Supplemental Information

Inch-size Cs₃Bi₂I₉ polycrystalline wafer with near-intrinsic

properties for ultralow-detection-limit X-ray detection

Nuo Bu,^a Shanshan Jia,^a Yingrui Xiao,^a Haojin Li,^a Nan Li,^a Xinmei Liu,^a Zhou Yang,^{a*} Kui Zhao,^{a*} Shengzhong (Frank) Liu^{a,b*}

^a Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education; Shaanxi Key Laboratory for Advanced Energy Devices; Shaanxi Engineering Lab for Advanced Energy Technology; Institute for Advanced Energy Materials; School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710119, China.

^b Dalian National Laboratory for Clean Energy; Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.



Figure S1. Photograph of the $Cs_3Bi_2I_9$ wafer.



Figure S2. (a) and magnified (b) plan-view SEM image of the $Cs_3Bi_2I_9$ wafer.



Figure S3. (a-e) Cross-sectional SEM images of the $Cs_3Bi_2I_9$ wafer with different magnification.



Figure S4. The fitted response current under X-ray illumination to determine the $\mu\tau$ product.



Figure S5. Schematic of the Cs₃Bi₂I₉ polycrystalline-based X-ray detector structure.



Figure S6. (a-e) ON/OFF photocurrent response of $Cs_3Bi_2I_9$ polycrystalline-based X-ray detector at different dose rates (0.97, 1.83, 3.70, 7.33 and 14.60 μ Gy_{air} s⁻¹) and different electric field (5, 10, 20, 30, 40 V mm⁻¹).



Figure S7. (a, b) I-T photocurrent response of the $Cs_3Bi_2I_9$ X-ray detector under 40 V mm⁻¹ electric field and various dose rates.



Figure S8. $Cs_3Bi_2I_9$ X-ray detector operational stability against continuous X-ray irradiation under a dose rate of 42.885 μGy_{air} s⁻¹ with 40 V mm⁻¹ electric field.

Materials	Source	Electric Field	Sensitivity	Detection limit	Ref
			$(\mu C \ Gy_{air}^{-1} \ cm^{-2})$	$(nGy_{air} s^{-1})$	
Cs ₂ AgBiBr ₆ Single	50 kV	/	105	59.7	1
Crystal			(25 V mm ⁻¹)	(2.5 V mm ⁻¹)	
(BA) ₂ CsAgBiBr ₇ Single	70 keV	5 V mm ⁻¹	4.2	/	2
Crystal					
Cs ₃ Bi ₂ I ₉ Single Crystal	40 kV	50 V mm ⁻¹	1652.3	130	3
Cs ₃ Bi ₂ I ₉ Single Crystal	/	/	964	44.6	4
			(120 V mm ⁻¹)	(60 V mm ⁻¹)	
Cs ₃ Bi ₂ I ₉ Single Crystal	80 kV	450 V cm ⁻¹	111.9	/	5
Cs ₃ Bi ₂ Br ₉ Single Crystal	50 kV	/	230.4 (200 V)	/	6
Rb ₃ Bi ₂ I ₉ Single Crystal	50 kV	300 V mm ⁻¹	159.7	8.32	7
MA3Bi2I9 Single Crystal	40 kV	60 V mm ⁻¹	1947	83	8
FA3Bi2I9 Single Crystal	45 kV	/	598.1 (500 V)	200 (180 V)	9
(NH ₄) ₃ Bi ₂ I ₉ Single	50 keV	/	8.2×10^{3}	55	10
Crystal					
(H ₂ MDAP)BiI ₅ Single	70 keV	5 V mm ⁻¹	~1	/	11
Crystal					
(DMEDA)BiI5 Single	50 kV	494 V mm ⁻¹	72.5	/	12
Crystal					
Cs ₂ AgBiBr ₆ Wafer	50 keV	0.5 V mm ⁻¹	250	93.6	13
$Cs_3Bi_2Br_3I_6$	/	/	~2 (200 V)	10700 (50 V)	14
MA ₃ Bi ₂ I ₉ Wafer	45 kV	2100 V cm ⁻¹	563	9.3	15
(F-PEA) ₃ BiI ₆ Wafer	120 kV	100 V mm ⁻¹	118.6	30	16
Ba ₂ AgIO ₆ Wafer	50 keV	5 V mm ⁻¹	18.9	/	17
Cs ₃ Bi ₂ I ₉ Wafer	40 kV	40 V mm ⁻¹	230.46	61.25	This
					work

Table S1. The X-ray detection performance of the lead-free perovskite detectors.

