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350 ps Ultrafast room-temperature scintillation realized on CsPbBr₃-based single crystals *via* Br₂ over-doping

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Ultrafast scintillators are essential for next-generation radiation detection, positron emission tomography, and high-speed medical imaging. All-inorganic CsPbBr₃ perovskites are attractive candidates because of their high stopping power, and excellent optical quality, yet their long carrier lifetimes result in slow scintillation responses on the order of hundreds of nanoseconds. Here, we demonstrate that controlled over-doping with Br₂ produces CsPbBr_{3.03} single crystals with sub-nanosecond scintillation at room temperature while preserving crystal quality. Single crystals grown by the Bridgman method exhibit high transparency and maintain the orthorhombic perovskite structure. Br₂ over-doping induces a slight lattice expansion (about 0.42% increase in unit-cell volume) while maintaining the orthorhombic perovskite phase and high optical transparency. Optical absorption reveals a slight redshift of the absorption edge after Br₂ introduction, indicating a modified defect landscape. Time-resolved photoluminescence and radioluminescence measurements show that Br₂ doping creates dense and efficient recombination centers that reduce the scintillation decay time from more than 100 ns in undoped crystals to 350 ps under 5.486 MeV α -particle excitation, and the scintillation decay time decreases by two orders of magnitude. The doped crystals also achieve a spatial resolution of 12 lp mm⁻¹ in X-ray imaging. These results reveal a defect-engineering route for achieving ultrafast scintillation in halide perovskites and highlight the potential of Br₂-modified CsPbBr₃ for fast timing applications.

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1. Introduction

A scintillator is a class of materials capable of converting high energy radiation into visible light,^{1–3} with extensive applications

in nuclear security screening, high energy physics experiments, and medical imaging systems.^{4–7} However, the performance of scintillator materials directly determines detector capabilities. An ideal scintillator material should possess the following characteristics:^{8,9} (1) high stopping power (elevated effective atomic number, Z_{eff}); (2) short scintillation decay time (*e.g.* few ns); (3) substantial light yield; (4) excellent chemical and thermal stability and facile processability. As shown in Table 1, which summarizes the performance parameters of several conventional scintillator crystals, traditional scintillator materials generally exhibit prolonged luminescence decay times. These over-long >18 ns scintillation decay times limit their applications in ultrafast dynamic medical imaging and ultrafast pulsed radiation detection, which demands ultra-fast scintillation.¹⁰ The scientific community has initiated exploration of novel scintillator materials with sub-nanosecond decay times. Ouyang and co-workers successfully synthesized 2-inch diameter ZnO:Ga crystals *via* hydrothermal methods, achieving an ultrafast scintillation decay time of 600 ps under α particle irradiation.¹¹ Concurrently, Tao and co-workers realized remarkable performance in Cs₃Cu₂I₅:Mn²⁺ single crystals through Mn²⁺ doping, attaining a light yield of

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Table 1 Key technical specifications of conventional and commercial scintillator crystals

Materials	Light yield (Photons per MeV)	Decay time (ns)	Scintillation center wavelength (nm)	Energy resolution (%)	Ref.
NaI:Tl	42 000	230	415	5.4 (662 keV)	27,28
CsI:Tl	87 000	800	550	4.8 (662 keV)	27
Bi ₄ Ge ₃ O ₁₂ :Ce	8800	300	480	8.52 (662 keV)	29,30
Lu ₂ SiO ₅ :Ce	39 000	42	420	9.1 (662 keV)	31
Gd ₃ Al ₂ Ga ₃ O ₁₂ :Ce	28 000	50	515	9.43 (662 keV)	32,33
(Lu _x Y _{1-x}) ₂ SiO ₅ :Ce	30 000	42	410	7 (662 keV)	34,35
LaBr ₃ :Ce	63 000	18	358	2.6 (662 keV)	36
(Lu, Gd)AlO ₃ :Ce	21 000	60	373	14.2 (662 keV)	37
Gd ₂ SiO ₅ :Ce, P	11 850	43	450	10.8 (662 keV)	38

95 772 photons/MeV, energy resolution of 3.79% and scintillation decay time of 3 ns under 662 keV γ -ray excitation.¹²

Since 2013, Kanatzidis and co-workers showed that CsPbX₃ (X = Cl, Br) perovskite semiconductors function as excellent gamma-ray and X-ray detectors,^{13–15} and that their performance stems from properties such as high defect tolerance, long carrier lifetimes, long diffusion lengths, and low-cost crystal growth.^{16–20} The octahedral framework of perovskite materials, combined with divalent group-14 cations like Pb²⁺ with their dynamic lone pairs, gives these compounds remarkable defect tolerance and long recombination times. These features make them ideal platforms for further optimization of the material and, ultimately, its radiation detection performance.^{21–23} High-quality CsPbBr₃ perovskite single crystals were grown using an improved melt-growth method. With an asymmetric electrode design, the resulting semiconductor detectors delivered strong performance, reaching energy resolutions of 1.4% for 662 keV ¹³⁷Cs and 3.9% for 122 keV ⁵⁷Co at room temperature.^{23,24} Perovskite materials have become a major research focus in both academia and industry, emerging as high-performance, low-cost semiconductor materials for radiation detection.²⁵ However, their ultrafast scintillation behavior at room temperature remains largely uninvestigated. This work aims to develop perovskite-based scintillators with sub-nanosecond decay times (<1 ns) suitable for room-temperature operation. Previous studies have shown that in high-quality cesium lead bromide single crystals, longer carrier lifetimes result in extended decay times, often reaching hundreds of nanoseconds, highlighting the need for strategies to accelerate recombination dynamics.²⁶ This study focuses on resolving the key challenge of achieving high crystal quality while simultaneously shortening the scintillation decay time in perovskites. We present a “defect engineering” strategy and grow CsPbBr_{3,03} single crystals with excess Br₂ doping by the vertical Bridgman method. Excess Br₂ introduces efficient exciton recombination centers, which sharply reduces the scintillation decay time without compromising single-crystal quality. This approach yields an ultrafast scintillator with a decay time in the sub-nanosecond regime.

