Identifying carrier behavior in ultra-thin indirect-bandgap CsPbX₃ nanocrystal films for use in UV/visible-blind high-energy detectors

*Bin Xin, Naresh Alaal, Somak Mitra, Ahmad Subahi, Yusin Pak, Dhaifallah Almalawi, Norah Alwadai, Sergei Lopatin, Iman S. Roqan**

Dr. B. Xin, Dr. N. Alaal, Dr. S. Mitra, Dr. Y. Pak, D. Almalawi, N. Alwadai, Prof. I. S. Roqan*

¹Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

*E-mail: iman.roqan@kaust.edu.sa

Prof. A. Subahi

King Saud Bin Abdulaziz University for Health Sciences, Jeddah 22384, Saudi Arabia.

Dr. S. Lopatin

Imaging and Characterization Core Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.

D. Almalawi

Physics Department, Faculty of Science, Taif University, 21974 Taif, P. O. Box 888, Saudi Arabia.

N. Alwadai

Department of Physics, College of Sciences, Princess Nourah bint Abdulrahman University (PNU), Riyadh 11671, Saudi Arabia.

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Abstract

High-energy radiation detectors such as x-ray detectors with low light photoresponse characteristics are used for several applications including, space, medical and military devices. Here, an indirect bandgap inorganic perovskite-based x-ray detector is reported. We reveal the indirect bandgap nature of perovskite materials through optical characterizations, time-resolved photoluminescence (TRPL), and theoretical simulations, demonstrating that the differences in temperature-dependent carrier lifetime related to CsPbX_3 ($X = \text{Br}, \text{I}$) perovskite composition are due to the changes in the bandgap structure. TRPL, theoretical analyses, and x-ray radiation measurements reveal that the high response of the UV/visible-blind yellow-phase CsPbI_3 under high-energy x-ray exposure is attributed to the nature of the indirect bandgap structure of CsPbX_3 . The yellow-phase CsPbI_3 -based x-ray detector achieves a relatively high sensitivity of $83.6 \mu\text{CGy}_{\text{air}}^{-1}\text{cm}^{-2}$ (under $1.7 \text{ mGy}_{\text{air}}\text{s}^{-1}$ at an electron field of $0.17 \text{ V}\mu\text{m}^{-1}$ used for medical diagnostics) although the active layer is based solely on an ultra-thin ($\sim 6.6 \mu\text{m}$) CsPbI_3 nanocrystal film, exceeding the values obtained for commercial x-ray detectors, and further confirming good material quality. This CsPbX_3 -based x-ray detector is sufficient for cost-effective device miniaturization based on a simple design.

1. Introduction

High-energy radiation detectors including x-ray detectors are utilized in many fields, such as medical diagnostics, astronomy, security inspection, and industrial monitoring. In particular, UV/visible blind detectors are important for several applications, such as space and military. Among these applications, medical diagnostics is particularly significant, but it presently requires direct exposure to high doses of radiation, which is harmful to human health, increasing cancer risk, especially in children^[1, 2]. Hence, x-ray detectors possessing both high sensitivity and high resolution with a low light interface noise^[3, 4] are required to minimize the radiation exposure during routine medical diagnostics. In the pertinent literature, use of conventional semiconductors for direct x-ray detection has been reported by several groups, including amorphous Se^[5], crystalline Si^[6], Ge^[7], HgI₂^[8], CdTe^[9, 10] and CdZnTe^[9, 10], indicating that the most effective materials are indirect bandgap semiconductors^[5-10] that exhibit low light interference noise. However, as such devices possess low sensitivity due to the low atomic number values of their materials^[7], as well as they still require expensive fabrication and complex processing methods, there is a high industrial demand for cost-effective highly sensitive x-ray detectors that are more suited for mass production.

Ionic perovskite crystals can be processed from solution at low temperatures, in contrast to covalent bond semiconductors, which require a high-temperature crystallization process. Consequently, lead halogen perovskite has emerged as a promising candidate due to its cost-effectiveness, high crystal quality, high absorption cross-section, high illumination, and ability to form quantum dots^[11]. Moreover, these materials were conceived to act as an active layer for x-ray detectors due to the high absorption arising from the high-Z atoms^[12-19]. Owing to these beneficial characteristics, when perovskite materials are utilized in devices based on direct x-ray detection mode^[20-26], simpler system configuration compared to scintillators can be achieved^[27]. However, commercial x-ray detectors rely mostly on indirect bandgap

materials to mitigate the light interference, as medical diagnostics and other industrial applications require high sensitivity, which can only be attained at a high signal-to-noise ratio^[7]. Given that the high cross-sectional light absorption of perovskites (such as CsPbBr₃ and MAPI) and their highly sensitive response to UV/visible light characteristics^[11, 28-32] will increase the x-ray detector complexity as well as the production cost, there is a need for investigating x-ray detectors based on indirect bandgap perovskite-related materials. In particular, CsPbI₃-based x-detectors remains insufficiently studied.

Based on the x-ray detector fundamentals, semiconductor-based x-ray detectors rely on two key features (low density of mobile carriers in the absence of ionizing radiation such as x-rays, and high density of generated carriers with a long decay lifetime to ensure that the carriers can be collected before recombination). Besides, the high performance of x-ray detectors is indicative of high crystal quality^[7]. Therefore, the low quantum yield of the orthorhombic (δ) phase CsPbI₃ is not a measure of the material quality and x-ray detector performance. Recently, x-ray detectors based on γ -phase CsPbI₃ exhibiting very high response and sensitivity for x-ray radiation have been reported, which was attributed to its high resistivity and large (carrier mobility $\times$ lifetime) value^[33]. However, there is a paucity of research on orthorhombic (δ) phase CsPbI₃, as well as its optical properties and carrier mechanisms that produce low light photoresponse, even though its properties can be good for x-ray detectors^[34-37]. Furthermore, the correlation between the band structure of (δ) phase CsPbI₃ and its optical properties has never been conducted.

