

The Reaction Controlled Growth with Formic Acid for High-Quality Cs₃Cu₂I₅ Single Crystal

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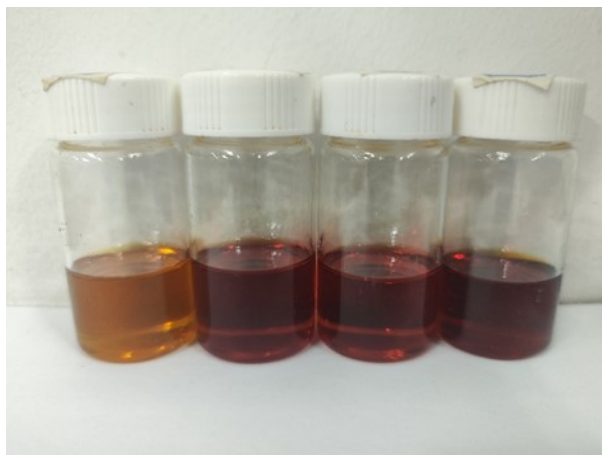


Figure S1. Photographs of precursor solutions with different concentrations of formic acid added (0%, 2.5%, 5%, 10%).

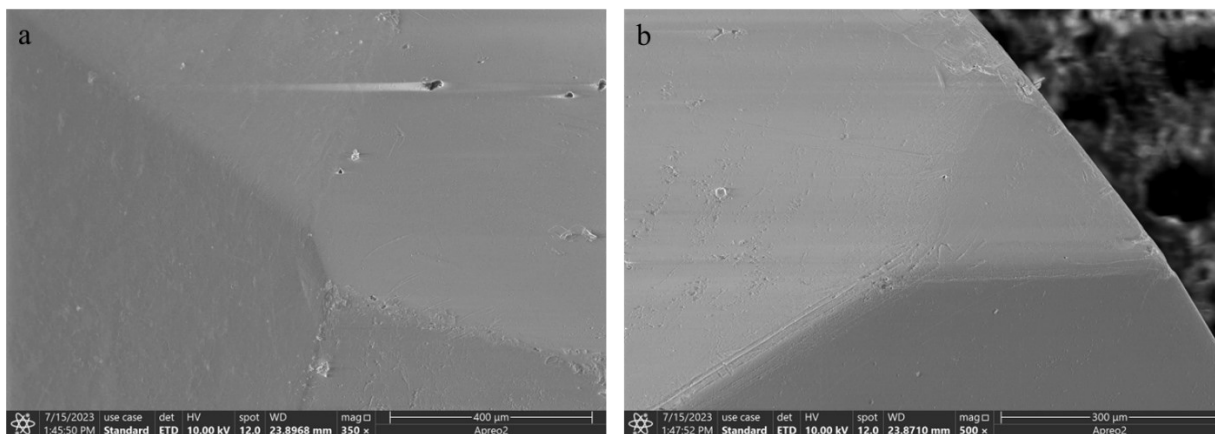


Figure S2. Scanning electron microscopy (SEM) images of Cs₃Cu₂I₅.

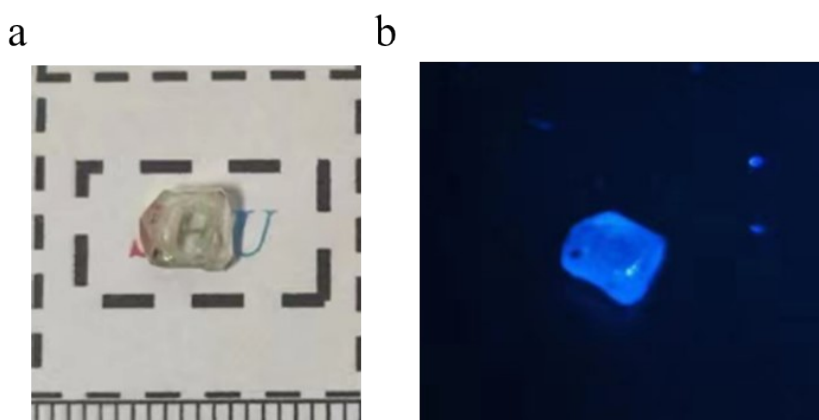


Figure S3. Photographs of the Cs₃Cu₂I₅ single crystal grown without formic acid. a) Under natural light. b) Under 365 nm UV light irradiation.