2. Results and discussion

The chemical reagents used in this research include (1) cesium bromide 99.999%, aladdin; (2) lead bromide 99.999%, aladdin;

(3) cesium tribromide (synthesized by the chemical reaction of liquid bromine and cesium bromide, as shown in Fig. 1(a). (The details of synthesis are elaborated in the SI, and the PXRD pattern of CsBr₃ is presented in Fig. S1).

Stoichiometric amounts of CsBr, PbBr₂, and CsBr₃ precursors were loaded into quartz tubes for the synthesis of pure-phase CsPbBr₃ and CsPbBr_{3,03}. During the reaction, the CsBr₃ dopant decomposes *in situ* to CsBr and Br₂ gas, introducing bromine into the structure as the active dopant. This approach eliminates the need to handle hazardous elemental bromine directly. The loading of precursors was conducted in a glove box filled with inert gas to prevent impurity contamination. Initially, homogeneous polycrystalline raw materials were synthesized using a tube

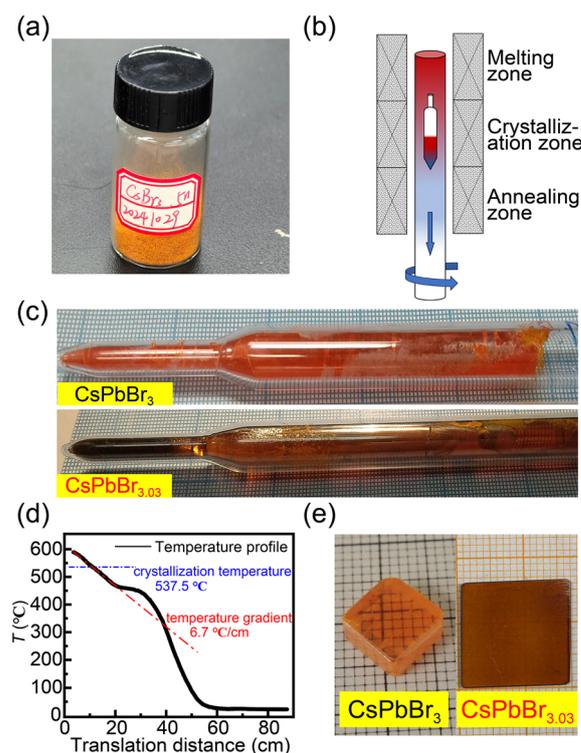


Fig. 1 (a) As-synthesized CsBr₃ powder. (b) Schematic diagram of the three-temperature zone vertical Bridgman furnace for single crystal growth. (c) The as-grown single crystal ingots of CsPbBr_{3,03} and CsPbBr₃. (d) Temperature-position curve of crystal growth. (e) Polished dark orange CsPbBr_{3,03} and orange CsPbBr₃ single crystals.



furnace. Subsequently, the quartz tubes were placed in a vertical gradient freeze furnace for single crystal growth.

Fig. 1(b) schematically illustrates crystal growth by the Bridgman method.³⁹ Based on the setup shown, the large sealed silica tube is connected to an electric motor that rotates the ingot at 8 rpm while it simultaneously descends at a preset rate. The entire assembly passes sequentially through the melting zone, the crystallization zone, and the annealing zone. Fig. 1(d) presents the temperature profile within the furnace chamber. Based on Fig. 1(b) and (d), the crystal growth process is divided into three steps: first, move downward at a translation rate of 5.0 mm h⁻¹ for 14 h before solidification; second, move downward at a translation rate of 0.5 mm h⁻¹ for 240 h during solidification; third, move downward at a translation rate of 5.0 mm h⁻¹ for 50 h after solidification; finally, downward at a translation rate of 2.0 mm h⁻¹ for 60 h for annealing. Under the same synthesis and crystal growth conditions, CsPbBr₃ crystals without Br₂ doping were grown as the reference sample. The final obtained crystal ingots are shown in Fig. 1(c). Crystal ingots with excellent light transmittance can be produced by the Bridgman method. After Br₂ doping, the ingots take on a darker, deeper orange hue, in contrast to the bright orange appearance of the undoped crystals. We further performed atomic force microscopy (AFM) on the polished single crystal surfaces (Fig. S2). The white spots correspond to residual polishing agents, while the black lines represent deeper scratches, indicating that abrasives with lower hardness should be used in subsequent polishing. Notably, excessive Br doping did not introduce any special Br rich morphologies, such as pores or well define geometry shapes, on the surface or in the bulk, confirming that doping does not compromise the material's structural integrity.

The two crystals were analyzed by powder X-ray diffraction, which shows only the CsPbBr₃ phase. No additional phases are observed upon Br₂ doping. This suggests that the excess bromine does not form a separate crystalline phase and may instead be accommodated within the lattice, for example at interstitial sites. To assess the effect of Br₂ doping on the lattice parameters, the PXRD patterns were refined using TOPAS software.⁴⁰ The lattice parameter refinement results are shown in Fig. 2(a) and (b). Table S1 compares the room-temperature lattice constants before and after doping. Br₂ over-doping results in a slight lattice expansion, with increases in *a*, *b*, and *c* and an overall 0.42% increase in unit cell volume. This observation is consistent with the introduction of additional bromine-related species into the lattice, plausibly *via* interstitial incorporation, although complementary chemical and spectroscopic evidence would be needed to identify the specific defect form. Scanning electron microscopy (SEM) characterization was conducted on the CsPbBr₃ and CsPbBr_{3.03} samples, as illustrated in Fig. S3. The Br atomic content of the sample CsPbBr_{3.03} is slightly higher than that of the sample CsPbBr₃, thus enabling the qualitative confirmation of successful Br₂ doping. Furthermore, elemental mapping results revealed a uniform distribution of Br without observable aggregation or agglomeration.