In this work, we address this gap in extant research by performing advanced optical, theoretical, and structural analyses. Specifically, we used advanced optical time-resolved spectroscopy analyses to explore the changes in the carrier lifetime stemming from the change in perovskite CsPbBr_xI_{3-x} composition. We found that such effects can be attained by engineering the band structure from direct bandgap perovskite CsPbBr₃ to indirect bandgap

orthorhombic (δ) phase CsPbI_3 . We also successfully developed a UV/visible-blind x-ray detector based on the indirect bandgap ultra-thin CsPbI_3 active layer with higher device sensitivity compared to the commercial devices. As this device demonstrates high response, it satisfies two key x-ray detector prerequisites (negligible response to UV/visible light in the absence of ionizing radiation).

2. Results and Discussion

2.1. Synthesis and characterization of CsPbX_3 perovskite.

For the present investigation, we prepared different inorganic perovskites by synthesizing four CsPbX_3 ($X = \text{I}, \text{Br}$) nanocrystals (NCs) by a modified room-temperature co-precipitation method reported by G. Konstantatos *et al.*^[38]. Even though the nominal elemental ratio of the resulting NCs for $\text{CsPbBr}_x\text{I}_{3-x}$ is not very accurate, those four perovskite samples are denoted as CsPbI_3 , CsPbBrI_2 , CsPbBr_2I and CsPbBr_3 , respectively, based on the molar ratio of the halogen element used during chemical synthesis.

As shown in the high-resolution transmission electron microscopy (TEM) images presented in Figure S1a–S1d (in supporting information), the as-synthesized NCs with different Br/I ratios exhibit markedly different shapes depending on the weight of the halogen element. Generally, there are two types of CsPbX_3 NC morphology—nanorod and nanosheet (**Figure 1**). Figure 1a–1c shows the high resolution TEM (HR-TEM) images and corresponding electron energy loss spectroscopy (EELS) mapping as well as the NC profile, respectively, which confirm the quality and the shape of the CsPbBr_3 NCs. The thickness of these NC was estimated to be $\sim 1.2\text{--}2.3$ nm along the z -direction, which is much smaller than the dimensions in the xy -plane (tens to hundreds of nanometers), thus forming two-dimensional (2D) NC structures, as shown in Figure 1a–1c. On the other hand, CsPbI_3 NCs possess a nanorod structure of 150–1,000 nm length, as indicated in their HR-TEM image, EELS map and the corresponding NC profile shown in Figure 1d–1f, respectively. Figure 1f shows that the CsPbI_3

nanorod diameter is ~ 15 nm. The HR-TEM images shown in the insets of Figure 1a and 1d confirm that both NC types exhibit crystalline structure, suggesting high crystal quality.

Figure 1. (a) HR-TEM image of nanosheet (CsPbBr_3 NCs), with the HR-TEM of CsPbBr_3 NCs shown in the inset. (b) EELS mapping corresponding to the TEM image in Figure 1a. (c) The corresponding profile image of CsPbBr_3 NCs demarcated by the dashed rectangle in Figure 1b, confirming the nanosheet feature and the mean free path (λ) estimates (using 300 kV) 60–70 nm x-y dimensions for CsPbBr_3 NC. (d) HR-TEM image of nanorods (CsPbI_3 NCs), with the HR-TEM of CsPbI_3 NCs shown in the inset. (e) EELS mapping corresponding to the TEM image in Figure 1a. (f) The corresponding profile image of CsPbI_3 NCs demarcated by the dotted line shown in Figure 1e, indicating nanorod structure. (g) EDX mapping for CsPbBr_2I ,

where the colored and black patterns indicate the elemental distributions. (h) XRD spectra for CsPbI₃, CsPbBrI₂, CsPbBr₂I, and CsPbBr₃, respectively.

The dramatically different size of these two NC types is determined by the colloidal dispersion in solution, which ranges from weak (CsPbI₃) to strong (CsPbBr₃) as the Br/I ratio increases. The scanning electron microscope (SEM) images of films produced by drop-casting these CsPbX₃ NCs (Figure S1e–S1h in supporting information) are consistent with the corresponding TEM results (Figure S1a–S1d in supporting information). CsPbI₃ films are formed by nanorod stacking (Figure S1e in supporting information), whereas the CsPbBr₃ film surface (Supporting Figure S1h) is much smoother due to the inherent nanosheet structure, which is in line with our recent findings^[39]. The TEM and SEM images of the mixed halogen (CsPbBr₂I and CsPbBrI₂) perovskite reveal structures combining those two morphology types.

To elucidate the chemical composition contribution to the NC morphology, energy-dispersive x-ray spectroscopy (EDX) measurements were carried out and the findings indicate that the Cs/Pb/Br/I elemental ratios are about 1:1:0:2.3, 1:1:1:1.5, 1:1:2.3:0.65 and 0.6:1:3:0, for CsPbI₃, CsPbBr₂I, CsPbBrI₂, and CsPbBr₃, respectively, as shown in Figure S2 in supporting information. We attributed the reduced Cs ratio in the CsPbBr₃ sample to the fact that the Cs ion surface is replaced by a surfactant^[40]. The EDX mapping of the CsPbBr₂I sample (shown in Figure 1g as an example) indicates that the color mapping contrast (denoting elemental distribution) between Pb and Br is much clearer than that pertaining to Cs, implying that Cs drifts more easily than the bonded lead–halide framework (PbBr₄²⁻ tetrahedron).

Figure 1h shows the θ – 2θ x-ray diffraction (XRD) scans of the four perovskite samples. Using the ICSD-181287 and ICSD-27979 XRD data, it can be determined that the CsPbBr₃ structure has a cubic phase that belongs to the *Pm-3m* group, whereas the CsPbI₃ structure has orthorhombic δ -phase (non-perovskite yellow phase) that belongs to the *Pnma* group, in line

with the previously reported findings^[41]. The XRD measurements suggest that both NC types have good crystal quality without secondary phases, which is in line with the findings yielded by the HR-TEM analysis. The peaks at 7.5° and 11.2° (noted by green arrows in Figure 1j) in the CsPbBrI₂, CsPbBr₂I, and CsPbBr₃ spectra are ascribed to the ordered stacking of NCs or superstructures corresponding to the nanosheet morphology evident from the SEM and HR-TEM images, as discussed in our previous work^[42]. However, it should be noted that both CsPbBrI₂ and CsPbBr₂I comprise of a mixture of cubic and yellow phases. Moreover, their lattice constants can be increased by changing the I concentration, as confirmed by the slight shift of the peaks located at 21.5° and 31.5°, which are indicated by the pink- and cyan-colored arrows in Figure 1h.