Figure S4. Photographs of precursor solutions without formic acid after two days.

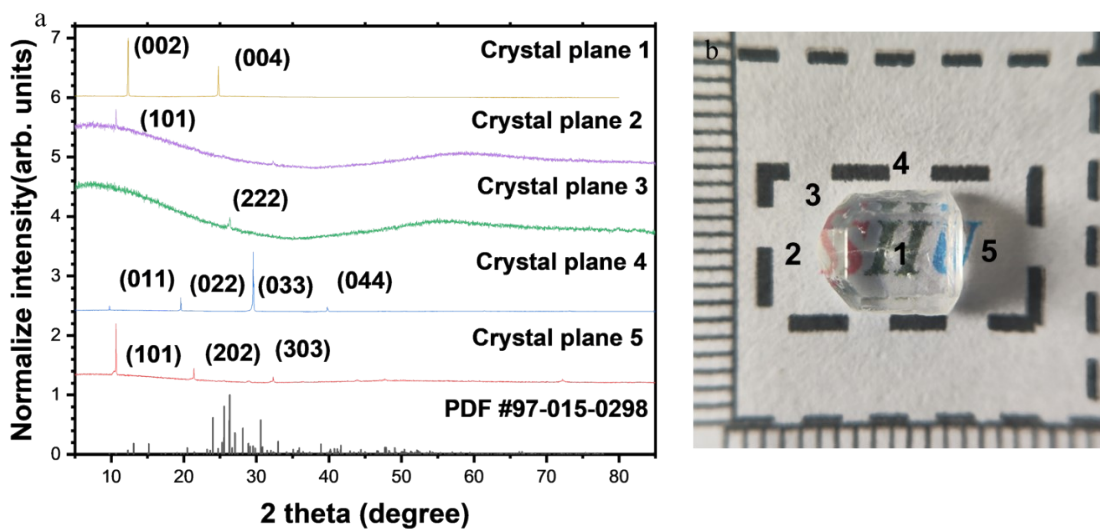


Figure S5. a) X-ray diffraction curve of the $\text{Cs}_3\text{Cu}_2\text{I}_5$ Single crystal with different surface plane. b) Photograph of the $\text{Cs}_3\text{Cu}_2\text{I}_5$ Single crystal.

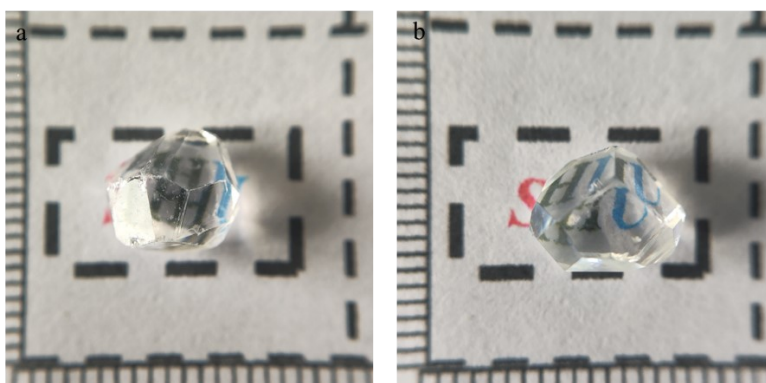


Figure S6. Photographs of the $\text{Cs}_3\text{Cu}_2\text{I}_5$ single crystals.

