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

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Hybrid formamidinium (FA) lead halide perovskites ($FAPbX_3$, 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 $FAPbI_3$ single crystals (SCs): low noise level and dark current, high mobility-lifetime product (1.8×10^{-2} cm^2 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) $FAPbI_3$ 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_3 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 pm, $r_{Pb^{2+}}$=119 pm and r_{I^-}=220 pm). Stable cubic perovskites typically exhibit a *GTF*=0.8-1 (*GTF*=0.987 for cubic $FAPbI_3$ at room temperature). Decreasing the *GTF* of $FAPbI_3$ can be obtained by replacing FA^+ cations by smaller Cs^+ ions, and/or by replacing I^- anions with smaller Br^- ions, likely leading to higher stability.

We will present a facile, inexpensive, solution-phase growth of cm-scale SCs of variable composition $Cs_xFA_{1-x}PbI_{3-y}Br_y$ (x=0-0.1, y=0-0.6). Comparing to the parent cubic $FAPbI_3$ 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 $Cs_xFA_{1-x}PbI_3$ SCs and of more than 4 months for quinary $Cs_xFA_{1-x}PbI_{3-y}Br_y$ SCs [2]. These SCs possess outstanding electronic quality, represented by a high carrier mobility-lifetime product (up to $1.2x10^{-1}$ cm^2 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.

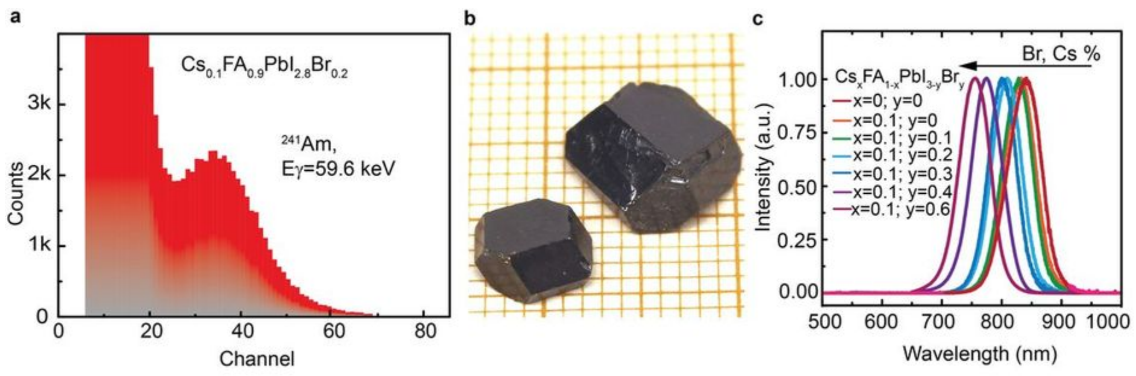

Figure 1. Energy resolved spectrum of an ^{241}Am source using perovskite SCs; (b) A photograph of typical 0.5-1 cm $Cs_xFA_{1-x}PbI_{3-y}Br_y$ SCs on a millimetre-grid paper; (c) Photoluminescence spectra of ground SCs.

[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.