

Spectroscopic Performance of CsPbBr₃ Perovskite γ -Ray Detectors Despite Grain Boundaries

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Abstract

The CsPbBr₃ perovskite has emerged as a promising material for next-generation γ -ray detection owing to its high stopping power, wide bandgap, and excellent charge-transport properties. Unlike conventional semiconductors, in which grain boundaries (GBs) degrade response, we observed that CsPbBr₃ retains functional spectroscopic performance in their presence, demonstrating remarkable defect tolerance. We systematically investigate the impact of GBs on the performance and stability of CsPbBr₃-based detectors. Detectors containing GBs exhibit measurable spectroscopic performance at room temperature, including resolved photopeaks at 59.5 keV (²⁴¹Am) and 122 keV (⁵⁷Co), along with hole mobility-lifetime products $(\mu\tau)_h$ on the order of $\sim 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1}$, highlighting the defect-tolerant nature of CsPbBr₃. Two-photon excitation PL microscopy shows asymmetric carrier diffusion near GBs (under zero field bias), indicative of impeded charge transport, while transient waveform analysis captures field-assisted detrapping that recovers charge collection on application-relevant timescales. Our measurements indicate that device engineering choices, pixel placement/size, guard rings, field shaping, and electrode work-function design can help drift paths and electric fields away from defects, and may reduce GB impacts.

Keywords: CsPbBr₃, Gamma-ray detection, Defect tolerance, Grain boundaries, Two-photon microscopy.

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1. Introduction

Gamma-ray detection plays an essential role in medical imaging, homeland security, nuclear non-proliferation, and high-energy physics.^[1] The performance of γ -ray detectors largely depends on the choice of materials, which must possess a high atomic number for efficient photon absorption, a wide bandgap to suppress thermal noise, and excellent charge transport properties for effective charge collection.^[2] Cadmium telluride (CdTe) and cadmium zinc telluride ($\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ (CZT)) have long been favored due to their high stopping power and ability to operate at room temperature.^[3] However, their widespread use is hindered by challenges in crystal growth, including poor stoichiometric control, secondary phase formation, unbalanced electron/hole transport, and high dislocation densities, all of which limit detector performance.^[4] Additionally, the high cost and difficulty in synthesizing large, high-quality single crystals of CZT further limit its broader application.^[5] High-purity germanium (HPGe) detectors, while offering excellent energy resolution (ER), require extremely pure germanium and cryogenic cooling to reduce thermal noise and dark current, making them both complex and costly to use.^[6] Similarly, thallium bromide (TlBr) radiation detectors face issues with ionic conductivity, which leads to polarization effects, and their hygroscopic nature necessitates protective encapsulation to prevent moisture-induced degradation.^[7] These limitations underscore the need for alternative materials that offer greater stability, simplified operation, and improved performance, paving the way for advancements in radiation detection technology.

In recent years, metal halide perovskites (MHPs) have attracted significant attention as promising materials for radiation detection, offering high absorption coefficients, excellent resistivity, and a high mobility-lifetime ($\mu\tau$) product.^[8] Among them, cesium lead bromide (CsPbBr_3 , CLB) stands out due to its superior properties compared to traditional compound semiconductors.^[8d, 9] With high atomic number elements (Cs: 55, Pb: 82, Br: 35), CLB exhibits strong X-ray and γ -ray absorption, ensuring efficient radiation detection.^[10] Its direct bandgap of approximately 2.3 eV enables low dark-current operation, while a high $\mu\tau$ product enhances charge collection efficiency (CCE).^[9a, 11] Unlike CZT, which is reported to suffer from material inhomogeneity and charge-transport anisotropy, as well as Te inclusions and precipitates, Zn segregation, intrinsically low hole $(\mu\tau)_h$ that necessitates single-polarity sensing and depth corrections, radiation-induced polarization at high flux, and device-to-device variability from low crystal-growth yields, CLB crystals can be grown with fewer compositional variations, fewer deep

traps, and improved uniformity.^[12] Furthermore, their defect-tolerant electronic structure reduces the impact of carrier traps that typically degrade the performance of conventional semiconductors, such as TlBr, HgI₂, BiI₃, and CZT.^[10, 13] While CLB shows great promise, structural imperfections, particularly grain boundaries, pose challenges to optimal detector performance, necessitating a deeper understanding of their impact.

Grain boundaries (GBs) in semiconductor materials have long been recognized as sites of enhanced carrier trapping and recombination due to localized states associated with atomic disorder, strain fields, and/or impurity segregation.^[14] Their presence is strongly correlated with asymmetric charge diffusion and reduced carrier lifetimes, both of which significantly impair CCE.^[15] In CZT, for example, GBs introduce potential barriers that hinder carrier drift, leading to increased charge loss and degraded detector performance.^[16] In TlBr, GBs and sub-GBs are likewise recognized as detrimental to detector performance, as X-ray diffraction and synchrotron topography on Bridgman-grown, detector-grade crystals show that regions with higher GB density exhibit the lowest resistivity and the poorest spectroscopic response, directly correlating GB density with degraded ER.^[17] Although strategies such as compositional engineering and passivation have been employed to minimize these effects in CZT^[16, 18], a comprehensive understanding of GB behavior in perovskite-based detectors to enable such mitigation remains underdeveloped. In contrast to conventional γ -ray detectors, like CZT and TlBr, halide perovskites demonstrate enhanced resilience to extended structural defects such as dislocations, stacking faults, and GBs.^[19] Materials tolerant to point defects generally exhibit reduced nonradiative recombination at such imperfections, a phenomenon directly observed in single-crystal halide perovskites, where optoelectronic properties remain largely unperturbed by structural disorder.^[19b] First-principles calculations reveal that in CLB, most native point defects induce shallow transition levels, while deep defects exhibit high formation energies and thus low concentrations. This electronic defect-tolerance stems from Br-p and Pb-s/p band-edge states that suppress mid-gap defects.^[20] Strong lattice anharmonicity further limits nonradiative capture, while high dielectric screening, large-polaron formation, defect self-compensation, and rapid ion migration collectively minimize trap activity in CLB.^[19b, 21] Collectively, these processes weaken carrier-trap coupling and/or eliminate radiation-induced Frenkel pairs.^[19b] Furthermore, recent theoretical studies suggest that applying compressive strain stabilizes GB configurations in CLB, suppresses large-scale structural fluctuations, and inhibits deep-trap formation, pointing to practical strategies for

minimizing GB impacts in γ -ray detectors.^[22] Given the rapid advancements in perovskite-based radiation detectors, a fundamental understanding of how GBs influence charge transport and long-term stability in CLB detectors is essential. A systematic investigation of their electrical and spectroscopic properties will be key to guiding performance improvements and fully utilizing the intrinsic robustness of this material.

