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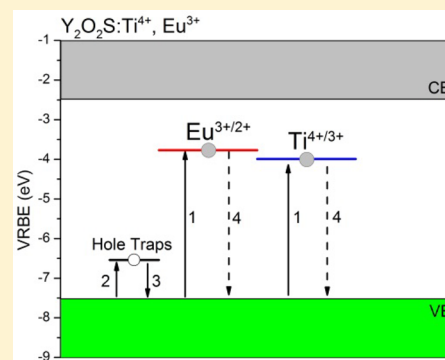
Charge Carrier Trapping Processes in $\text{RE}_2\text{O}_2\text{S}$ (RE = La, Gd, Y, and Lu)

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S Supporting Information

ABSTRACT: Two different charge carrier trapping processes have been investigated in $\text{RE}_2\text{O}_2\text{S}:\text{Ln}^{3+}$ (RE = La, Gd, Y, and Lu; Ln = Ce, Pr, and Tb) and $\text{RE}_2\text{O}_2\text{S}:\text{M}$ (M = Ti^{4+} and Eu^{3+}). Cerium, praseodymium and terbium act as recombination centers and hole trapping centers while host intrinsic defects provide the electron trap. The captured electrons released from the intrinsic defects recombine at Ce^{4+} , Pr^{4+} , or Tb^{4+} via the conduction band. On the other hand, Ti^{4+} and Eu^{3+} act as recombination centers and electron trapping centers while host intrinsic defects act as hole trapping centers. For these codopants we find evidence that recombination is by means of hole release instead of electron release. The released holes recombine with the trapped electrons on Ti^{3+} or Eu^{2+} and yield broad Ti^{4+} yellow-red charge transfer (CT) emission or characteristic Eu^{3+} 4f–4f emission. We will conclude that the afterglow in $\text{Y}_2\text{O}_2\text{S}:\text{Ti}^{4+}$, Eu^{3+} is due to hole release instead of more common electron release.



1. INTRODUCTION

Charge carrier trapping and detrapping processes are of great interest in the luminescence research field both for an application and for a theoretical point of view.¹ Afterglow phosphors require that the captured electrons or holes are spontaneously released at room temperature to recombine at the luminescence center. Neither a too shallow nor a too deep trap will produce room temperature afterglow.^{2,3} For storage materials used in X-ray imaging, deeper traps are needed to prevent thermal fading at room temperature.⁴

The lanthanide dopant can either act as an electron or as a hole trapping center. Such electron trapping was reported as early as in the 1960s by McClure et al., who found that trivalent lanthanides in CaF_2 can be reduced to divalent under γ -irradiation.⁵ In 2005, Dorenbos proposed that when the divalent lanthanide 4fⁿ ground state levels are below the conduction band (CB) the corresponding trivalent ions may act as electron trapping centers and as a function of type of lanthanide codopant there is a predictable variation in trap depth.⁶ Later, this hypothesis was experimentally confirmed by thermoluminescence (TL) studies of $\text{YPO}_4:\text{Ce}^{3+}$, Ln^{3+} (Ln = Pr, Nd, Sm, Dy, Ho, Er, Tm, and Yb) by Bos et al.⁷ Here, Ce^{3+} acts as the hole trapping center as well as the recombination (luminescence) center while the selected lanthanide codopants are the electron trapping centers. During the TL readout, the trapped electrons are released and move freely in the CB to eventually recombine at Ce^{4+} . Different lanthanide codopants have different TL glow peak maxima indicating different trap depth. The same phenomenon has been reported later in $\text{Sr}_3\text{Al}_2\text{Si}_{1-x}\text{O}_5:\text{Ce}^{3+}$, Ln^{3+} (Ln = Er, Nd, Sm, Dy, and Tm),⁸ $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ln}^{3+}$, RE^{3+} (Ln = Ce^{3+} , Pr^{3+} and Tb^{3+} ; RE = Eu^{3+} and Yb^{3+})⁹ and $\text{GdAlO}_3:\text{Ce}^{3+}$, Ln^{3+} (Ln = Pr, Er, Nd, Ho, Dy, and Tm).¹⁰

