Research article

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Tailoring the electron and hole dimensionality to achieve efficient and stable metal halide perovskite scintillators

<https://doi.org/10.1515/nanoph-2020-0624>

Received November 25, 2020; accepted January 26, 2021;

published online February 17, 2021

Abstract: Metal halide perovskites have recently been reported as excellent scintillators for X-ray detection. However, perovskite based scintillators are susceptible to moisture and oxygen atmosphere, such as the water solubility of CsPbBr₃, and oxidation vulnerability of Sn²⁺, Cu⁺. The traditional metal halide scintillators (NaI: Tl, LaBr₃, etc.) are also severely restricted by their high hygroscopicity. Here we report a new kind of lead free perovskite with excellent water and radiation stability, Rb₂Sn_{1-x}Te_xCl₆. The equivalent doping of Te could break the in-phase bonding interaction between neighboring octahedra in Rb₂SnCl₆, and thus decrease the electron and hole dimensionality. The optimized Te content of 5% resulted in high photoluminescence quantum yield of 92.4%, and low X-ray

detection limit of 0.7 μGy_{air} s⁻¹. The photoluminescence and radioluminescence could be maintained without any loss when immersing in water or after 480,000 Gy radiations, outperforming previous perovskite and traditional metal halides scintillators.

Keywords: electron and hole dimensionality; metal halide perovskite; scintillators; stable; tailoring.

1 Introduction

Metal halide perovskites have emerged as a new class of promising emitters for various applications of luminescence, such as electroluminescence, phosphors, lasers, scintillators etc [1–10]. The adjustable composition and defect tolerance nature endow perovskites with wide spectral tunability and high quantum efficiency. Several recent papers have demonstrated the use of CsPbBr₃ nanocrystals as promising scintillators with good X-ray attenuation coefficient, tunable emission wavelength and low temperature solution processing [11–13]. The self-trapped exciton emitters of low dimensional perovskites (Rb₂CuBr₃, Bmpip₂SnBr₄) have also been utilized as scintillators and shown high radioluminescence, benefiting from the negligible self-absorption effect [14, 15]. For example, Kovalenko and co-workers found that Bmpip₂SnBr₄ exhibited ~1.7 times higher radioluminescence intensity than commercial NaI:Tl scintillator [15]. Scintillators have wide applications in detection of high-energy radiations, including X-rays and gamma rays. During the detection, scintillators firstly convert X-ray or gamma ray into visible photons, which are then collected by photosensors to give spatial or temporal information.

However, the currently reported perovskite related scintillators are susceptible to moisture and oxygen atmosphere, such as the water solubility of CsPbBr₃, and oxidation vulnerability of Sn²⁺, Cu⁺. The traditional scintillators, NaI: Tl, LaBr₃, are also severely restricted in

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practical applications by their high hygroscopicity [16]. It is of great significance to explore lead-free perovskite scintillators with excellent stability toward oxygen and moisture, as well as high radioluminescence intensity.

We speculate $A_2\text{SnX}_6$ ($A=\text{Cs, Rb}$; $X=\text{Cl, Br, I}$) as a possible candidate considering its negligible water solubility and stable valence states of Sn^{4+} . However, although each Sn-X octahedron is completely separated from the neighbors, previous studies have illustrated that the band structure of $A_2\text{SnX}_6$ does not follow the same behavior and no luminescence could be observed [17]. Taking Cs_2SnI_6 as an example, the conduction band minimum (CBM) is from the antibonding of $\text{Sn } 5s$ and $\text{I } 5p$ orbitals [18]. At the Γ point, the antibonding orbital is in phase with that of adjacent cell, resulting in a bonding interaction between neighboring octahedra and disperse projection of halide p orbital into the inter-octahedral voids.

We note that for efficient emissions, the CBM and valence band maximum (VBM) should both have low electronic dimensionality. Otherwise, the electron and hole orbital overlap and transition dipole moment will be decreased according to Fermi's golden rule, $\mu = \langle \varphi_h | \hat{\mu} | \varphi_e \rangle$, where $\hat{\mu}$ is the electric dipole operator, φ_h and φ_e are the hole and electron wavefunctions, respectively [19]. The delocalized CBM in above case of Cs_2SnI_6 is responsible for its negligible luminescence. Thereby it is desired to introduce equivalent ions to partially replace Sn^{4+} for reduced electronic dimensionality to boost emissions, and such study has not been reported as far as we are concerned.