The DTA curve was measured to examine how excessive Br₂ doping affects both the melting point and the phase transition

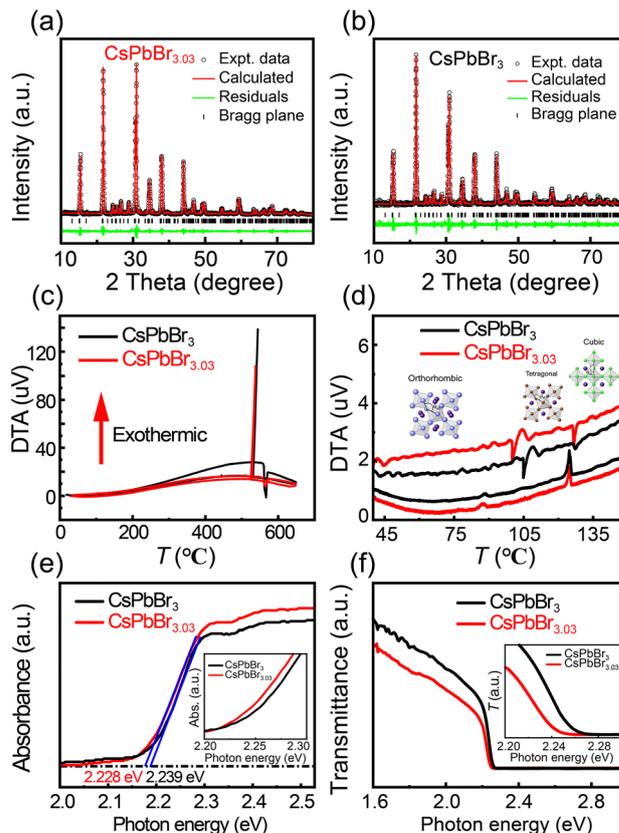


Fig. 2 (a) and (b) TOPAS refinement results of the pure phase CsPbBr₃ crystal and Br₂ over-doped CsPbBr_{3.03} crystal. (c) Differential thermal analysis (DTA) curves of CsPbBr₃ and CsPbBr_{3.03} crystals from 25 to 650 °C. (d) Differential thermal analysis (DTA) curves of CsPbBr₃ and CsPbBr_{3.03} crystals from 40 to 150 °C. (e) UV-Vis optical absorption spectra of CsPbBr₃ and CsPbBr_{3.03} crystals. (f) UV-Vis optical transmission spectra of CsPbBr₃ and CsPbBr_{3.03} crystals.

temperatures. As shown in Fig. 2(c) and (d), the CsPbBr_{3.03} crystal melts at 564.2 °C and crystallizes at 537.5 °C, while the CsPbBr₃ crystal melts at 566.6 °C and crystallizes at 544.0 °C. During the cooling process, CsPbBr_{3.03} crystals undergo phase transitions similar to those of undoped CsPbBr₃ crystals. CsPbBr_{3.03} transforms from the cubic phase to the tetragonal phase at 126.9 °C, and then transforms from the tetragonal phase to the orthorhombic phase at 87.2 °C.⁴¹

Lattice expansion leads to increased atomic spacing, weakening the interatomic interactions, reducing electron wave function overlap, and consequently decreasing the energy required for electrons to transition from the valence band to the conduction band, thereby resulting in a reduced band gap in semiconductor materials.^{42–44} Therefore, the band gap of the material was determined by ultraviolet-visible optical absorption spectrum with and without Br₂ doping. Fig. 2(e) shows the comparison diagram of the band gap before and after Br₂ doping. After Br₂ doping, the band gap decreases from 2.239 eV to 2.228 eV. The slight narrowing of the band gap is consistent with the darker color of the CsPbBr_{3.03} crystal. As shown in Fig. 2(f), the reduction of the band gap can also be observed from the transmission spectrum of a finely polished wafer with a thickness of 1.5 mm. Due to



high transparency, both polished crystals have high light transmittance, which is crucial for scintillators to reduce the self-absorption of scintillation light.

To further probe the effect of Br over-doping on the electronic structure of CsPbBr₃, X-ray photoelectron spectroscopy (XPS) characterization was performed, as illustrated in Fig. S4. Table S2 summarizes the core-level binding energies of key elements in undoped CsPbBr₃ and CsPbBr_{3.03} samples. The most prominent change was observed at the Cs site: the binding energies of the Cs 3d_{5/2} and 3d_{3/2} peaks decreased systematically by ~3.13 eV, indicative of a notable increase in the electron cloud density around Cs atoms. In contrast, the Pb-Br units forming the perovskite framework remained highly stable: the binding energies of Pb 4f and Br 3d orbitals exhibited negligible shifts (≤ 0.06 eV), all within the instrumental error margin. This distinct selective shift implies that the introduction of excess Br did not significantly perturb the local bonding or electronic structure of the [PbBr₆]⁴⁻ octahedral framework.

We constructed a CsPbBr₃ supercell model and performed calculations using the density functional theory (DFT) method. Specifically, in our modeling Br atoms and Br₂ molecules were introduced at interstitial sites, respectively, with their corresponding three-dimensional configurations depicted in Fig. 3(a)–(c). It is observed that Br and Br₂ reside in the interstitial space among four octahedra, where it exerts mutual compressive interactions with the Cs ions present at this site. Table S3 summarizes the supercells' volumes and formation energies. Notably, when a single interstitial site is occupied by a Br₂ molecule other than Br atom, the volume expansion rate of the model is 0.36%, which is closer to the TOPAS-corrected expansion value of 0.42%. Additionally, the formation energy of the lattice with Br₂ occupancy is 0.164 eV (as the reference state: the formation energy of the undoped model is set to 0), which is significantly lower than the 0.301 eV observed when the site is occupied by Br atoms. Furthermore, the CsPbBr₃ cells were removed from the model, leaving only two excess Br atoms. The energies of the two isolated Br atoms and the Br₂ molecule were calculated separately. The results indicate that the energy of Br–Br is –2.847 eV, whereas the energy of the two isolated Br atoms is –0.244 eV. It is evident that the presence of Br in the form of

Br₂ within the lattice reduces the formation energy by approximately 1.30 eV per atom, thereby enhancing the structural stability. As observed in Fig. 3(c), excess Br₂ localizes near Cs atomic sites. In comparison to adjacent Pb ions, the occupancy site of Br₂ lies closer to Cs ions. The high electronegativity of Br₂ is likely to induce a reduction in the binding energy of Cs 3d electrons. Consequently, the occupancy environment assumed in the calculations is consistent with the measured results of XPS binding energies.

