

## Supporting Information

### Printable Thick Junctions based Lead-Free Perovskite Single Crystal Powders for X-ray Detection

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## 1. Experimental section

**Materials:** Cesium bromide (CsBr, 99.5%), Nickel (II) acetate tetrahydrate ( $\text{NiC}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$ , 99%), hydrobromic acid (HBr, 48%wt), and sucrose octaacetate ( $\text{C}_{28}\text{H}_{38}\text{O}_{19}$ ) were purchased from Aladdin. Bismuth bromide ( $\text{BiBr}_3$ , 99%) was purchased from Alfa Aesar, and silver bromide (AgBr, 99.9%) was purchased from Macklin Biochemical Co., Ltd. Acetonitrile (ACN, 99.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Fullerene- $\text{C}_{70}$  ( $\text{C}_{70}$ , 99.9%) was purchased from Advanced Election Technology Co., Ltd. Bathocuproine (BCP, >99%) was purchased from Xi'an Polymer Light Technology Corp. All the reagents were used directly without purification.

**Crystal growth and preparation of perovskite suspensions:**  $\text{Cs}_2\text{AgBiBr}_6$  crystal was prepared via solution cooling crystallization method. 0.426 g CsBr, 0.449 g  $\text{BiBr}_3$ , 0.188 g AgBr and 13 mL HBr (48%wt) were mixed in an airtight glass bottle and heated at 180°C for 3 h to obtain a light brown clarification solution. The solution was then cooled to room temperature, and the precipitated red crystals were washed three times with ethanol, followed by drying at 50°C for 3 h. After thoroughly grinding the crystals, 0.7966 g  $\text{Cs}_2\text{AgBiBr}_6$  microcrystalline powders were dispersed in 500  $\mu\text{L}$  ACN with different SO concentrations (0  $\text{mg mL}^{-1}$ , 10  $\text{mg mL}^{-1}$ , 30  $\text{mg mL}^{-1}$ , and 50  $\text{mg mL}^{-1}$ ). The slurry was then stirred at 60°C and 1200 rpm for 1 h to get a flowable suspension for blade coating.

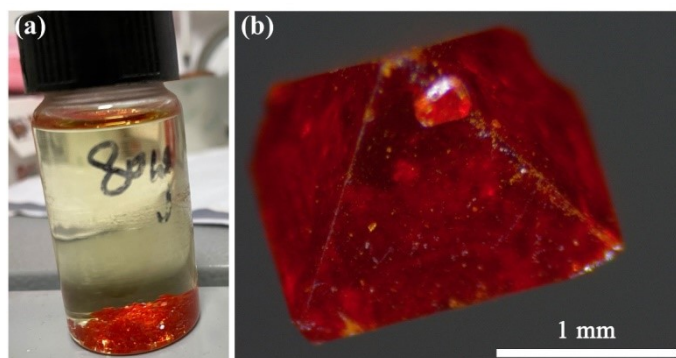
**Device fabrication:** The ITO substrates were brushed with a cleaning solution and cleaned sequentially with ethanol, water, and ethanol in ultrasonic bath for 20 min, respectively. Then, the ITO substrates were treated with UV-ozone for 20 min to remove any chemical residuals and enhance the surface wettability. To prepare the  $\text{NiO}_x$  precursor solution, 49.75 mg nickel (II) acetate tetrahydrate was dissolved with 12  $\mu\text{L}$  2-aminoethanol in 1 mL ethylene glycol monomethyl ether and stirred at 70°C for 2 h. The obtained  $\text{NiO}_x$  solution was spin-coated on the substrate at a speed of 3000 rpm in air for 30 s to form a hole transport layer. Subsequently, the  $\text{NiO}_x$ -coated substrate was pre-annealed on a hot plate at 150°C for 5 minutes and then annealed in

a muffle furnace at 300°C for 60 minutes. Before blade-coating, the ITO substrate was preheated at 60°C, and the perovskite suspension was stirred at 800 rpm for 30 min at 60°C to make the suspension uniformly dispersed. The fluxible suspension was blade coated onto the substrate, and the wet film was then transferred to a 60 °C hot plate to cure for 10 min. Subsequently, the film surface was covered with an equal-sized glass and pressed at 0.6 MPa for 10 min. Finally, the C<sub>70</sub> (70 nm, 0.2 Å s<sup>-1</sup>), BCP (3 nm, 0.1 Å s<sup>-1</sup>), and Cu (130 nm, 0.3 Å s<sup>-1</sup>) were evaporated onto the thick film under 6 × 10<sup>-4</sup> Pa. The effective electrode area was 0.05 cm<sup>2</sup>.

