

# PHOTONICS Research

## Indium-doped perovskite-related cesium copper halide scintillator films for high-performance X-ray imaging

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Scintillators are widely utilized in high-energy radiation detection in view of their high light yield and short fluorescence decay time. However, constrained by their current shortcomings, such as complex fabrication procedures, high temperature, and difficulty in the large scale, it is difficult to meet the increasing demand for cost-effective, flexible, and environment-friendly X-ray detection using traditional scintillators. Perovskite-related cesium copper halide scintillators have recently received multitudinous research due to their tunable emission wavelength, high photoluminescence quantum yield (PLQY), and excellent optical properties. Herein, we demonstrated a facile solution-synthesis route for indium-doped all-inorganic cesium copper iodide ( $\text{Cs}_3\text{Cu}_2\text{I}_5$ ) powders and a high scintillation yield flexible film utilizing indium-doped  $\text{Cs}_3\text{Cu}_2\text{I}_5$  powders. The large area flexible films achieved a PLQY as high as 90.2% by appropriately adjusting the indium doping concentration, much higher than the undoped one (73.9%). Moreover, benefiting from low self-absorption and high PLQY, the  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  films exhibited ultralow detection limit of 56.2 nGy/s, high spatial resolution up to 11.3 lp/mm, and marvelous relative light output with strong stability, facilitating that  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  films are excellent candidates for X-ray medical radiography. Our work provides an effective strategy for developing environment-friendly, low-cost, and efficient scintillator films, showing great potential in the application of high-performance X-ray imaging. © 2024 Chinese Laser Press

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### 1. INTRODUCTION

X-ray detection can be divided into direct detection and indirect detection [1–5], and widely used in the fields of medical diagnosis [6,7], safety inspection [8], non-destructive testing [9], aerospace [10], etc. Direct detection has the advantage of high spatial resolution. However, its low attenuation efficiency ( $\alpha\text{-Se}$ ) [11], low stopping power for X-ray energy above 60 keV, and high operating voltage seriously hinder its further applications [12,13]. In indirect X-ray detection, the top scintillator absorbs X-rays to achieve fluorescence conversion while the bottom photodetector array undergoes photoelectric conversion under fluorescence to generate electrical signals, making it a mainstream since it has great stability, high detection efficiency, and low cost [14]. Over the past decades, many

scintillators have been commercialized, such as thallium-doped cesium iodide ( $\text{CsI:Tl}$ ) [15,16], cerium-doped lutetium yttrium ortho-silicate (LYSO) [16,17],  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  (BGO) [18],  $\text{LaBr}_3:\text{Ce}$  [19], and Tb-doped  $\text{Gd}_2\text{O}_2\text{S}$  (GOS) [20]. Despite obtaining significant success, these materials still have boundedness in real applications. They usually involve time-consuming and complex manufacturing processes [21] and require high-temperature and high-vacuum environments [22], which are neither scalable nor environment-friendly. There is an urgent need to explore new scintillator materials with scalable manufacturing processes, high light yields, low cost, and short decay time [23].

Lead halide perovskite materials have been reported as a promising X-ray scintillator due to their simple preparation methods, strong X-ray attenuation ability, and high PLQY

[24,25]. In 2018, the first CsPbBr<sub>3</sub> perovskite scintillator device prepared by the thermal injection method was reported, exhibiting a detection limit 420 times lower than typical X-ray medical imaging doses [26]. However, the light yield of CsPbBr<sub>3</sub> nanocrystals was only 21,000 photons/MeV [23], much lower than the traditional scintillators such as CsI:Tl (54,000 photons/MeV) [15] and GOS (60,000 photons/MeV) [27]. The severe self-absorption effect caused by the small Stokes shift of CsPbBr<sub>3</sub> scintillators leads to low luminescence efficiency [23]. The stability of lead halide perovskite is also a great challenge for practical applications [28]. Thus, researchers tried to replace lead with low toxicity or toxicity-free elements to prepare a series of lead-free metal halide scintillator materials to overcome these problems [29–32].