When the trivalent lanthanide 4fⁿ ground state levels are close above the VB, these ions may act as hole trapping centers. The captured holes can be released to recombine with a luminescence center via the VB or as a migrating V_k center. Compared to the many reports on electron trapping and detrapping processes, there are much less reports that discuss hole trapping and detrapping processes. One of the few is by Chakrabarti et al. in the 1980s who found that during UV irradiation of $\text{MgS}:\text{Ce}^{3+}$, Sm^{3+} the holes are captured by cerium and electrons by samarium. After hole release, they recombine with samarium producing Sm^{3+} characteristic emission during the TL readout.¹¹ The other example is from our own studies on $\text{Gd}_{1-x}\text{La}_x\text{AlO}_3:\text{Eu}^{3+},\text{Tb}^{3+}$ where Tb^{3+} acts as the hole trapping center and Eu^{3+} as the electron trapping center. The captured holes release from Tb^{4+} earlier than electrons from Eu^{2+} and recombine with Eu^{2+} producing Eu^{3+} characteristic 4f–4f emission. Another example of hole detrapping is given by Bos et al. in $\text{YPO}_4:\text{Tb}^{3+}$, RE^{3+} (RE³⁺ = Nd, Ho, and Dy) where again Tb^{3+} is acting as a hole trapping center and RE^{3+} as electron trapping center.⁷

Eu^{2+} and Ce^{3+} are the most widely used recombination (luminescence) centers in afterglow materials. For instance, $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$,¹² $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$,¹³ $\text{CaS}:\text{Eu}^{2+},\text{Dy}^{3+}$,¹⁴ $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+},\text{Tm}^{3+}$ ¹⁵ and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+},\text{Cr}^{3+}$.¹⁶ The 5d excited levels of divalent europium or trivalent cerium are located very close to the CB in those compounds, and therefore excited electrons are easily released into the CB and subsequently caught by a trivalent lanthanide or Cr^{3+} cation.¹ The trapped electrons are released slowly and recombine with

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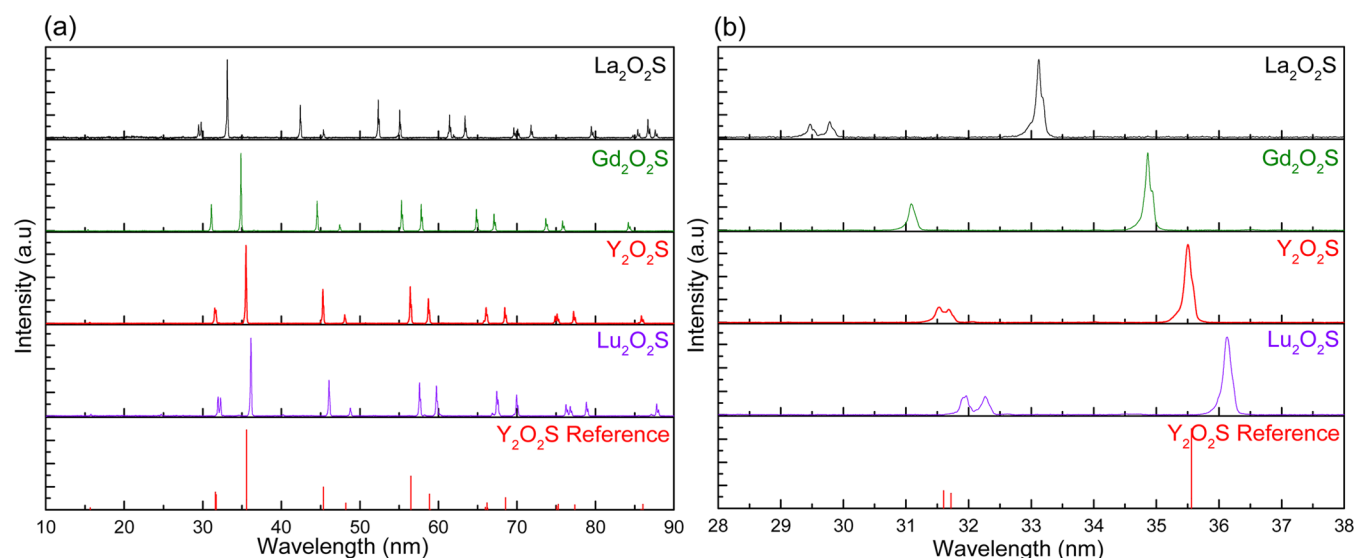


Figure 1. (a) XRD patterns of the as-prepared samples of $\text{La}_2\text{O}_2\text{S}$, $\text{Gd}_2\text{O}_2\text{S}$, $\text{Y}_2\text{O}_2\text{S}$, and $\text{Lu}_2\text{O}_2\text{S}$. (b) Detailed XRD patterns in the range from 28 to 38° .

the europium or cerium recombination center to generate Eu^{2+} or Ce^{3+} emission. In these cases, the afterglow mechanism is due to the electron trapping and electron release.