In this work, we report a new lead-free double perovskite $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$ with efficient X-ray scintillation, and ultra-high stability against moisture and high energy radiations. Te^{4+} could partially substitute Sn^{4+} in the structure. At the CBM, $\text{Te } 5p$ orbital interacts with $\text{Cl } 3p$ orbital, which could break the in-phase bonding interaction between neighboring octahedra in Rb_2SnCl_6 . The electronic dimensionality is thereby reduced, and we experimentally observed the self-trapped exciton emission in the alloy $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$. When the Te content is 5%, the products exhibited wide emission spectra (peak at ~ 580 nm), high photoluminescence quantum yield of 92.4%, and photoluminescence lifetime of 1.16 μs . Under X-ray excitation, the radioluminescence intensity is 39% of commercial $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ scintillators ($66,500$ photons MeV^{-1}) and the detection limit is as low as $0.7 \mu\text{Gy}_{\text{air}} \text{ s}^{-1}$. The photoluminescence and radioluminescence could be maintained without any loss when immersing in water or after 480,000 Gy radiations, outperforming previous perovskite and traditional metal halides scintillators. Considering its excellent stability, $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$ may find vast

applications as scintillators for radiography and radiosensitizers for *in vivo* radiodynamic therapy.

2 Results and discussions

The series of products $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$ were synthesized by dissolving designed stoichiometric ratio of RbCl , SnCl_4 , TeCl_4 into HCl solution in a hydrothermal autoclave. The solution was heated and then slowly cooled down to room temperature. The resulting powder crystals were washed by isopropanol to remove surface-adsorbed ions. Figure 1a shows the schematic crystal structure of $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$. Each Sn^{4+} (Te^{4+}) is coordinated with six Cl^- ions, and the formed $\text{Sn}(\text{Te})\text{-Cl}$ octahedra are completely separated from each other by the presence of Rb^+ . Such structure could also be viewed as vacancy ordered double perovskites. Figure 1b shows the powder X-ray diffraction (PXRD) patterns of $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$ samples. The diffraction patterns of all $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$ follow the structure type of K_2PtCl_6 (space group: $Fm\bar{3}m$), where $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$. The calculated lattice constant (a) of pure Rb_2SnCl_6 is 10.088 Å and that of Rb_2TeCl_6 is 10.148 Å, consistent with the ionic radius of Sn^{4+} (0.69 Å) and Te^{4+} ion (0.97 Å). From the peaks with asterisks in the right panel, as Te^{4+} increases, the (111) diffraction peak moves to the left. The alloys exhibit pure phase and the lattice constant gradually increases upon the introduction of Te^{4+} , demonstrating the random replacement of Sn^{4+} by Te^{4+} to yield solid solutions.

The tetravalent oxidation state of Te and Sn were confirmed by X-ray photoelectron spectroscopy (XPS) measurements (Figure 1c and Figure S1). The peaks at 576.36 and 586.66 eV are attributed to $\text{Te}^{4+} 3d_{5/2}$ and $3d_{3/2}$, and those at 486.86 and 496.36 eV correspond to $\text{Sn}^{4+} 3d_{5/2}$ and $3d_{3/2}$, respectively. Also, the energy dispersive spectrometer (EDS) mapping of $\text{Rb}_2\text{Sn}_{0.8}\text{Te}_{0.2}\text{Cl}_6$ in Figure 1d shows the homogeneous distributions of rubidium (Rb), tin (Sn), tellurium (Te) and chlorine (Cl) elements in the product, also confirming the random occupation of Te^{4+} on Sn^{4+} lattice sites.

UV-vis absorption and photoluminescence (PL) spectra are shown in Figure 2a and b. It is clearly observed that the absorption within the region of 300–500 nm is enhanced with the increase of Te contents. The origin of band gap change will be discussed later. As shown in Figure 2b, for photoluminescence upon excitation at 380 nm, $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$ shows a broad yellow emission. Upon increasing the Te content, the emission peak red shifted from 566 to 586 nm, which are caused by the decreased band gaps [17]. In addition, the full-width-at-half-maximum (FWHM) increased from 108 to 122 nm.

Figure 1: (a) Schematic crystal structure of $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$ double perovskites. (Dark green octahedron: $[\text{SnCl}_6]^{2-}$; purple octahedron: $[\text{TeCl}_6]^{2-}$). (b) Powder X-ray diffraction (PXRD) for the series of $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$, and the peaks with asterisks in the left picture are displayed with enlarged abscissa on the right. (c) X-ray photoelectron spectroscopy (XPS) and peak fitting for Sn 3d and Te 3d orbitals, respectively. (d) Energy dispersive mapping of elements Rb, Sn, Te and Cl for the prepared powders.