Excess Br doping can introduce defect levels into the electronic structure, which in turn can significantly alter the background carrier concentration and therefore the resistivity. As shown in Fig. 4(a) and (b), the resistivity of the CsPbBr_{3.03} sample is $1.2 \times 10^{10} \Omega \text{ cm}$. After doping, the resistivity decreases significantly to $1.51 \times 10^8 \Omega \text{ cm}$. This two-order-of-magnitude reduction likely reflects an increase in the effective carrier concentration, but it may also arise from changes in defect chemistry and transport associated with Br-rich growth. In particular, the slight lattice expansion could modestly weaken Pb–Br bonding and facilitate ion migration, which can contribute to an apparent increase in conductivity under applied bias. Consistent with this picture, the excess bromine introduced during growth may be accommodated in the lattice, plausibly at interstitial sites, although the specific defect form cannot be established from these measurements alone.

Photoluminescence is a sensitive probe of recombination pathways and defect-related processes in semiconductors. As shown in Fig. 5(a), when excited with a 375 nm laser, the sample emits bright green light. The emission bands of both samples exhibit a full width at half maximum of about 18.0 nm. The PL peak intensity of the CsPbBr_{3.03} sample closely matches that of the CsPbBr₃ sample, indicating that Br₂ doping does not quench the luminescence. Our experimental results demonstrate a slight redshift in the optical band gap upon doping, providing evidence that the modified defect environment impacts the electronic structure. However, current measurement techniques are insufficient to resolve the precise nature and energy levels of bromine-induced defects.

To investigate its luminescence dynamics, we first probed the recombination mechanism of the material *via* PL decay measurements. PL decay data were acquired from the emission signals of the two samples at their respective peak wavelengths. Fig. 5(b) and (c) present the time-resolved PL decay curves of

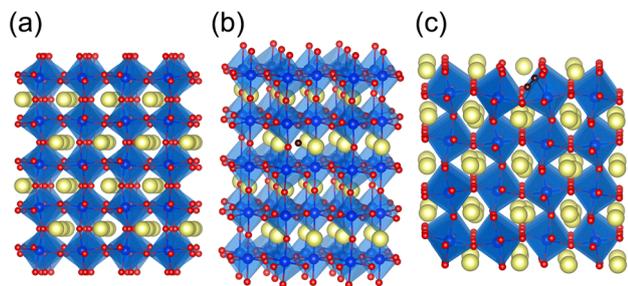


Fig. 3 (a) Schematic illustration of the $2\sqrt{2} \times 2\sqrt{2} \times 2$ supercell structure of CsPbBr₃. (b) Schematic illustration of the $2 \times 2 \times 2$ supercell structure of CsPbBr₃ doped with one excess Br atom. (c) Schematic illustration of the $2\sqrt{2} \times 2\sqrt{2} \times 2$ supercell structure of CsPbBr₃ doped with one excess Br₂. The excess-doped Br atoms are represented by brown symbols.

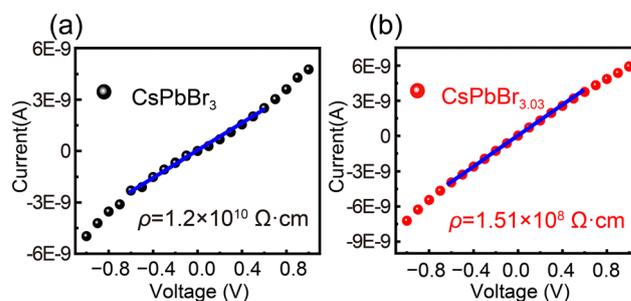


Fig. 4 (a) Current and voltage (I – V) curve of pure phase CsPbBr₃ crystals. (b) Current and voltage (I – V) curve of CsPbBr_{3.03} crystals.



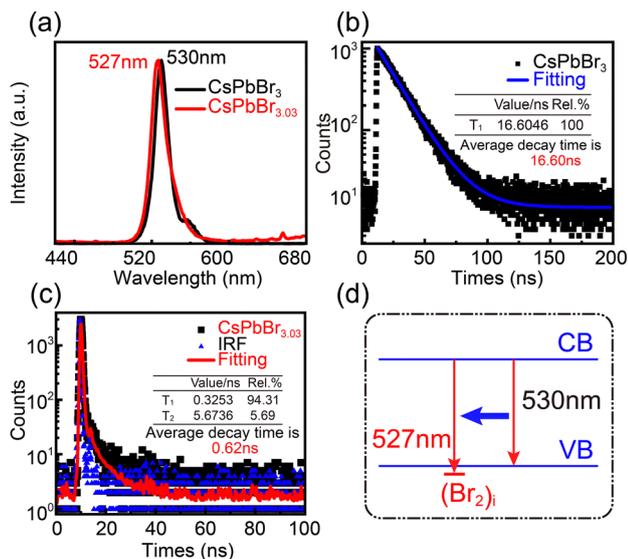


Fig. 5 (a) PL spectra of CsPbBr₃ and CsPbBr_{3.03} crystals. (b) Time-resolved PL decay time of the CsPbBr₃ crystal under 375 nm laser with a power of 5 mW. (c) Time-resolved PL decay time of the CsPbBr_{3.03} crystal under 375 nm laser with a power of 5 mW. (d) A schematic illustration of the defect charge transition energy levels.