In 2003, Kang et al. reported on the afterglow material of $\text{Y}_2\text{O}_2\text{S}:\text{Mg}^{2+}, \text{Ti}^{4+}$ that shows a unique orange broad band persistent luminescence centered at ~ 595 nm after 380 nm UV excitation.¹⁷ After that, dozens of reports were published to modify or improve this material. For instance, $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}, \text{Mg}^{2+}, \text{Ti}^{4+}$ ¹⁸ and $\text{Gd}_2\text{O}_2\text{S}:\text{Eu}^{3+}, \text{Mg}^{2+}, \text{Ti}^{4+}$ ¹⁹ were synthesized and show afterglow emission both from Eu^{3+} and Ti^{4+} .

Different to Eu^{2+} and Ce^{3+} , Eu^{3+} can only act as an electron acceptor. The same applies to Ti^{4+} with the $3d^0$ electron configuration. If neither Eu^{3+} nor Ti^{4+} can be an electron donor then what is the electron donor in phosphors like $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}, \text{Mg}^{2+}, \text{Ti}^{4+}$ and $\text{Gd}_2\text{O}_2\text{S}:\text{Eu}^{3+}, \text{Mg}^{2+}, \text{Ti}^{4+}$? Where and how are the electrons captured? How are these electrons released and why is the afterglow from Ti^{4+} and Eu^{3+} ?

Several studies were carried out to analysis the afterglow mechanism of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}, \text{Mg}^{2+}, \text{Ti}^{4+}$. Hölsä et al. found that the afterglow emission is from Eu^{3+} and Ti^{3+} but did not explain the afterglow mechanism.²⁰ Zhou et al. observed that the afterglow is from Eu^{3+} and Ti^{4+} , and the traps that contribute to the afterglow are complex Ti related traps.¹⁸ Lei et al. studied the thermoluminescence of $\text{Gd}_2\text{O}_2\text{S}:\text{RE}^{3+}, \text{Ti}, \text{Mg}$ (RE = Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, and Yb).²¹ Lei et al. proposed that UV-light exposure causes an electronic transition from the ground state of the RE^{3+} to the excited state, and simultaneously electrons and holes are created in the host. Then the captured electrons return back to the excited states of RE^{3+} at room temperature resulting in characteristic f–f persistent afterglow emission. Since the $4f^n$ states of the lanthanide ions are localized impurity states, after excitation of RE^{3+} to the excited state one may not interpret that the $4f$ state leaves a hole in the host lattice that can be filled by another electron.²² Therefore, the transition suggested by Lei et al. is highly unlikely.

The objective of this study is to reveal the trapping and detrapping processes of electrons and holes in $\text{RE}_2\text{O}_2\text{S}:\text{M}$ (RE = La, Gd, Y and Lu; M = Ce^{3+} , Pr^{3+} , Tb^{3+} , Eu^{3+} , and Ti^{4+})

materials. Photoluminescence emission (PL) and excitation (PLE) spectra of Eu^{3+} or Ti^{4+} single-doped samples have been measured to construct the vacuum referred binding energy (VRBE) diagrams showing the lanthanide and titanium levels within the band gap. Thermoluminescence emission (TLEM) and thermoluminescence (TL) measurements were performed to identify the recombination centers and to derive the trap depths. Thermoluminescence excitation (TLE) spectra were measured to analyze the charging process of Eu^{3+} or Ti^{4+} single-doped samples. Finally, to show how the obtained knowledge can be applied, the results are used to propose the persistent luminescence mechanism of $\text{Y}_2\text{O}_2\text{S}:\text{Ti}^{4+}, \text{Eu}^{3+}$.

2. EXPERIMENTAL SECTION

All starting materials were purchased from Sigma-Aldrich and used without further treatment. The materials were synthesized by mixing of 5 N (99.999%) purity rare earth oxides, S (99.5%), TiO_2 (99.99%) and Na_2CO_3 (99.99%) and fired from 1150 to 1250 $^\circ\text{C}$ during 4–8 h one or two times in a corundum crucible in CO atmosphere. The obtained compounds were washed by deionized water a couple of times to remove the Na_2CO_3 flux. The content of Na_2CO_3 is 7% by weight.