2.2. Advanced optical analysis and the band structure of perovskite.

The four studied perovskite samples exhibit different optical properties due to the chemical phase differences, as shown in the normalized room temperature (RT) photoluminescence (PL) and absorption spectra (Tauc plots) in **Figure 2a** and **2b**. The PL peaks (excited by the $\lambda = 400$ nm line) located within the 500~525 nm range exhibit a very slight shift as I and Br composition changes. However, The PL integrated peak intensities of all samples shown in Figure S3 in supporting information indicate a significant emission decline as the I composition increases, as the 3:17:100:2000 intensity ratio is obtained for the CsPbI₃, CsPbBrI₂, CsPbBr₂I, and CsPbBr₃ emission peaks. The CsPbI₃ sample produces very weak emission under the weak excitation of the UV lamp source at RT, while the laser excitation induces a broad peak emission from this sample at RT, as shown in Figure S3c in supporting information. A redshift from the absorption edge is observed for the emission peaks of all materials, which is indicative of the Stokes shift^[43]. The color change in CsPbX₃ as a result of varying the halogen element composition ratio is not observed, countering the previously reported findings^[11].

It can also be observed that the absorption edge becomes very broad as the I composition increases. CsPbBr₃ NCs show a much sharper absorption edge, indicating its direct bandgap behavior, relatively, perovskite containing iodine (PCI) NCs deemed as indirect bandgap^[44-46], which is in line with the emission peaks that is proved by our theoretical estimation. The corresponding Tauc plot^[47-49] as shown in Figure 2b reveal the samples bandgap from 2.15 eV (CsPbI₃) to 2.46 eV (CsPbBr₃). Consequently, as shown in the inset of Figure 2a, under UV light illumination, the color brightness of the material declines rapidly, from significantly bright (CsPbBr₃) to completely dark (no emission from CsPbI₃), as I concentration increases. On the other hand, the inset of Figure 2a shows that the material color becomes either yellow or orange under room light, corresponding to the absorption spectra shown in Figure S3b in supporting information.

Figure 2. (a) Normalized PL spectra and absorption of CsPbX₃ samples. (b) Tauc plots of CsPbX₃ samples, the plots show the characteristics of indirect bandgaps for CsPbI₃, CsPbBrI₂, and CsPbBr₂I, and a direct bandgap for CsPbBr₃. The band structure of (c) yellow-phase CsPbI₃ and (d) cubic CsPbBr₃.

To elucidate the differences in the CsPbBr₃ optical properties compared to those characterizing PCI samples incorporating I, the band structure was revealed using density functional theory (DFT) calculations^[50] and the related carrier dynamics of the studied materials were investigated carefully. Orthorhombic δ -CsPbI₃ (yellow phase), cubic CsPbBr₃, orthorhombic γ -CsPbI₃ (black phase), and cubic CsPbI₃ were examined by applying DFT. As can be seen from the band structure of yellow-phase CsPbI₃ shown in Figure 2c, it is an indirect bandgap material, as its valence band maximum (VBM) is situated between the highly symmetric Brillouin zone Γ and Y k -points, and its conduction band minimum (CBM) is located at a different point (X k -point). However, cubic CsPbBr₃ exhibits direct bandgap material properties, as both CBM and VBM are located at the R k -point (Figure 2d). Unlike the yellow-phase CsPbI₃, γ -CsPbI₃ and cubic CsPbI₃ (Figure S4a and S4b in supporting information) exhibit direct bandgap nature, similar to CsPbBr₃ (shown in Figure 2c). However, for γ -CsPbI₃, both CBM and VBM occur at the Γ point. These results align with the absorption measurements, confirming that the yellow-phase CsPbI₃ is an indirect bandgap material.

As typical indirect bandgap materials (such as CsPbI₃) produce very low emission at RT, whereas direct bandgap samples produce much intense emission^[47], we study the optical properties and carrier dynamics of both samples CsPbBr₃ and CsPbI₃. Temperature-dependent PL measurements using laser excitation were performed on CsPbI₃ and CsPbBr₃, as shown in **Figure 3a** and **3b**, indicating that the CsPbBr₃ peak remained relatively intense and sharp as the temperature increased from 4 K to RT, whereas the CsPbI₃ peak was much broader and weaker. In addition, as the temperature increased to RT, the emission produced by CsPbI₃ became weaker and exhibited a broader spectrum. A similar PL signature has been observed for high-quality indirect bandgap materials which indicated that the low emission was due to the nature of the indirect bandgap and was unrelated to the material quality.

Figure 3. Temperature-dependent PL spectra for (a) CsPbBr₃ and (b) CsPbI₃ excited by 400 nm laser line. (c) Room temperature and (d) low temperature TRPL spectra of both CsPbBr₃ and CsPbI₃ NCs. The lifetimes at low temperature (5 K) and room temperature (300 K) for (e) yellow-phase CsPbI₃ and (f) cubic CsPbBr₃.

The carrier dynamics of CsPbI₃ and CsPbBr₃ samples were investigated using time-resolved photoluminescence (TRPL) measurements to further confirm our findings and better understand the optical phenomena observed in Figure 3c and 3d (Table S1 shows the RT TRPL parameters). The total decay lifetime was fitted with bi-exponential decay functions (comprising both fast and slow decay components) due to the presence of multiple recombination centers^[51, 52], as shown in Table S1. Results indicated that the total lifetime was dominated by the slow decay component, which is indicative of high-quality materials. Based on the available literature, the fast decay component is dominant in materials characterized by low crystal quality^[53, 54], as it has been attributed to hot carrier–phonon interactions and optical phonon decay.

Notably, the RT decay lifetime of CsPbBr₃ ($\tau = 9.7 \sim 10$ ns) is almost two orders of magnitude greater than the values obtained for the CsPbI₃ sample (0.26 ns). On the other hand, at low-temperature (5 K), the decay lifetime trend reverses of the CsPbI₃ sample compared to that of CsPbBr₃; the carrier lifetime of CsPbI₃ at 5 K increased significantly and became significantly longer than that of CsPbBr₃ as shown in the TRPL measurements presented in Figure 3d. For CsPbI₃, the total lifetime increased from 0.265 ns at RT to 0.748×10^3 ns at 5 K (an increase of three orders of magnitude), as shown in Figure 3c and 3d, respectively, whereas a minimal change in the total lifetime of CsPbBr₃ was observed as the temperature increased from 5 K (5.2 ns) to RT (9.7 ns). The TRPL parameters are reported in Table S2.