Furthermore, the photoluminescent quantum yields (PLQYs) were also recorded. As shown in Figure 2c, the reference (black curve) of a quartz plate and $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$ were put in an integrating sphere and excited by 380 nm light. The PLQY value was obtained via dividing integrated emission intensity by the absorbance. Figure 2d shows the PLQYs for the series of solid solution. PLQY gets enhanced upon introducing higher Te content, and reaches its maximum value of 92.4% at 5% Te content. Such PLQY is among the highest values for all kinds of metal halide perovskites [20–22].

In addition, to verify the mechanism of radiative recombination process, we also tested the photoluminescence (PL) and photoluminescence excitation (PLE) spectra of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ as a function of the excitation and emission wavelengths, respectively. As exhibited in Figure 3a, both PL and PLE spectra show identical shapes. Above phenomenon indicates that the emission comes from the same excited states, excluding the influence of defect emissions. The Stokes shift is

estimated around 140 nm. The negligible overlap between PL and PLE indicates that the self-absorption effect is not significant for the products, which is ideal for efficient light out-coupling and achieving high radioluminescence. For the time-resolved PL spectrum (Figure 3b), we could fit the curve through a double exponential function. The two lifetimes are 0.19 and 3.32 μs , and the average decay time is 1.16 μs . The large Stokes shift and long lifetime imply the possible formation of self-trapped excitons (STEs).

We evaluate the electron-phonon coupling and self-trapped excitons by recording the temperature-dependent FWHM spectrum. The curve is fitted based on the phonon broadening model, while the fitting function is shown in the inset of Figure 3c [23]. The electron-phonon coupling could be quantitatively studied by Huang-Rhys factor S , where a large value of S means strong electron-phonon coupling and favorable formation of STEs. The obtained Huang-Rhys factor S is 30.7, and $\hbar\omega_{\text{phonon}}$ is 18.5 meV. The S value of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ is one order of magnitude higher than

Figure 2: (a) UV-vis absorption spectra of $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$. (b) PL spectra of $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$, while no emission could be observed for Rb_2SnCl_6 . (c) The PL spectra of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ for PLQY measurement. (d) The PLQY values of $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$ with various x values.

Figure 3: (a) Wavelength-dependent PLE and PL spectra for $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$. (b) PL decay and fitting curve of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ powders. (c) Fitting results of full width at half maximum (FWHM) as a function of temperature from 83 to 353 K derived from the PL spectra. For the fitting equation, S is Huang-Rhys factor, $\hbar\omega_{\text{phonon}}$ is the phonon frequency ($\hbar$, reduced Planck constant), k_B is the Boltzmann constant. (d) Transient absorption spectra of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ (laser pulse of 400 nm and $4 \mu\text{J cm}^{-2}$), while the decay curve is for the wavelength of 456 nm $\Delta T/T$ is the transmittance change.

traditional emitters like CdSe (1), ZnSe (0.3), CsPbBr_3 (3.2), and slightly lower than $\text{Cs}_2\text{Ag}_{0.16}\text{Na}_{0.84}\text{InCl}_6$ (51.0) [24–26]. Hence, we infer that the large electron-phonon coupling could promptly transform the excited excitons into the self-trapped states, which then radiatively recombine to produce broad emissions.

The transient absorption measurements on $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ provide the formation kinetics of STEs (Figure 3d). Upon excitation at 400 nm, the sample showed a broad featureless photo-induced absorption (PIA) signal from 430 to 480 nm. The PIA signal rises within ~ 300 fs, suggesting an ultrafast exciton self-trapping process. According

to the previously obtained phonon frequency (18.5 meV), we could estimate the self-trapping time as $\tau = \frac{2\pi}{\omega_{\text{phonon}}} = 223$ fs. The consistency of the observed and estimated self-trapping time also confirms the self-trapped exciton emissions.

