

Supplementary Material

A novel Li⁺-doped CsCu₂I₃ Single Crystal for dual gamma-neutron detection

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1. Crystal growth

Anhydrous high-purity CuI (99.999%, ALDRICH) and CsI and ⁶LiI (99.99%, ⁶Li enrichment above 95%, APL Engineered Materials, INC.) were used as starting materials. The high-quality Li⁺-doped CsCu₂I₃ single crystals with a size of Φ12 mm*30 mm were grown successfully by self-seeding vertical Bridgman technique with capillary tube. In order to obtain the single crystal, the 30 mm length of capillary tube was chosen, as shown in Fig S1a (Supplementary Material). Before loading raw materials, the quartz crucible was cleaned with deionized water and acetone to remove impurities on the inner surface before loading raw materials. Then, the washed quartz crucible was dried at 180°C for 16 hours under an oven to remove residual water and oxygen impurities. These starting materials were weighted according to the stoichiometric ratio, and then mixed and loaded into a quartz crucible in a glove box with <0.1 ppm moisture and <0.1 ppm oxygen. Due to the similar Shannon radii, Li⁺ is assumed to substitute for Cu⁺ (d10). Then, the quartz crucible was vacuumed to 5 × 10⁻⁵ mbar and sealed with a hydrogen-oxygen flame. And then, the quartz crucible was transferred to a single-temperature zone vertical Bridgman method crystal growth furnace. The melting point of CsCu₂I₃ crystal is about 371°C. To fully melt the raw material, the high temperature zone is set about 400°C and the quartz crucible was held in the high-temperature zone for 24 h. The temperature field of furnace for CsCu₂I₃ growth is shown in the Fig S1b. The temperature gradient is 20 °C/cm. The position is located at 4 cm to 5 cm below the edge of the temperature gradient zone. The bottom of capillary tube is located the upper of the

temperature gradient, which is the initial position of crystal growth. The experiment results show that the CsCu₂I₃ crystal is easy to crack during the cooling and machining process, as shown in Figure S 1c. The annealing and cooling rate (<5°C/h) are crucial for a high-quality CsCu₂I₃ crystal. The growth speed is about 0.5 mm/h.

2. Characterization methods

The crystal structure and phase purity of different samples were measured in a SmartLab SE XRD with Cu K α radiation ($\lambda = 0.1541$ nm). The Li element content of CsCu₂I₃:Li single crystals, dissolved in nitrohydrochloric acid aqueous solution, were measured by inductively coupled plasma-optical emission spectrometer (ICP-MS, Agilent Technologies 5100).

The photoluminescence excitation (PLE) spectra, photoluminescence (PL) spectra and decay time measurements under UV light were recorded on a FLS1000 spectrometer with pulsed nano-LED. The slits for both excitation and emission measurement were all set as 2.5 nm and the scan speed was fixed at 240 nm/min. The XEL spectra were recorded on an Omni- λ 3027i-EMM spectrometer. A Moxtek MAGPRO X-ray tube (50 kV, 100 μ A) with W target was used as the excitation source. The PLQY were performed with a Hamamatsu quantum yield measurement system C9920-02G.

The ¹³⁷Cs energy spectra for energy resolutions were recorded with a Hamamatsu model R6231-100 PMT (operation voltage of -1000 V) that was connected to an Ortec 672 spectroscopy amplifier and a model 927 ASPEC MCA instrument. A pulse shaping time of 10 μ s was used to ensure complete integration of the scintillation pulses. The relative light yield of pure and Li⁺-doped CsCu₂I₃ were estimated by using the CsI(Tl) crystal standard sample (56000 photons/MeV). Under the excitation of ¹³⁷Cs, the R6231PMT and Tektronix DPO 5104 oscilloscopes were used to collect each scintillation signal of the crystal, and on this basis, by using the program to calculate the average waveform collected. The decay time constant is fitted according to the average waveform obtained. The gamma-ray and neutron waveforms were recorded at a sampling rate of 1 GSPS using a CAEN DT5751 digitizer under a ²⁵²Cf source excitation, and the pulse shape discrimination (PSD) performance was evaluated by off-line processing.