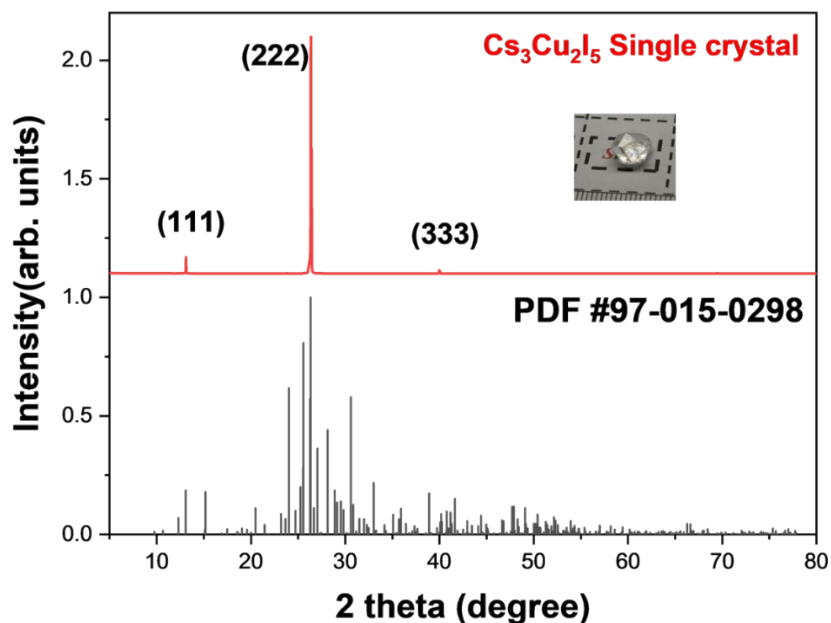


Figure S7. X-ray diffraction curve of a $\text{Cs}_3\text{Cu}_2\text{I}_5$ Single crystal with a (111) surface plane.

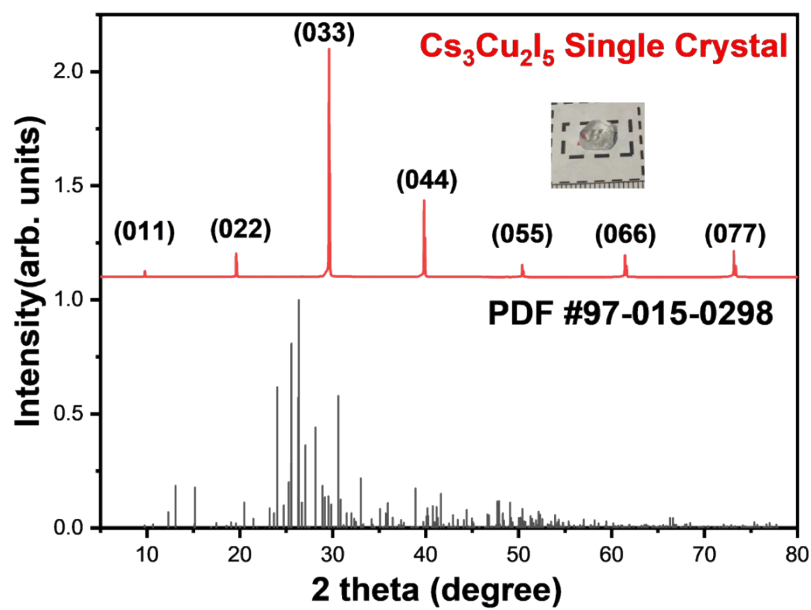


Figure S8. X-ray diffraction curve of a $\text{Cs}_3\text{Cu}_2\text{I}_5$ Single crystal with a (011) surface plane.

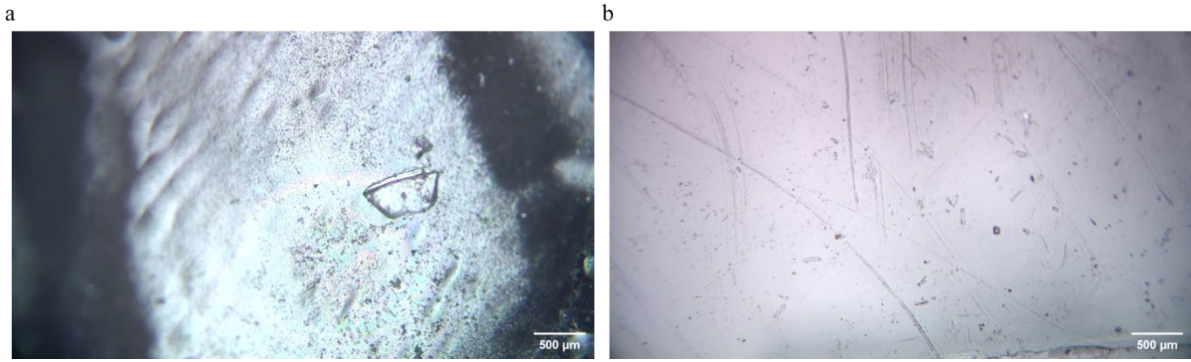


Figure S9. Optical images of the $\text{Cs}_3\text{Cu}_2\text{I}_5$ single crystals grown a) without formic acid. b) with formic acid.