This study investigates the impact of GBs on the γ -ray detection performance and stability of CLB detectors. Interestingly, all detectors exhibited functional γ -ray spectra under ^{241}Am and ^{57}Co irradiation, underscoring the intrinsic defect tolerance of CLB. The GB-free detector demonstrated the lowest dark current, the highest hole mobility-lifetime $(\mu\tau)_h$ product, the best energy resolution (ER), and stable performance over 18 hours. Detectors containing GBs showed only modest performance variations, with the most pronounced effects observed in the parallel GB configuration, including increased charge trapping and ER drift. Two-photon excitation optical luminescence microscopy shows symmetric diffusion in GB-free wafers and asymmetric diffusion across GBs, indicating their role in limiting charge transport; however, applied fields facilitate charge recovery, preserving functional γ -ray spectroscopic performance. Importantly, our measurements suggest that optimizing electrode geometry, such as pixel size and placement, can further minimize the detrimental impact of GBs, enabling good spectroscopic performance even in the presence of GBs. These findings reinforce CLB's exceptional resilience to defects.

2. Results and Discussion

The CLB ingot was grown using the Bridgman method, which enables controlled crystallization via slow melt cooling after thorough purification to ensure high wafer quality for radiation detection. The formation of GBs in CLB ingots grown by this method was observed and likely occurred randomly due to solidification instabilities, uncontrolled nucleation, and thermal or mechanical perturbations during growth, resulting in the development of misoriented grains.^[12b, 23] To investigate the impact of GBs on CLB-based detectors, we systematically studied wafers with and without GBs, examining their structural, electrical, and spectroscopic properties.

Figure 1a presents a CLB ingot (schematic) alongside the extracted wafers from the ingot grown using the Bridgman method. Three wafers were selected: Wafer-1 has dimensions $5.2 \times 4.5 \times 1.27 \text{ mm}^3$ and contains no GB; Wafer-2 measures $7.0 \times 6.0 \times 1.23 \text{ mm}^3$ with a GB perpendicular

($\perp$) to the large surface; and Wafer-3 measures $7.5 \times 8.5 \times 2.75 \text{ mm}^3$ with a GB parallel ($\parallel$) to the large surface. The phase of CLB was confirmed by powder X-ray diffraction (PXRD), as shown in **Figure S1a**, indicating the monoclinic phase belonging to the $P2_1/m$ space group at room temperature (RT), which is consistent with the recent literature.^[24] The RT photoluminescence (PL) spectrum of the CLB wafer exhibits a sharp emission peak at 531 nm (**Figure 1b**). PL mapping reveals a peak position variation of less than 1.3 nm across $\sim 0.45 \text{ mm}^2$ (**Figure S1b**), indicating excellent compositional uniformity. The inset of **Figure 1b** presents the Tauc plot calculated from the transmission spectra, indicating an optical band gap of $\sim 2.23 \text{ eV}$ for the CLB wafer, which is consistent with reported values within the error margin for CLB.^[24-25]

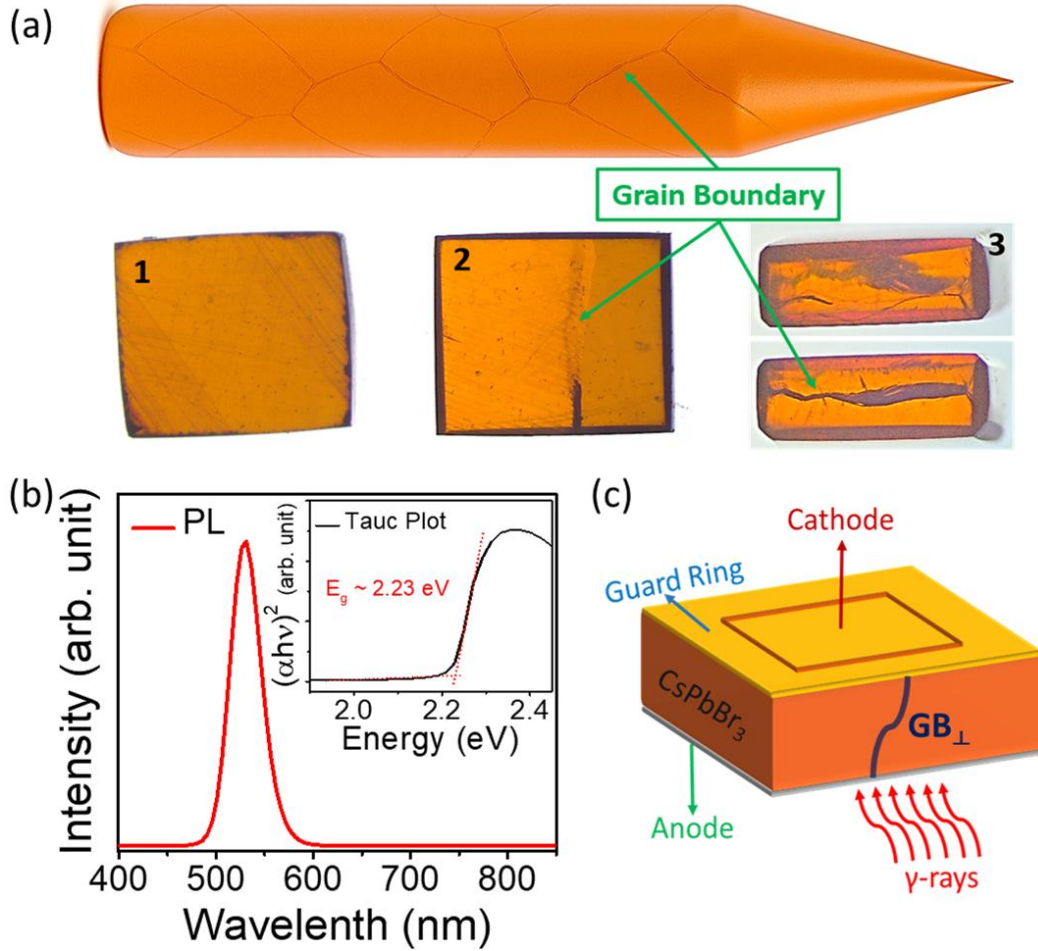


Figure 1. (a) Schematic of the CLB ingot alongside the extracted wafers, highlighting Wafers 2 and 3 with different GB configurations ($\text{GB}_\perp$: perpendicular to the large area, and $\text{GB}_\parallel$: parallel to the large area) grown via the Bridgman method. (b) Room-temperature PL spectrum of a clean CLB wafer at $\sim 380 \text{ nm}$ excitation wavelength, with the inset showing the Tauc plot. (c) Schematic

of a Schottky-type Au/CLB/Alloy detector with a guard-ring configuration and illustrating the general direction of a GB in a perpendicular orientation.