To understand such carrier lifetime behavior in both materials, radiative and non-radiative components were analyzed^[51, 55], and the results are reported in Figure 3e-3f, , while Tables S1 and S2 show the calculated values using the equation in section S1. As shown in Figure 3d, the lifetime of CsPbBr₃ at RT was dominated by radiative recombination (as it is in the same ns range of the total lifetime). By contrast, TRPL analysis of CsPbI₃ NCs (Figure 3f) revealed that the non-radiative recombination, τ_{nr} , was 0.279 ns at RT, which is comparable to the total recombination value (0.265 ns), though the radiative recombination lifetime was very long ($\tau_r = 325 \times 10^3$ ns), suggesting more non-radiative recombination contribution that is usually observed in the indirect bandgap material^[53]. Similar decay behavior has been reported in pertinent literature for typical direct- and indirect bandgap materials.^[51, 54] Since radiative recombination is independent of temperature, the total lifetime did not change significantly for CsPbBr₃ in contrast to that in CsPbI₃.^[42, 53, 56] These findings revealed the reason behind the more intense PL emission and longer RT total lifetime decay of CsPbBr₃ compared to that of CsPbI₃.

At low temperatures, we observed that the carrier lifetime was considerably longer in indirect bandgap CsPbI₃ materials compared to that of direct bandgap CsPbBr₃ materials. This

may be due to the contribution of phonon interactions in the generation/recombination processes, allowing for momentum conservation^[56] to transfer the carriers from the CBM at the X k -point to the VBM at the k -point between Γ and Y, as shown in the band structures of CsPbI₃ in Figure 3a. This stands in contrast to the recombination/generation processes in direct bandgap CsPbBr₃ that do not require phonon interaction (the CBM and VMB at the same K-point). Similar long lifetime behavior has been observed in several indirect bandgap materials at low temperatures, though the RT lifetime is very short as the phonon is highly dependent on temperature^[53]. Therefore, the phonon interaction in the indirect bandgap structure of CsPbI₃ led to a shorter lifetime at RT and a longer lifetime at low temperature compared to those of direct bandgap materials.^[57, 58]

Figure 4. (a) The detector structure, with the working energy level shown in the inset. (b) The ON/OFF transient measurements of CsPbI₃ and CsPbBr₃ under 53 mW/cm² visible light illumination. (c) The ON/OFF transient measurements of CsPbI₃ and CsPbBr₃ under 158.5 mW/cm² UV laser illumination at 244 nm.

2.3. Detector performance under Vis/UV/X-ray illumination.

Four perovskite samples were prepared by drop-casting 100 ml of colloid solution on interdigitated contact electrode (IDE) (Au/SiO₂/Si substrate). Au was used as an ohmic contact in the horizontal metal–semiconductor–metal (MSM) structures, as shown in **Figure 4a**. The energy level plotted in Figure S5a in supporting information is based on the 6.35 eV Pt work

function and the CsPbBr₃ CBM and VBM energy levels of -4.1 eV and -6.3 eV, respectively^[59]. The active layer was exposed to the excitation source (visible light, UV light, or x-ray radiation), which generated carriers, thereby enhancing the current produced when a bias voltage is applied to the two electrodes.

Figure 4b shows the on-off current curve obtained when the photodetectors were exposed to visible light, while the curve depicted in Figure 4c was produced by exposing the devices to UV radiation at 1 V bias voltage. The visible light was generated by a 53 mW/cm² white LED (operating in the 400 nm ~ 700 nm wavelength range), whereas a 244 nm, 158.5 mW/cm² UV laser served as the UV light source. CsPbBr₃ produced the photocurrent of 3 nA and 8.3 nA, under visible light and UV light, respectively. CsPbI₃ yielded a much lower photocurrent (0.2 nA), which is equivalent to ~7% of the photocurrent obtained from CsPbBr₃ under visible light exposure. Similarly, 0.22 nA was obtained for CsPbI₃ under UV light, corresponding to ~2.5% of the value measured for CsPbBr₃.

Figure 5. (a) Calculation of the mass absorption of Si, CdTe, MAPbI₃, and CsPbI₃ as a function of x-ray energy (the region marked by the dashed rectangle is shown in the inset). (b) The I–T curve of the CsPbBrI₂ detector at different voltages when subjected to a 60 kV, 200 mA, 2 s x-ray pulse. (c) Sensitivity of devices based on CsPbI₃, CsPbBrI₂, CsPbBr₂I, and CsPbBr₃ as a

function of electric field. (d) Sensitivity of devices based on CsPbI₃, CsPbBrI₂, CsPbBr₂I, and CsPbBr₃ as a function of x-ray dose. (e) A schematic diagram of the x-ray carrier generation process. (f) The I–T curve of the CsPbI₃ detector as a function of dose, which was varied by controlling the x-ray tube current, while the x-ray tube acceleration bias was maintained at 60 kV.

The I–V curves of the PCI samples shown in Figure S5b and S5c in supporting information indicate that their response produced by UV/visible excitation almost coincides with that under dark conditions, which implies highly unfavorable response to UV/visible illumination and is in line with the previously reported findings^[35]. Such photoresponse is most likely due to the nature of the indirect bandgap structure of the PCI materials, rather than reflecting the material quality. We attribute the poor response of the PCI samples and the favorable response of CsPbBr₃ to the fact that, unlike the former, the latter is a direct bandgap material, characterized by higher generated carrier density due to direct carrier transitions from the VB to the CB. Conversely, in indirect bandgap materials, the energy absorbed from the incident light is dissipated through phonon interactions, leading to poor device response. It is well known that indirect bandgap materials are not suitable for optoelectronic applications because the generation and recombination processes of electron-hole pairs require not only photon involvement, but also necessitates momentum conservation via a phonon, which significantly reduces the probability of photoelectric conversion.