Among them, inorganic cuprous halide perovskite-related compounds have been extensively studied [33,34] and bloomed into a great deal of optoelectronic devices [35,36]. Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> is widely used in X-ray detection due to its high luminous efficiency and good stability [13]. The Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> single crystals fabricated by the Bridgman method showed a light yield of 32,000 photons/MeV [37], and the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> films made of ball-milled powders realized the X-ray imaging spatial resolution of 6.8 lp/mm [38]. Researchers continuously explore higher light yield and resolution of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> to meet the long-term application in X-ray imaging [39]. Metal ion doping provides an efficacious way to improve the scintillation performance of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> [40,41]. Qu *et al.* prepared Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:Zn nanocrystals by hot-injection with a detection limit of 310 nGy/s and spatial resolution up to 15.7 lp/mm [42], while the material yield of the hot-injection-based nanocrystal fabrication process was low and the energy consumption of the vacuum evaporation procedures was relatively high. Wang *et al.* reported the In<sup>+</sup> doped Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> single crystals by the vertical Bridgman method showing a high light yield of 53,000 photons/MeV and a low detection limit of 96.2 nGy/s [43]. However, the synthesis of single crystals also requires high cost and complex procedures. Meanwhile, some researchers doped Tl<sup>+</sup> into Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> to improve its scintillation yields [40,44]. But Tl<sup>+</sup> doping will significantly lead to a very long scintillation decay time, and the doping of highly toxic Tl elements is undesirable [43]. A more efficacious way to prepare Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> with excellent scintillation yield, high spatial resolution X-ray imaging, simple fabrication procedures, and low cost is needed.

In this work, we demonstrated a facile solution-synthesis route for In<sup>+</sup>-doped Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> powders, which were mixed after grinding completely with PDMS at a ratio of 45% to obtain a flexible film with arbitrary sizes by spin-coating. Appropriately adjusting the indium-doped concentration could significantly improve the PLQY of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> films from 73.9% to 90.2%. Profiting from the high PLQY and ultralow self-absorption, the indium doped Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> films obtained a high relative light output, more than five times higher than that of the BGO. The Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films exhibited an ultralow detection limit with the doses of 56.2 nGy/s, approximately 98 times lower than the dose of the typical X-ray medical imaging. A high resolution of 11.3 lp/mm was achieved, facilitating Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films to be excellent candidates for X-ray medical radiography. Moreover, our Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films

exhibited excellent radiation stability, cycle stability, and water tolerance, enabling high-resolution imaging in various complicated environments.

## 2. EXPERIMENT

### A. Materials

Cesium iodide (CsI, 99.9%), copper iodide (CuI, 99.95%), indium iodide (InI, 99.99%), dimethyl sulfoxide (DMSO, AR), isopropanol (IPA, AR), and polydimethylsiloxane (PDMS) were purchased from Aladdin. All chemicals were used as received without further purification.

### B. Preparation of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In Powders and Flexible Films

In a typical synthesis of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:0.4%In powders, 2494.2 mg CsI, 1218.8 mg CuI, 3.1 mg InI, and 4 mL DMSO were added to a 10 mL bottle. The mixture was stirred at 75°C for 2 h to fully dissolve the powders. The precursor solution was mixed 1:1 with isopropanol and vigorously vibrated to completely dissolve them. After that, the solution was centrifuged at 9500 r/min for 5 min and the supernatant was discarded to obtain Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> powders. Wash the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> powders three times with isopropanol to remove remains on the surface. Indium-doped Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>-PDMS flexible films were prepared by a simple spin-coating method. The prepared Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> powders were hand-grinding in an agate mortar to obtain uniform size distribution powders. The PDMS was prepared by mixing two components of Sylgard 184 at a volume ratio of 10:1 and stirred vigorously to mix evenly. After that, the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> powders were added at a mass ratio of 45%, and the mixture was stirred for 2 h to disperse completely. A little mixture was sucked, quickly dripped onto the glass slide, and then cured for 1 h at 140°C to form the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>-PDMS flexible film. The thickness of the films can be easily controlled by adjusting the spin-coating speed from 100 to 800 r/min.