Figure 1c shows the schematic of a Schottky-type Au/CLB/Alloy detector architecture with a guard ring configuration^[26] operating in hole collection mode. Here, the eutectic alloy Bi-In-Pb-Sn was chosen as the anode as it combines a low melting point of ~ 59.2 °C and a low work function of ~ 4.4 eV (**Figures S2a, b**). When paired with a high work function Au cathode (~ 5.1 eV), it establishes a built-in potential of ~ 0.7 eV, which can suppress the dark current and enhance the CCE.^[12a] Moreover, its low melting point enables reflow onto the polished CLB wafer surface without exceeding the phase-transition temperature, ensuring compatibility with the thermally sensitive CLB during detector fabrication. A high voltage (HV) is applied to the anode (alloy), and when high-energy photons interact with the CLB, they generate electron-hole pairs. For hole collection, the photogenerated holes drift through the wafer under the applied electric field, reach the gold cathode, and are extracted to generate a measurable current in the external circuit.

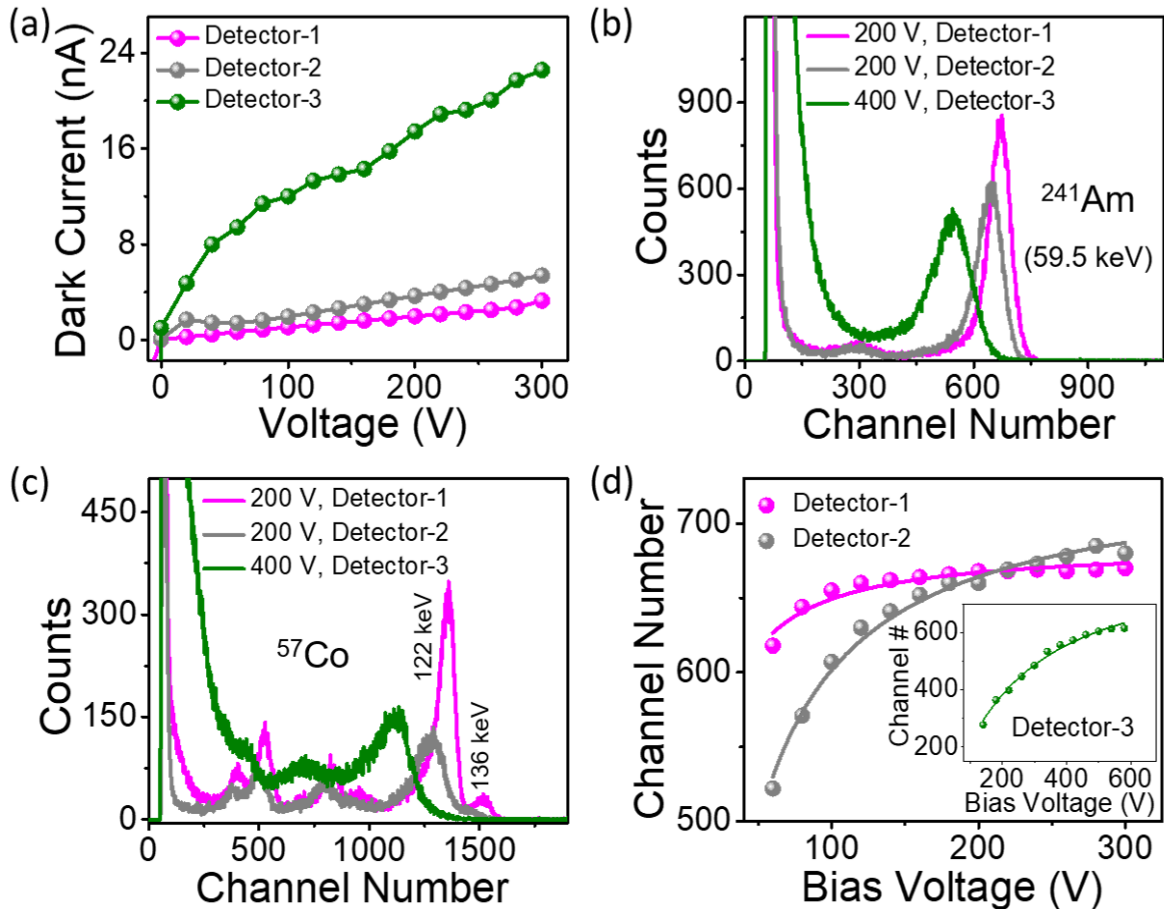


Figure 2. (a) Typical I–V characteristics of Au/CLB/Alloy guard ring detectors under positive bias: Detector-1, Detector-2, and Detector-3. (b) Energy spectrum of the ^{241}Am (59.5 keV) γ -ray source recorded with a 3 μs shaping time, the specified bias, and a 300 s acquisition time in hole collection mode. (c) Energy spectrum of the ^{57}Co (122 keV) γ -ray source recorded with a 3 μs shaping time, the specified bias, and a 300 s acquisition time in hole collection mode. (d) Hole mobility-lifetime products $(\mu\tau)_h$ for Detector 1 and 2 (Detector-3 shown in the inset), estimated by fitting the Hecht equation to the spectral responses.

To evaluate the electrical and γ -ray response characteristics, guard ring detectors were fabricated from CLB wafers with and without GBs, following the configurations shown in **Figure 1c**. Optical images of the wafers and corresponding detectors are provided in **Figure S3**. The complete current-voltage (I–V) characteristics are shown in **Figure S4**, with the positive bias region expanded in **Figure 2a**. At an applied bias of +300 V, the dark current varied with GB presence and orientation: ~ 3.3 nA in the GB-free Detector-1, ~ 5.4 nA in Detector-2 with GB perpendicular ($\perp$) to the electrodes, and ~ 22.6 nA in Detector-3 with GB parallel ($\parallel$) to the electrodes. This trend suggests that a parallel GB can act as a continuous leakage path under bias due to its cross alignment with the electric field, while a perpendicular GB only partially interrupts charge transport.