The electronic band structures have been theoretically calculated. As shown in Figure 4a, using a self-energy corrected shGGA-1/2 method [27, 28], the band gap of Rb_2SnCl_6 was determined as 3.71 eV, consistent with the experimental results (~ 3.9 eV). By introducing a certain amount (6 Te per 64 Sn, 9.375%) of Te, the calculated band gap decreased to 2.89 eV. One could identify the origin of the band structure through partial density of states analysis. Considering the electronic configuration of Sn^{4+} ($5s^0 5p^0$), the VBM comes from the non-bonding Cl 3p orbitals for pure Rb_2SnCl_6 , while the CBM consists of the antibonding states between Sn 5s and Cl 3p orbitals. In order to differentiate the degree of localization for carriers, we further performed $4 \times 4 \times 1$ supercell calculations. The charge density isosurfaces shown in Figure 4c, evaluated at the Γ point, reveal that

the charges at VBM are completely isolated. In contrast, although Sn–Cl octahedra are isolated from each other, dispersive CBM states are observed, indicating that the electrons at the CBM tend to be delocalized. Neilson and co-workers previously utilized the simplified orbital bonding picture to explain the above abnormal phenomenon, which can also be applied in this work (Figure 4d) [15]. For CBM, the Sn 5s orbital hybridizes with Cl 3p orbital with a σ bonding type, while the A_{1g} antibonding orbital is in phase with the neighboring A_{1g} orbital in the adjacent cell. Thereby there is a bonding interaction between adjacent Sn–Cl octahedra. Due to the dispersive projection of halide p orbitals, the bonding interaction extends to the inter-octahedral void. As stated in the introduction part, such behavior would decrease the electron and hole orbital overlap, lowering the emission efficiency accordingly.

The influence of Te^{4+} doping over the electronic dimensionality especially for CBM is further studied. Firstly, for pure Rb_2TeCl_6 , the $5s^2 5p^0$ electron configuration

Figure 4: Theoretical calculation results of Rb_2SnCl_6 (a–d) and $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$ (e–h). (a, e) Band structures and density of states. (b, f) Charge density isosurface of CBM. (c, g) Charge density isosurface of VBM. (d, h) Simplified molecular orbital picture.

of Te^{4+} adds two more electrons to occupy the antibonding states from Te 5s and Cl 3p, and the higher binding energy of Te 5s orbital also lowers the energy level of the antibonding states. Hence, the CBM is composed of high-energy antibonding state of Te 5p and Cl 3p orbitals.

For the case of $\text{Rb}_2\text{Sn}_{1-x}\text{Te}_x\text{Cl}_6$, we introduced six Te atoms into the supercell, corresponding to a doping content of 9.37%. The CBM consists of Sn 5s and Cl 3p orbitals, and the presence of Te will create barriers for the delocalization of electrons. It is straightforward that the electronic dimensionality will be reduced, as the yellow circle in Figure 4f indicates. Moreover, the VBM is then comprised by antibonding states of Te 5s and Cl 3p orbitals, and we could clearly observe that the holes are strongly confined around Te–Cl octahedra (Figure 4g). The simultaneous decrease of electronic dimensionality for electrons and holes contribute to the emission enhancement. Provided that the Te content is too large, the electrons and holes will

be separately confined onto Sn–Cl octahedra and Te–Cl octahedra, respectively, which nevertheless would decrease the overlap of electrons and holes again, explaining the worsened PLQY when Te contents in excessive.

Figure 5a depicts the schematic process of X-ray scintillation. The high energy X-rays interact with the inner shell electrons through photoelectric ionization. The generated energetic electrons can excite other secondary or tertiary electrons, which thermally relax to the conduction band edge via interaction with optical and acoustic phonons. Then the electrons and holes could radiatively recombine to emit visible photons. The radioluminescence spectrum of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ has been measured under 50 kV X-ray excitation (Figure S2). The spectrum is similar to that under 380 nm UV-light, which demonstrates that the same radiative recombination channel is taken under either X-ray or UV excitation.

Figure 5: (a) Schematic diagram of the scintillation mechanism. (b) Absorption coefficients of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$, Si, $\text{Lu}_{1.8}\text{Y}_{0.2}\text{SiO}_5:\text{Ce}$ (LYSO), CsI: Tl and $\text{Gd}_2\text{O}_2\text{S: Tb}$ (GOS) as a function of photon energy, from 1 keV (soft X-rays) to 100 MeV (gamma radiation) (c) Response voltage of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ and GOS as a linear function of dose rate. The inset is the photograph of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ under neutral light and X-ray irradiation, separately. (d) Statistics of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ scintillation response before and after radiation dose of 480,000 Gy.

The absorption coefficient of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ was plotted in Figure 5b, with comparison to other typical scintillators (Si, LYSO, CsI:Tl and GOS) in a wide photon energy range, according to the photon cross-section database [29]. Considering the density as 3.24 g cm^{-3} and the light element composition, the absorption coefficient is lower than LYSO, CsI:Tl and GOS, but higher than silicon.