2.4. Detector performance under x-ray exposure.

The CsPbI₃ x-ray absorption spectrum was compared to that of traditional semiconductors over a broad range of photon energies using the photon cross-section database^[60], as shown in **Figure 5a**. The remaining CsPbX₃ structures exhibit similar absorption properties, as shown in Figure S6a in supporting information, confirming a high quality of PCI similar to that of

CsPbBr₃, which results in similar high-performance devices. The x-ray absorption coefficient is determined by $\alpha=Z^4/E^3$, where Z is the atomic number and E is the radiation energy. As Cs, Pb, I, and Br are heavy elements, this results in efficient x-ray attenuation (Figure S6b in supporting information), as well as improved signal current, as x-ray radiation is readily absorbed by the material in the x-ray path. For example, the CsPbI₃ absorption coefficient across the entire examined energy range (excluding 3.7~5.2 keV and 26.7~36 keV) is slightly higher than that of CdTe (shown in the inset of Figure 5a). Its performance is also superior to that reported for inorganic perovskite MAPbI₃ and is much better than the performance of traditional Si-based detectors.

The performance of x-ray detectors based on the four studied perovskites was investigated using a dark-environment clinical diagnostics tube, as shown in Figure S7 in supporting information. The I–T curve obtained for CsPbBrI₂ under different bias voltages is shown in Figure 5b, as the remaining three samples produced a similar response (Figure S8 in Supporting information). The repeated on/off current cycles are characterized by the same intensity and are capable of reversible and rapid switching between the dark and under the x-ray exposure, indicating stable device performance as shown in Figure S8. We found that the current increases as voltage increases (linearly), suggesting good device stability. No device degradation was observed when we repeated the on/off measurements under different applied bias and several x-ray exposure. Thus, we demonstrated the performance and high stability of our devices under x-ray exposure using different voltages and different x-ray doses (Figure S8 and Figure 5f, respectively). The on-current exhibited much greater fluctuations than those induced by visible light or UV light, which could be attributed to x-ray tube ripple or random carrier generation in the perovskite active layer^[16]. When the x-ray measurements were repeated after a few weeks, similar I–V results were obtained to those shown in Figure S5b and S5c in supporting

information. This evidence confirms that inorganic CsPbX₃ is sufficiently stable under x-ray exposure.

By using the $S = Q/AX$ sensitivity formula, where A is the exposed area and X is the radiation exposure^[5], it can be shown that the sensitivity of the four studied devices can be described by a linear function of the electric field strength, as demonstrated in Figure 5c. Here, x-ray intensity was calculated using Rad Pro Calculator^[61] and the findings are reported in Table S3. Dose-dependence experiments were conducted by varying the x-ray tube current. As shown in Figure 5d, the sensitivity of all studied devices followed a very similar trend, increasing with the dose rate reduction.

The highest sensitivity (up to 83.6 $\mu\text{CGy}_{\text{air}}^{-1}\text{cm}^{-2}$) was obtained for the CsPbI₃ (the indirect bandgap material) sample under 1.7 $\text{mGy}_{\text{air}}\text{s}^{-1}$ at an electron field of 0.17 $\text{V}\mu\text{m}^{-1}$ (which is within the range used in medical diagnostics, given that the medical hospital system shown in Figure S7 in supporting information was used in the present investigation). It can thus be concluded that the x-ray detector sensitivity increases as the electric field increases and the dose rate decreases. Device sensitivity can also be calculated via the linear fitting of the current density as a function of dose rate^[18], as shown in Figure S8 and Figure S9 in supporting information. For all devices, the sensitivity of about 21 $\mu\text{CGy}_{\text{air}}^{-1}\text{cm}^{-2}$ was derived from the slope of the fitted line. Moreover, the fitting results indicate that -5.48 $\text{mGy}_{\text{air}}\text{s}^{-1}$ is the lowest detectable dose rate. This negative value could be attributed to the non-linear relationship between the current density and the dose rate, especially in the low dose rate region. We believe that the lowest detectable dose rate calculated by this method is not of practical significance, because most detectors are characterized by a distinct signal-to-noise ratio.

We expect that the x-ray absorption would be governed by the core electrons in each of the constituent elements. As the four samples contain both Cs and Pd, the x-ray response is expected to arise primarily from Pd, as it is a much larger atom, dominating the response of

other elements (as confirmed by the elemental x-ray absorption analyses presented in Figure S6b). Figure S6a represents the calculated x-ray absorption values of all four samples, which are equal, leading to the conclusion that the devices exhibit comparable performance. As shown in Figure 5e, when x-rays are incident on the active atoms, photons eject electrons from the inner orbitals (i.e., the L or K shell)^[62]. These ejected electrons either become free electrons or may be captured by other atoms. In either case, the resulting holes in the lower orbitals will be filled by electrons from an outer shell (M shell), each creating a hole that would act as a carrier. Although perovskite materials typically exhibit a highly sensitive response to UV/visible light, such wavelengths will produce noise in x-ray detectors.

The data related to CsPbI₃, CsPbBrI₂, CsPbBr₂I, and CsPbBr₃ under visible light (53 mWcm⁻²) and UV light (158.5 mWcm⁻²), as well as under x-ray radiation (26.5 mGy_{air}S⁻¹), shown in Figure S8 and Figure S9 confirm that the device based on indirect bandgap perovskite has a high x-ray response similar to that obtained from devices based on direct bandgap perovskite (Figure S10 in supporting information), while also indicating the superior quality of the four materials. However, the CsPbBr₃ current signal produced by vis/UV light is much higher than that obtained under x-ray exposure, while it is markedly suppressed for the remaining three PCI samples. Hence, our devices could operate under a very high light exposure without any further modifications to their structure or additional signal modulation. These findings confirm that CsPbI₃ is capable of eliminating solar light interference to ensure that the detector would meet the criteria imposed by its intended applications.