the two samples under 375 nm laser excitation, revealing that the Br₂-doped sample exhibits a notably faster decay rate than the undoped counterpart. The decay curves were fitted using exponential functions, with the relevant fitting parameters summarized in the inset tables of Fig. 5(b) and (c). The Br₂-doped sample shows an average decay time of 0.62 ns, consisting of a fast component (0.31 ns, with a relative amplitude contribution of 94.31%) and a slow component (5.67 ns). The presence of this ultrafast decay component indicates the existence of an extremely rapid radiative recombination pathway within the material. Conventional scintillation processes typically involve multiple sequential steps: ionization radiation generates primary electron-hole pairs; hot carriers relax *via* phonon scattering and other mechanisms; carriers are trapped by luminescent centers; and photons are finally emitted through recombination. Among these steps, carrier relaxation and trap-mediated recombination usually take a relatively long time (ranging from nanoseconds to microseconds). However, the sub-nanosecond ultrafast PL decay observed in this study suggests that under optical excitation, the radiative recombination of the material is dominated by an unconventional ultrafast pathway. This fast pathway may be associated with specific defect states in the material, which allow excitons or carriers to recombine before undergoing complete relaxation and trapping processes. Thus, the ultrafast luminescence component observed in the Br₂-doped sample provides a crucial mechanistic basis for its ultrafast scintillation response. Instead, photoexcitation initially produces a high density of electron-hole pairs in the crystal. The calculations and the fluorescence measurements are consistent with strong electronegativity interstitial Br₂ (Fig. 5(d)) introducing an electron-accepting trap level. In this picture, Br₂ preferentially captures photogenerated

electrons (or equivalently withdraws electron density from the host), which suppresses radiative recombination and leaves behind an elevated population of mobile holes in the valence band.

To investigate the potential mechanisms of PL and elucidate the origins of radiative transitions, power-dependent PL spectra were recorded (Fig. 6(a) and (c)). The power-dependent PL spectra of samples CsPbBr₃ and CsPbBr_{3.03}, measured at room temperature, are displayed in Fig. 6(a) and (c). All spectra exhibit a single emission peak centered at 533 nm and 527 nm, respectively. As shown in Fig. 6(a), the PL intensity increases with rising laser power, indicating a direct correlation between excitation power and emission intensity. This observation offers valuable insights into the underlying radiative recombination mechanisms as follows. As the excitation intensity (I) increases, the PL intensity (I) shows a power-law dependence described by $I \propto L^k$, where the exponent k governs the scaling behavior.⁴⁵ When the photon energy of the excitation light exceeds the band-gap energy, the value of the slope k generally falls into one of the following two ranges: $0 < k < 1$ or $1 < k < 2$.^{45,46} In the case of $0 < k < 1$, the emission band can be ascribed to donor-acceptor pair recombination (DAP) or free-bound radiative recombination. When $1 < k < 2$, the emission stems from transitions of free excitons or bound excitons.

As shown in Fig. 6(b) and (d), for sample CsPbBr₃, the value of k is 1.37, while for sample CsPbBr_{3.03}, $k = 1.45$. The k value lies within the scope of free or bound exciton emission. When this is connected with the sub-nanosecond luminescence decay time of sample CsPbBr_{3.03}, it can be deduced that the emission mechanism of sample CsPbBr_{3.03} pertains to bound exciton emission.

To conduct a more in-depth study of the exciton-phonon interaction within CsPbBr₃ and CsPbBr_{3.03} samples, we

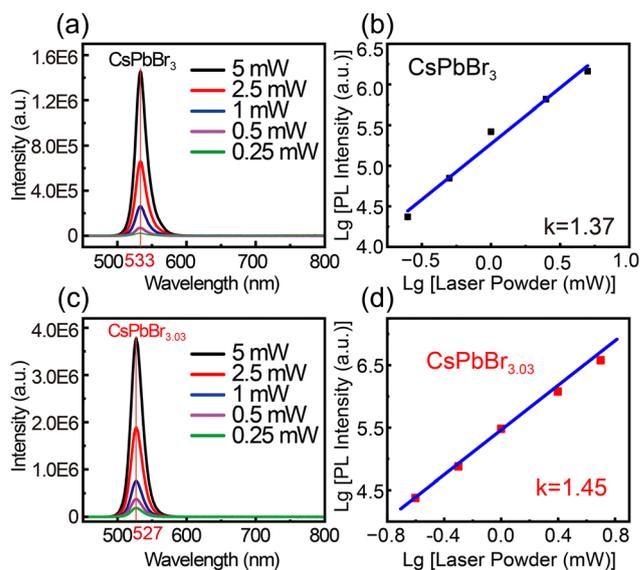


Fig. 6 (a) Power-dependent PL spectra of the CsPbBr₃ single crystal at room temperature. (b) Linear fitting of lg (375 nm laser power)-lg (PL intensity) from a cleaved sample of the CsPbBr₃ single crystal. (c) Power-dependent PL spectra of the CsPbBr_{3.03} single crystal at room temperature. (d) Linear fitting of lg (375 nm laser power)-lg (PL intensity) from a cleaved sample of the CsPbBr_{3.03} single crystal.



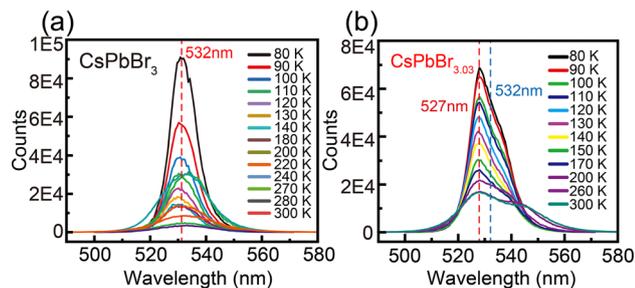


Fig. 7 (a) Temperature-dependent PL spectra of the CsPbBr₃ crystal under excitation from a 5 mW 375 nm laser. The emission peak is located near 532 nm. (b) Temperature-dependent PL spectra of the CsPbBr_{3.03} crystal under excitation from a 5 mW 375 nm laser. Each PL spectrum can be deconvoluted into Peak 1 centered at 527 nm and Peak 2 centered at 532 nm.

acquired temperature-dependent PL spectra spanning from 80 K to 300 K (Fig. 7). Owing to phonon-assisted relaxation processes, the intensity of the PL gradually increases as the temperature goes lower. When excited by a 375 nm laser with a power of 5 mW, the PL spectra within this temperature range exhibit a green emission band. As depicted in Fig. 7, the band-edge emission peaks of the CsPbBr₃ sample exhibit relatively low sensitivity to temperature. However, the linewidth broadening is attributed to the carrier-LO phonon scattering interaction. For the samples with Br₂ over-doping, a notable redshift of the side peaks at 532 nm is observed.