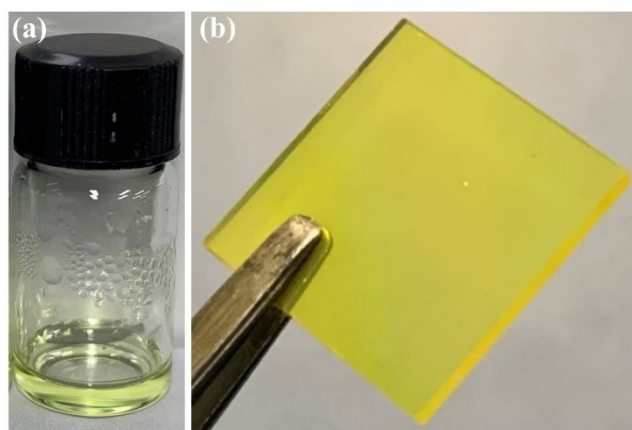
**Material characterization:** X-ray diffraction (XRD) patterns were obtained using a D8 Advance X-ray diffractometer (Cu K $\alpha$  radiation, 1.5418 Å) with a scanning speed of 10 degrees per minute. Steady-state PL spectra were performed using a fiber optic spectrometer (Ideaoptics, NOVA-EX) excited with a 405 nm CW laser. Time-resolved microwave conductivity (TRMC) was performed using a FieldFox Handheld Microwave Analyzer (Keysight, N9915A) microwave source. The samples were pumped with a tunable OPO laser and excited with a wavelength and intensity tunable nanosecond laser. The thickness and roughness of the obtained perovskite films were measured by a step profiler (Alpha-Step D-500, KLA).

**Device performance measurement:**  $I$ - $V$  and  $I$ - $t$  curves of devices under white light illumination were recorded using a semiconductor analyzer (Keysight, B1500A). Noise spectra were calculated from a fast Fourier transform of the dark current. X-ray photons with a peak energy of 35 keV were produced using a commercial tungsten anode X-ray tube (Source-Ray, Inc. SB-80-1K). The accelerating voltage was fixed at 60 kV, the X-ray dose rate was controlled by adding copper sheets and adjusting the tube's input current. The dose rate was carefully calibrated using a standard dosimeter (Suhe Instrument Technology Co. LTD, XH-3525). Detectors were placed in a dark lead chamber to minimize noise from electromagnetic radiation and ambient light.

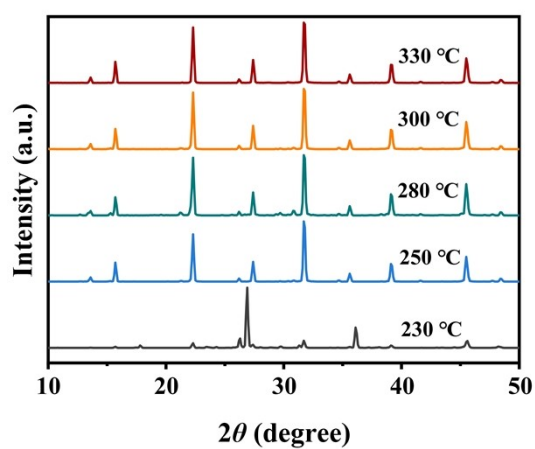
## 2. Supporting figures



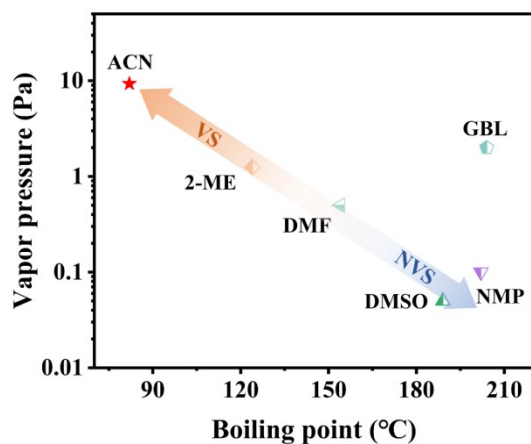
**Fig. S1** (a) Cs<sub>2</sub>AgBiBr<sub>6</sub> single crystals were obtained through solution cooling crystallization. (b) The photograph of Cs<sub>2</sub>AgBiBr<sub>6</sub> single crystal.