### C. Characterization Methods

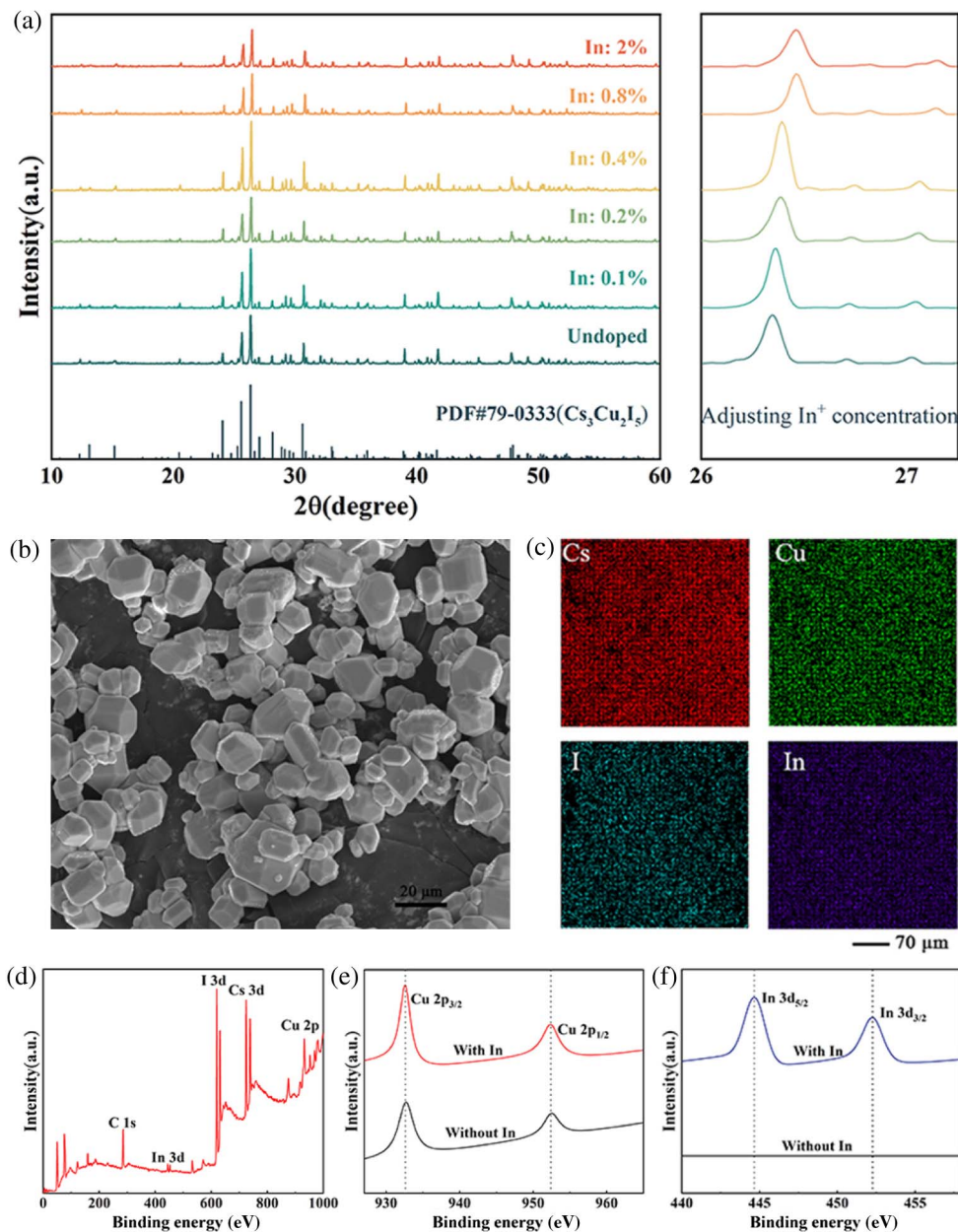
The crystallinity characterization of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> was analyzed by PANalytical BV X-ray diffraction (XRD). The morphologies of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> powders were analyzed by scanning electron microscopy (SEM) on a Nova NanoSEM 450. The X-ray photon spectroscopy (XPS) profile was measured by AXIS-ULTRA DLD-600W. PL and photoluminescence excitation (PLE) spectra were collected on a fluorescence spectrofluorometer (QuantaMaster 8000). The time-resolved PL (TRPL) spectra and PLQY were measured by the fluorescence spectrofluorometer with an integrating sphere. The excitation wavelength was set at 311 nm. The radioluminescence (RL) spectra were taken by a spectrometer (HORIBA FluoroMax-4/Plus) equipped with a photomultiplier tube (PMT, Hamamatsu R928P) and an X-ray tube (tungsten target, HORIBA FluoroMax-4/Plus). The detection slit was set at 3 nm, and the X-ray outlet was set to 9 cm away from the samples for all spectral measurements. The X-ray doses were controlled by adjusting the input voltage and current values. A high sensitivity X-ray ion chamber dosimeter (Radcal Accu-Gold+) was used for calibration. To ensure no radiation leakage, all tests were conducted in a lead cabinet shielded from radiation.