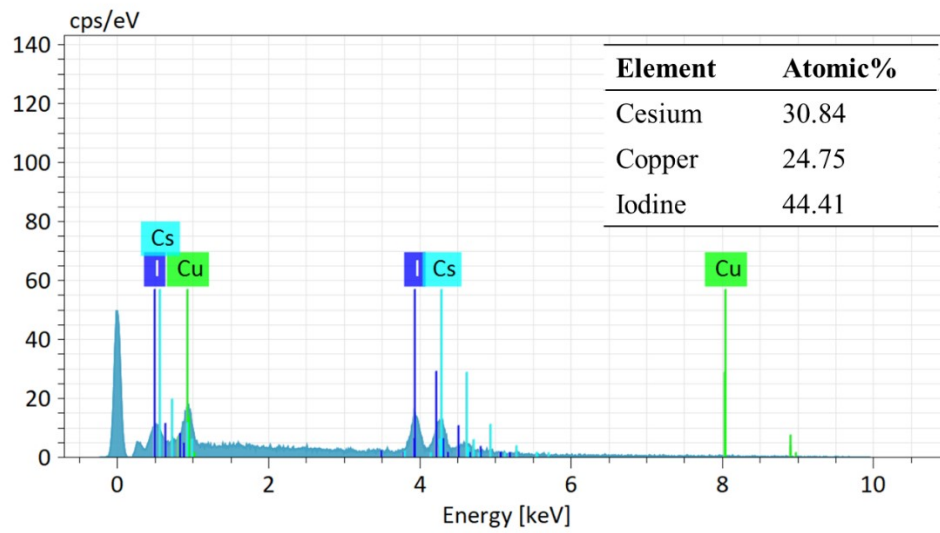


Figure S10. EDX spectrum analysis results of $\text{Cs}_3\text{Cu}_2\text{I}_5$.

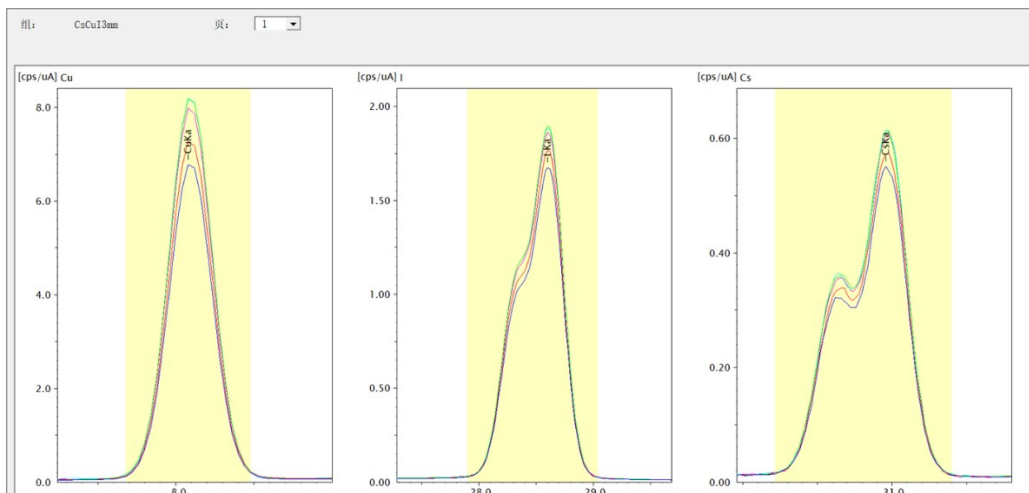


Figure S11. X-ray fluorescence (XRF) results of $\text{Cs}_3\text{Cu}_2\text{I}_5$.

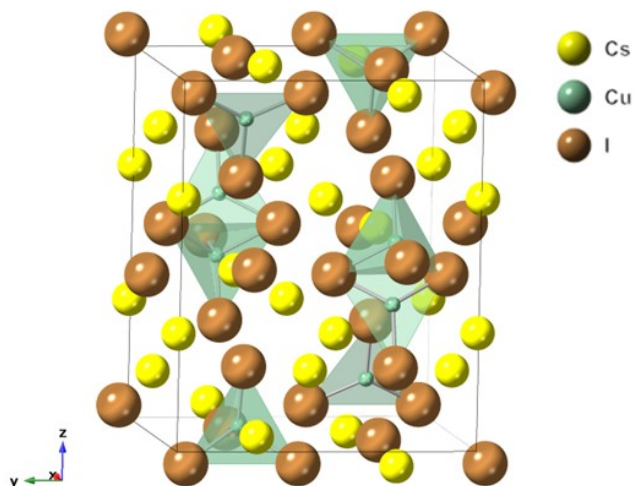


Figure S12. Crystal structure of Cs₃Cu₂I₅.