These detectors were evaluated for γ -ray detection using ^{241}Am and ^{57}Co sources in hole collection mode. Under a 59.5 keV ^{241}Am irradiation (**Figure 2b**), all three detectors exhibited a well-resolved spectroscopic response. At +200 V bias (~ 1.57 kV/cm) across the 1.27 mm-thick wafer, Detector-1 achieved an ER of $\sim 9.6\%$. Detector-2, biased similarly (~ 1.63 kV/cm), exhibited a broader ER of $\sim 11.9\%$, likely due to moderate charge trapping at the perpendicular GB. In Detector-3, operated at +400 V (~ 1.45 kV/cm) across a 2.75 mm-thick wafer, the ^{241}Am ER broadened further to $\sim 21.1\%$, attributed to the combined effects of longer carrier drift distance, higher dark current, increased low-energy tailing, and incomplete charge collection. **Figure 2c** presents the spectral response of the ^{57}Co source, following the same trend observed for the ^{241}Am response. For 122 keV peak of ^{57}Co , Detector-1 achieves an ER of $\sim 5.9\%$, Detector-2 degrades to $\sim 11.0\%$, and Detector-3 to $\sim 16.3\%$. Notably, Detector-1 resolved the 136 keV ^{57}Co peak, indicating low noise and efficient charge transport. Detector-2 exhibited a slight shoulder,

suggesting moderate GB-induced trapping, while Detector-3's inability to resolve this peak indicates more trapping and increased spectral broadening.^[27] All detectors, irrespective of GB presence, delivered operational spectroscopic performance, reinforcing the intrinsic defect tolerance of CLB.

The charge carrier mobility-lifetime product ($\mu\tau$) is a key metric for evaluating the charge transport efficiency of a radiation detectors. The hole-collection photopeak of the 59.5 keV ^{241}Am γ -ray response was used to fit the Hecht equation^[28] as shown in **Figure S5a–c**. The mobility-lifetime products for holes ($\mu\tau$)_h were estimated to be $1.47 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1}$ for Detector-1, $3.62 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1}$ for Detector-2 and $2.12 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1}$ for Detector-3 (**Figure 2d**). Normalized to Detector-3, the ($\mu\tau$)_h values scale as Detector-1:Detector-2:Detector-3 $\approx 6.93:1.71:1$, indicating a systematic decrease from the GB-free to GB-containing detector configurations. Notably, Detector-2 exhibited a continuous increase in the photopeak channel number up to 260 V, likely reflecting the field-induced release of carriers initially trapped at the GB.^[14] Based on field-driven collection efficiency, the mean drift length $L_d = \mu\tau E$ for holes is approximately 23 mm in Detector-1 at +200 V, which is about 18 $\times$ its 1.27 mm thickness, ensuring nearly complete charge collection. In Detector-2, $L_d \approx 5.9$ mm at +200 V, roughly 4.9 $\times$ its 1.23 mm thickness, remains sufficient but shows a modest trapping. Detector-3 exhibits $L_d \approx 3.1$ mm at +400 V, nearly matching (1.1 $\times$) its 2.75 mm thickness, indicating decreased charge collection, while still maintaining resolvable γ -ray peaks. We also performed electron backscatter diffraction (EBSD) on Wafer-2 to classify GBs and micro-structural arrangement, which is extensively used for halide perovskites.^[29] Orientation indexing (monoclinic $P2_1/m$)^[30] shows that the two grains differ by 16.30°, indicating a high-angle GB (HAGB). **Figure S6** presents the foreshatter detector (FSD) image of Wafer-2 and inverse pole figure (IPF) maps along the X, Y, and Z sample axes; the matching IPF-Z colors but subtly different IPF-X and IPF-Y colors indicate a misorientation with a rotation axis near Z. Despite this structural classification, Detector-2 exhibits spectroscopic performance under the applied bias, suggesting that the GB in this orientation is electronically benign, consistent with the defect-tolerant behavior often observed in CLB. **Table 1** summarizes performance from Detector-1 to Detector-3, showing a monotonic increase in dark current and FWHM broadening for the 59.5 keV (^{241}Am) and 122 keV (^{57}Co) peaks, while all detectors retain resolvable spectroscopic response at both energies.

Table 1: Electrical and Spectroscopic Parameters of Detector 1–3

Parameters	Detectors		
	Detector-1	Detector-2	Detector-3
Wafer Details	No GB	GB $\perp$ to electrode	GB $\parallel$ to electrode
Dimensions (mm ³)	$5.2 \times 4.5 \times 1.27$	$7.0 \times 6.0 \times 1.23$	$7.5 \times 8.5 \times 2.75$
Dark Current (nA)	3.3 @+300V	5.4 @+300V	22.6 @+300V
²⁴¹ Am ER (59.5 keV)	9.6%	11.9%	21.1%
⁵⁷ Co ER (122 keV)	5.9%	11.0%	16.3%
$(\mu\tau)_h$ (cm ² ·V ⁻¹)	1.47×10^{-3}	3.62×10^{-4}	2.12×10^{-4}

To further evaluate detector stability, we performed 18 hours continuous-bias tests under 59.5 keV ²⁴¹Am irradiation to assess CCE and spectral response. All three detectors retained the qualitative behavior observed in short-term measurements and remained spectroscopically functional, with performance drift correlated with GB presence and wafer thickness. Detector-1 exhibited excellent stability, maintaining a peak channel near 666 and an ER of ~10.2% at +200 V with a 3 μ s shaping time, with slight improvement over time (**Figure S7a–b**). Detector-2 settled at a peak channel near 631, while ER drifted modestly from ~12.1% to ~15.0% (average ~14.2%) at +200 V and 3 μ s (**Figure S7c–d**). Detector-3 showed the most considerable drift, stabilizing at a peak channel near 535, while ER broadened from ~17.4% to ~22.8% (average ~21.3%) at +400 V and 3 μ s (**Figure S7e–f**). The long-term drift in GB-containing detectors likely reflects continued ion migration and trap filling at GBs, which elevate dark current and shot noise, while increased thickness introduces additional field nonuniformity that further impacts CCE and ER.^[8a]

