

Article

Spin-Selective Up-Conversion Ho^{3+} Luminescence by Fe^{3+} Doping in $\text{Cs}_2\text{NaScCl}_6\text{:Ho}^{3+}$ Crystals and Its Highly Sensitive X-Ray Detection Performance

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Abstract

This study investigated the effect of magnetic coupling of Fe^{3+} on Ho^{3+} luminescence in the double perovskite $\text{Cs}_2\text{NaScCl}_6$. Under 980 nm laser excitation, red emission from Ho^{3+} ions was observed in $\text{Cs}_2\text{NaScCl}_6\text{:Ho}^{3+}/\text{Fe}^{3+}$ samples. We propose that this arises from spin-selective up-conversion mediated by magnetic polarons (EMPs). However, green emission from the $^5\text{F}_4/^5\text{S}_2$ levels was not observed in this system. The experimental results suggest that localized EMPs form via ferromagnetic short-range ordering between Fe^{3+} and Ho^{3+} or among Fe^{3+} ions. These EMPs can be directly excited to higher energy levels via a biexciton absorption transition, then relaxed to the $^5\text{F}_5$ level of Ho^{3+} through ferromagnetic coupling. Under X-ray excitation, the characteristic emission peaks of Ho^{3+} in $\text{Cs}_2\text{NaScCl}_6\text{:Ho}^{3+}/\text{Fe}^{3+}$ become smoother, lose fine structure, and significantly decrease in intensity with increasing Fe^{3+} concentration. Based on this, we prepared Fe^{3+} -free $\text{Cs}_2\text{NaScCl}_6\text{:Ho}^{3+}$ and explored its excellent scintillation performance, with a detection limit as low as $37.73 \text{ nGy}_{\text{air}} \text{ s}^{-1}$, below the medical diagnostic dose, surpassing the performance of commercial scintillators such as LuAG:Ce and BGO. This work reports the phenomenon of using Fe^{3+} as a sensitizer to achieve up-conversion sensitization in chloride double perovskites and demonstrates the application potential of Fe-free systems in ultra-low-dose X-ray imaging.

Keywords: up-conversion sensitized luminescence; magnetic polarons; X-ray detectors; Ho^{3+} phosphor; spin-related emission



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1. Introduction

In the field of luminescence, Fe^{3+} has long been regarded as a quenching center. Due to its d–d transitions and half-filled $3d^5$ electronic configuration, it readily acts as a luminescence quencher [1,2]. However, this same electronic configuration also endows Fe^{3+} with high-spin characteristics. If magnetically coupled with other ions that also possess magnetic moments, the role of Fe^{3+} may no longer be limited to conventional luminescence quenching. To deeply explore the influence of magnetic coupling of Fe^{3+} on luminescence in materials, a single luminescence mode is insufficient. By comparing the differences in Stokes, up-conversion, and X-ray-excited luminescence of the same host before and after Fe^{3+} doping, one can investigate the effect of Fe^{3+} magnetic coupling on luminescence from multiple dimensions under strictly controlled experimental conditions. $\text{Cs}_2\text{NaScCl}_6$

is an ideal host that meets this concept. It has a direct bandgap of approximately 4 eV, which facilitates efficient recombination of photoexcited electron–hole pairs. Meanwhile, its low phonon energy effectively suppresses non-radiative recombination, which is key to achieving Stokes and up-conversion luminescence [3–6]. The high atomic number of Cs ($Z = 55$) in the lattice provides a high X-ray absorption cross-section, laying the physical foundation for X-ray imaging [7–13]. These excellent physical properties make $\text{Cs}_2\text{NaScCl}_6$ an ideal host for Stokes, up-conversion, and X-ray-excited luminescence. Furthermore, $\text{Cs}_2\text{NaScCl}_6$ is compatible with a variety of rare-earth ions and can also be extended to transition metal and alkali metal ions, providing conditions for constructing co-doped systems and tuning energy transfer pathways within the same host. These properties enable $\text{Cs}_2\text{NaScCl}_6$ to meet the experimental requirements for multi-dimensional exploration of the effect of Fe^{3+} magnetic coupling on luminescence.

In addition to the choice of host, the selection of the luminescence center is equally important. Ho^{3+} , as an important luminescence center, typically produces red emission at 665 nm ($^5\text{F}_5 \rightarrow ^5\text{I}_8$) and green emission at 540 nm ($^5\text{F}_4/^5\text{S}_2 \rightarrow ^5\text{I}_8$) under 450 nm excitation, providing a basis for observing the effect of magnetic coupling before and after Fe^{3+} doping. However, under 980 nm laser excitation, the up-conversion performance of Ho^{3+} is poor due to the absence of energy levels that directly match the photon energy, thus requiring the assistance of a sensitizer. Conventionally, Yb^{3+} is commonly used as an up-conversion sensitizer, and its energy transfer mechanism has been systematically studied. Moreover, achieving a transition metal-mediated spin-selective up-conversion mechanism would provide new ideas for the design of up-conversion materials. Ho^{3+} has a 4f^{10} electronic configuration and possesses a magnetic moment, while the transition metal Fe^{3+} has a 3d^5 electronic configuration and also carries a magnetic moment. Relevant studies have shown that Fe^{3+} doping can enhance the absorption near 980 nm. Therefore, based on the potential magnetic exchange interaction and the enhanced absorption near 980 nm, Fe^{3+} doping is expected to establish a spin-selective energy transfer channel in $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}$, thereby improving the up-conversion luminescence of Ho^{3+} . In addition, under X-ray excitation, Ho^{3+} can effectively capture charge carriers generated in the host, enabling X-ray-excited luminescence, which provides another excitation pathway to explore the magnetic coupling of Fe^{3+} .