### 3. RESULTS AND DISCUSSION

#### A. Preparation and Characterization Details of $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$ Powders

$\text{Cs}_3\text{Cu}_2\text{I}_5$  consists of zero-dimensional electronic structures. According to previous theoretical calculations, Cu 3d orbitals dominantly contribute to the valence band maximum (VBM), while the conduction band minimum (CBM) is mainly composed of Cu 4s and I 5p orbitals [45]. Therefore, exciton transition in  $\text{Cs}_3\text{Cu}_2\text{I}_5$  occurs mainly in the Cu-I structures. The substitution of  $\text{Cu}^+$  or  $\text{I}^-$  ions has become the main strategy for modulating the electronic structure and optical properties of  $\text{Cs}_3\text{Cu}_2\text{I}_5$ . Considering the ionic radius and spatial configuration

of  $\text{Cu}^+$ ,  $\text{In}^+$  was proved to be an excellent dopant [43]. In this work, we introduce an additional exciton recombination center in  $\text{Cs}_3\text{Cu}_2\text{I}_5$  by doping  $\text{In}^+$  to improve RL efficiency. The phase purity of undoped and In-doped  $\text{Cs}_3\text{Cu}_2\text{I}_5$  powders was measured by XRD. The prepared  $\text{Cs}_3\text{Cu}_2\text{I}_5$  powders matched the standard diffractions (PDF#79-0333) exactly, without the existence of impurities [Fig. 1(a)]. With the increase of  $\text{In}^+$  doping concentration, the XRD peaks shifted continuously toward the higher values of  $2\theta$ . Compared with the undoped  $\text{Cs}_3\text{Cu}_2\text{I}_5$ , the strongest diffraction peak of  $\text{Cs}_3\text{Cu}_2\text{I}_5:2\%\text{In}$  shifted from 26.341 to 26.459 deg implied that  $\text{In}^+$  doping decreased the interplanar spacing. Figure 1(b)



**Fig. 1.** Characterization details of the  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  powders. (a) XRD patterns of the  $\text{Cs}_3\text{Cu}_2\text{I}_5$  powders samples doped with different indium concentrations (top), compared with the orthorhombic  $\text{Cs}_3\text{Cu}_2\text{I}_5$  at the bottom (PDF#79-0333). (b) SEM image of the  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  powders. (c) Elemental mapping images of the  $\text{Cs}_3\text{Cu}_2\text{I}_5:2\%\text{In}$  powders. (d) XPS survey spectrum of the  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  powders. (e), (f) High-resolution XPS profiles of Cu ( $2p_{3/2}$  and  $2p_{1/2}$ ) and In ( $3d_{5/2}$  and  $3d_{3/2}$ ) of the  $\text{Cs}_3\text{Cu}_2\text{I}_5$  powders synthesized with and without In, respectively.

shows the morphology of the  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  powders, an irregular micrometer spherical shape with an average size of 4.16  $\mu\text{m}$ .

The energy dispersive spectroscopy (EDS) and elemental mapping images of the  $\text{Cs}_3\text{Cu}_2\text{I}_5:2\%\text{In}$  powders are shown in Fig. 1(c), respectively, confirming that the proportions of Cs, Cu, and I atoms were 32.45%, 17.93%, and 48.15%, respectively, close to the stoichiometric ratio (3:2:5). The  $\text{In}^+$  dopant was also detected at 1.47%. To further determine the composition and chemical state of the elements, we conducted XPS on the  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  powders, showing peaks of the constituting elements C 1s, In 3d, Cs 3d, Cu 2p, and I 3d [Fig. 1(d)]. The valence state of Cu ions in the  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  powders was analyzed in Fig. 1(e). The two peaks located at 932.5 and 952.3 eV were characteristic peaks of  $\text{Cu}^+ 2p_{3/2}$  and  $\text{Cu}^+ 2p_{1/2}$ . Moreover, no characteristic satellite peak of  $\text{Cu}^{2+}$  was observed (approximately 943 eV), further ruling out the presence of  $\text{Cu}^{2+}$  in the  $\text{Cs}_3\text{Cu}_2\text{I}_5$  powders. Two additional peaks in the InI-doped  $\text{Cs}_3\text{Cu}_2\text{I}_5$  powders appearing at 444.7 and 452.3 eV attributed to the In 3d further confirmed that  $\text{In}^+$  was doped into the  $\text{Cs}_3\text{Cu}_2\text{I}_5$  powders [Fig. 1(f)]. These results provided further support for the successful synthesis of the  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  powders.