**Fig. S2** (a) The precursor solution is formed by dissolving Cs<sub>2</sub>AgBiBr<sub>6</sub> single-crystal powders in DMSO. (b) Cs<sub>2</sub>AgBiBr<sub>6</sub> thin film spin-coated on a glass substrate.



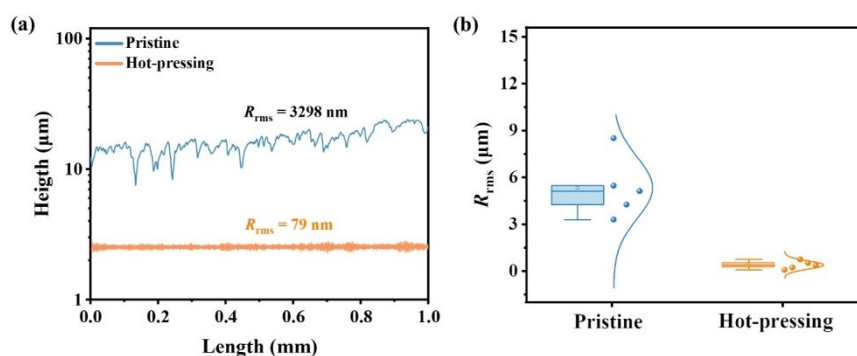
**Fig. S3** XRD spectra of Cs<sub>2</sub>AgBiBr<sub>6</sub> thin films at different annealing temperatures.



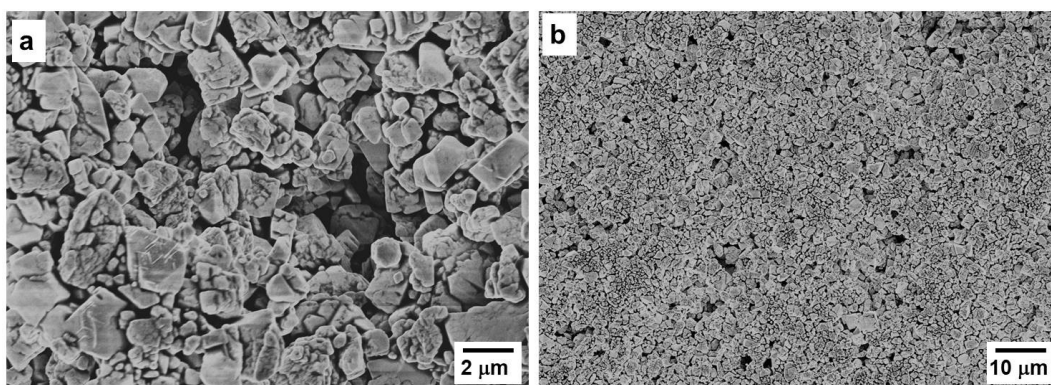
**Fig. S4** Statistics of surface vapor pressure versus boiling point for common volatile and non-volatile solvents (VS and NVS) at room temperature<sup>S1, S2</sup>.



**Fig. S5**  $\text{Cs}_2\text{AgBiBr}_6$  single-crystal powders were dispersed in ACN, yielding a viscous suspension.



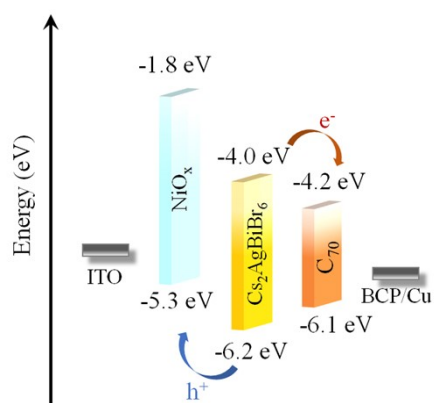
**Fig. S6** (a) Surface roughness scan of the  $\text{Cs}_2\text{AgBiBr}_6$  thick films with and without hot-pressing. (b) Statistical diagram of surface roughness in different regions of the thick films.