To gain a deeper understanding of the luminescence mechanism, the relationship between the intensity of the samples' emission peaks and temperature was analyzed using the following formula. The goal was to estimate the thermal activation energy of the sample by fitting the data with the Arrhenius equation:⁴⁷

$$I(T) = \frac{I_0}{1 + Ae^{-E_a/K_B T}}$$

where $I(T)$ and I_0 are the PL intensities at temperatures T and the value at a given temperature. This equation also includes E_a , the thermal activation energy, and K_B , the Boltzmann constant, which has a value of 8.6×10^{-5} eV K⁻¹. Initially, the PL spectra of the samples were subjected to Gaussian peak fitting. The fitting results are presented in Fig. 8. The intensity and FWHM of each peak were meticulously recorded. In addition, the PL peak of sample CsPbBr₃ appears symmetric and does not necessitate peak deconvolution, whereas each emission peak of sample CsPbBr_{3.03} can be deconvoluted into two distinct sharp peaks. Subsequently, the aforementioned formula was employed to conduct Arrhenius fitting for these data. The thermal activation energy E_a of the sample CsPbBr₃ is estimated to be 33.81 MeV,⁴⁸ showing a close proximity to the estimated value of 40 MeV. The thermal activation energy of Sample CsPbBr_{3.03} is estimated at 28.93 MeV and 42.24 MeV, respectively. At 527 nm, the thermal activation energy is lower than that of the undoped sample, indicating the formation of new luminescent centers and the establishment of a more efficient energy transfer pathway. At 532 nm, the thermal activation energy increases, likely because

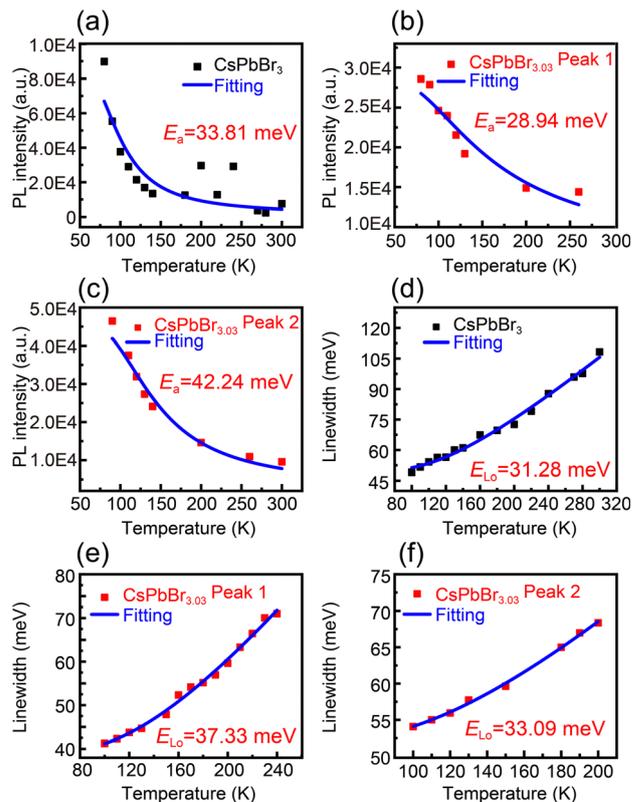


Fig. 8 (a) Arrhenius fitting of the temperature-dependent PL intensity of the CsPbBr₃ sample. (b) Arrhenius fitting utilized to analyze the temperature-dependent intensity of peak 1 of sample CsPbBr_{3.03}. (c) Arrhenius fitting utilized to analyze the temperature-dependent intensity of the peak 2 of sample CsPbBr_{3.03}. (d) Arrhenius fitting used to analyze the temperature-dependent FWHM of the emission peak of CsPbBr₃ sample. (e) Arrhenius method used to analyze the temperature-dependent FWHM of the peak 1 in CsPbBr_{3.03}. (f) Arrhenius method used to analyze the temperature-dependent FWHM of the peak 1 in CsPbBr_{3.03}.

the introduction of Br₂ passivates the original intrinsic luminescent centers, thereby enhancing their stability. On the other hand, the carrier-LO phonon scattering interaction of the samples was explored by measuring the variation of the PL linewidth of the samples with temperature. As depicted in Fig. 7(a) and (b), a notable broadening of the linewidths of both samples was witnessed. This phenomenon can be ascribed to the carrier-LO phonon scattering interaction. For perovskite materials, the temperature-dependent linewidth of PL emission is characterized by the following expression:

$$\Gamma(T) = \Gamma_{\text{inh}} + \Gamma_{\text{LO}}(e^{E_{\text{LO}}/k_B T} - 1)^{-1}$$

Here, the first term, Γ_{inh} , is the inhomogeneous broadening contribution, an Γ_{LO} describes the interactions of carrier-optical phonon contributions to the linewidth broadening. The LO phonon energies (E_{LO}) of the CsPbBr₃, CsPbBr_{3.03} peak 1 and CsPbBr_{3.03} peak 2 samples were determined as 31.28, 37.33 and 33.09 MeV, respectively, based on the temperature-dependent PL spectra of the samples. The relatively higher LO phonon energy observed in the Br₂ doped samples implies a more pronounced



scattering interaction between carriers and LO phonons. This phenomenon can be attributed to the fact that Br₂ doping induces lattice expansion. As a consequence, carrier scattering centers are introduced, and the phonon energy is augmented.

To investigate the scintillation behavior of the Br₂-doped samples, we measured the RL spectra and decay curves under excitation by 5.31 MeV α particles from a ²¹⁰Po source with an activity of 5 mCi. As shown in Fig. 9(a), the emission peaks of the CsPbBr_{3.03} and CsPbBr₃ samples are located at 547 nm and 549 nm, respectively. The RL decay time of the samples was tested. As shown in Fig. 9(b) and (c), the average decay time obtained from the time-resolved radioluminescence (TRRL) test of the sample with excessive Br₂ doping at 547 nm is 0.59 ns which is still on the level of sub-nanosecond, and the average decay time of the undoped sample at 549 nm is 122.48 ns.