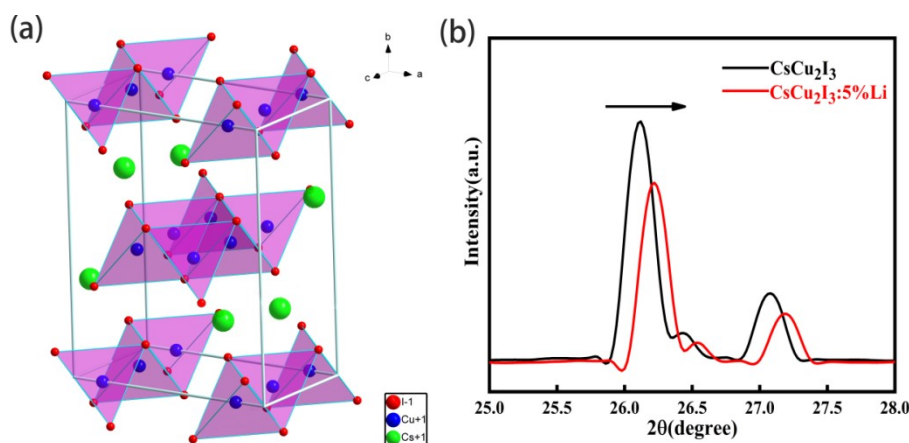
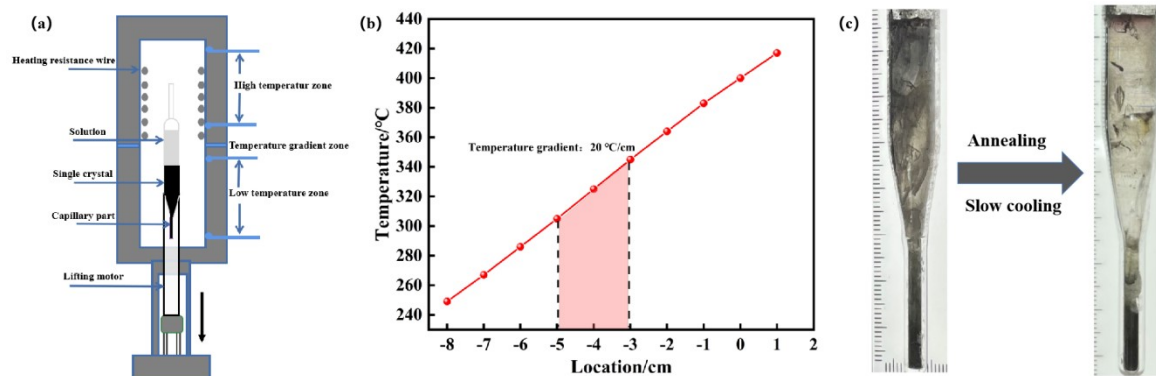


Figure S2 (a) Crystal structure of $\text{CsCu}_2\text{I}_3:5\text{mol}\%\text{Li}$ crystal. (b) Comparison of diffraction peaks in a narrow range.

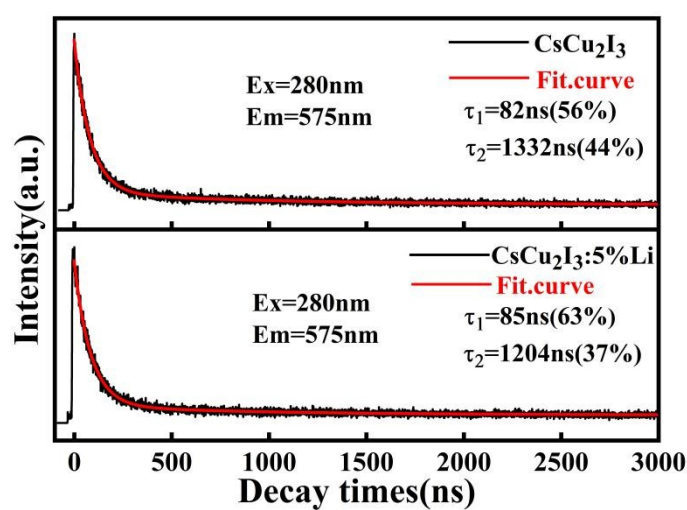


Figure S3 Decay profiles of CsCu_2I_3 and $\text{CsCu}_2\text{I}_3:5\text{mol}\%\text{Li}$.

Table S1. ICP-MS results of CsCu₂I₃:5mol%Li at different positions.

Sample serial number	1	2	3	4	5
Primitive position of samples (mm ³)	15	25	30	35	37.5
The volume position after the diameter processing Z' (mm ³)	228	1056	1689	2323	2640
Calculated concentration $C_L(\text{Li})$			0.05		
Sampling position Li concentration $C_s(Z')$	0.0292	0.0364	0.0428	0.0465	0.0513
K_{Li}			0.445		