Growth window optimization for large-size quasi two-dimensional Dion-Jacobson type perovskite

Yinghao Fan[a], Hang Yin[b], Xinyi Li[a], Jiafu Yu[a], Yue Hu[c], Yuting Gao[a], Guangda Niu[b]**

[a]Engineering Research Center of Nano-Geomaterials of the Ministry of Education, Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan, 430074, China.
[b]Wuhan National Laboratory for Optoelectronics and School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, China.
[c]School of Chemistry, University of Edinburgh, Kings Buildings, Edinburgh EH9 3FJ, U.K.

*Corresponding Authors: Yuting Gao, Guangda Niu.

Email: gaoyt@cug.edu.cn, guangda_niu@hust.edu.cn.

METHODS

Materials preparation

Lead (II) bromide ($PbBr_2$, 99.5%), hydrobromic acid (HBr, 48 wt%), 3-(aminomethyl)pyridine (3AMPY, 99 wt%), and methylamine bromide (CH_6BrN, 98%) were purchased from Anegi Reagent Co. Ltd (Shanghai, China). All reagents and solvents in this experiment were of reagent grade and could be used without further purification.

Preparation of (3AMPY) (MA) Pb_2Br_7 SCs

To prepare (3AMPY)(MA)Pb_2Br_7 microcrystals, 3 mmol of $PbBr_2$ (1.101 g) was dissolved in 12 mL of HBr solution. Subsequently, 0.5 mmol of 3AMPY (0.0476 g) was added to the solution, resulting in the formation of a light yellow precipitate. After warming the solution and allowing the precipitate to dissolve, 3 mmol (0.2026 g) of methylamine bromide was added. The mixture was then heated with constant stirring on a magnetic stirrer at 120 °C until the precipitate completely dissolved, producing a clarified solution. The (3AMPY)(MA)Pb_2Br_7 microcrystals were obtained by rapidly

cooling this solution. To grow larger (3AMPY)(MA)Pb_2Br_7 single crystals, the saturated solution was transferred to a glass vial and placed in an electrically heated, constant-temperature drying oven at 80 °C and cooled from 80-50 °C at 2 °C per day, Then cooled to room temperature (25 °C) at a rate of 1 °C per day. The ambient temperature was 21 °C, and the humidity was 48%.

Materials characterization

XRD patterns were collected by a Bruker D8 Advance diffractometer in 1° steps. The photoluminescence spectra were tested by a steady-state/transient fluorescence spectrometer (FLS 1000). The absorption spectra were obtained by a UV−vis−NIR spectrophotometer (Shimadzu UV-3600i Plus). SCXRD data at room temperature were collected by using a Bruker D8 Venture diffractometer with Mo Ka radiation (λ =0.77 Å). The crystal structures of (3AMPY)(MA)Pb_2Br_7 were solved by the direct methods and then refined with the full-matrix least-squares technique based on F2 using SHELXLTL software package.

Detector performance measurement

To apply different bias voltages, we utilized the Keithley 6517B Source Meter. For evaluating X-ray detection performance, we employed the Amptek Mini-X2 tube with an Au target (Newton Scientific M237) as the X-ray source. Additionally, we utilised a horizontal displacement stage to move the samples in the X-Y direction. Dose rates were calibrated using accu-diode ionization chambers, including DDX6-W and DDX6-WL (Accu-Gold+, Radcal).

Table S1. Crystal data and structure refinement for (3AMPY)(MA)Pb_2Br_7.

Empirical formula	$C_7H_{16}Br_7N_3Pb_7$
Formula weight	1115.98
Temperature/K	296(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	15.559(2)
b/Å	17.143(2)
c/Å	8.2450(11)
α/°	90
β/°	97.367(3)
γ/°	90
Volume/Å^3	2181.1(5)
Z	4
ρ_{calc} Mg/m^3	3.398
μ/mm^{-1}	28.233
F(000)	1952
Crystal size/mm^3	0.220×0.200×0.180
θ Range for date collection/°	2.376 to 28.355
Index ranges	-20<=h<=18, -22<=k<=22, -11<=l<=10
Reflections collected	34760
Independent reflections	5417 [R(int) = 0.1281]
Date/restraints/parameters	5417 / 1 / 176
Goodness-of-fit on F^2	1.006
Final R indexes [I>=2σ(I)	R1 = 0.0576, wR2 = 0.1051
Final R indexes [all data]	R1 = 0.1489, wR2 = 0.1347
Largest diff. peak/hole/e Å^{-3}	1.951 and -2.747

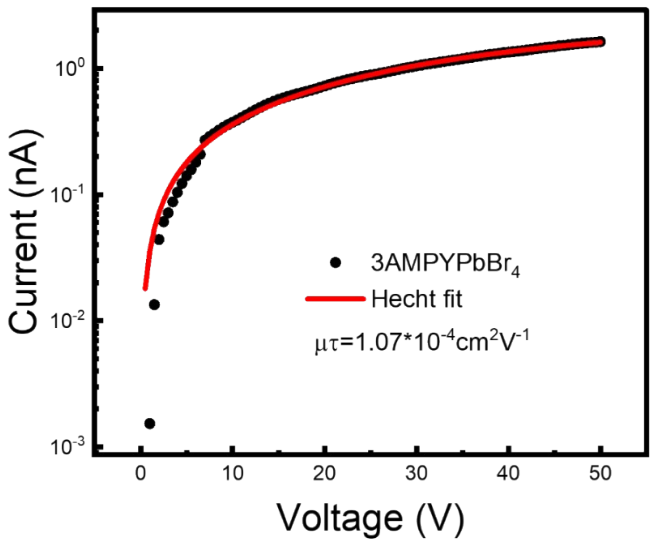

Figure S1. 3AMPYPbBr$_4$ crystal μτ test results.