Based on the above rationale, we prepared the $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$ system and investigated the effect of Fe^{3+} magnetic coupling on luminescence by comparing the luminescence behaviors before and after Fe^{3+} doping. Under 980 nm excitation, Fe^{3+} promoted red up-conversion emission of Ho^{3+} at 665 nm, in contrast to the fluorescence quenching observed under Stokes luminescence [14–16]. Calculations suggest that Fe^{3+} transfers energy to the $^5\text{F}_5$ level of Ho^{3+} through biexciton absorption and ferromagnetic coupling [12,17–20]. Under X-ray excitation, the radioluminescence peaks of Ho^{3+} lost their fine structure, whereas the fine structure was retained under other excitation conditions, providing indirect evidence for $\text{Fe}^{3+}\text{--}\text{Ho}^{3+}$ magnetic coupling. Fe^{3+} doping weakened the luminescence of Ho^{3+} , possibly due to the opening of a non-radiative relaxation pathway. Based on these results, we prepared the Fe^{3+} -free $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}$ system, which is approximately 2.5 times that of BGO and comparable with that of $\text{LuAG}:\text{Ce}$ and a detection limit as low as $37.73 \text{ nGy}_{\text{air}} \text{ s}^{-1}$, far below the medical diagnostic dose of $5.5 \text{ } \mu\text{Gy}_{\text{air}} \text{ s}^{-1}$ [21–27]. This work reports the phenomenon of using Fe^{3+} as an up-conversion sensitizer and demonstrates the potential of the Fe^{3+} -free $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}$ system for ultra-low-dose X-ray imaging.

2. Experimental Section

Materials: Cesium chloride (CsCl , 99.9%), sodium chloride (NaCl , 99.9%), scandium oxide (Sc_2O_3 , 99.9%), iron(III) oxide (Fe_2O_3 , 99.99%), holmium(III) oxide (Ho_2O_3 , 99.99%),

and hydrochloric acid (HCl, 37 wt% in water) were purchased from Macklin reagent (Shanghai, China) and used without further purification.

Synthesis: We synthesized $\text{Cs}_2\text{NaScCl}_6\text{:Ho}^{3+}$ and $\text{Cs}_2\text{NaScCl}_6\text{:Ho}^{3+}/\text{Fe}^{3+}$ crystals by the hydrothermal method. In this process, 4 mmol of CsCl, 2 mmol of NaCl, 1 mmol of Sc_2O_3 , and 0.05 mmol of Ho_2O_3 were mixed in a 25 mL high-pressure reactor lined with polytetrafluoroethylene (PTFE). For the $\text{Cs}_2\text{NaScCl}_6\text{:Ho}^{3+}/\text{Fe}^{3+}$ sample, x mmol of Fe_2O_3 ($x = 0.025, 0.05, 0.075, 0.1$) was added to it, followed by the addition of 4 mL of hydrochloric acid. The mixture was then ultrasonicated for 5 min, and the high-pressure reactor was heated at 180 °C for 6 h and naturally cooled in the furnace for 12 h. The resulting product was washed with ethanol and dried in a 60 °C oven.

Film Preparation: We ground the $\text{Cs}_2\text{NaScCl}_6\text{:0.1Ho}^{3+}$ powder, sieved it through a 250-mesh screen, and uniformly mixed it with polydimethylsiloxane (PDMS) at a mass ratio of 1:2.5. The mixture was poured into a mold and cured at 60 °C for 4 h, resulting in a flexible composite film.

Characterization: The powder X-ray diffraction (XRD) patterns were measured using the Bruker D2 Phaser diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Morphology and elemental analysis were conducted using a Hitachi SU8020 scanning electron microscope (SEM) (Thermo Fisher Scientific, Waltham, MA, USA) in combination with an Oxford X-Max Aztec energy-dispersive X-ray spectrometer (EDS) (Oxford Instruments, Abingdon, UK). X-ray photoelectron spectroscopy (XPS) tests were performed using a Kratos AXIS Supra spectrometer (Kratos Analytical, Manchester, UK). The steady-state and temperature-dependent photoluminescence (PL) spectra, photoluminescence excitation (PLE) spectra, and decay lifetimes were measured using an Edinburgh Instruments FLS1000 spectrophotometer (Edinburgh Instruments, Livingston, UK) equipped with a microsecond flash lamp. Absorption spectra were measured on a PerkinElmer Lambda 750 UV/Vis/NIR spectrophotometer (PerkinElmer, Waltham, MA, USA). In the radioluminescence (RL) performance tests, the RL spectra were recorded using an Edinburgh FS5 instrument excited by a MOXTEK MAGPRO TUB00154-91-06 70 kV X-ray tube (Edinburgh Instruments, Livingston, UK). The detection limit of the dose rate was obtained from the slope of the fitted line, with a signal-to-noise ratio (SNR) of 3. At the same time, commercial LuAG:Ce and BGO chips were used as standard reference samples to estimate the light yield of the prepared scintillators. To further improve measurement accuracy, the relative light yield was calculated by integrating the X-ray-induced RL spectrum (corrected for the spectral response of the detection system). For imaging performance evaluation, a homemade X-ray imaging system was used to characterize the material's spatial resolution. The modulation transfer function (MTF) was obtained based on the edge method: first, the edge spread function (ESF) was extracted from the imaging results, then differentiated to obtain the line spread function (LSF), and finally, the MTF curve was obtained by performing Fourier transform on the LSF, thereby quantitatively analyzing the system's resolution.

3. Results and Discussion

3.1. Structure of $\text{Cs}_2\text{NaScCl}_6\text{:Ho}^{3+}/\text{Fe}^{3+}$ Perovskite

As shown in Figure 1a, $\text{Cs}_2\text{NaScCl}_6$ forms an $\text{A}_2\text{BB}'\text{X}_6$ double perovskite. The A site contains Cs^+ , while Na^+ and Sc^{3+} occupy the B and B' sites, respectively. As depicted in Table S1, the alternating arrangement of $[\text{NaCl}_6]^{5-}$ and $[\text{ScCl}_6]^{3-}$ octahedra forms a face-centered cubic space group ($\text{Fm}\bar{3}\text{m}$). Figure S1 shows that in the $\text{Cs}_2\text{NaScCl}_6\text{:Ho}^{3+}/\text{Fe}^{3+}$ structure, the formation energy for Ho^{3+} occupying the Sc^{3+} site and Fe^{3+} occupying the Sc^{3+} site is -5.53 eV . In another doping model, where Ho^{3+} occupies the Sc^{3+} site and two Fe^{3+} ions substitute the Na^+ and Sc^{3+} sites, respectively, in the same lattice, the