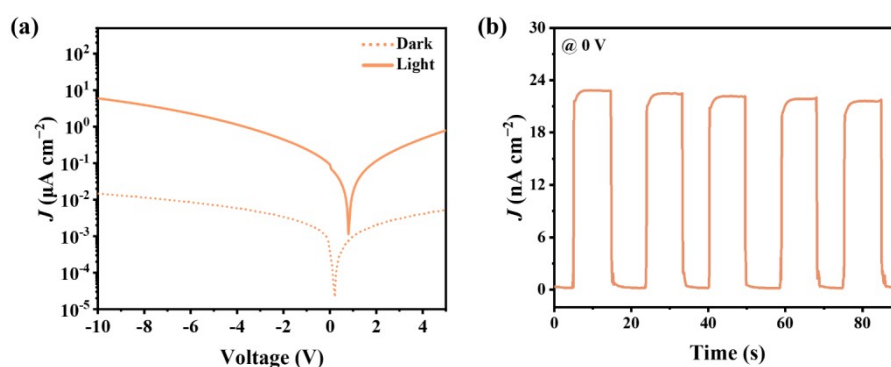
**Fig. S7** Surface SEM images of the  $\text{Cs}_2\text{AgBiBr}_6$  thick films.



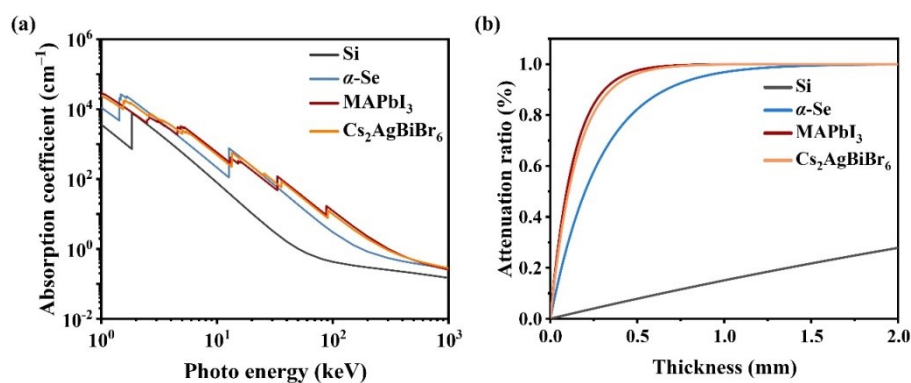
**Fig. S8** The  $\text{Cs}_2\text{AgBiBr}_6$  thick film with  $30 \text{ mg mL}^{-1}$  SO. A 100 g weight is attached to the surface of the film via PI tapes.



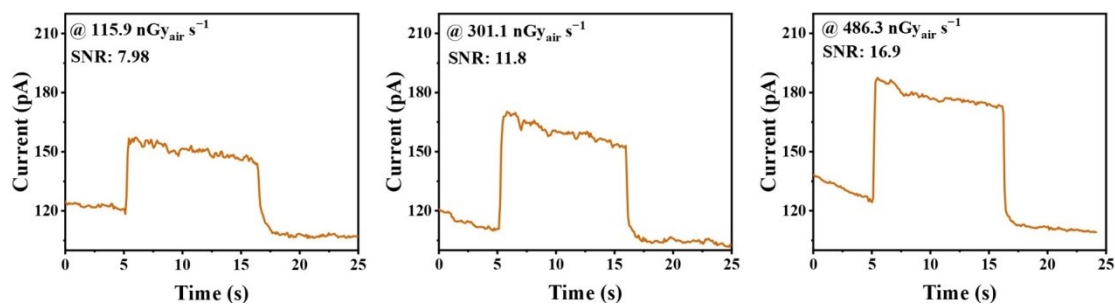
**Fig. S9** Schematic diagram of the device energy level.



**Fig. S10** (a)  $I$ - $V$  curves of the target devices in dark and under white light illumination. (b)  $I$ - $t$  curves of the target device under white light illumination without bias.



**Fig. S11** (a) Calculated attenuation coefficients of Si,  $\alpha$ -Se, MAPbI<sub>3</sub>, and Cs<sub>2</sub>AgBiBr<sub>6</sub>. (b) Attenuation efficiency of the semiconductors to 40 keV X-rays.



**Fig. S12**  $I$ - $t$  curves of the target device at low dose rates.

## References

S1. C. Wu, K. Wang, J. Li, Z. Liang, J. Li, W. Li, L. Zhao, B. Chi and S. Wang, *Matter*, 2021, **4**, 775-793.

S2. S. Sidhik, Y. Wang, M. De Siena, R. Asadpour, A. J. Torma, T. Terlier, K. Ho, W. Li, A. B. Puthirath, X. Shuai, A. Agrawal, B. Traore, M. Jones, R. Giridharagopal, P. M. Ajayan, J. Strzalka, D. S. Ginger, C. Katan, M. A. Alam, J. Even, M. G. Kanatzidis and A. D. Mohite, *Science*, 2022, **377**, 1425-1430.