All powders were checked with a PANalytical XPert PRO X-ray diffraction system with a $\text{Co K}\alpha$ ($\lambda = 0.178901$ nm) X-ray tube (45 kV, 40 mA). The PL spectra of Ti-doped samples were measured by a UV to VIS spectrometer (Ocean Optics, QE65000) with a UV LED (365 nm, 780 mW) excitation. The PLE spectra of Ti-doped samples and the PLE and PL spectra for all the Eu^{3+} -doped samples were measured with a setup that consists of an UV/vis branch with a 500W Hamamatsu CW Xe lamp and Gemini 180 monochromator. The PerkinElmer MP-1913 photomultiplier was exploited as a detector connected at the exit slit of a Princeton Acton SP2300 monochromator.

Low-temperature TL measurements (90–450 K) were recorded with a sample chamber operating under vacuum ($P = 10^{-7}$ mbar), a $^{90}\text{Sr}/^{90}\text{Y}$ β irradiation source having a dose rate of ~ 0.4 mGy s^{-1} and a PerkinElmer channel PM tube (MP-1393). Liquid nitrogen was used as a cooling medium. A 600 nm bandpass filter (600FS40–50, Andover Corporation) was placed between the sample and the PMT during the

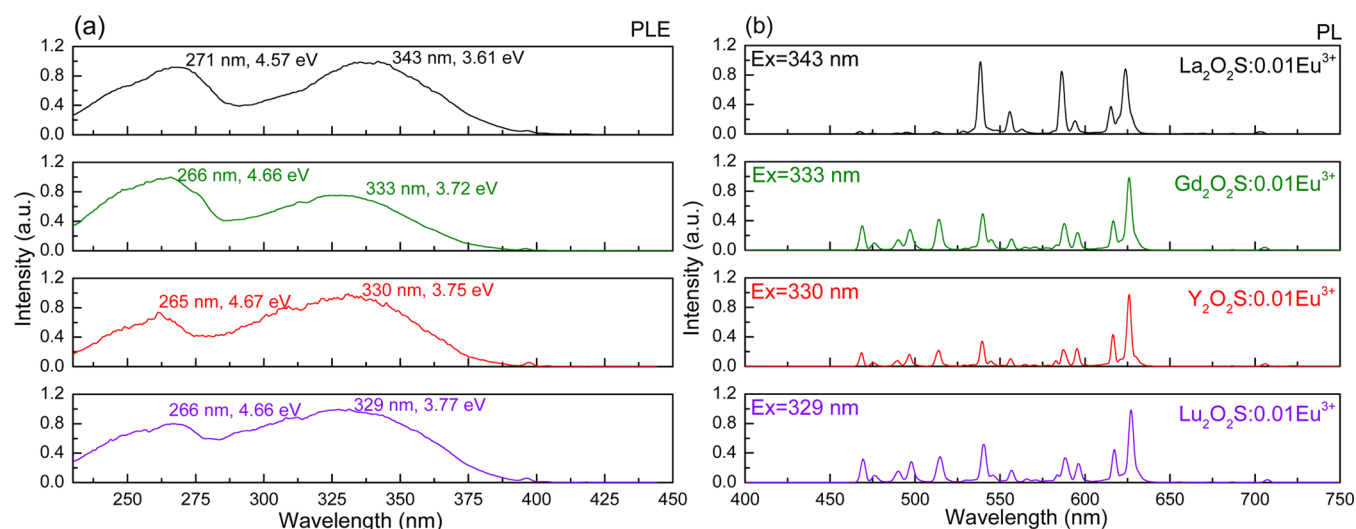


Figure 2. Room temperature PLE (a) and PL spectra (b) of $\text{La}_2\text{O}_2\text{S}:0.01\text{Eu}^{3+}$, $\text{Gd}_2\text{O}_2\text{S}:0.01\text{Eu}^{3+}$, $\text{Y}_2\text{O}_2\text{S}:0.01\text{Eu}^{3+}$, and $\text{Lu}_2\text{O}_2\text{S}:0.01\text{Eu}^{3+}$. The excitation spectra were recorded at 627 nm emission. The emission spectra were excited at the charge transfer peak maxima, which are labeled in the legend of part b. The numbers in part a show the host exciton excitation maxima (left) and the charge transfer maxima (right).