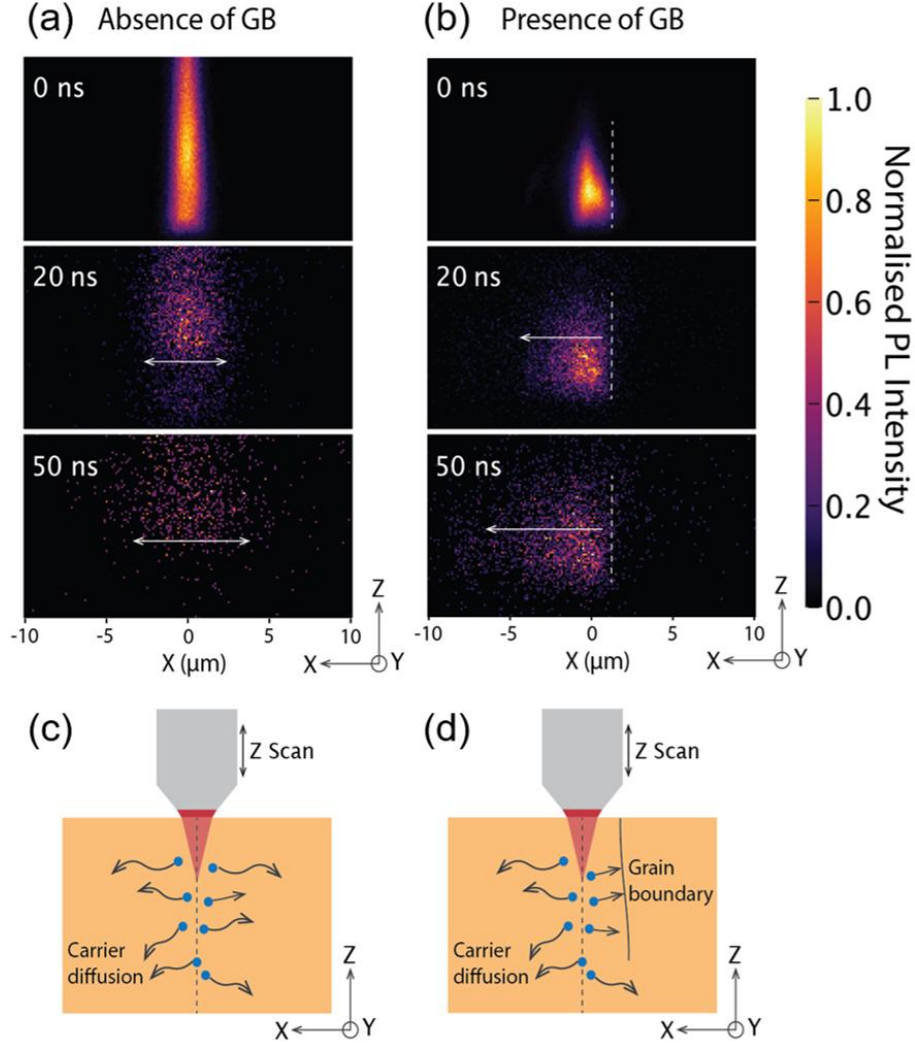


Figure 3. Carrier diffusion in the x-z direction (cross-section) using two-photon PL microscopy, with excitation focused at $x=0$, $y=0$: **(a)** Normalized PL diffusion maps in Wafer-1 at 0 ns, 20 ns, and 50 ns after pulsed excitation, showing symmetrical diffusion without any GBs. **(b)** Normalized PL diffusion maps in the Wafer-2 at 0 ns, 20 ns, and 50 ns after pulsed excitation, showing impeded diffusion next to the GB. Schematic illustration of carrier diffusion **(c)** in the absence of a GB and **(d)** in the presence of a GB. The 2P excitation was performed at 700 nm with a fluence of $1850 \mu\text{J cm}^{-2}$.

To investigate the influence of GBs on carrier transport within the bulk of CLB wafers, two-photon (2P) excitation PL microscopy was employed.^[31] Owing to the low two-photon absorption coefficient, this technique enables deep optical penetration and allows visualization of the temporal evolution of PL signals tens of micrometers beneath the wafer surface.^[32] By raster-

scanning both the excitation and emission in the xz-plane (perpendicular to the crystal surface), the cross-section of the CLB wafer was mapped to identify the lateral position of the GBs (**Figure S8–S9**). The excitation beam was then fixed in the x-direction, and the emission was scanned across the region of interest in the xz-plane. This configuration enabled monitoring of carrier diffusion by tracking the spatiotemporal broadening of the PL profile along the x-direction at various depths (z). Due to low outcoupling and signal loss through the confocal pinhole, the PL signals are inherently noisy, limiting precise extraction of diffusion coefficients compared with single-point measurements, where excitation remains fixed in z. Nevertheless, this approach reveals spatial variations in charge transport across GBs that are inaccessible to conventional single-point methods, providing valuable insight into the local influence of GBs on carrier transport.

In **Figures 3a–b**, we compare the 2P-PL diffusion results in the absence of visually apparent GBs (Wafer-1) and in proximity to a GB (Wafer-2). In Wafer-1 (**Figure 3a**), the PL profile broadens symmetrically on both sides of the excitation spot ($x = 0$) at later times, indicating uniform carrier diffusion in the absence of GBs (**Figure 3c**). In Wafer-2 (**Figure 3b**), by contrast, where a GB is located near the excitation spot on the right side (see **Figure S10**), the PL evolution shows asymmetric broadening. Over time, the PL expands preferentially to the left ($x < 0$) while remaining suppressed on the right ($x > 0$), indicating that the GB in CLB limits carrier transport but does not entirely block it, as evident at 20 ns and 50 ns (**Figure 3b**). To provide a quantitative analysis, each x-z diffusion map was summed over the z direction to obtain an averaged PL profile as a function of x at different times (**Figure S11**). Following the procedure reported in our recent work,^[33] the PL broadening in the presence of GB was fitted separately on the left ($x < 0$) and right ($x > 0$), resulting in diffusion coefficients of $0.73 \text{ cm}^2/\text{s}$ and $0.03 \text{ cm}^2/\text{s}$ for the left and right sides (**Figure S11d**), respectively. Given that GBs in halide perovskites are known to act as nonradiative recombination centers and barriers to carrier transport^[32, 34], an asymmetric diffusion pattern near GBs is consistent with this behavior (**Figure 3d**). As such, GBs oriented perpendicular to the charge collection direction can impair detector performance. These findings support the conclusion that GBs can act as local barriers to carrier diffusion, particularly when they are oriented parallel to the electrodes and intersect the full drift path under zero field bias. However, as we demonstrate in this work, applying an external bias can overcome these barriers and successfully inject carriers across the GBs.

The 2P excitation PL microscopy shows that, without an applied field, GBs act as localized barriers and only a delayed, minor fraction of carriers crosses the boundary. Accordingly, we investigated how applied electric field (bias) modulates carrier trapping and transport across GBs by analyzing hole-collection waveforms for Detector 1–3 under ^{241}Am γ -irradiation (**Figures S12a–c**). The moderate GB-related effect is observed in the pulse shape in the presence of the applied field. Detector-1 shows the sharpest leading edge, Detector-2 closely matches Detector-1 (consistent with the minimal impact of a $\perp$ -oriented GB), and Detector-3 exhibits a slower rise with a noticeable tail, yet pulse amplitudes remain comparable, indicating carrier transport across GBs. These observed behaviors in Detector-2 and especially Detector-3 indicate the initial capture of carriers into shallow GB-associated states, followed by field-assisted detrapping at modest fields^[35]; with increasing bias, the delayed release of carriers sharpens the leading edge.^[36]