formation energy is -5.22 eV, giving a difference of 0.31 eV. Both substitution models have negative formation energies, indicating that they are thermodynamically feasible, with Fe^{3+} predominantly occupying the Sc^{3+} sites and a small fraction occupying the Na^{+} sites [28]. To confirm the optimal doping concentration of Ho^{3+} , we measured the PL and PLE spectra of $\text{Cs}_2\text{NaScCl}_6:x\text{Ho}^{3+}$ ($x = 0-0.2$), which are shown in Figure S2. It can be seen that the PL and PLE intensities reach their maximum at a Ho^{3+} concentration of 0.1 . Subsequently, we synthesized $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/x\text{Fe}^{3+}$ ($x = 0-0.2$). Figure 1b shows the scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) imaging, which confirms that all elements in the $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$ crystal are uniformly distributed and the atomic ratio is close to the stoichiometric ratio (Figure S3, Table S2), indicating the successful synthesis of the $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/x\text{Fe}^{3+}$ ($x = 0-0.2$) fluorescent powder. Figure 1c,d represents XPS spectra, which confirm the presence of Fe^{3+} and Ho^{3+} , and it can be observed that the $2p$ orbital characteristic peaks of Fe^{3+} are at 723.4 eV and 737.3 eV, while the $4d$ orbital characteristic peaks of Ho^{3+} are at 158 eV and 163.4 eV [10,29]. Figure S4 represents the XPS spectra of other elements. Figure S5 represents the XRD spectrum of $\text{Cs}_2\text{NaScCl}_6$, indicating that the pure sample was successfully synthesized, and it matches the XRD data of the theoretical pure sample $\text{Cs}_2\text{NaScCl}_6$ [30]. As depicted in Figure 1e, the peak position at 23.9° in the XRD spectrum changes with doping. We believe this is due to the larger ionic radius of Ho^{3+} compared with Sc^{3+} ions, which causes the peak position of the doped sample to shift to a lower angle direction. Conversely, the ionic radius of Fe^{3+} is smaller than that of Na^{+} and Sc^{+} ions, so the peak position shifts to a higher angle direction.

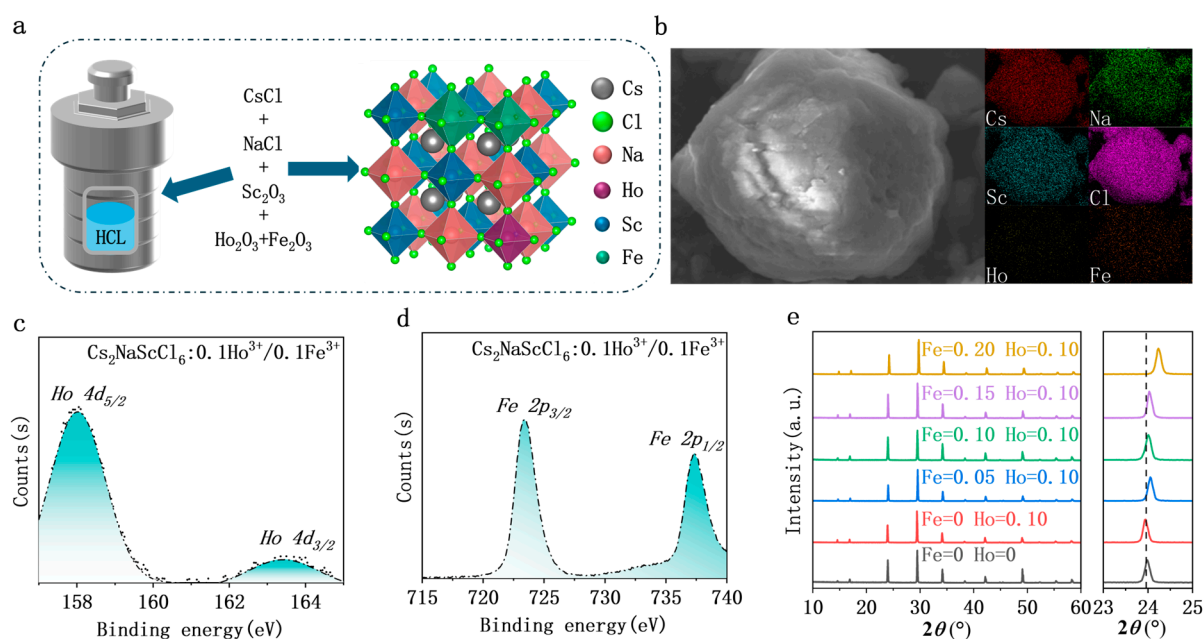


Figure 1. (a) $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$ double perovskite crystal structure. Here, the gray, green, red, purple, blue, and cyan spheres represent the elements of Cs, Cl, Na, Ho, Sc, and Fe, respectively. (b) The scanning electron microscopy (SEM) image and corresponding element distribution map of $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$. (c,d) XPS spectra of Ho $4d$ and Fe $2p$ for $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/0.1\text{Fe}^{3+}$. (e) X-ray diffraction (XRD) patterns of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/x\text{Fe}^{3+}$ ($x = 0, 0.05, 0.1, 0.15, 0.2$) compared with the standard card.

We further systematically characterized the optical properties of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/x\text{Fe}^{3+}$ ($x = 0-0.2$) and prepared $\text{Cs}_2\text{NaScCl}_6:\text{Fe}^{3+}$ as a reference. Typically, under 450 nm excitation, Ho^{3+} ions exhibit red emission at 665 nm via the $^5\text{F}_5 \rightarrow ^5\text{I}_8$ transition. As shown in Figure S6, no emission peaks were observed in the $500-680$ nm range for the $\text{Cs}_2\text{NaScCl}_6:0.1\text{Fe}^{3+}$ sample under 450 nm excitation, ruling out the possibility of self-emission from Fe^{3+} . Subsequently,