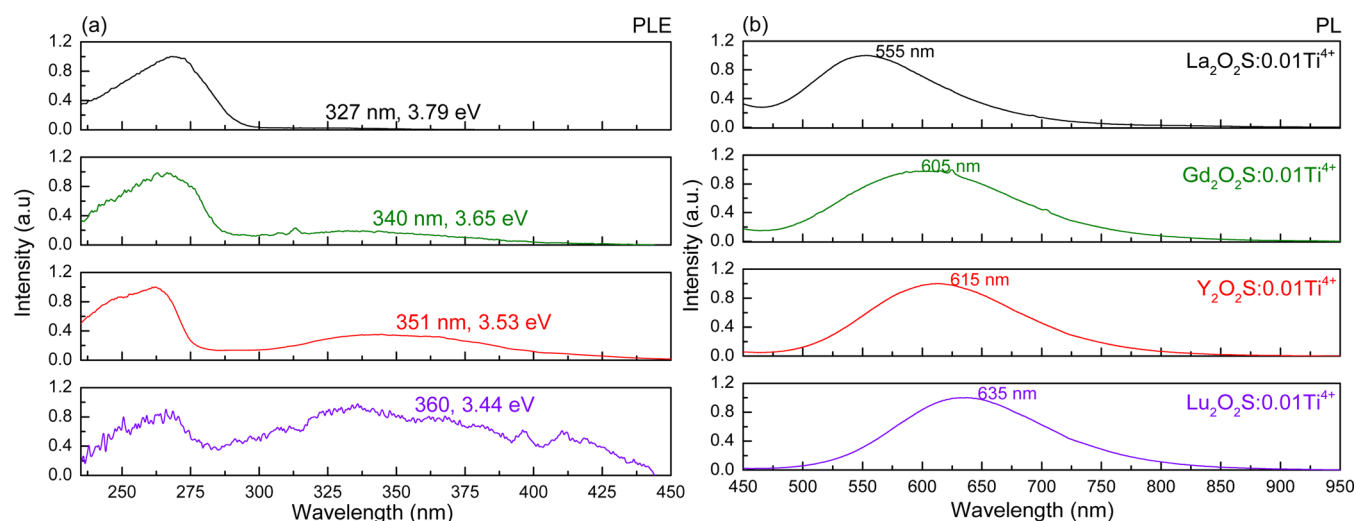


Figure 3. Room temperature PLE (a) and PL spectra (b) of $\text{La}_2\text{O}_2\text{S}:0.01\text{Ti}^{4+}$, $\text{Gd}_2\text{O}_2\text{S}:0.01\text{Ti}^{4+}$, $\text{Y}_2\text{O}_2\text{S}:0.01\text{Ti}^{4+}$ and $\text{Lu}_2\text{O}_2\text{S}:0.01\text{Ti}^{4+}$. The excitation spectra were measured at the emission maxima. The CT maxima are shown in the legend of part a. The emission spectra were recorded by a calibrated CCD spectrometer (Ocean Optics, QE65000) under the 365 nm UV-LED excitation.

measurements of Ce^{3+} , Pr^{3+} , Eu^{3+} , and Ti^{4+} singly doped samples to transmit the red emission from the above dopants. For the Tb^{3+} -doped samples, a 550 nm bandpass filter (550FS40–50, Andover Corporation) was placed between the sample and the PMT. TLEM spectra were measured using an UV to VIS spectrometer (Ocean Optics, QE65000) with a HR composite grating (300 lines/mm) and an entrance aperture of 100 μm resulting in a 3.3 nm (fwhm) wavelength resolution. Samples were irradiated with a ^{60}Co gamma source to an absorbed dose of ~ 1.6 kGy.²³

The TL excitation spectra (TLE) were measured by first illuminating the samples during 600 s with monochromatic photons from a 150 W xenon arc lamp (Hamamatsu L2273) filtered by a 1/8 monochromator (Oriel Cornerstone 130) with wavelength resolution of 0.8 nm/0.1 mm slit width. The slit width was selected as 1 mm and the wavelength step was fixed as 10 nm. Next, the system is programmed by LabVIEW to record all the TL glow curves from room temperature to 350 $^{\circ}\text{C}$ for excitation wavelengths between 200 and 450 nm. The

plot of the integrated TL glow peaks versus the excitation wavelength is called a TL excitation spectrum.²⁴ The TL spectra were all recorded by a RISØ TL/OSL reader model DA-15 and a controller model DA-20. The same 600 nm bandpass filter (600FS40–50) was placed between the sample and PMT.

3. RESULTS

3.1. X-ray Diffraction Spectra and Photoluminescence Spectroscopy. The X-ray diffraction (XRD) patterns of as-prepared $\text{RE}_2\text{O}_2\text{S}$ materials are shown in Figure 1. All samples are of single phase and match with the $\text{Y}_2\text{O}_2\text{S}$ reference card (No. 382242) due to the same crystal structure (space group: $P3\bar{m}1$). A slight shift of the XRD patterns can be observed in Figure 1b due to different lattice parameters.