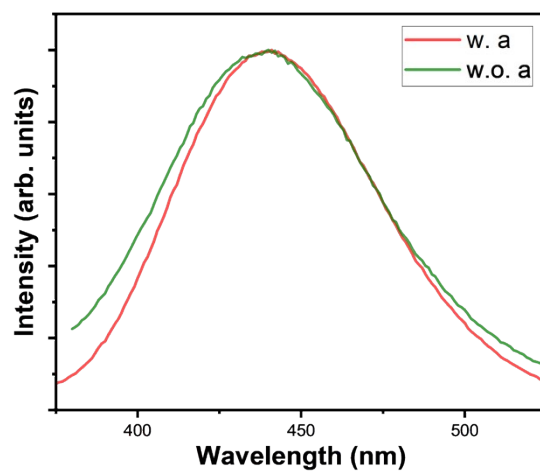


Figure S13. The PL spectra of the Cs₃Cu₂I₅ single crystals grown with and without formic acid.

Table S1. Summary of Cs₃Cu₂I₅ Single crystal scintillator performance.

Growth Method	Tl doped	PL decay time (ns)	Energy resolution	Light yield (photons/MeV)	Afterglow (ms)	Ref
Bridgman	No	968	3.6% @662KeV	25000	10 (0.03%)	1
Bridgman	Yes	2000	3.4% @662KeV	87000	10 (0.17%)	2
Bridgman	No	157 (12%) 956 (87%)	7.7 ± 0.3% @662KeV	18 000 ± 2000	-	3
	Yes	304 (15%) 893 (83%)	4.5% @662KeV		51000	
Bridgman	No	1000	4.4% @662KeV	41,500	-	4
	Yes	720	3.3% @662KeV	98200	-	
Inverse Temperature Crystallization	No	134 (33%) 1034 (67%)	9.1% @662KeV	-	-	5
Solution Temperature Lowering	No	1034	7.8% @511KeV 4.4% @662KeV	35000	15 (<0.1%)	6
Inverse Temperature Crystallization	No	1381	7.1% @511KeV	39000	-	This work

REFERENCES

- (1) Cheng, S.; Beitlerova, A.; Kucerkova, R.; Nikl, M.; Ren, G.; Wu, Y., Zero - Dimensional Cs₃Cu₂I₅ Perovskite Single Crystal as Sensitive X - Ray and γ - Ray Scintillator. *Phys. Status Solidi RRL* **2020**, *14*, 2000374.
- (2) Cheng, S.; Nikl, M.; Beitlerova, A.; Kucerkova, R.; Du, X.; Niu, G.; Jia, Y.; Tang, J.; Ren, G.; Wu, Y., Ultrabright and Highly Efficient All - Inorganic Zero - Dimensional Perovskite Scintillators. *Adv. Opt. Mater.* **2021**, *9*, 2100460.
- (3) Yuan, D., Air-stable bulk halide single-crystal scintillator Cs₃Cu₂I₅ by melt growth: intrinsic and Tl doped with high light yield. *ACS applied materials & interfaces* **2020**, *12*, 38333-38340.

- (4) Stand, L.; Rutstrom, D.; Koschan, M.; Du, M.-H.; Melcher, C.; Shirwadkar, U.; Glodo, J.; Van Loef, E.; Shah, K.; Zhuravleva, M., Crystal growth and scintillation properties of pure and Tl-doped Cs₃Cu₂I₅. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2021**, *991*, 164963.
- (5) Xu, Q.; Wang, J.; Zhang, Q.; Ouyang, X.; Ye, M.; Xie, W.; Yan, X.; Li, D.; Ouyang, X.; Tang, X., Solution-processed lead-free bulk 0D Cs₃Cu₂I₅ single crystal for indirect gamma-ray spectroscopy application. *Photonics Research* **2021**, *9*, 351-356.
- (6) Yao, Q.; Li, J.; Li, X.; Zheng, X.; Wang, Z.; Tao, X., High - Quality Cs₃Cu₂I₅ Single - Crystal is a Fast - Decaying Scintillator. *Adv. Opt. Mater.* **2022**, *10*, 2201161.