The performance of the undoped and doped samples in scintillation-based X-ray imaging was evaluated, as depicted in Fig. 10(a) and (b). Upon irradiation with X-rays, both samples presented emission peaks in the vicinity of 540 nm. In comparison with the PL spectra excited by a 375 nm laser, the main emission peak underwent a red shift. As the temperature increases, the energy of the main peak initially rises and then gradually declines. The Br₂ doped sample demonstrated a more intense X-ray radioluminescence than the undoped (approximately 7 times) under a temperature of 7 K and RL conditions, indicating that the radioluminescence intensity was significantly enhanced after bromine doping. This could be attributed to the lower thermal activation energy in the doped system ($E_a = 28.94$ MeV). Subsequently, X-ray imaging tests were performed on the Br₂ doped samples. Fig. 10(c) shows a schematic diagram of the X-ray imaging system (tube voltage 50 kV). A metal spring enclosed in a black plastic housing was chosen as the imaging subject and positioned between the sample and the X-ray source. Upon X-ray irradiation, the low-density plastic housing was penetrated, whereas the metal effectively blocked the X-rays. The fluorescence image generated by CsPbBr_{3.03} was captured by a CMOS camera equipped with a 20-megapixel sensor. The exposure time was set at 60 s, and the radiation dose rate was 62 mGy s⁻¹, the tube voltage at 50 kV, and the tube current at 1000 μ A. X-ray imaging of the item in Fig. 10(d) was carried out using the CsPbBr_{3.03} sample, and the corresponding photographs are presented in Fig. 10(e) and (f). As can be observed, the optimal spatial resolution is around 12 lp mm⁻¹.

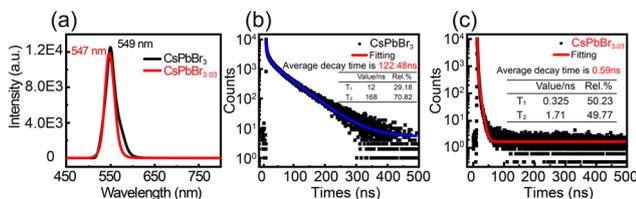


Fig. 9 (a) RL spectra of CsPbBr₃ and CsPbBr_{3.03} crystals irradiated by 5.31 MeV α particles (5 mCi). (b) Time-resolved RL decay time of the CsPbBr₃ crystal irradiated by 5.31 MeV α particles (5 mCi). (c) Time-resolved RL decay time of the CsPbBr_{3.03} crystal irradiated by 5.31 MeV α particles (5 mCi).

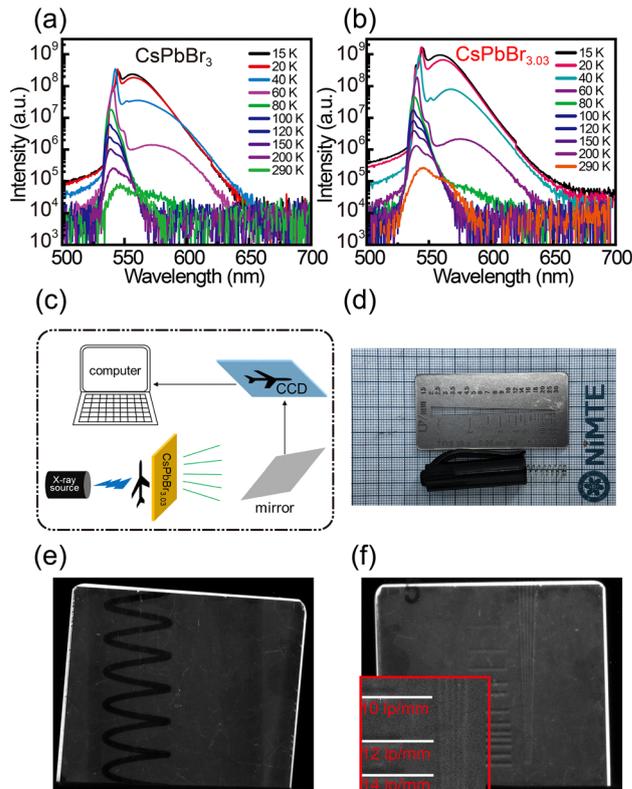


Fig. 10 (a) Temperature-dependent RL spectra of the CsPbBr₃ sample excited by X-rays. (b) Temperature-dependent RL spectra of the CsPbBr_{3.03} sample excited by X-rays. (c) Schematic diagram of the X-ray imaging system. (d) The physical image of the spring and wire phantom for X-ray imaging applications, the crystal employed has a thickness of 0.8 mm and an area of 16 mm \times 17 mm. (e) X-ray fluorescence images of a metallic spring within a black plastic shell. (f) The spatial resolution of the CsPbBr_{3.03} wafer measured by a line pair test pattern.

The aforementioned research findings suggest that CsPbBr_{3.03} single crystals hold promising potential for applications in X-ray imaging.

Due to the gradient variation of Br₂ concentration in the crystal, we observed that the crystals at the tail end exhibited a lower light yield, and CsPbBr_{3.03} was unable to resolve the full energy peak of ²⁴¹Am α particles (Fig. S5). We attribute this degradation primarily to the increased defect density and non-radiative recombination centers induced by the non-stoichiometric Br₂ excess. This excess Br₂, likely in the form of unreacted precursors or secondary phases (e.g., CsPb₂Br₅, Cs₄PbBr₆) at the crystal surface/grain boundaries, could act as effective compound point for charge carriers or excitons. In this scenario, when an excited Br₂ is in close proximity to another Br₂ in the ground state, the excited Br₂ may transfer its energy to the ground state Br₂. As a result, neither of the two Br₂ can emit photons. Instead, the energy is converted into heat and released through lattice vibrations. Moreover, a high doping ratio also enhances the formation of quenching centers within the crystal, which are caused by defects, impurities, etc. In addition, the high concentration of luminescent centers shortens the energy



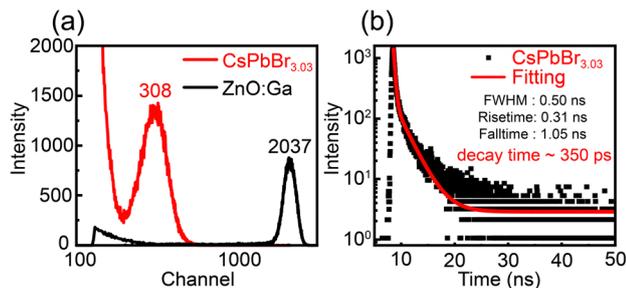


Fig. 11 (a) The pulse height spectra of the CsPbBr_{3.03} samples and the standard sample ZnO:Ga when excited by the 5.486 MeV α particles emitted from ²⁴¹Am. (The CsPbBr_{3.03} wafer is cut along the growth direction of the crystal ingot). (b) Single-particle time-resolved spectrum of CsPbBr_{3.03} excited by 5.486 MeV α particles emitted from ²⁴¹Am.

migration path. Consequently, the likelihood that excitations encounter quenching centers increases significantly. We have successfully observed the full energy peak of ²⁴¹Am α particles in the tip region crystallizing first.

