cm$^2$ V$^{-1}$ s$^{-1}$ which is two orders of magnitude higher than pure FAPbBr$_3$. This suggests that Cl inclusion may be a useful approach to enhance the mobility. In the case of FAPb$_{1-x}$Sn$_x$Br$_3$ we find a mobility of 0.22 cm$^2$ V$^{-1}$ s$^{-1}$. This is a moderate increase compared to MA based analogues which exhibits a two order of magnitude increase for 3% Sn inclusion (Fig. S10, ESI†).

### Conclusion

In summary, the ITC method was successfully generalized to synthesize large single crystals of FAPbBr$_3$–Cl and doped FAPb$_{1-x}$Sn$_x$Br$_3$ mixed perovskites with only minor variations in preparation technique. Structural and optical characterizations were carried out to obtain a highly tuneable bandgap for mixed halide and doped metal single crystal perovskite grown using ITC. In addition, FAPbBr$_{1-x}$Cl$_x$ single crystals with degradated surfaces were successfully repaired using a simple anti-solvent treatment, leading to enhanced PL emissions. The conductivity was found to increase with the inclusion of only 1–3% Sn for FAPb$_{1-x}$Sn$_x$Br$_3$ based perovskites, similar to their MA analogues. Overall the trap density for our single crystals perovskites is between $10^9$–$10^{11}$ cm$^{-3}$ which is exceptionally low. The mobility of the mixed halide and doped metal perovskites increased upon both Cl and Sn inclusion, suggesting that Cl and Sn inclusion could lead to an enhancement in the charge transport properties for FA based single crystals. This demonstrates that ITC can be generalized to grow a wide variety of high quality formamidinium perovskite single crystals in a matter of days.

### Conflicts of interest

There are no conflicts to declare.

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### Notes and references

1. G. C. Xing, N. Mathews, S. Y. Sun, S. S. Lim, Y. M. Lam, M. Gratzel, S. Mhaisalkar and T. C. Sum, *Science*, 2013, **342**, 344–347.
2. S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith, *Science*, 2013, **342**, 341–344.
3. Q. F. Dong, Y. J. Fang, Y. C. Shao, P. Mulligan, J. Qiu, L. Cao and J. S. Huang, *Science*, 2015, **347**, 967–970.
4. C. C. Stoumpos, C. D. Malliakas and M. G. Kanatzidis, *Inorg. Chem.*, 2013, **52**, 9019–9038.
5. C. S. Ponseca, T. J. Savenije, M. Abdellah, K. B. Zheng, A. Yartsev, T. Pascher, T. Harlang, P. Chabera, T. Pullerits, A. Stepanov, J. P. Wolf and V. Sundstrom, *J. Am. Chem. Soc.*, 2014, **136**, 5189–5192.
6. S. De Wolf, J. Holovský, S. J. Moon, P. Loper, B. Niesen, M. Ledinsky, F. J. Haug, J. H. Yum and C. Ballif, *J. Phys. Chem. Lett.*, 2014, **5**, 1035–1039.
7. M. I. Saidaminov, A. L. Abdelhady, B. Murali, E. Alarousu, V. M. Burlakov, W. Peng, I. Dursun, L. F. Wang, Y. He, G. Maculan, A. Goriely, T. Wu, O. F. Mohammed and O. M. Bakr, *Nat. Commun.*, 2015, **6**, 7586.
8. D. Shi, V. Adinolfi, R. Comin, M. J. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent and O. M. Bakr, *Science*, 2015, **347**, 518–522.
9. Y. H. Shao, Z. G. Xiao, C. Bi, Y. B. Yuan and J. S. Huang, *Nat. Commun.*, 2014, **5**, 5784.
10. Y. Y. Dang, Y. Liu, Y. X. Sun, D. S. Yuan, X. L. Liu, W. Q. Lu, G. F. Liu, H. B. Xia and X. T. Tao, *CrystEngComm*, 2015, **17**, 665–670.
11. Y. J. Fang, Q. F. Dong, Y. C. Shao, Y. B. Yuan and J. S. Huang, *Nat. Photonics*, 2015, **9**, 679–686.
12. M. I. Saidaminov, A. L. Abdelhady, G. Maculan and O. M. Bakr, *Chem. Commun.*, 2015, **51**, 17658–17661.
13. G. Maculan, A. D. Sheikh, A. L. Abdelhady, M. I. Saidaminov, M. A. Hague, B. Murali, E. Alarousu, O. F. Mohammed, T. Wu and O. M. Bakr, *J. Phys. Chem. Lett.*, 2015, **6**, 3781–3786.
14. Y. C. Liu, Z. Yang, D. Cui, X. D. Ren, J. K. Sun, X. J. Liu, J. R. Zhang, Q. B. Wei, H. B. Fan, Y. Y. Yu, X. Zhang, C. M. Zhao and S. Z. Liu, *Adv. Mater.*, 2015, **27**, 5162–5183.
15. Q. F. Han, S. H. Bae, P. Y. Sun, Y. T. Hsieh, Y. Yang, Y. S. Rim, H. X. Zhao, Q. Chen, W. Z. Shi, G. Li and Y. Yang, *Adv. Mater.*, 2016, **28**, 2253–2258.
16. A. A. Zhumekevych, M. I. Saidaminov, M. A. Haque, E. Alarousu, S. P. Sarmah, B. Murali, I. Dursun, X. H. Miao, A. L. Abdelhady, T. Wu, O. F. Mohammed and O. M. Bakr, *ACS Energy Lett.*, 2016, **1**, 32–37.
18 Y. Rakita, N. Kedem, S. Gupta, A. Sadhanala, V. Kalchenko, M. L. Bohm, M. Kulbak, R. H. Friend, D. Cahen and G. Hodes, Cryst. Growth Des., 2016, 16, 5717–5725.