Our experimental results also indicate that the detector was sensitive to a lower dose of 1.7 mGy_{air}S⁻¹ with an on/off ratio of 4, as shown in Figure 5e. This on/off ratio is similar to that reported by Shrestha^[17] under a much higher dose (5.86 mGy_{air}S⁻¹) and a higher electron field (0.2 Vμm⁻¹), indicating superior characteristics of our devices. In addition, the highest sensitivity of the CsPbI₃ device (83.6 μCGy_{air}⁻¹cm⁻²) is more than ten times higher than that

reported for an amorphous silicon detector ($0.3 \mu\text{CGy}_{\text{air}}^{-1}\text{cm}^{-2}$)^[6] as well as Cd(Zn)Te single-crystal detectors and much higher than α -Se detectors ($20 \mu\text{CGy}_{\text{air}}^{-1}\text{cm}^{-2}$)^[5], while it is comparable to the results reported by Wei and Pan^[18] (as shown in Table S4). Our devices exhibit a higher sensitivity compared to semiconductor devices because the x-ray attenuation coefficient (α) or stopping power of a material is very sensitive to its atomic number (Z) (as $\alpha \propto Z^4/E^3$), where E is the x-ray photon energy. Therefore, although commercial single-crystalline semiconductor-based (e.g. Si, Se and Cd(Zn)Te) detectors possess large (charge mobility $\times$ carrier lifetime) value, their sensitivity remains low due to the small Z values.^[63] It is worth noting that this is the first report on an x-ray detector based on ultra-thin perovskite (about $6.6 \mu\text{m}$ for CsPbI₃, as shown in Figure S11 in supporting information). Recently CsPbI₃ microwire-based x-ray detector was reported to exhibit high sensitivity^[33].

Perovskite-based x-ray detector has a similar device structure to photodetectors but requires a much thicker active layer for absorbing x-rays efficiently. Thus, the perovskite layer thickness is a crucial determinant of device sensitivity. However, when the perovskite layer is too thick, it will be challenging to obtain high spatial resolution. Therefore, we fabricated devices based on an ultra-thin CsPbX₃ active layer ($\sim 6.6 \mu\text{m}$). In all previous reports, the active layer was up to 1000 times thicker than that utilized in our study (a detailed comparison is given in Table S4 in Supporting Information). In addition, the sensitivity of our device is better than that currently achieved in commercial devices in which the active layer thickness ranges from $100 \mu\text{m}$ to a few mm^[15, 18]. Even though it is expected that our device architecture and ultra-thin film thickness to result in lower sensitivity, the response is still superior compared to that reported for other devices^[15, 18]. These characteristics can be beneficial for portable cost-effective UV/visible blind x-ray detectors powered by solar cells that require high sensitivity and simple design. Owing to the high x-ray absorption of CsPbX₃, even a thin layer of this material could yield high sensitivity (Figure 5a). Further investigations focusing on optimizing

the active layer thickness and reducing the dark current (i.e., by adding a hole-block layer) should, in principle, significantly boost the performance of our devices.

3. Conclusions

We reported on a novel concept based on applying solution-processed iodine CsPbX₃ NCs for high-energy (mainly x-ray) detection. The properties of these NCs have been studied by HR-TEM and TRPL that revealed different carrier dynamics and band structures of CsPbX₃ when X changes. We showed that although the carrier lifetime of CsPbBr₃ is much longer than that of CsPbI₃ at RT, the lifetime trend reverses at 5K, which was attributed to their band structure nature. For the first time, the fabrication of UV/visible blind and high sensitivity x-ray detectors based on yellow phase PbCsI₃ operating under ambient conditions was demonstrated. We show that the x-ray detector exhibits higher sensitivity ($83.6 \mu\text{CGy}_{\text{air}}^{-1}\text{cm}^{-2}$) compared to commercial semiconductor-based x-ray devices, though a much thinner active layer ($\sim 6.6 \mu\text{m}$) was adopted, confirming sufficient evidence of the device's excellent performance. Our findings showed that the fabrication process of our x-ray device is simple and cost-effective, it does not require the complex integration of several filter layers and can be used for producing portable detectors, revealing the potential for adopting indirect bandgap iodine CsPbX₃ materials for practical applications.

4. Method

Chemicals: Lead(II) bromide (PbBr₂, 99.999% trace metals basis), lead(II) iodide (PbI₂, 99.999% trace metals basis), cesium acetate (CsAc, 99.99% trace metals basis), octylamine (OcAm, 99%), hexanoic acid (HexAc, 99%), isopropanol (IPA, 99%), n-hexane (Hex, 99%) and toluene (TOL, 99.8%) were purchased from Sigma-Aldrich. All chemicals were used without any further purification.

Synthesis and purification of CsPbX₃ nanocrystals: CsPbX₃ (CsPbI₃, CsPbBrI₂, CsPbBr₂I, and CsPbBr₃) NCs were synthesized by a modified procedure reported by G. Konstantatos *et al.*^[38]. Typically, Cs precursor and PbX₂ precursor were prepared separately, and the reaction was initiated by injecting the latter into the former. First, Cs precursor solution was prepared by dissolving 32 mg CsAc in 1 mL IPA in a 20 mL vial under stirring in air at RT, followed by addition of 6 mL Hex and 2 mL IPA. Next, PbX₂ precursor solution was prepared by dissolving 0.167 mmol PbX₂ (307.5 mg PbI₂ for CsPbI₃, 81.6 mg PbBr₂ and 205 mg PbI₂ for CsPbBrI₂, 163.2 mg PbBr₂ and 102.5 mg PbI₂ for CsPbBr₂I, and 245 mg PbBr₂ for CsPbBr₃) into a mixture solution of 0.45 mL IPA, 0.45 mL hexanoic acid and 0.45 mL OcAm at 90 °C in air under vigorous stirring. The hot PbX₂ precursor was subsequently swiftly injected into the Cs precursor under vigorous stirring at RT. The reaction was completed in 120 s. High illumination was noted under UV exposure for CsPbBr₃ and CsPbBrI₂. The CsPbX₃ NCs were isolated by centrifugation at 3,000 rpm for 180 s, and the pellet was dispersed into 3 mL of toluene. As a result of centrifugation, CsPbBrI₂ NCs lose the illumination ability, as indicated by the phase change during dispensation.

Characterization: XRD measurements were conducted using a Bruker D8 Advance X-ray diffractometer equipped with monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The samples were prepared by drop-casting the nanosheet on a glass slide before drying the specimen at RT. HR-TEM was performed using a Titan CT (with 200 kV), while Cary 6000i UV-Vis-NIR spectrophotometer was used for absorption measurements. RT PL measurements were performed utilizing Edinburgh FLS980 Photoluminescence Spectrometer attached to a 1,000 W Xenon lamp (Newport 66923). ZEISS SEM (with 5 kV) was employed for SEM, and EDX analysis was carried out using an X-ACT detector from Oxford Instruments coupled with SEM (20 kV). The samples for SEM measurements were prepared by drop-casting colloidal NCs on a Si wafer and drying under ambient air conditions, with a 3 nm-thick iridium layer serving as the conductive coating.