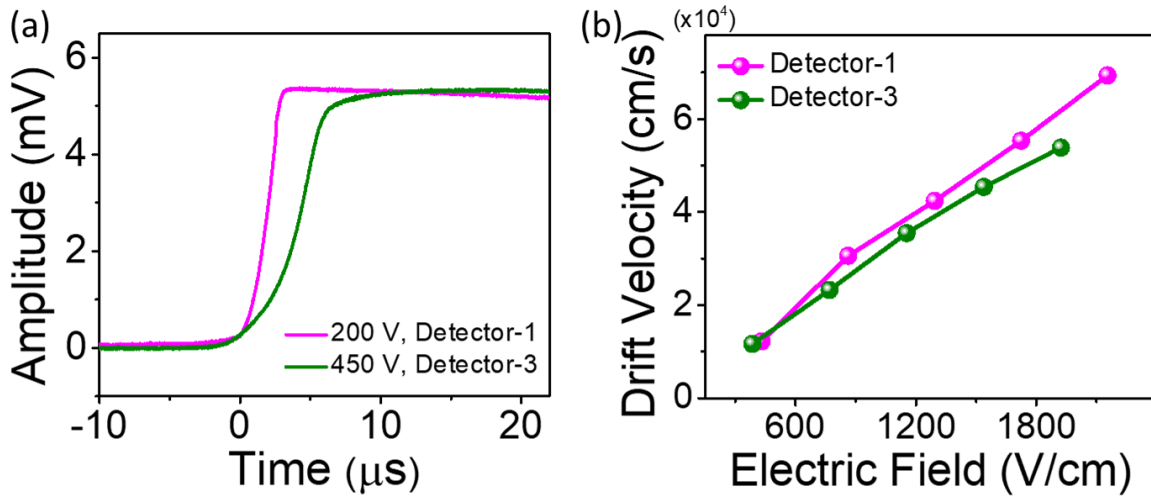


Figure 4. (a) Representative hole-collection pulses under ^{241}Am (59.5 keV) irradiation for Detector-1 and Detector-3. (b) Hole drift velocity as a function of electric field for Detector-1 and Detector-3.

To isolate microstructural effects, we show Detector-1 and Detector-3 pulse waveforms at electric fields in close proximity (**Figure 4a**), revealing hole rise times of 2.1 μs for Detector-1 and 5.1 μs for Detector-3. Furthermore, approximately $7.48 \pm 0.11\%$ of carriers undergo trapping followed by delayed release, resulting in the long, rising tail between 8 and 18 μs for Detector-3. Drift velocities for these two detectors, extracted from the 10–90% rise times across multiple applied fields (**Figure 4b**), scale linearly with field, indicating a mobility-limited regime. At an applied

field of 1.5 kV/cm, the hole drift velocity is estimated to be 4.85×10^4 cm/s for Detector-1 and 4.44×10^4 cm/s for Detector-3. Similarly, the hole mobilities were calculated to be $33.58 \pm 1.65\%$ $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for Detector-1 and $31.08 \pm 0.36\%$ $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for Detector-3, indicating only a slight reduction due to carrier scattering at the boundary. The drift velocities and hole mobilities are broadly comparable, with a modest reduction in Detector-3 because holes must traverse a $\parallel$ -oriented GB en-route to the cathode, a trend also reflected in its γ -ray spectrum. Overall, GBs modulate transport but do not entirely prevent spectroscopic operation in CLB from being observed, and modest bias levels are sufficient to recover trapped charges and maintain functional ER.