Regarding the measurement of the single particle pulse height spectrum of the CsPbBr_{3.03} samples under α particles excitation, we observed that the channel number of the full energy peak was positively correlated with the scintillation light yield of the specific ray, as shown in Fig. 11(a). When comparing the channel number of the full energy peak of the CsPbBr_{3.03} crystal with that of the commercial scintillator of polycrystalline ZnO:Ga, the former was approximately 15.1% of the latter. Through relative light yield calculations, the light yield of the CsPbBr_{3.03} single crystal was estimated to be ~ 875 photons/(MeV ns), and the light yield of ZnO employed for comparison is 3333 photons/(MeV ns). The relevant equations are presented as follows:

$$Y_{\text{sample}} = Y_{\text{ref}} \frac{P_{\text{sample}}}{P_{\text{ref}}}$$

where Y represents the light yield and P represents the position of the full energy peak in the energy spectrum. Combined with Fig. S6, the relatively low light extraction efficiency of CsPbBr_{3.03} single crystals can be ascribed to their strong self-absorption effect, as evidenced by the large overlap area between the fluorescence emission and optical absorption spectra of the CsPbBr_{3.03} single crystal sample in Fig. S6. Furthermore, we polished crystals with varying thicknesses and observed that thinning can effectively mitigate the drawback, as illustrated in Fig. S7. From Fig. S7(a)–(c), the resolution improves significantly as the wafer thickness decreases. And an alternative strategy involves enhancing the light yield through doping with rare earth elements as activation ions. Then, we bombarded the CsPbBr_{3.03} wafers with 5.486 MeV α particles sourced from a ²⁴¹Am radioactive source (11 000 Bq). Fig. 11(b) depicts the typical waveform of the CsPbBr_{3.03} sample acquired using the single photon counting technique. Through effective noise suppression, the superposition of coincidence events was successfully achieved. In Fig. 11(b), the luminescence rise time is 0.31 ns, the FWHM is 0.50 ns, and the decay tail exhibits a two-exponential behavior.

This clearly demonstrates that the results accurately reflect the time response characteristics of the sample. By fitting the afterglow curve with the single exponential function:

$$y = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2} + A_3 e^{-x/t_3}$$

The decay time τ of the CsPbBr_{3.03} single crystal was determined to be approximately 350 ps.

In addition, electrical measurements (see SI, Fig. S8) reveal that heavily Br₂-doped wafers exhibit high dark currents and unstable photo response under applied bias. This behavior is consistent with the presence of a dense population of fast recombination centers and confirms that such doping suppresses long-lived carrier transport. These findings reinforce the interpretation that Br₂ creates molecular-level defects that accelerate recombination for fast timing scintillation but render the material unsuitable for semiconductor detector operation.

3. Conclusions

CsPbBr₃-based single crystals with Br-rich conditions (nominal composition CsPbBr_{3.03}) were grown from the melt using the vertical Bridgman method, yielding transparent, phase-pure ingots with only a modest lattice expansion relative to undoped CsPbBr₃. Br-rich growth introduces a high density of fast recombination pathways that strongly suppress the slow radioluminescence component and enable ultrafast scintillation at room temperature. Under α -particle excitation, the Br-rich crystals exhibit sub-nanosecond radioluminescence dynamics and a single-particle time response with a decay time as short as ~ 350 ps (compared with the undoped sample, the scintillation decay time reduces by two orders of magnitude), demonstrating that halide perovskites can be driven into a timing regime relevant for fast scintillation and time-resolved detection. In addition, the CsPbBr_{3.03} wafers function as scintillation screens for X-ray imaging, achieving a spatial resolution of ~ 12 lp mm⁻¹ under the conditions tested. At the same time, the electrical measurements indicate that the Br-rich crystals exhibit increased dark current and unstable photoresponse under applied bias, consistent with the introduction of dense recombination centers that accelerate radiative dynamics but degrade long-range charge transport. Therefore, this Br-rich defect-engineering approach is best viewed as a strategy to optimize perovskites for ultrafast scintillation timing rather than for semiconductor detector operation. Future work should focus on identifying the specific bromine-related defect species responsible for the prompt recombination channel, improving compositional uniformity along the ingot, and increasing light yield by mitigating self-absorption and concentration-related quenching while preserving the ultrafast response. At present, we do not understand the microscopic mechanism by which a minute excess of Br drives the scintillation decay into the sub nanosecond regime. Deciphering this will require dedicated future studies, including ultrafast spectroscopy and carrier dynamics modeling, to identify the relevant Br-related defects



and to quantify the carrier generation, transport, trapping, and recombination pathways that set the observed 350 ps response.

4. Author contributions

Z. L. and W. L. designed and accomplished the synthesis, crystal growth, characterization, and measurement of optical properties. Z. L. also conducted data analysis and wrote the manuscript. W. L. designed and supervised the project, and provided assistance in organizing the entire manuscript. Additionally, W. L. carried out the synthesis, crystal growth, doping, and most of the characterization experiments at ANL. Y. H. conducted the γ -ray spectroscopy response tests, Z. C. reviewed, and edited the work. W. L., D. Y. C., and M. G. K. conceived the work and wrote the manuscript. X. O. and F. W. conducted tests on the single photon response of the material. T. B. completed the calculation part.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

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

Supplementary information is available. See <https://doi.org/10.1039/d5tc00101g>.

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