## B. Ultraviolet Detection Performance of $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$ Films

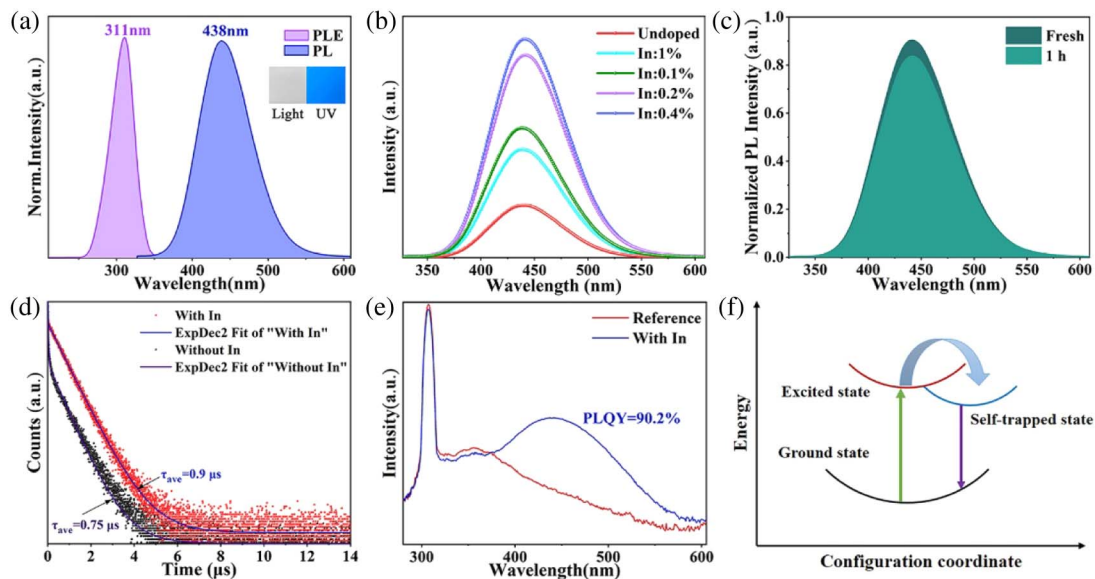
Figure 2(a) shows the optical properties of  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  films. The PLE spectrum of the films showed an excitation peak at 311 nm, while the PL spectrum exhibited strong blue emission at 438 nm with a full-width at half-maximum (FWHM) of 84 nm and a Stokes shift of 127 nm. There was almost no spectral overlap between the PLE and PL spectra, indicating that the prepared  $\text{Cs}_3\text{Cu}_2\text{I}_5$  materials exhibited ultralow self-absorption [46], which was an indispensable parameter for

high-performance scintillators. The PL spectral peaks measured at different doping concentrations showed the same shape but different intensities, indicating that the observed blue emission was caused by radiation recombination in the same excited state [Fig. 2(b)]. As shown in Fig. 2(c), after immersion in deionized water for 1 h, the PL intensity of the films only suffered a slight decay.

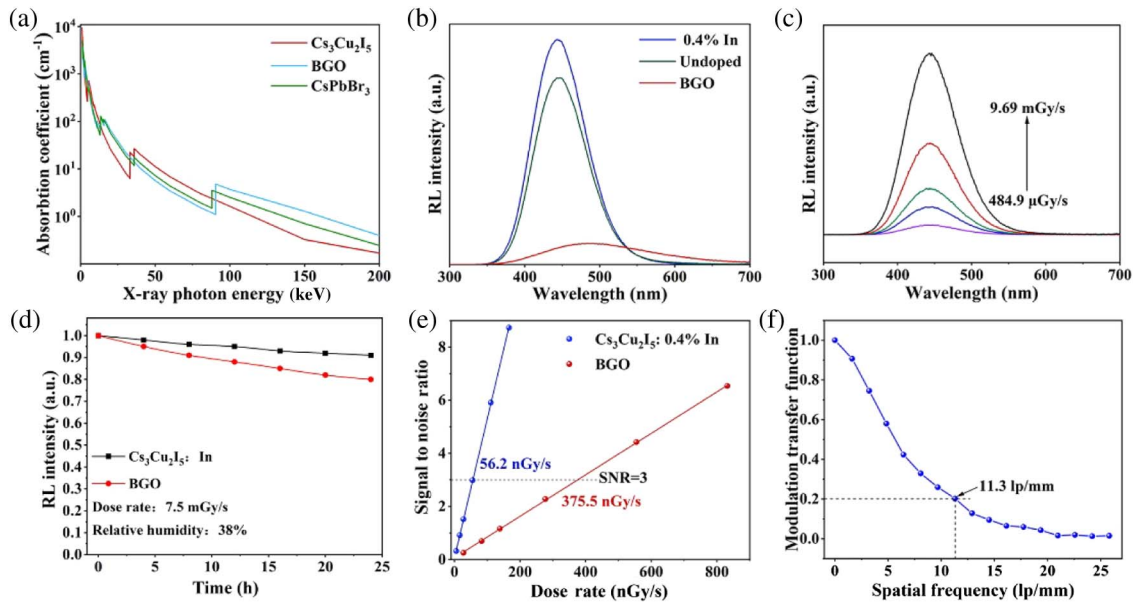
The corresponding TRPL decay curves of the doped and undoped films were measured in Fig. 2(d). The PL lifetime of the  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  films was 0.9  $\mu\text{s}$ , longer than that of the undoped  $\text{Cs}_3\text{Cu}_2\text{I}_5$  films (0.75  $\mu\text{s}$ ), implying that after indium doping, the capture of excited electrons by surface states was inhibited. The efficient utilization of the excited carriers resulted in a high PLQY as well as a long lifetime. A high PLQY of 90.2% was achieved in the  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  films [Fig. 2(e)]. We propose that extra incorporation of  $\text{In}^+$  brings a new radiative recombination channel and accelerates the energy transfer, improving the utilization of excitons, as well as the PLQY. The high PLQY of the scintillation films ensures a subsequent high RL light yield [44]. Figure 2(f) shows the self-trapped exciton (STE) emission mechanism of the  $\text{Cs}_3\text{Cu}_2\text{I}_5$ . Under the excitation of an external light source, electrons transitioned from the valence band to the conduction band, and the excited state underwent transient lattice distortion under strong electron phonon coupling, forming the STE state [47]. Due to the low STE barrier, a quantity of electrons relaxed to the STE state, ultimately combining with holes to produce bright blue emissions.