we measured the photoluminescence excitation (PLE) spectra monitored at 665 nm and the photoluminescence (PL) spectra under 450 nm excitation for $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/x\text{Fe}^{3+}$, which are presented in Figure S7. The PLE spectra exhibit three excitation bands centered at 450, 460, and 465 nm, attributed to the f–f transitions of Ho^{3+} ions [31,32]. The PLE intensity decreases significantly with increasing Fe^{3+} concentration. The PL intensity shows the same decreasing trend as the Fe^{3+} concentration increases. Figure S8 combines the PL, PLE, and absorption spectra of the $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$ samples. It shows that as the Fe^{3+} doping concentration increases, the absorption in the 220–573 nm range significantly enhances, opposite to the trends observed in PL and PLE. We propose that in the low Fe^{3+} doping concentration regime, 450 nm photons can directly excite Ho^{3+} or indirectly transfer energy to Ho^{3+} through the host matrix, resulting in Ho^{3+} luminescence. However, in the high Fe^{3+} doping concentration regime, the antiferromagnetic coupling between adjacent $[\text{FeCl}_6]^{3-}$ octahedra is enhanced, promoting non-radiative energy transfer among Fe^{3+} ions [33]. Meanwhile, the 450 nm excitation light falls exactly within the 220–573 nm broadband absorption range. Consequently, broadband self-absorption and Fe^{3+} – Fe^{3+} antiferromagnetic coupling jointly hinder energy transfer to Ho^{3+} , leading to concentration quenching upon Fe^{3+} doping. Furthermore, considering that Mn^{2+} shares the same $3d^5$ electronic configuration as Fe^{3+} , subsequent experiments compare the Mn^{2+} -doped $\text{Cs}_2\text{NaScCl}_6$ and $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}$ systems with the Fe^{3+} -doped system described above. Figures S9 and S10 show the excitation and emission spectra of Mn^{2+} – Mn^{2+} pairs at 632 nm arising from ferromagnetic coupling in $\text{Cs}_2\text{NaScCl}_6:0.1\text{Mn}^{2+}$ [34], which differ significantly from the $\text{Cs}_2\text{NaScCl}_6:0.1\text{Fe}^{3+}$ system. Figure S11 presents the PLE spectrum of the $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/0.1\text{Mn}^{2+}$ sample monitored at 665 nm, and the strongest excitation peak at 265 nm was selected as the excitation wavelength. Its PL spectrum (Figure S12) simultaneously contains the characteristic Ho^{3+} emission at 665 nm, the host emission at 445 nm, and the Mn^{2+} – Mn^{2+} pair emission at 632 nm. Figure S13 shows the lifetime decay curve of this sample monitored at 632 nm, indicating that the lifetime of the Mn^{2+} – Mn^{2+} pair is 4 μs . In sharp contrast, in the $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/x\text{Fe}^{3+}$ system, the introduction of Fe^{3+} not only fails to promote luminescence but rather suppresses the characteristic Ho^{3+} emission due to Fe^{3+} – Fe^{3+} antiferromagnetic coupling and broadband self-absorption.

3.2. Optical Properties Under 980 nm CW Laser Excitation

Although the photoluminescence performance of $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$ under 450 nm excitation is inferior to that of $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Mn}^{2+}$ under 265 nm excitation, under 980 nm laser excitation, $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/0.1\text{Fe}^{3+}$ exhibits characteristic emission from Ho^{3+} ions at 665 nm ($^5\text{F}_5 \rightarrow ^5\text{I}_8$), and the emission intensity is 73 times higher than that of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}$ (Figure S14). However, under the same excitation, no characteristic emission from Ho^{3+} ions is observed in the $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/0.1\text{Mn}^{2+}$ sample (Figures S15 and S16), indicating that the sensitization effect of Fe^{3+} is ion-specific. To investigate this sensitization mechanism, we first ruled out the possibility that the emission originates from Fe^{3+} itself: as shown in Figure S17, under 980 nm laser excitation, no characteristic emission of Fe^{3+} is detected in the $\text{Cs}_2\text{NaScCl}_6:0.1\text{Fe}^{3+}$ sample in the wavelength range of 500–680 nm. This proves that the emission observed in $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/0.1\text{Fe}^{3+}$ indeed comes from Ho^{3+} ions. Meanwhile, the absorption spectra in Figures 2a and S18 show that the absorption intensity of the co-doped sample near 980 nm gradually increases with increasing Fe^{3+} concentration. Correspondingly, Figures 2b and S19 show the PL spectra of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/x\text{Fe}^{3+}$ ($x = 0$ – 0.2) under 980 nm laser excitation as a function of Fe^{3+} concentration, indicating that the emission intensity of Ho^{3+} ions at 665 nm increases with Fe^{3+} concentration and reaches a maximum at $x = 0.1$. This dependence of emission intensity on Fe^{3+} doping concentration suggests that Fe^{3+} transfers the absorbed 980 nm excitation energy to Ho^{3+} ions. Further increasing the Fe^{3+} doping concentration leads to

a decrease in Ho^{3+} emission intensity, which we attribute to the concentration quenching effect of Fe^{3+} [35]. Theoretically, under 980 nm laser excitation, $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$ should exhibit green characteristic emission from Ho^{3+} ions via phonon-assisted relaxation because the two-photon energy of 980 nm is 2.53 eV, which is higher than the 2.27 eV of the green emission level. However, no green characteristic emission from Ho^{3+} ions is observed in the present system, indicating that such a non-radiative relaxation pathway does not exist in this system. Therefore, the luminescence of this system is highly pure red, and its CIE color coordinate diagram is shown in Figure S20.