To evaluate the radioluminescence intensity, we assembled an integrating sphere into the system in Figure S3. We note that such system will exclude the influence of photon out-coupling effect, compared with our previously adopted method without integrating sphere [12]. Moreover, to strictly compare the scintillation performance, we strongly recommend to pay attention to the area, geometry and position of the samples. As shown in Figure S3, the reference and samples should have the same thickness, area and shapes. Here we pressed commercial GOS and our $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ powders into small pellets. During the measurement, we posited these two pellets onto the same position to avoid the influence of nonuniformity and anode effect of X-ray tubes. Considering the nonlinearity of Si-PM in high response range, we decreased the radiation dose rates. As shown in Figure 5c, the response voltage was measured at different dose rates for determining the linear response range to the X-ray dose rate. The linear response of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ covers a wide range from $0.97 \mu\text{Gy}_{\text{air}}/\text{s}$ to at least $6.79 \mu\text{Gy}_{\text{air}}/\text{s}$. When SNR is 3, we can get the detection limit of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ is $700.5 \text{ nGy}_{\text{air}}/\text{s}$ from the linear fitting curve, which is about eight times lower than the requirement of X-ray diagnosis ($5.5 \mu\text{Gy}_{\text{air}}/\text{s}$). The inset of Figure 5c shows the photograph of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ under neutral light and X-rays irradiation. Upon the irradiation of X-rays, the sample emits clear yellow-green light in the dark.

At last, in terms of the stability, we immersed $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$, CsPbBr_3 and Rb_2CuBr_3 separately into three bottles with water. $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ could hardly dissolve into water and we can still observe the photoluminescence and radioluminescence of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ after several hours. In sharp contrast, CsPbBr_3 and Rb_2CuBr_3 completely dissolved and no RL could be observed in seconds (Figure S4).

Moreover, we also record the radiation stability of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ (Figure 5d). The scintillator powders were unencapsulated and directly exposed to ^{60}Co radiation source ($^{60}\text{Co} \rightarrow ^{60}\text{Ni} + \text{beta rays} (0.317 \text{ MeV}) + \text{gamma rays} (1.17, 1.33 \text{ MeV})$). In order to accurately compare the scintillation response before and after

radiation, we separated the pristine scintillator powder into two parts, one was for radiation and the other one served as the control. After radiation for 480,000 Gy, the two samples were weighted equivalently and pressed into pellets with exactly the same size. It should be noted that the adopted total radiation dose is large enough, 10^7 times higher than the dose for computed tomography (10 mGy for each inspection). Then the scintillation response of these pellets was measured. The control samples (six pellets for statistics) exhibited an average response of $98.6 \pm 6.2 \text{ mV}$, and the samples after radiation exhibited almost unchanged response of $95.6 \pm 3.0 \text{ mV}$. Such good stability benefits from the all-inorganic composition and no hygroscopicity of $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$.

3 Conclusions

In summary, this work establishes the tailoring of electron and hole dimensionality as an effective strategy to enhance photoluminescence and radioluminescence. The equivalent substitution of Sn^{4+} by Te^{4+} ions can break the in-phase bonding interaction between neighboring octahedra in Rb_2SnCl_6 , and induce the formation of self-trapped excitons via strong electron-phonon coupling effect. As a result, $\text{Rb}_2\text{Sn}_{0.95}\text{Te}_{0.05}\text{Cl}_6$ exhibited wide emission spectra (peak at $\sim 580 \text{ nm}$), high photoluminescence quantum yield of 92.4%, and photoluminescence lifetime of $1.16 \mu\text{s}$. The scintillation response is 39% of commercial $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ scintillators ($66,500 \text{ photons MeV}^{-1}$) and the detection limit is $0.7 \mu\text{Gy}_{\text{air}} \text{ s}^{-1}$. More importantly, the excellent stability toward water and large dose radiations render this material with great promise in the field of X-ray imaging panels and radiosensitizers for *in vivo* radiodynamic therapy.

Acknowledgment: The authors thank the Analytical and Testing Center of HUST and the facility support of the Center for Nanoscale Characterization and Devices, WNLO.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work was financially supported by National Key R&D Program of China (2016YFB0700702, 2018YFA0703200), National Natural Science Foundation of China (51761145048, 51702107, 61905082, 61725401, 51902113), China Post-doctoral Science Foundation (2018M632843) and the Innovation Fund of WNLO.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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Supplementary Material: The online version of this article offers supplementary material (<https://doi.org/10.1515/nanoph-2020-0624>).