## C. X-Ray Detection Performance of $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$ Films

The high PLQY, short decay time, low preparation cost, good stability, and simple large area preparation process of the  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  films promise their application in large-scale



**Fig. 2.** Ultraviolet detection performance of the  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  films. (a) PL and PLE spectra of the  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  films. (b) PL emission spectra of the  $\text{Cs}_3\text{Cu}_2\text{I}_5$  films doped with different indium concentrations. (c) Comparison of the PL spectra of the films before and after being soaked in deionized water for 1 h. (d) PL decay spectra of the  $\text{Cs}_3\text{Cu}_2\text{I}_5$  films with and without  $\text{In}^+$ . (e) PLQY spectra of the  $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{In}$  films. (f) Configuration coordinate diagram of the photophysical dynamics in  $\text{Cs}_3\text{Cu}_2\text{I}_5$ .



**Fig. 3.** X-ray detection performance of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In powders. (a) X-ray absorption coefficients of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> film, the CsPbBr<sub>3</sub> film, and commercial BGO scintillator as a function of photon energy. (b) RL spectra of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:0.4%In films, the undoped Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> films, and the BGO films (dose rate, 4.85 mGy/s; voltage, 50 kV). The size (1 cm × 1 cm) and thickness (1 mm) of the films are the same. (c) Dose-rate-dependent RL spectra of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films. (d) Normalized RL intensity of Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films and BGO under 24 h continuous radiation irradiation with an X-ray dose rate of 7.5 mGy/s. (e) Signal-to-noise ratio of X-ray response of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films at different irradiation dose rates. (f) MTF of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films, measured by the slanted-edge method.

practical X-ray radiography. To effectively evaluate the performance of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> films, the absorption coefficients of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> film, commercial BGO scintillator, and CsPbBr<sub>3</sub> film under the same conditions were recorded and compared horizontally [Fig. 3(a)]. The absorption coefficient of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> film was much higher than that of the CsPbBr<sub>3</sub> film and commercial BGO scintillator from 33 to 60 keV covered by the clinical radiology area, which means that lower detection doses can be achieved in medical testing. The commercial BGO scintillator was used as a reference to estimate the light yield of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> films [48] since the RL spectral range of BGO is similar to Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>. The films were fabricated to keep the same size and thickness as the BGO wafer, and RL curves were obtained using the spectrometer under an identical configuration [Fig. 3(b)]. The results showed that the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:0.4%In film exhibited the strongest RL response, 5.34 times higher than that of the BGO (with a light yield of 10,000 photons/MeV), and the undoped Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub> film was also 4.49 times that of the BGO. The RL strength of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films exhibited a perfect linear relationship from 484.9 μGy/s to 9.69 mGy/s [Fig. 3(c)]. There was no significant difference between the RL spectrum and the PL spectrum, implying identical composite framework under UV irradiation and X-ray irradiation. After 24 h of irradiation with an X-ray dose rate of 7.5 mGy/s, the RL intensity could still be maintained at about 90%, while for BGO scintillators, its RL intensity decreased to 80% of its initial intensity, implying that the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films had good X-ray tolerance [Fig. 3(d)]. In addition, under a signal-to-noise ratio (SNR) of 3, the detection limit was 56.2 nGy/s [Fig. 3(e)], which was lower than that of