Figure 2 displays the PLE (a) and PL (b) spectra of Eu^{3+} single-doped $\text{RE}_2\text{O}_2\text{S}$. All the samples have the characteristic Eu^{3+} 4f–4f emission. The host exciton creation energy

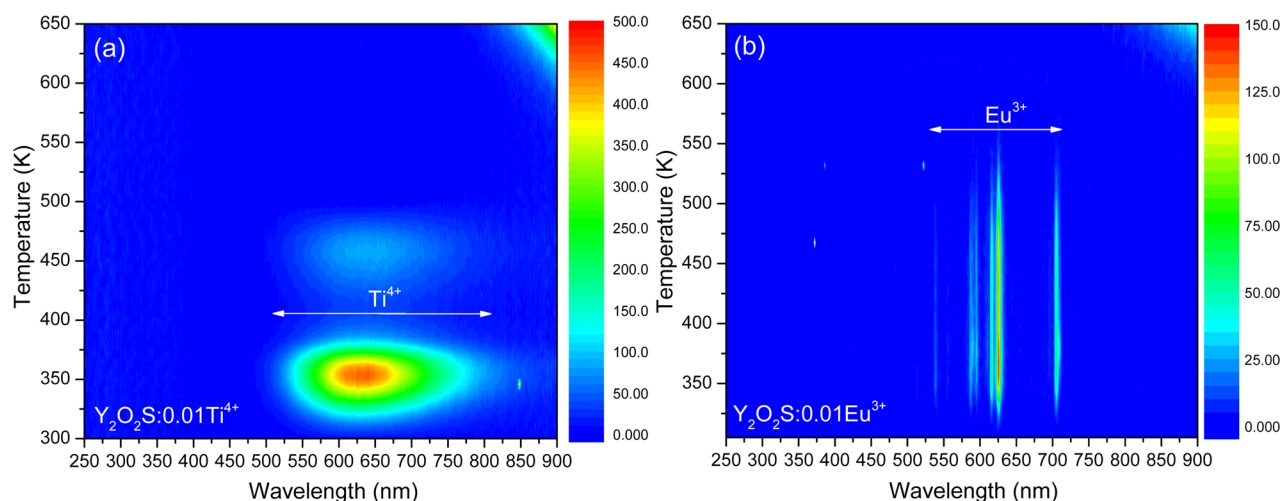


Figure 4. Thermoluminescence emission (TLEM) spectra of (a) $\text{Y}_2\text{O}_2\text{S}:0.01\text{Ti}^{4+}$ and (b) $\text{Y}_2\text{O}_2\text{S}:0.01\text{Eu}^{3+}$. The heating rate is 1 K/s after and each sample has been exposed to an irradiation dose of 1.6 kGy from a ^{60}Co source.