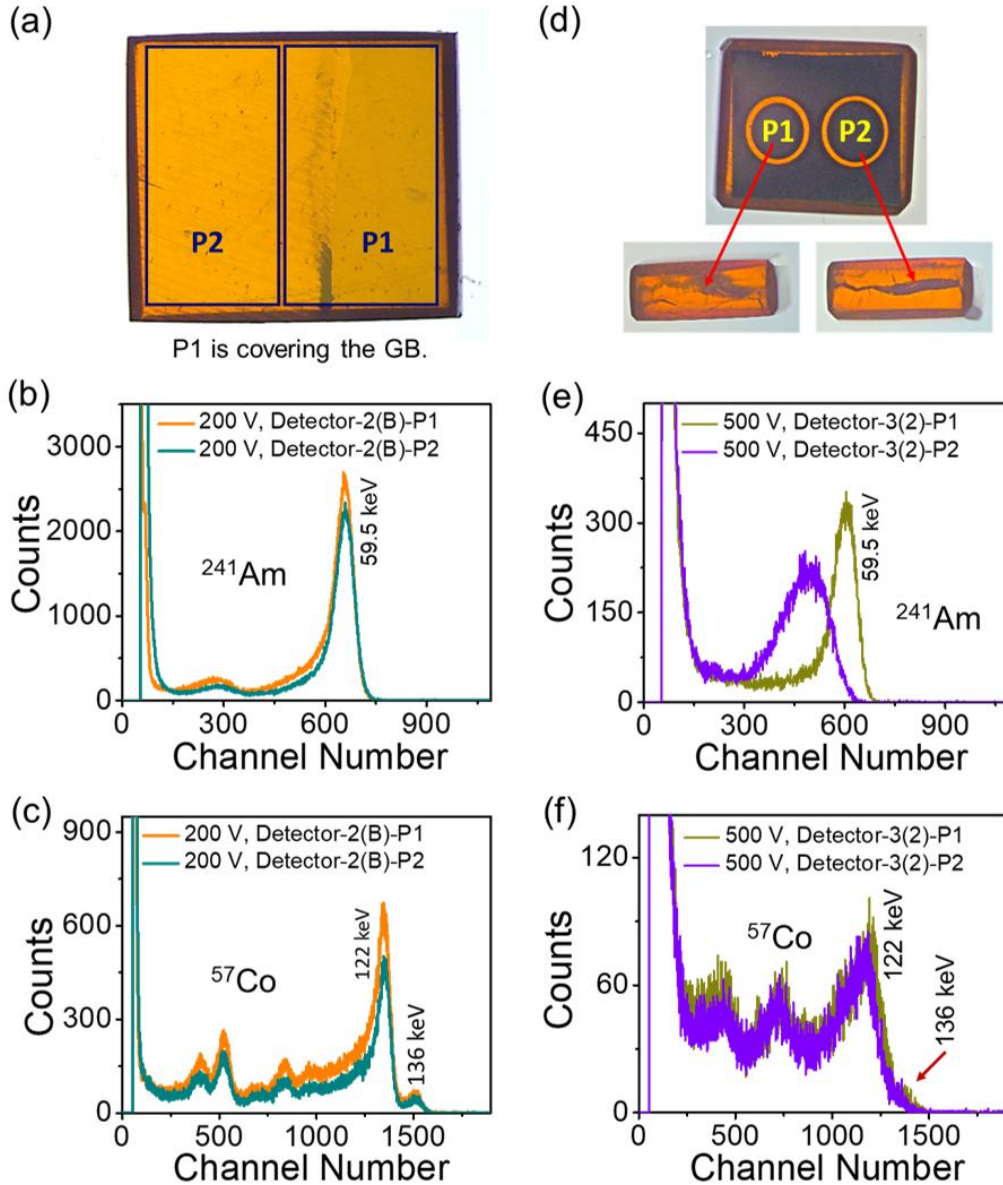


Figure 5. (a) Schematic of two electrodes deposited on the surface of Wafer-2 (Detector-2(B), thickness: 1.28 mm); P1 covers the GB, while P2 does not. **(b–c)** Energy spectrum of the 59.5 keV ^{241}Am γ -ray source and 122 keV ^{57}Co γ -ray source, respectively, recorded with a 3 μs shaping time, +200 V bias, and a 300 s acquisition time in hole collection mode. **(d)** Photograph of two pixels deposited on the surface of Wafer-3 (thickness: 2.70 mm) on Detector-3(2). **(e–f)** Energy spectrum of the 59.5 keV ^{241}Am γ -ray source and 122 keV ^{57}Co γ -ray source, respectively, recorded with a 3 μs shaping time, +500 V bias, and a 300 s acquisition time in hole collection mode for both pixels of Detector-3(2).

To investigate the effects of electrode placement, we examined GB-bearing CLB detectors with varied electrode/pixel layouts and sizes, systematically evaluating their impact on γ -ray detection performance. **Figure 5a–c** illustrates the comparative performance of two adjacent electrodes of Detector-2(B), which was fabricated before using Wafer-2 to fabricate pixelated Detector-2. **Figure 5a** shows that P1 overlays a GB ($\perp$ to the electrode), whereas P2 does not, fabricated on a 1.28 mm-thick Wafer-2 (see **Figure S13a**). In the I–V measurements (**Figure S13b**), P1 exhibits a dark current of 9.86 nA at +300 V, compared to 8.64 nA for P2. Under a 59.5 keV ^{241}Am source irradiation (**Figure 5b**), P1 achieves an ER of 9.9%, while P2, benefiting from its GB-free local region, resolves the peak more sharply at 9.3%. Similarly, for the 122 keV ^{57}Co peak (**Figure 5c**), P1 and P2 achieve ER of 7.4% and 6.9%, respectively. These responses are slightly better for P2 and confirm that even a localized GB can slightly degrade detector performance; still, a GB perpendicular to the electrode surface does not dramatically alter overall behavior.

To further examine the effect of a GB running parallel to the electrodes, Detector-3(2) was fabricated on Wafer-3 by patterning two adjacent pixels (P1 and P2) on the same face: P1 over a region where the GB contrast fades and P2 directly atop the clearly visible GB (**Figure 5d**). **Figure S14b** confirms the GB's variable prominence, and dark current measurements at +300 V revealed 5.72 nA for P1 versus 7.20 nA for P2, indicating slightly enhanced leakage along the intact boundary. **Figure 5e** shows the 59.5 keV ^{241}Am response for pixels P1 and P2 at +500 V, yielding ER of 17.0% for P1 and 45.0% for P2. Similarly, **Figure 5f** displays the 122 keV response from ^{57}Co , with ERs of 16.7% and 19.8% for P1 and P2, respectively, at the same bias. The detector was further subjected to an 18-hour long-term stability test under a 59.5 keV ^{241}Am γ -ray source at +500 V and a 3 μs shaping time. Both pixels exhibited notable instability: P1 averaged ~ 495

channel numbers with an ER of $\sim 34.2\%$ (**Figure S15a–b**), while P2 averaged ~ 448 channel numbers with an ER of $\sim 45.7\%$ (**Figure S15c–d**). Both pixels showed performance degradation over time. Thus, pixels located directly on the intact GB region exhibit higher leakage currents, degraded ER, and long-term instability compared to pixels positioned away from the intact boundary.

The pixel-size effect was probed by patterning 1 mm (P1) and 2 mm (P2) pixels directly on top of the GB of Wafer-4 ($7.5 \times 6.0 \times 1.46 \text{ mm}^3$; **Figure S16a**). At +300 V, pixel P1's dark current was 0.7 nA, whereas pixel P2's rose to 1.9 nA (**Figure S16b**). The energy spectra of the 59.5 keV ^{241}Am γ -ray source are shown in **Figure S16c**. Pixel P1 samples only the most trap-dense GB region; it suffers from reduced CCE and a broader ER of 12.5%. In contrast, the larger pixel P2 encompasses both the boundary and adjacent lower-trap-density areas, thereby boosting its effective $\mu\tau$ and sharpening the ER to 10.3%. Thus, increasing pixel size mitigates the adverse effects of GBs by averaging over lower-trap-density regions, thereby improving charge collection and energy resolution.

Finally, it is known that even modest concentrations of GBs or microcracks in CZT and TlBr can severely restrict charge transport and suppress signal,^[14, 16–17] whereas CLB detectors continue to deliver measurable γ -ray response despite GBs. This desirable behavior is attributed to the material's intrinsically benign defect energetics, strong dielectric screening, and partial self-passivation enabled by ionic conductivity. Moving forward, efforts to grow large, GB-free CLB crystals and design electrode architectures that steer electric fields away from extended defects will remain important for achieving high energy resolution and long-term operational stability in CLB γ -ray detectors. The observation that GBs do not critically limit spectroscopic performance suggests that some constraints required for MHPs detector technologies may be relaxed for some applications, potentially simplifying detector fabrication.

3. Conclusion

CsPbBr₃ detectors retain room-temperature spectroscopic performance despite grain boundaries: GBs modestly raise dark current, slightly reduce $(\mu\tau)_h$, and broaden energy resolution, yet the photopeak is preserved; the largest penalty occurs when a boundary intersects the drift path. At

room temperature, all configurations produced resolvable γ -ray spectra for ^{241}Am (59.5 keV) and ^{57}Co (122 keV), confirming that GBs modulate charge transport, but do not entirely stop spectroscopic operation in CsPbBr_3 . During 18 hours of continuous bias testing, GB-bearing detectors exhibited modest, GB-correlated peak drift and energy-resolution broadening, whereas the GB-free detector remained stable. Two-photon excitation PL microscopy showed asymmetric carrier diffusion near GBs, indicative of limitation in carrier transport under zero field bias, while transient waveform analysis captured field-assisted detrapping that recovers charge collection on application-relevant timescales. Moreover, device-engineering strategies including pixel placement and size, guard rings, field shaping, and electrode work-function design can steer drift paths and electric fields away from defects, thereby minimizing the severe impact of GBs. The operational defect tolerance of CsPbBr_3 reveals a resilience that contrasts with CZT and TlBr , where comparable GB/crack densities have been reported to quench charge transport. Perovskite-based detectors are therefore promising candidates for advanced high-resolution γ -ray detection applications.