the BGO scintillator (375.5 nGy/s) and approximately 98 times lower than the dose of the typical X-ray medical imaging (5.5 μGy/s) [49–52]. Due to its excellent scintillation performance, the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films achieved an ideal spatial resolution of 11.3 lp/mm at the MTF value of 0.2 [Fig. 3(f)], slightly higher than some recently reported X-ray scintillators [38,53,54]. Table 1 summarizes the scintillation performance of the studied Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In at the PDMS flexible scintillator screen and other reported scintillator materials. Compared with other copper-based perovskites and lead containing perovskites, the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films exhibited stronger relative light output, lower detection limit, and higher spatial resolution. The Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films could maintain better radiation stability compared to lead perovskites. Meanwhile, the solution method is more economical and environment friendly than hot injection, cooling crystallization, evaporation method, etc.

#### D. Construction and Application of High-Performance X-Ray Testing System

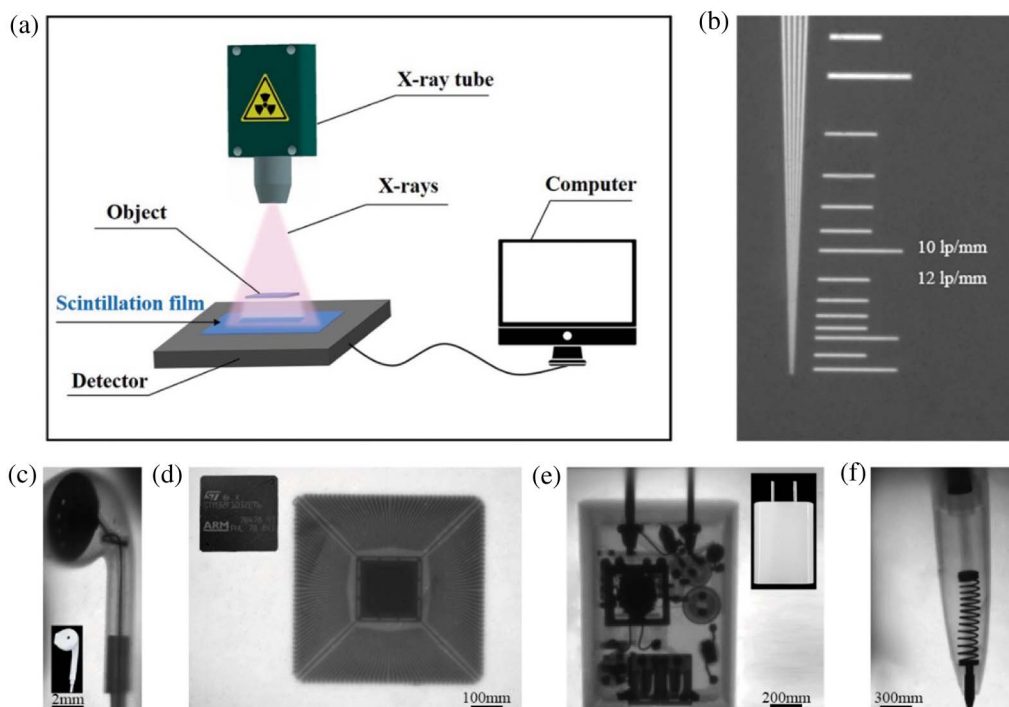
To demonstrate the potential application of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films in X-ray scintillation, an X-ray image system was constructed with an X-ray source, an X-ray detector, and a computer placed in sequence [Fig. 4(a)]. As a proof-of-concept experiment, the self-made system based on the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In scintillator film with 220 μm thickness was used to evaluate the X-ray imaging performance. The standard resolution test sample was placed on the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films, and we observed the resolution limit of 10 lp/mm, as shown in Fig. 4(b), coinciding well with the calculated MTF result in Fig. 3(f). Through X-ray imaging systems, we could clearly see the fine