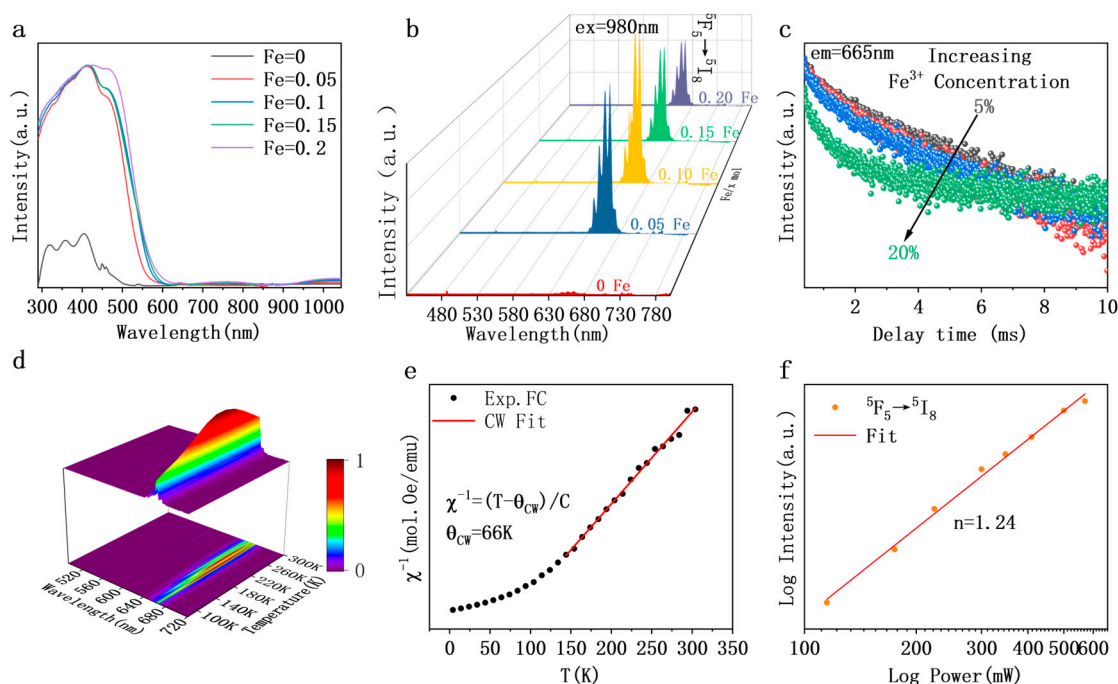


Figure 2. (a) Absorption spectrum of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/x\text{Fe}^{3+}$ ($x = 0, 0.05, 0.1, 0.15, 0.2$). (b) Photoluminescence (PL) spectrum of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/x\text{Fe}^{3+}$ ($x = 0, 0.05, 0.1, 0.15, 0.2$) under 980 nm laser excitation, with the emission peak at 665 nm. (c) Lifetime decay curve of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/x\text{Fe}^{3+}$ ($x = 0, 0.05, 0.1, 0.15, 0.2$) at 665 nm monitored under 980 nm laser excitation. (d) Temperature-dependent PL spectrum of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/0.1\text{Fe}^{3+}$ at 665 nm emission. (e) Relationship diagram of inverse magnetization (χ^{-1}) of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/0.1\text{Fe}^{3+}$ with temperature variation. (f) Double logarithmic plot of up-conversion photoluminescence (UCPL) intensity of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/0.1\text{Fe}^{3+}$ at 665 nm under 980 nm continuous wave laser excitation and excitation power.

Furthermore, the luminescence decay at the 665 nm wavelength follows a biexponential model [36]:

$$I = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

Here, I represents the luminescence intensity, t represents time, and A_1 and A_2 are constants. τ_1 and τ_2 represent the rapid and slow lifetime components, respectively. We propose that the inhomogeneous distribution of Fe^{3+} ions in the lattice may create two distinct local environments for Ho^{3+} ions: Ho^{3+} sites adjacent to Fe^{3+} contribute to the faster decay component (τ_1), whereas those without Fe^{3+} neighbors exhibit the slower intrinsic decay component (τ_2). The average lifetime τ_{ave} can be calculated using the following formula:

$$\tau_{ave} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (2)$$

The decay curves in Figures 2c and S21 show that the average photoluminescence time constant (τ_{ave}) of the sample decreases from 2.59 ms to 0.84 ms with increasing Fe^{3+} concentration (Table S3). Interestingly, the short lifetime component τ_1 first increases and then decreases, which is consistent with the trend of photoluminescence intensity. This indicates that, within the low doping concentration range, appropriately increasing the Fe^{3+} doping concentration is beneficial for the formation of $\text{Fe}^{3+}\text{-Ho}^{3+}$ pairs, thereby promoting the luminescence of the system; however, further increasing the Fe^{3+} concentration at high levels instead leads to the formation of $\text{Fe}^{3+}\text{-Fe}^{3+}$ pairs, which intensifies the antiferromagnetic coupling, enhances the non-radiative relaxation of the system, shortens τ_1 and τ_2 , and causes luminescence quenching. To further understand the luminescence behavior of this system, we measured temperature-dependent photoluminescence spectra. Figures 2d and S22 show that the emission intensity at 665 nm reaches a maximum at a temperature of 220 K. Figure S23 presents the fitting curve of the Huang–Rhys factor, and the formula used is as follows [37]:

$$FWHM = 2.36\sqrt{S\hbar\omega}\sqrt{\coth\left(\frac{\hbar\omega}{2k_B T}\right)} \quad (3)$$

Here, $FWHM$ represents the half-width at half-maximum, $\hbar$ is the reduced Planck constant, T is the temperature, and ω is the phonon frequency. The fitting yields a Huang–Rhys factor S of 0.046 and a phonon energy ($\hbar\omega$) of 19.58 meV, which corresponds to a temperature of approximately 227.2 K, basically close to the 220 K observed in the temperature-dependent PL. Therefore, strong electron–phonon coupling is not the dominant factor for the luminescence quenching of the sample at high temperatures. Figure S24 shows the Raman spectra of $\text{Cs}_2\text{NaScCl}_6\text{:0.1Ho}^{3+}$ and $\text{Cs}_2\text{NaScCl}_6\text{:0.1Ho}^{3+}/\text{0.1Fe}^{3+}$. In the $\text{Cs}_2\text{NaScCl}_6\text{:0.1Ho}^{3+}$ sample, a Raman peak located at 146 cm^{-1} can be observed. Interestingly, the Raman peak of the $\text{Cs}_2\text{NaScCl}_6\text{:0.1Ho}^{3+}/\text{0.1Fe}^{3+}$ sample splits at 157.63 cm^{-1} , which is attributed to the magnetic interaction between Fe^{3+} and Ho^{3+} . Correspondingly, Figure 2e presents the temperature-dependent inverse magnetic susceptibility (χ^{-1}) curve of $\text{Cs}_2\text{NaScCl}_6\text{:0.1Ho}^{3+}/\text{0.1Fe}^{3+}$, and the Curie–Weiss law is used to fit the linear region [38]:

$$\chi^{-1} = \frac{T - \theta_{cw}}{C} \quad (4)$$

Here, θ_{cw} represents the Curie temperature, C is the Curie constant, and T is the temperature. The fitted θ_{cw} value obtained is 66 K, which proves that this material exhibits long-range ferromagnetic order below 66 K, and the system transforms into paramagnet above 66 K. Figure S25 shows the hysteresis loop of $\text{Cs}_2\text{NaScCl}_6\text{:0.1Ho}^{3+}/\text{0.1Fe}^{3+}$ at 298.15 K, indicating that this material is paramagnet at 298.15 K. Since 66 K is below the temperature range of 80–220 K where the temperature-dependent PL enhancement occurs, we attribute the enhanced PL phenomenon in the temperature-dependent PL to the local dynamic short-range ferromagnetic fluctuations formed by the electron magnetic polarons (EMPs) in the $\text{Cs}_2\text{NaScCl}_6\text{:0.1Ho}^{3+}/\text{0.1Fe}^{3+}$ sample. These fluctuations are triggered by the $\text{Fe}^{3+}\text{-Ho}^{3+}$ coupling or the non- 180° superexchange interactions between Fe^{3+} ions, and this non- 180° superexchange interaction leads to a certain ferromagnetic coupling between $\text{Fe}^{3+}\text{-Fe}^{3+}$, a phenomenon that is common in Fe^{3+} ion-doped samples. Within the temperature range of 80–220 K, the increase in temperature helps stabilize and diffuse the EMPs, thereby enhancing the luminescence. However, if the temperature exceeds 220 K, the excessive temperature disrupts the local magnetic correlation and causes thermal quenching in $\text{Cs}_2\text{NaScCl}_6\text{:0.1Ho}^{3+}/\text{0.1Fe}^{3+}$, which is consistent with the EMP dissociation phenomenon¹².