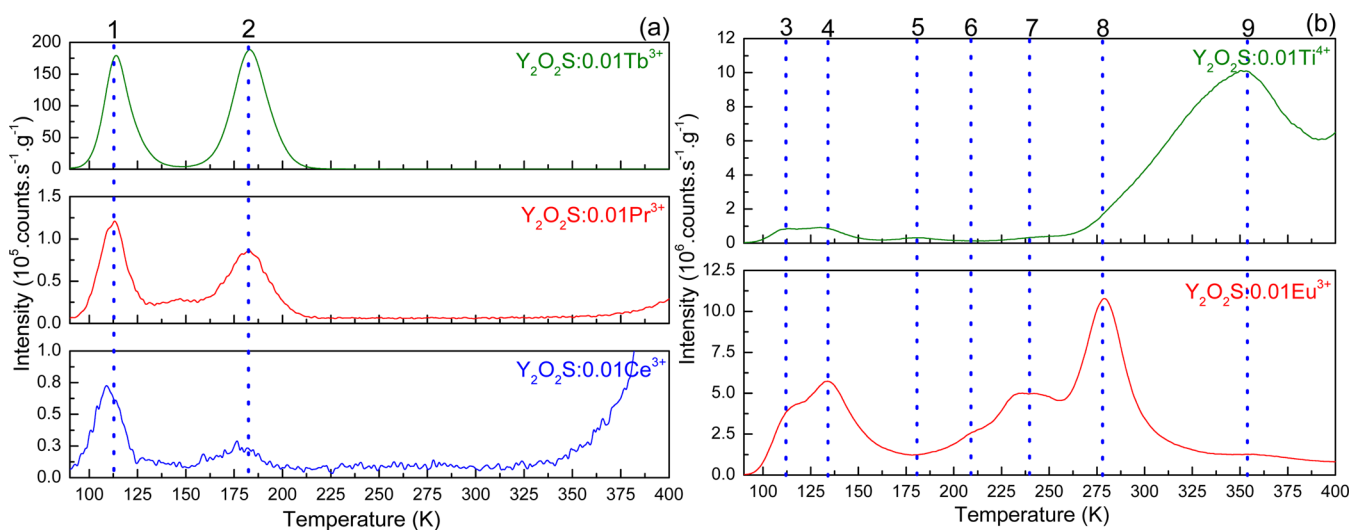


Figure 5. Low temperature thermoluminescence glow curves of (a) $\text{Y}_2\text{O}_2\text{S}:0.01\text{Tb}^{3+}$, $\text{Y}_2\text{O}_2\text{S}:0.01\text{Pr}^{3+}$, and $\text{Y}_2\text{O}_2\text{S}:0.01\text{Ce}^{3+}$ and (b) $\text{Y}_2\text{O}_2\text{S}:0.01\text{Ti}^{4+}$ and $\text{Y}_2\text{O}_2\text{S}:0.01\text{Eu}^{3+}$. The heating rate was 1 K/s for all TL-recordings. The peak intensities are normalized by the mass of the sample.

increases from 4.57 eV (271 nm) for $\text{La}_2\text{O}_2\text{S}$ to 4.66 eV (266 nm) for $\text{Lu}_2\text{O}_2\text{S}$. Those exciton energies are similar to that in previous reports, i.e., 4.60 eV for $\text{La}_2\text{O}_2\text{S}$ ²⁵ and 4.71 eV for $\text{Lu}_2\text{O}_2\text{S}$.²⁶ The broad excitation band near 320–400 nm originates from electron transfer from the valence band (VB) to Eu^{3+} , also called the charge transfer (CT) band. It increases from 3.61 eV (343 nm) for $\text{La}_2\text{O}_2\text{S}$ to 3.77 eV (329 nm) for $\text{Lu}_2\text{O}_2\text{S}$ and shows the same tendency as the host exciton creation energy. The CT bands of Eu^{3+} in $\text{RE}_2\text{O}_2\text{S}$ have fwhm (full width at half-maximum) around 0.8 eV which is quite typical for Eu^{3+} CT bands.^{27,28}

Figure 3 illustrates the PLE (a) and PL (b) spectra of Ti^{4+} single-doped $\text{RE}_2\text{O}_2\text{S}$. All samples show a broad band emission with fwhm around 0.5 eV. The broad emission bands originate from the Ti^{4+} charge transfer emission. The Ti^{4+} emission red shifts from 555 nm for $\text{La}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ to 635 nm for $\text{Lu}_2\text{O}_2\text{S}:\text{Ti}^{4+}$. Here a calibrated CCD spectrometer was used to measure the emission spectra since the PerkinElmer MP-1913 photomultiplier we used is not sensitivity to the red light. A comparison of $\text{Y}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ emission spectra measured by the

PerkinElmer MP-1913 PMT and the CCD are shown in Figure S1 in the Supporting Information.