Advanced optical characterizations: TRPL measurements were performed using a mode-locked Ti:sapphire laser (Coherent Mira 900), with a 1.90 W laser power at 800 nm. A second harmonic generator (APE) was used to excite the samples by 400 nm (150 fs pulse width and 76 MHz pulse repetition rate). Laser power on the sample was $> 1 \text{ mW}$ (60 μm spot diameter). Emission produced by the samples was detected by the monochromator attached to a Hamamatsu C6860 streak camera with a temporal resolution of 2 ps. The single sweep mode was used for 5 K measurements, whereas the synchroscan mode was used for RT measurements. For the single sweep mode, a pulse picker (PulseSelect APE) was utilized to reduce the frequency from 76 to 2 MHz.

Ab initio electronic structure calculations of different phase CsPbX₃: First principles-based DFT calculations were performed using VASP software package as it is very good tool to obtain the electronic properties and band structures^[64, 65] and other of the orthorhombic δ -CsPbI₃ (yellow phase), orthorhombic γ -CsPbI₃ (black phase), cubic CsPbI₃, and cubic CsPbBr₃. The electron-ion interaction was described by projected augmented wave (PAW) method^[66]. The

Perdew–Burke–Ernzerhof functional^[67] was used as the exchange and correlation potential. A kinetic energy cut-off of 500 eV was chosen for the plane wave basis sets. All atoms in the unit cell were relaxed until the force on each atom declined below 0.01 eV/Å, and 10⁻⁵ eV total energy convergence was chosen for the electronic relaxation. A gamma-centered k-point mesh of 6×6×6 and 8×8×6 dimensions was adopted for cubic and orthorhombic crystal structures, respectively.

Detectors – fabrication and measurements: An 80 nm thick electrode was deposited on SiO₂/Si substrates of 200 nm thickness by thermal evaporation assisted with shadow masks.^[68, 69] The interdigitated contact electrode (ICE) comprised of four close parallel branches extending from two separate trunks. The channel length between the branches and the branch width was 30 μm and 950 μm, respectively. The CsPbX₃ solution was drop-casted on the electrode. After the solution had dried, the sample was placed on a hot plate for thermal annealing in ambient air at 110 °C for 10 minutes. Keithley DC power supply was used as the voltage source for I–V measurements, whereby the photocurrent was recorded via LABVIEW program (current vs. time frame) and ReRa Solutions Tracer I–V curve software was employed for data acquisition. For the experiments, white light / UV light and x-ray radiation sources were supplied by a 53 mW/cm² visible light source and 158.5 mW/cm² UV laser, respectively. A filter was placed in the light path to obtain visible or UV light.

X-ray tube experiment: For practical purposes, this experiment was conducted under a Definium 8000 system produced by GE Healthcare with a Maxiray 100 x-ray tube, whereby 2 mm Al filtration (SIEMENS AL01C II) acted as the collimator. In an x-ray tube, electrons are accelerated in a vacuum by an electric field towards a metal target. Because x-rays are emitted as the electrons decelerate in the metal, the output signal consists of a continuous bremsstrahlung spectrum, with additional sharp characteristic peaks associated with the atoms in the target. For tungsten, an L-shell electron filling a K-shell vacancy results in a

characteristic x-ray energy: $E_{K-shell} - E_{L-shell} = 69.5 \text{ keV} - 10.2 \text{ keV} = 59.3 \text{ keV}$. The shape of this continuous spectrum is approximately described by Kramers' law.

Supporting information:

TEM, EELS mapping of CsPbBr₃; EDX spectrum; PL absorption spectrum; TRPL parameters; Band structures; Low-temperature TRPL parameters; Device work function; X-ray absorption coefficient; X-ray detector setup; X-ray doses; X-ray generated photocurrent; Performance comparison; I–T curve of CsPbI₃; Cross films; Comparison form.

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Conflict of interests

The authors declare no competing interests.

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Table of contents

High-energy radiation detectors, such as x-ray detectors with low light photoresponse characteristics are crucial for several application in medical diagnostics, astronomy, military and industrial monitoring. The carrier dynamics of an indirect-bandgap perovskite was revealed, which can be used for UV/visible-blind x-ray detectors with high and stable photoelectric response under high-energy x-ray exposure.

B. Xin, N. Alaal, S. Mitra,¹A. Subahi, Y. Pak, D. Almalawi, N. Alwadai, S. Lopatin, I. S. Roqan

Identifying carrier behavior in ultra-thin indirect-bandgap CsPbX₃ nanocrystal films for use in UV/visible-blind high-energy detectors

Supporting Information

Identifying carrier behavior in ultra-thin indirect-bandgap CsPbX₃ nanocrystal films for use in UV/visible-blind high-energy detectors

Bin Xin,¹ Naresh Alaal,¹ Somak Mitra,¹ Ahmad Subahi,² Yusin Pak,¹ Dhaifallah Almalawi,^{1,3} Norah Alwadai,^{1,4} Sergei Lopatin,⁵ Iman S. Roqan^{1,*}

¹Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

²King Saud Bin Abdulaziz University for Health Sciences, Jeddah 22384, Saudi Arabia.

³Physics Department, Faculty of Science, Taif University, 21974 Taif, P. O. Box 888, Saudi Arabia.

⁴Department of Physics, College of Sciences, Princess Nourah bint Abdulrahman University (PNU), Riyadh 11671, Saudi Arabia

⁵Imaging and Characterization Core Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.

*E-mail: iman.roqan@kaust.edu.sa

S1: SEM and TEM images

Figure S1. (a–d) TEM images of CsPbI_3 , CsPbBrI_2 , CsPbBr_2I , and CsPbBr_3 , respectively. (e–h) SEM images of CsPbI_3 , CsPbBrI_2 , CsPbBr_2I , and CsPbBr_3 , respectively. It is noteworthy that the nanorods in mixed halogen perovskite (of μm length) are longer than those observed in CsPbI_3 (~ 200 nm).