In addition, we have made a variation excitation power diagram as shown in Figure S26 regarding the relationship between excitation power and up-conversion photoluminescence (UCPL) intensity and converted it into a PL and power-related double logarithmic plot, as exhibited in Figure 2f, where the slope $n = 1.24$, indicating that this up-conversion process is not an ideal two-photon process ($n = 2$). We attribute this value to EMP-mediated up-conversion, in which EMP absorbs the energy from two Fe^{3+} ions and transfers the energy to Ho^{3+} , thereby generating red light up-conversion.

3.3. Calculation of Energy Band Structure and Density of States

To further investigate the luminescence mechanism of $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$, we calculated the electronic band structures and density of states of the pure and doped samples. Figure S27 presents the band structure analysis of $\text{Cs}_2\text{NaScCl}_6$, showing that this double perovskite is a direct bandgap semiconductor with a bandgap of 3.94 eV. In contrast, the co-doped sample exhibits differences in its energy levels. Figure 3a,b display the band structures of the spin-up and spin-down channels of $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$, respectively. It can be observed that the bandgap of the spin-up channel also remains 3.94 eV. Interestingly, two spin-polarized intermediate states appear within the bandgap of the spin-down channel [39]. Analysis of the total density of states and the projected density of states in Figures S28 and 3c reveals that these two spin-down intermediate states originate from the hybridization of Fe-3d and Cl-2p atomic orbitals. Due to the localized nature of the 4f electrons of Ho^{3+} , the contribution from Ho^{3+} is relatively small. It can be seen that the energy difference between the lower intermediate state and the valence band maximum is 1.27 eV, which matches well with the 980 nm photon energy of 1.26 eV. This indicates that the absorption of 980 nm photons by the material is spin-selective. Meanwhile, the energy of the higher intermediate state (referred to as the biexciton state hereafter) is 2.17 eV. Importantly, the biexciton absorption process itself relies on the ferromagnetic parallel alignment between Fe^{3+} ions. This biexciton state then transfers energy to Ho^{3+} through the magnetic coupling between Fe^{3+} and Ho^{3+} , achieving spin-selective up-conversion. Furthermore, this energy lies above the $^5\text{F}_5$ red emission level of Ho^{3+} (1.86 eV) and below the $^5\text{F}_4/^5\text{S}_2$ green emission levels (2.27 eV), which may consequently lead to the absence of green emission in the system. In addition to the energy levels, their corresponding effective magnetic moments can also provide an explanation for this selective emission. The green emission corresponds to the $^5\text{F}_4/^5\text{S}_2$ levels, whose total angular momentum quantum numbers are $J = 4$ and $J = 2$, respectively. The red emission $^5\text{F}_5$ has a total angular momentum of $J = 5$. According to the formula:

$$\mu_{eff} = g_J \sqrt{J(J+1)} \mu_B \quad (5)$$

The calculated effective magnetic moment of the $^5\text{F}_5$ level is 7.67 μ_B , which is larger than 6.04 μ_B for $^5\text{F}_4$ and 4.90 μ_B for $^5\text{S}_2$. Therefore, the $^5\text{F}_5$ level is more prone to exchange magnetic coupling with Fe^{3+} , which provides theoretical support for the presence of only red emission and the spin-selective nature of the up-conversion process in this system. Furthermore, to verify the existence of the 2.17 eV biexciton state in the system, we measured the photoluminescence excitation (PLE) spectra of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}$ and $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/0.1\text{Fe}^{3+}$ monitored at 665 nm, as shown in Figure S29. The results show that although weak red emission can be generated in $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}$ under 593 nm excitation, its intensity is significantly lower than that of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/0.1\text{Fe}^{3+}$. The energy corresponding to 593 nm is close to 2.17 eV, and under 980 nm laser excitation, the luminescence intensity of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/0.1\text{Fe}^{3+}$ is enhanced by approximately 73 times (Figure S14). Therefore, this sensitization pathway

exists in $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/0.1\text{Fe}^{3+}$, transferring the 980 nm photon energy to Ho^{3+} ions. In addition, the spin asymmetry in the orbitals of Fe^{3+} , Cl^- , and Ho^{3+} provides a theoretical basis for local Fe^{3+} - Ho^{3+} magnetic coupling and the formation of EMPs in the paramagnetic phase (Figure 3c) [40,41].

