

## Solution grown caesium-formamidinium lead halide perovskites for detection of gamma photons

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Hybrid formamidinium (FA) lead halide perovskites (FAPbX<sub>3</sub>, X=I or Br/I) gained considerable popularity due to their excellent performance as photovoltaic and high energy photon-detecting materials [1]. The detection of gamma photons is enabled by high electronic quality of FAPbI<sub>3</sub> single crystals (SCs): low noise level and dark current, high mobility-lifetime product ( $1.8 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1}$ ), and high absorptivity of high-energy photons by Pb and I [1]. The difficulties arise from the phase instability of the desired three-dimensional (3D) FAPbI<sub>3</sub> cubic perovskite phase that undergoes a phase transition to non-perovskite 1D hexagonal lattice. The reason lies in the large size and spatial geometry of FA cation. The Goldschmidt tolerance factor (*GTF*) concept is a useful tool in estimation of the compositionally-dependent stability of 3D perovskites with ABX<sub>3</sub> general formula and idealized cubic lattice.  $GTF = (r_A + r_X) / [\sqrt{2}(r_B + r_X)]$ , where  $r_A$ ,  $r_B$  and  $r_X$  represent the ionic radii of each lattice site constituent (in this case,  $r_{FA^+} = 253 \text{ pm}$ ,  $r_{Pb^{2+}} = 119 \text{ pm}$  and  $r_I = 220 \text{ pm}$ ). Stable cubic perovskites typically exhibit a  $GTF = 0.8-1$  ( $GTF = 0.987$  for cubic FAPbI<sub>3</sub> at room temperature). Decreasing the *GTF* of FAPbI<sub>3</sub> can be obtained by replacing FA<sup>+</sup> cations by smaller Cs<sup>+</sup> ions, and/or by replacing I<sup>-</sup> anions with smaller Br<sup>-</sup> ions, likely leading to higher stability. We will present a facile, inexpensive, solution-phase growth of cm-scale SCs of variable composition Cs<sub>x</sub>FA<sub>1-x</sub>PbI<sub>3-y</sub>Br<sub>y</sub> ( $x=0-0.1$ ,  $y=0-0.6$ ). Comparing to the parent cubic FAPbI<sub>3</sub> compound these SCs show improved phase stability with shelf life (the time before hexagonal phase impurities could be detected) of up to 20 days for quaternary Cs<sub>x</sub>FA<sub>1-x</sub>PbI<sub>3</sub> SCs and of more than 4 months for quinary Cs<sub>x</sub>FA<sub>1-x</sub>PbI<sub>3-y</sub>Br<sub>y</sub> SCs [2]. These SCs possess outstanding electronic quality, represented by a high carrier mobility-lifetime product (up to  $1.2 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1}$ ) and a low dark carrier density allowing the sensitive detection of gamma radiation. With stable operation up to 30 V, these novel SCs have been used in a prototype of a gamma-counting dosimeter.

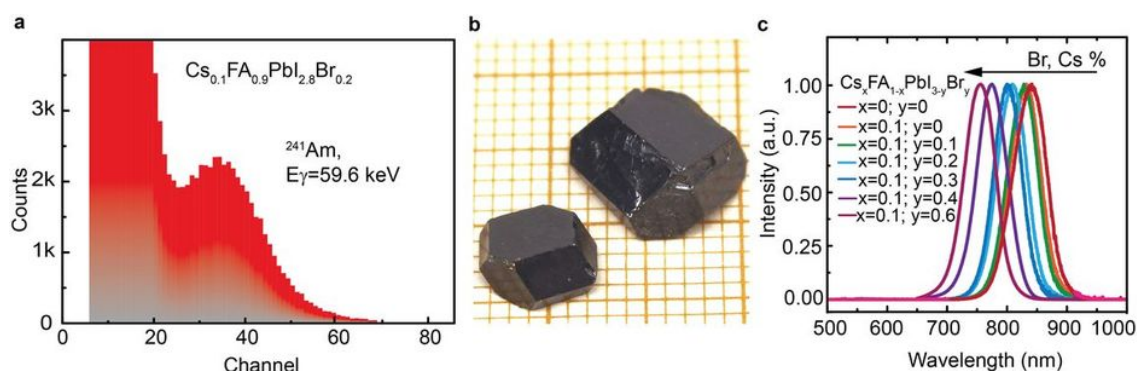


Figure 1. Energy resolved spectrum of an <sup>241</sup>Am source using perovskite SCs; (b) A photograph of typical 0.5-1 cm Cs<sub>x</sub>FA<sub>1-x</sub>PbI<sub>3-y</sub>Br<sub>y</sub> SCs on a millimetre-grid paper; (c) Photoluminescence spectra of ground SCs.

[1] S. Yakunin, D. N. Dirin, Y. Shynkarenko, V. Morad, I. Cherniukh, O. Nazarenko, D. Kreil, T. Nauser, M. V. Kovalenko. Nat. Photon. **2016**, 10 (9), 585-589. [2] O. Nazarenko, S. Yakunin, V. Morad, I. Cherniukh, M. V. Kovalenko. NPG Asia Mater., **2017**, 9, e373.