Remarks: kV: tube voltage; keV: energy of electron after acceleration voltage.

Reference

- W. Pan, H. Wu, J. Luo, Z. Deng, C. Ge, C. Chen, X. Jiang, W.-J. Yin, G. Niu, L. Zhu, L. Yin, Y. Zhou, Q. Xie, X. Ke, M. Sui and J. Tang, *Nat. Photonics*, 2017, **11**, 726-732.
- Z. Xu, X. Liu, Y. Li, X. Liu, T. Yang, C. Ji, S. Han, Y. Xu, J. Luo and Z. Sun, Angew. Chem. Int. Ed., 2019, 58, 15757-15761.
- Y. Zhang, Y. Liu, Z. Xu, H. Ye, Z. Yang, J. You, M. Liu, Y. He, M. G. Kanatzidis and S. F. Liu, *Nat. Commun.*, 2020, 11, 1-11.
- S. Wei, S. Tie, K. Shen, T. Zeng, J. Zou, Y. Huang, H. Sun, L. Luo, X. Zhou, A. Ren, X. Zheng, D. Zhao and J. Wu, *Adv/ Opt/ Mater/*, 2021, 9, 2101351.
- Q. Sun, Y. Xu, H. Zhang, B. Xiao, X. Liu, J. Dong, Y. Cheng, B. Zhang, W. Jie and M. G. Kanatzidis, *J. Mater. Chem. A*, 2018, 6, 23388-23395.
- 6. X. Li, X. Du, P. Zhang, Y. Hua, L. Liu, G. Niu, G. Zhang, J. Tang and X. Tao, *Sci. China Mater.*, 2021, **64**, 1427-1436.
- M. Xia, J. H. Yuan, G. Niu, X. Du, L. Yin, W. Pan, J. Luo, Z. Li, H. Zhao, K. H. Xue, X. Miao and J. Tang, *Adv. Func. Mater.*, 2020, **30**, 1910648.
- Y. Liu, Z. Xu, Z. Yang, Y. Zhang, J. Cui, Y. He, H. Ye, K. Zhao, H. Sun, R. Lu, M. Liu, M. G. Kanatzidis and S. F. Liu, *Matter*, 2020, 3, 180-196.
- 9. W. Li, D. Xin, S. Tie, J. Ren, S. Dong, L. Lei, X. Zheng, Y. Zhao and W.-H. Zhang, *J. Phys. Chem. Lett.*, 2021, **12**, 1778-1785.
- 10. R. Zhuang, X. Wang, W. Ma, Y. Wu, X. Chen, L. Tang, H. Zhu, J. Liu, L. Wu, W. Zhou, X. Liu and Y. M. Yang, *Nat. Photonics*, 2019, **13**, 602-608.
- K. Tao, Y. Li, C. Ji, X. Liu, Z. Wu, S. Han, Z. Sun and J. Luo, *Chem. Mater.*, 2019, 31, 5927-5932.
- 12. L. Yao, G. Niu, L. Yin, X. Du, Y. Lin, X. Den, J. Zhang and J. Tang, *J. Mater. Chem. C*, 2020, **8**, 1239-1243.
- B. Yang, W. Pan, H. Wu, G. Niu, J. H. Yuan, K. H. Xue, L. Yin, X. Du, X. S. Miao, X. Yang, Q. Xie and J. Tang, *Nat. Commun.*, 2019, 10, 1989.
- 14. M. Daum, S. Deumel, M. Sytnyk, H. A. Afify, R. Hock, A. Eigen, B. Zhao, M. Halik, A. These and G. J. Matt, *Adv. Func. Mater.*, 2021, **31**, 2102713.
- 15. S. Tie, W. Zhao, D. Xin, M. Zhang, J. Long, Q. Chen, X. Zheng, J. Zhu and W.-H. Zhang, *Adv. Mater.*, 2020, **32**, 2001981.
- 16. M. Li, H. Li, W. Li, B. Li, T. Lu, X. Feng, C. Guo, H. Zhang, H. Wei and B. Yang, *Adv. Mater.*, 2021, 2108020.
- 17. L. Yang, J. Pang, Z. Tan, Q. Xiao, T. Jin, J. Luo, G. Niu and J. Tang, Front. Optoelectron., 2021, 1-9.