**Table 1. Summary of X-Ray Scintillation Performances of Scintillators**

Materials	Light Yield [photons MeV <sup>-1</sup> ]	Detection Limit [nGy s <sup>-1</sup> ]	Spatial Resolution [lp mm <sup>-1</sup> ]	Radiation Stability	Preparation Method	Reference
CsPbBr <sub>3</sub>	21,000	–	–	2 h (unchanged)	Hot injection	[23]
CH <sub>3</sub> NH <sub>3</sub> PbBr <sub>3</sub>	–	16	5.4	21 h (>80%)	Solution method	[55]
TPP <sub>2</sub> MnBr <sub>4</sub>	78,000	8.8	15.7	–	Antisolvent method	[56]
Rb <sub>2</sub> CuBr <sub>3</sub>	91,056	121.5	–	–	Cooling crystallization	[27]
(C <sub>8</sub> H <sub>20</sub> N) <sub>2</sub> MnBr <sub>4</sub>	24,400	24.2	4.9	250 min (>95%)	Evaporation method	[32]
K <sub>2</sub> CuBr <sub>3</sub>	23,806	132.8	–	–	Solution method	[30]
CsCu <sub>2</sub> I <sub>3</sub>	21,580	–	7.5	100 h (unchanged)	Cooling crystallization	[57]
Cs <sub>3</sub> Cu <sub>2</sub> I <sub>5</sub>	46,000	96.54	8.6	–	Solution method	[54]
Cs <sub>3</sub> Cu <sub>2</sub> I <sub>5</sub> :Zn	–	310	15.7	–	Hot injection	[42]
Cs <sub>2</sub> ZrCl <sub>6</sub>	49,400	65	18	120 min (>94%)	Solution method	[49]
Cs <sub>2</sub> Ag <sub>0.6</sub> Na <sub>0.4</sub> In <sub>1-γ</sub> Bi <sub>γ</sub> Cl <sub>6</sub>	39,000 ± 7000	19	4.4	50 h (unchanged)	Hydrothermal method	[58]
Cs <sub>2</sub> Na <sub>0.9</sub> Ag <sub>0.1</sub> LuCl <sub>6</sub> :Dy <sup>3+</sup>	8332	123.79	11.2	–	Hydrothermal method	[59]
Cs <sub>3</sub> Cu <sub>2</sub> I <sub>5</sub> :In	≈53,400	56.2	11.3	24 h (>90%)	Solution method	This work

structures inside the earphone that could not be directly recognized by eyes [Fig. 4(c)]. The internal circuitry of the microchip was revealed in detail, indicating that the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films possessed immense potential for application in industrial flaw detection [Fig. 4(d)]. We also imaged the charger and could see its internal structure very clearly, further indicating the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films have great potential in imaging detection

[Fig. 4(e)]. To evaluate the imaging effect on non-planar objects, we covered a pen with the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films. The spring and fill inside the pen could be clearly displayed, and there was no haloing or ghosting [Fig. 4(f)], indicating that the films also had a good imaging effect on the curved surface. This further proved that the flexible films had excellent mechanical stability and could maintain good imaging quality on non-planar



**Fig. 4.** Construction and application of a high-performance X-ray testing system. (a) Schematic diagram of the X-ray imaging system. (b) X-ray imaging of the Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>:In films on the standard resolution card. (c) Photograph and X-ray image (dose rate, 963 μGy/s; tube voltage, 50 kV; beam current, 200 μA; exposure time, 10 s) of internal structure of the earphone; (d) internal circuitry of the microchip; (e) internal structure of the charger; (f) internal spring and filling of the pen.

objects. These results demonstrated that the  $\text{Cs}_3\text{Cu}_2\text{I}_5$ :In films can realize X-ray imaging in complex environments.

#### 4. CONCLUSION

In summary, we demonstrated a facile solution-synthesis route to synthesize high-performance indium-doped perovskite-related  $\text{Cs}_3\text{Cu}_2\text{I}_5$  X-ray scintillator powders and a flexible scintillator film of  $\text{Cs}_3\text{Cu}_2\text{I}_5$ :In/PDMS at an arbitrary size for X-ray imaging. The  $\text{Cs}_3\text{Cu}_2\text{I}_5$ :In film exhibited bright blue light emission with a large Stokes shift of 127 nm and a high PLQY of 90.2%, and achieved good environmental stability. After continuous X-ray irradiation, soaking in deionized water, and continuous bending and stretching, the luminescence and imaging properties of the films remained stable. Benefiting from ultralow self-absorption and high PLQY, a high relative light output was obtained, more than 5 times higher than that of the BGO. The  $\text{Cs}_3\text{Cu}_2\text{I}_5$ :In films achieved an ultralow detection limit of 56.2 nGy/s, approximately 98 times lower than the dose of typical X-ray medical imaging. The films also exhibited outstanding X-ray imaging performance, with a high resolution of 11.3 lp/mm, excellent stability under ambient conditions, and undistorted non-planar imaging. To sum up, the presented low-cost, stable, and high-luminous-efficiency  $\text{Cs}_3\text{Cu}_2\text{I}_5$ :In flexible scintillator films have great application prospects in high-performance X-ray imaging.

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

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