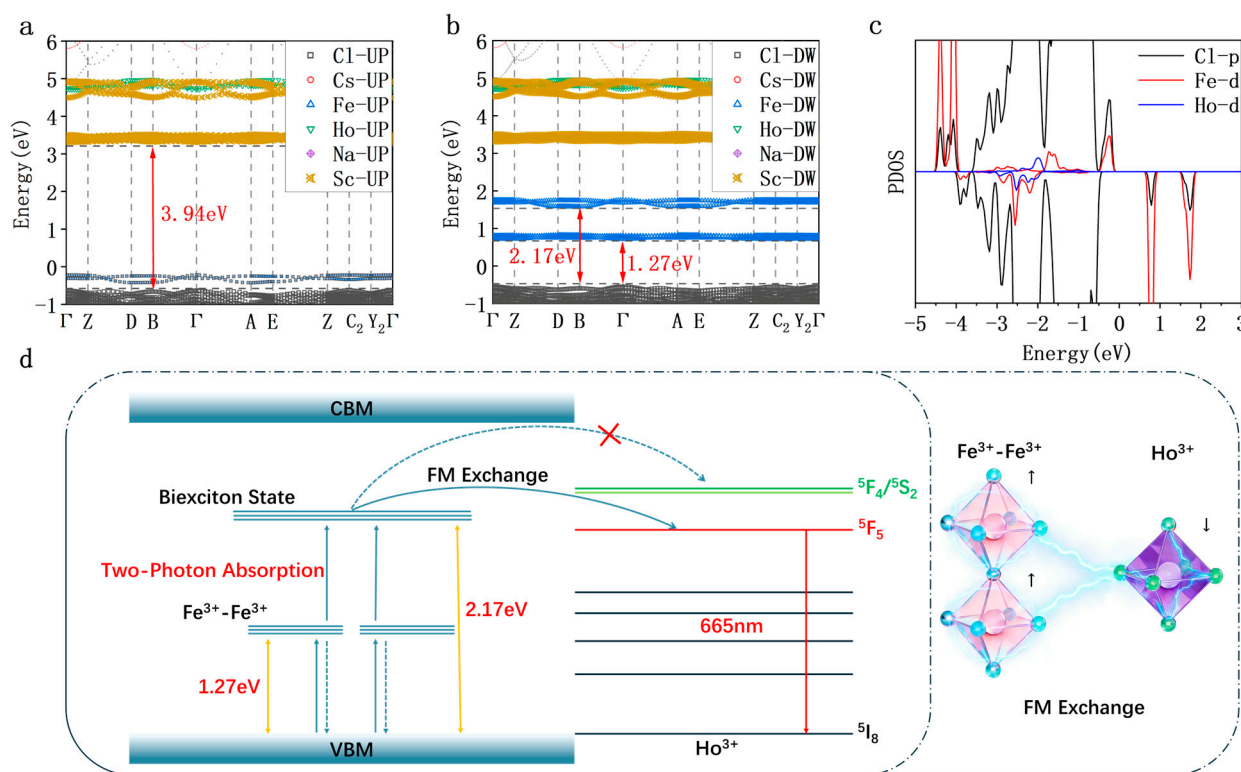


Figure 3. (a) Spin-up channel band structure of $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$. (b) Spin-down channel band structure of $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$. (c) Wave function density plots of $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$. (d) Up-conversion luminescence mechanism of $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$ under 980 nm laser excitation.

Furthermore, for $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Mn}^{2+}$, a system that exhibits no red emission under 980 nm laser excitation, we analyzed its spin-up and spin-down band structures as well as the projected density of states, and the results are shown in Figures S30–S32. It can be seen that there are no energy levels capable of absorbing 980 nm photons in either the spin-up or spin-down channels of $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Mn}^{2+}$. Consequently, no Ho^{3+} emission can be observed in this system.

Based on the above calculations, a schematic diagram of the up-conversion luminescence mechanism of $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$ is presented in Figure 3d. Within the bandgap of this system, there exist two spin-polarized intermediate states. The lower-energy intermediate state absorbs 980 nm photons, while the biexciton state absorbs the energy from two Fe^{3+} ions, and then relaxes the energy to the $^5\text{F}_5$ level of Ho^{3+} through a ferromagnetic exchange process, thereby increasing the population of the red emission level. Meanwhile, due to the weak electron–phonon coupling in $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$ and the fact that the effective magnetic moments of the $^5\text{F}_4/^5\text{S}_2$ levels are smaller than that of the $^5\text{F}_5$ level, the transition from the biexciton state to the $^5\text{F}_4/^5\text{S}_2$ levels of Ho^{3+} is blocked; hence, no green emission exists in this system, achieving spin-selective red up-conversion. In addition, the doping concentration of Fe^{3+} and the temperature variation have a significant impact on the luminescence of the system. At low Fe^{3+} doping concentrations, Fe^{3+} acts as a sensitizer, transferring energy to Ho^{3+} and promoting its luminescence; at higher Fe^{3+} concentrations, the antiferromagnetic coupling and cross-relaxation of Fe^{3+} - Fe^{3+} pairs intensify the non-radiative transitions of the system, leading to concentration quenching. In the low

temperature range, heating facilitates the formation and diffusion of EMPs, thus enhancing the luminescence; however, excessively high temperatures cause EMP dissociation and weaken the luminescence.

3.4. Ho^{3+} -Doped $\text{Cs}_2\text{NaScCl}_6$ Scintillator for X-Ray Imaging

Since $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}/\text{Fe}^{3+}$ achieves up-conversion via the EMP mechanism under 980 nm laser excitation, we further explored its luminescence behavior under X-ray excitation. However, the radioluminescence (RL) spectra in Figure S33 show that with increasing Fe^{3+} concentration, the emission intensity decreases significantly, and the characteristic emission peaks of Ho^{3+} lost their fine structure while remaining narrow. Generally, static lattice distortion would cause the Ho^{3+} emission to become smoother under all excitation conditions. Nevertheless, under 450 nm and 980 nm excitation, the Ho^{3+} emission does not lose its fine structure, thus excluding the dominant role of static lattice distortion. We attribute the X-ray-induced spectral smoothing to the magnetic coupling between Fe^{3+} and Ho^{3+} : under X-ray excitation, a large number of electron–hole pairs are generated in the lattice; they are captured at Fe^{3+} and Ho^{3+} sites, producing a local exchange field that broadens the Stark levels of Ho^{3+} , leading to spectral smoothing. At the same time, this magnetic coupling opens non-radiative energy transfer channels between Fe^{3+} and Ho^{3+} , quenching the luminescence. Therefore, although under 980 nm laser excitation Fe^{3+} ions can enhance the emission through EMP-mediated spin-selective up-conversion, under X-ray and Stokes excitation they act as quenching centers, and their magnetic coupling effect is detrimental. Hence, we removed Fe^{3+} ions, prepared $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}$, and systematically investigated its scintillation performance.

As shown in Figure 4a, $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}$ has a high absorption coefficient, which is comparable with LuAG:Ce, BGO, and CsPbBr₃ in the figure, indicating its strong absorption capacity for X-ray photons [42]. Figure 4b presents the RL spectrum of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}$ under X-ray excitation. To quantitatively evaluate its scintillation efficiency, we measured the RL spectra of commercial LuAG:Ce and BGO crystals (with the same sample dimensions) under identical irradiation conditions as references. The integrated RL intensity of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}$ is approximately 2.5 times that of BGO and comparable with that of LuAG:Ce, demonstrating its highly competitive X-ray-to-visible conversion efficiency [43]. Additionally, as shown in Figure S34, the RL intensity increases linearly with the X-ray dose rate, and it can be observed that their relationship shows a linear increasing trend. Next, we measured the detection limit of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}$. Figure 4c shows the variation of the signal-to-noise ratio (SNR) of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}$ with X-ray dose rate. By linearly fitting the data and extrapolating to $\text{SNR} = 3$, we obtained a detection limit of $37.73 \text{ nGy}_{\text{air}} \text{ s}^{-1}$. This value is much lower than the standard of $5.5 \mu\text{Gy}_{\text{air}} \text{ s}^{-1}$ required for medical imaging diagnosis, demonstrating the potential of this material for application in ultra-low-dose X-ray detection. Then, we combined $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}$ with PDMS to form a flexible scintillation film as demonstrated in Figure S35 and applied it to X-ray imaging. As exhibited in Figure 4d, the internal capsule with a spring and the key under $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}/\text{PDMS}$ X-ray imaging can clearly show its internal structure. The modulation transfer function (MTF) analysis in Figure 4e indicates that the spatial resolution of this scintillation film reaches 12.1 lp/mm at an MTF value of 0.2, which exceeds the performance of scintillators such as CsPbBr₃ (9.8 lp/mm) [44], $\text{Cs}_2\text{NaTbCl}_6$ (10 lp/mm) [45], and $\text{Cs}_2\text{HfCl}_6:\text{Mo}^{4+}$ (12 lp/mm) [46] reported previously.