S2: Energy-dispersive x-ray (EDX) measurement

Figure S2. (a~d). EDX for CsPbI_3 , CsPbBrI_2 , CsPbBr_2I and CsPbBr_3 , respectively.

S3: Optical characterizations

Figure S3. PL spectrum for CsPbX₃ in logarithmic form with lamp excitation. (b) Absorption spectrum for CsPbX₃. (c) PL spectrum of CsPbI₃ excited with Ti:sapphire ($\lambda=400$ nm) laser, the result is similar with Reference [1]

S4: Theoretical calculations

Figure S4. The band structures of (a) cubic CsPbI_3 and (b) black CsPbI_3 . It is noteworthy that, among cubic CsPbI_3 , black CsPbI_3 , yellow CsPbI_3 , and cubic CsPbBr_3 examined in this work, only yellow CsPbI_3 is an indirect bandgap material.

S5: TRPL fitting parameters:

Table S1 Fitting results pertaining to the RT TRPL spectrum in Figure 3c-d, whereby the average lifetime was calculated using $t = (A_1t_1^2 + A_2t_2^2 + \dots)/(A_1t_1 + A_2t_2 + \dots)$

Parameter	CsPbI ₃	CsPbBr ₃
A ₁	897	6621.5
t ₁ (ps)	40.2	6960
A ₂	2014.6	635.3
t ₂ (ps)	279	19880
Lifetime (ps)	264.6	9739.1

S6: Temperature-dependent TRPL lifetime values

Table S2 Fitting results pertaining to the TRPL spectrum in Figure 3c–3d. Two parameters are applied for CsPbBr₃ fitting, whereas three parameters are utilized for CsPbI₃ fitting.

Parameter	CsPbBr ₃ (5 K)	CsPbI ₃ (5 K)
A ₁	5493.6	1996.9
t ₁ (ns)	1.59	102.1
A ₂	371.6	1580.8
t ₂ (ns)	12.2	351.1
A ₃		199
t ₃ (ns)		1755.9
Lifetime (ns)	5.22	748.19

S7: I-V measurements under light illumination

Figure S5. (a) the work energy level of devices, Logarithmic I-V curve of CsPbX_3 under (b) visible light and (c) UV light.

S8: The x-ray absorption coefficient

Figure S6. (a) The absorption coefficient for CsPb(Br_xI_{1-x})₃. In theory, elemental iodine is a better X-ray absorber than bromine. But CsPbI₃ is slightly better absorption than CsPbBr₃ in all X-ray range for the different absorption edge of I and Br. (b) The absorption coefficients for Cs, I, Br, and Pt as references.

S9: The experimental setup for x-ray detector

Figure S7. The experimental setup used for the X-ray detector test. The X-ray source is a clinical angiography tube from Siemens Healthineers. It is mounted on the ceiling of a shielded room and the device under test is placed 30 inches away from the focal spot. The focal spot size is $4\text{ cm} \times 4\text{ cm}$. The experiments were conducted in dark environment.

S10: The voltage dependence of I-T curves

Figure S8: The voltage dependence of I-T curves of CsPbI₃, CsPbBrI₂, CsPbBr₂I and CsPbBr₃, which have similar response with same X-ray dose of 21.2 mGy_{air}s⁻¹ (60 KV, 200 mA, 2 s x-ray pulse)

S11: the X-ray dose calculations

Table S3 The X-ray dose calculated by Rad Pro Calculator

RadPro Calculator is a freely available online tool. Using 2 mm Al filter in the fittings, and 30 inch distance between the target and our devices. The parameters, X-ray tube current and voltage, imported into the Rad Pro calculator. The results reported as below.

Voltage (kV)	60	60	60	60	60	60	60
Current (mA)	250	200	160	100	50	25	16
Dose-rate (mGy_{air}s⁻¹)	26.5	21.2	16.9	10.6	5.3	2.6	1.7

S12: X-ray generated current at various dose rates

Figure S9. (a) X-ray generated current at various dose rates for CsPbI₃, CsPbBrI₂, CsPbBr₂I and CsPbBr₃, respectively. The fitting results for photocurrent as a function of dose rate for (b) CsPbI₃ (c) CsPbBrI₂, (d) CsPbBr₂I, and (e) CsPbBr₃, respectively.

S13: The X-ray signal intensity compared to the photoresponse under light.

Figure S10. The X-ray signal intensity produced by CsPbI₃, CsPbBrI₂, CsPbBr₂I, and CsPbBr₃ compared under UV or Vis light noise. Here the intensity of visible light is 53 mWcm⁻², UV light is 158.5 mWcm⁻² and X-ray radiation is 26.5 mGy_{air}S⁻¹, respectively.

S14: the thickness of the active nanocrystal layer.

Figure S11. The cross-sectional SEM image of (a) CsPbI₃, (b) CsPbBrI₂, (c) CsPbBr₂I and (d) CsPbBr₃ (sample thicknesses are 6.6, 9.4, 4.1, 3.6 μm, respectively). Although the thickness is not uniform, material sensitivity is similar, which we attribute to the differences in film density. For example, CsPbBr₃ is denser than CsPbI₃, as indicated by the SEM image. We further note that CsPbI₃ and CsPbBrI₂ are much thicker than CsPbBr₃ for their loose stack of NCs. Sintering method is supposed to reduce sample thickness without affecting its X-ray absorption capacity².

S15: performance comparison with literature

Table S4 Properties of perovskite for X-ray detection

Material	Thickness (μm)	Lowest detectable dose rate ($\mu\text{Gy}_{\text{air}}\text{s}^{-1}$)	Sensitivity $\mu\text{CGy}_{\text{air}}^{-1}\text{cm}^{-2}$	Remark
CsPbX₃ NCs (X = I, Br)	~ 6.6 (CsPbI₃)	-5480 (calculated) 1700 (experiment)	83.6	This work
MAPbI ₃	60	---	25 ³	Ref 3
MAPbBr ₃ Crystal	2000~3000	0.5	80	Ref 4
MAPbI ₃	1000	---	2527	Ref 2
MAPbBr ₃ Crystal	2000	< 0.1	2.1×10^4	Ref 5
MAPbI ₃	830	---	11	Ref 6
Cs ₂ AgBiBr ₆	2000	0.059	105	Ref 7
Commercial X-ray detector	> 100		0.3	Ref 8
Si			20	Ref 9
Se				

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