19 M. I. Saidaminov, M. A. Haque, J. Almutlaq, S. Sarmah, X. H. Miao, R. Begum, A. A. Zhumekenov, I. Dursun, N. Cho, B. Murali, O. F. Mohammed, T. Wu and O. M. Bakr, Adv. Opt. Mater., 2017, 5, 1600704.

20 T. Y. Zhang, M. J. Yang, E. E. Benson, Z. J. Li, J. van de Lagemaat, J. M. Luther, Y. F. Yan, K. Zhu and Y. X. Zhao, Chem. Commun., 2015, 51, 7820–7823.

21 Y. C. Liu, X. D. Ren, J. Zhang, Z. Yang, D. Yang, F. Y. Yu, J. K. Sun, C. M. Zhao, Z. Yao, B. Wang, Q. B. Wei, F. W. Xiao, H. B. Fan, H. Deng, L. P. Deng and S. Z. Liu, Sci. China: Chem., 2017, 60, 1367–1376.

22 H. T. Wei, D. DeSantis, W. Wei, Y. H. Deng, D. Y. Guo, T. J. Savenije, L. Cao and J. S. Huang, Nat. Mater., 2017, 16, 826–833.

23 W. F. Wang, J. Su, L. Zhang, Y. Lei, D. Wang, D. Lu and Y. Bai, CrystEngComm, 2018, 20, 1635–1643.

24 Y. X. Zhang, Y. C. Liu, Y. J. Li, Z. Yang and S. Z. Liu, J. Mater. Chem. C, 2016, 4, 9172–9178.

25 H. R. Byun, D. Y. Park, H. M. Oh, G. Namkoong and M. S. Jeong, ACS Photonics, 2017, 4, 2813–2820.

26 F. Y. Zhang, B. Yang, X. Mao, R. X. Yang, L. Jiang, Y. J. Li, J. Xiong, Y. Yang, R. X. He, W. Q. Deng and K. L. Han, ACS Appl. Mater. Interfaces, 2017, 9, 14827–14832.

27 A. L. Abdelhady, M. I. Saidaminov, B. Murali, V. Adinolfi, O. Voznyy, K. Katsiev, E. Alarousu, R. Comin, I. Dursun, L. Sinatra, E. H. Sargent, O. F. Mohammed and O. M. Bakr, J. Phys. Chem. Lett., 2016, 7, 295–301.

28 Z. Zhang, L. X. Ren, H. Yan, S. J. Guo, S. H. Wang, M. Wang and K. X. Jin, J. Phys. Chem. C, 2017, 121, 17436–17441.

29 G. E. Eperon, S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz and H. J. Snaith, Energy Environ. Sci., 2014, 7, 982–988.

30 F. C. Hanusch, E. Wiesenmayer, E. Mankel, A. Binek, P. Angloher, C. Fraunhofer, N. Giesbrecht, J. M. Feckl, W. Jaegermann, D. Johrendt, T. Bein and P. Dacampo, J. Phys. Chem. Lett., 2014, 5, 2791–2795.

31 W. Rehman, R. L. Milot, G. E. Eperon, C. Wehrenfennig, J. L. Boland, H. J. Snaith, M. B. Johnston and L. M. Herz, Adv. Mater., 2015, 27, 7938–7944.

32 D. X. Ju, Y. Y. Dang, Z. L. Liu, H. B. Liu, C. C. Chueh, X. S. Li, L. Wang, X. B. Hu, A. K. Y. Jen and X. T. Tao, Chem. Mater., 2018, 30, 1556–1565.

33 A. Rose, Phys. Rev., 1955, 97, 1538–1544.

34 R. H. Bube, J. Appl. Phys., 1962, 33, 1733–1737.

35 H. S. Rao, W. G. Li, B. X. Chen, D. B. Kuang and C. Y. Su, Adv. Mater., 2017, 29, 1602639.

36 B. Wenger, P. K. Nayak, X. M. Wen, S. V. Kesava, N. K. Noel and H. J. Snaith, Nat. Commun., 2017, 5, 590.