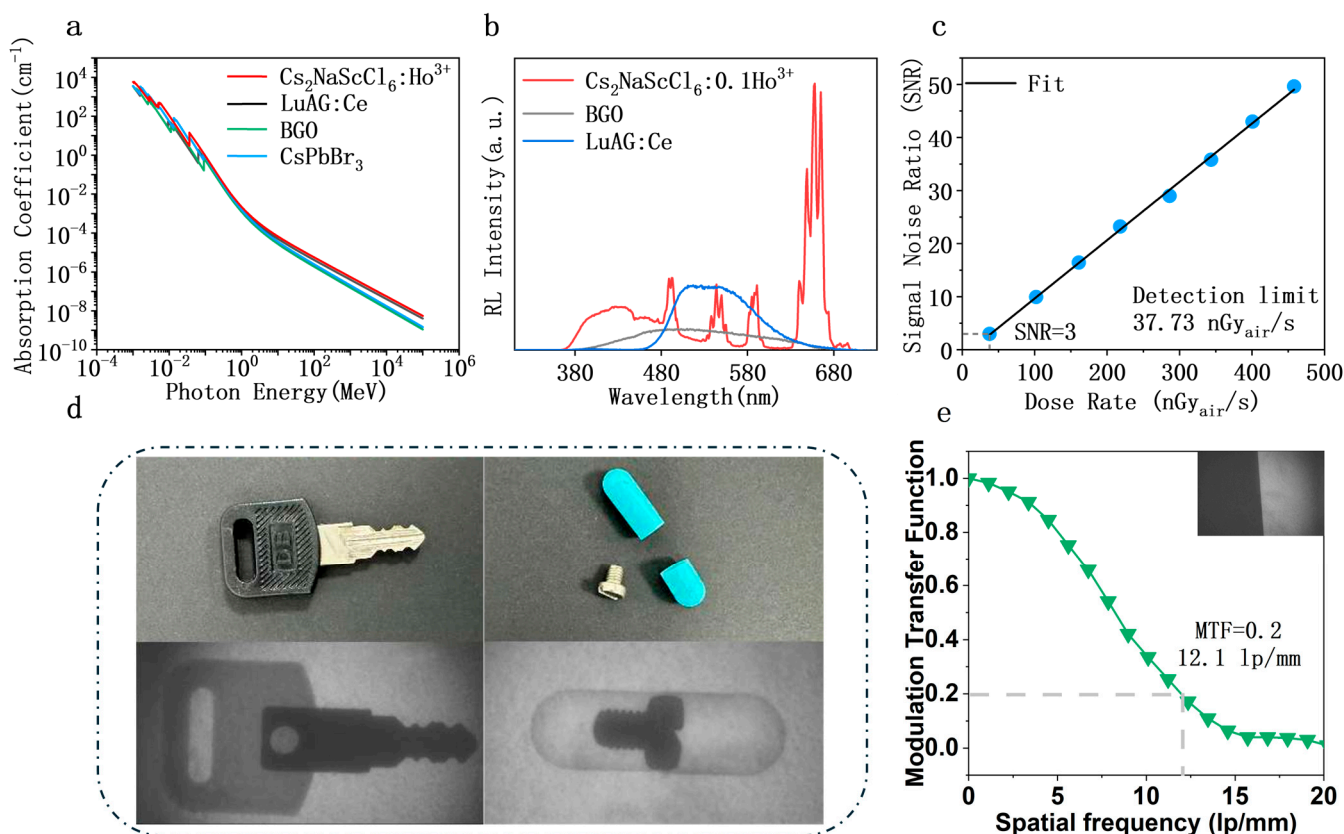


Figure 4. (a) Graph showing the variation of X-ray absorption coefficients of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}$, LuAG:Ce, BGO, and CsPbBr_3 with X-ray photon energy. (b) Fluorescence spectra of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}$ /PDMS, BGO, and LuAG:Ce phosphors under an X-ray excitation dose rate of $50 \text{ mGy}_{\text{air}} \text{ s}^{-1}$. (c) Graph showing the relationship of the signal-to-noise ratio (SNR) of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}$ with X-ray dose rate. (d) X-ray imaging of different objects. (e) Modulation transfer function MTF curve for X-ray imaging using the flexible film of $\text{Cs}_2\text{NaScCl}_6:0.1\text{Ho}^{3+}$ /PDMS.

4. Conclusions

This work investigates the influence of Fe^{3+} magnetic coupling on Ho^{3+} luminescence in $\text{Cs}_2\text{NaScCl}_6$ under different excitation conditions. The results indicate that Fe^{3+} doping introduces spin-polarized intermediate states in the bandgap and forms electron magnetic polarons (EMPs) in the material under 980 nm excitation. These EMPs subsequently transfer energy to the $^5\text{F}_5$ level of Ho^{3+} via $\text{Fe}^{3+}\text{-Ho}^{3+}$ magnetic coupling, resulting in spin-selective red up-conversion emission without green emission. Moreover, under this condition, the $\text{Fe}^{3+}\text{-Ho}^{3+}$ magnetic coupling may open a non-radiative energy relaxation pathway, thereby quenching the luminescence. Based on these observations, we prepared Fe^{3+} -free $\text{Cs}_2\text{NaScCl}_6:\text{Ho}^{3+}$, report its excellent scintillation performance (the integrated RL intensity is approximately 2.5 times that of BGO and comparable with that of LuAG:Ce and a detection limit of $37.73 \text{ nGy}_{\text{air}} \text{ s}^{-1}$), and demonstrate its potential for flexible X-ray imaging.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst16070472/s1>.

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