4. Experimental Section

Precursor Synthesis and Ingot Growth Process: CLB was synthesized following our lab's optimized protocol and established literature procedures by initially preparing the binary precursors, CsBr and PbBr_2 .^[12b] For CsBr, cesium carbonate (Cs_2CO_3 , 100 g, 3N, Sigma-Aldrich) was carefully dissolved in aqueous hydrobromic acid (HBr, 100 ml, 48%, ProChem Inc.) under continuous stirring. Acetone was then added to precipitate CsBr, resulting in a white powder. This powder was thoroughly washed with excess acetone to remove impurities, dried initially at 120 °C in a drying oven, and subsequently subjected to vacuum drying at 220 °C. PbBr_2 was prepared by dissolving lead(II) acetate trihydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, 100 g, 4N, Sigma-Aldrich) in aqueous HBr (100 ml) with continuous stirring. Ethanol was added to induce precipitation of PbBr_2 , producing a white powder, which was rinsed 3-4 times with ethanol. The PbBr_2 powder was dried at 120 °C in an oven and then further dried under vacuum at 220 °C to remove residual moisture and solvents. The CLB ingot was grown using a sequential, double-purification Bridgman method. Initially, CsBr and PbBr_2 precursors were combined in a stoichiometric ratio of 1:1, sealed in quartz ampoules under a vacuum of approximately 3×10^{-3} Torr, and heated in a vertical furnace to 700 °C. Black impurities were observed on the bulk ingot's surface and removed, along with the

top and bottom sections of the ingot, before the next stage of ingot growth. Following this purification step, growth was conducted at a rate of 3 mm/h. The resulting CLB Bridgman ingot exhibited GBs in certain regions, likely arising from recrystallization dynamics within the sealed environment.

Detector Fabrication and Electrical Characterization: The CLB ingot was sectioned into wafers using a Struers Accutom 50 diamond blade saw to ensure precise cutting. Each wafer was subjected to sequential mechanical polishing using sandpapers with grit sizes of 2400, 4000, 8000, and 12,000 to achieve smooth surfaces with nanoscale roughness. Detectors were fabricated from Bridgman-grown CLB wafers in three configurations: GB-free, GB perpendicular ($\perp$) to the electrode interfaces, and GB parallel ($\parallel$) to the electrode interfaces. For detector fabrication, a low-melting eutectic alloy (Bi-In-Pb-Sn) was manually applied as an anode. A 150 nm thick gold (Au) layer was deposited as the cathode using the SuPro sputtering system. Detectors were fabricated by connecting the electrodes with copper wire using fast-drying conductive carbon glue (TED Pella) and mounting them on electrically insulating glass substrates. After that, each detector was encapsulated in paraffin wax to protect the wafer and contacts from environmental exposure and ensure measurement stability. Electrical characterization was performed under dark conditions across a bias voltage range of -300 V to $+300$ V. Current-voltage (I–V) characteristics were measured using a Keithley 6517B electrometer.

Two-photon Photoluminescence Microscopy: We used a confocal microscope setup (PicoQuant, MicroTime 200) to acquire the PL mapping and diffusion measurements. To achieve two-photon excitation, a 700-nm (below the CsPbBr₃ bandgap) pulsed laser (SpectraPhysics InSight DS+, ~ 100 fs pulse width) was focused through an air objective (100x, 0.8 NA) with a repetition rate of 5MHz and a fluence of $1070 \mu\text{J}/\text{cm}^2$ and $1850 \mu\text{J}/\text{cm}^2$ for mapping and diffusion, respectively. The FWHM of the excitation spot size is approximately 515 nm. A 670 nm shortpass dichroic mirror (T670spxrxt, Chroma) and a 680 nm shortpass filter were used to separate the emission signals from the excitation sources. The filtered emission was then directed through a 75 μm pinhole before being focused onto a photomultiplier detector (PicoQuant, Hybrid PMA) for time-correlated single photon counting. To obtain the PL intensity maps of the entire region of interest, both excitation and emission were scanned pixel by pixel over the region of interest. A Galvano scanner was used to raster scan in the x-direction, and the z-direction was scanned by rapidly moving the objective using a piezo stage. In diffusion measurements, the emission signals

were scanned pixel-by-pixel in the x-direction using a Galvano scanner. The excitation source reached the sample through another path to remain at a fixed x position, while the z-direction was scanned in the same way as mapping using the piezo stage.

γ -ray Experiments: γ -ray detection measurements were performed using ^{241}Am and ^{57}Co sources, each with an activity of $\sim 1\ \mu\text{Ci}$. An eV-550 (Kromek Ltd.) single-channel preamplifier was employed for independent signal readout from the cathode's central electrode. The detector was biased using an ORTEC high-voltage supply (0 to $\pm 5000\ \text{V}$), with a positive bias applied to the anode, and γ -ray photons incident on the same side, followed by hole collection at the cathode. The output signal was first amplified and shaped using an ORTEC 572A amplifier at varying shaping times, then processed by a dual 16K-input multichannel analyzer (ASPEC-927) and an analog-to-digital (ADC) converter. The data collection time was 300 s, and the gain was 80x for all measurements unless otherwise specified. For long-term stability analysis, data were recorded every 10 minutes over 18 hours. The resulting spectra were acquired and analyzed using MAESTRO-32 software. For waveform analysis, pulses generated by γ -ray irradiation from a ^{241}Am source were recorded at various bias voltages using a PicoScope 5444D (Pico Technology Ltd.). For each voltage, 1,000 pulses were acquired, averaged, and normalized using a custom Python program.

Supporting Information

Supporting Information is available free of charge on the Wiley Online Library.

Acknowledgment

This work received financial support from the Defense Threat Reduction Agency (DTRA) under the interaction of Ionizing Radiation with Matter University Research Alliance (IIRM-URA) under contract number HDTRA1-20-2-0002. EBSD performed at the Center for Nanoscale Materials (a U.S. DOE Office of Science User Facility) is supported by the Office of Basic Energy Sciences under Contract DE-AC02-06CH11357. This work utilized the NUFAB and EPIC facilities at the NUANCE Center, Northwestern University. Z.W. and S.D.S. acknowledge the Leverhulme Trust (Project No: RPG-2021-191). S.D.S. acknowledges the Royal Society and Tata Group UF150033, URF\R\221026.

Conflict of Interest

Mercouri G. Kanatzidis is a co-founder of Actinia, Inc., which develops perovskite-based radiation detectors.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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