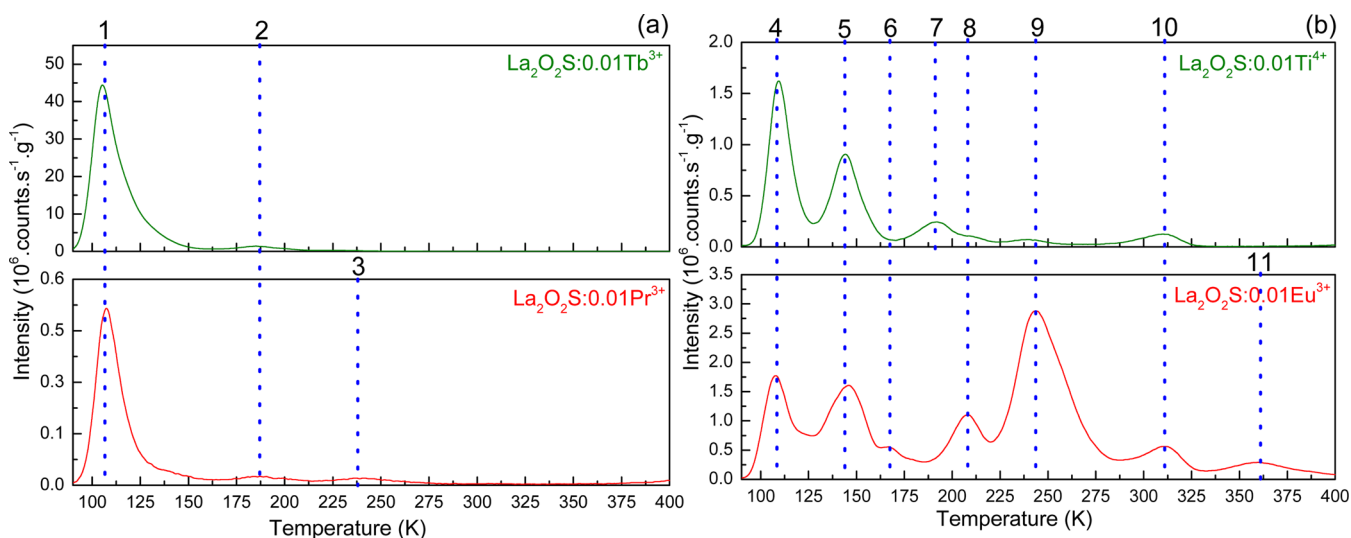
The excitation spectra of Ti^{4+} are shown in the Figure 3a. Similar to that for Eu^{3+} , the broad band near 265 nm is the host exciton creation band and the one near 320–380 nm is the VB $\rightarrow \text{Ti}^{4+}$ charge transfer. The relative intensity of the Ti^{4+} CT excitation band (the ratio of Ti^{4+} CT intensity to the host exciton intensity) increases from $\text{La}_2\text{O}_2\text{S}$ to $\text{Lu}_2\text{O}_2\text{S}$. The Ti^{4+} CT excitation band of $\text{La}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ is weak at room temperature. Therefore, the low-temperature (10 K) photoluminescence excitation spectrum of $\text{La}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ was measured and shown in Figure S2.

Figure S2 shows that at 10 K Ti^{4+} CT excitation band locates at ~ 327 nm (3.79 eV). Figure S3 shows that the temperature $T_{0.5}$ where Ti^{4+} emission intensity is quenched by 50% is at ~ 165 K. The activation energy for thermal quenching can be derived from²⁹

$$I(T) = \frac{I(0)}{1 + C \exp\left(-\frac{E}{kT}\right)} \quad (1)$$

Table 1. Peak Number, Frequency Factor s (s^{-1}), Peak Maxima T_m (K), and Trap Depth E (eV) of the TL Glow Peaks Recorded at $\beta = 1$ K/s from $\text{RE}_2\text{O}_2\text{S}$ (RE = La, Gd, Y, and Lu)

		1	2	3	4	5	6	7	8	9	10	11
$\text{La}_2\text{O}_2\text{S}$	s						1.1×10^{13}					
	T_m	105	185	240	110	145	165	190	208	245	312	360
	E	0.28	0.51	0.66	0.30	0.39	0.45	0.52	0.57	0.68	0.87	1.0
$\text{Gd}_2\text{O}_2\text{S}$	s						1.3×10^{13}					
	T_m	115	115	130	180	203	220	250	288	335	370	
	E	0.31	0.31	0.35	0.50	0.56	0.61	0.70	0.80	0.94	1.0	
$\text{Y}_2\text{O}_2\text{S}$	s						1.3×10^{13}					
	T_m	115	182	113	134	181	210	240	278	350		
	E	0.31	0.50	0.31	0.37	0.50	0.58	0.67	0.78	0.98		
$\text{Lu}_2\text{O}_2\text{S}$	s						1.4×10^{13}					
	T_m	108	170	267	105	160	200	223	320			
	E	0.29	0.47	0.75	0.29	0.44	0.61	0.62	0.90			

**Figure 6.** Low-temperature thermoluminescence glow curves of (a) $\text{La}_2\text{O}_2\text{S}:0.01\text{Tb}^{3+}$ and $\text{La}_2\text{O}_2\text{S}:0.01\text{Pr}^{3+}$ and (b) $\text{La}_2\text{O}_2\text{S}:0.01\text{Ti}^{4+}$ and $\text{La}_2\text{O}_2\text{S}:0.01\text{Eu}^{3+}$. The heating rate was 1 K/s for all TL-recordings. The peak intensities are normalized by the mass of the sample.

where $I(T)$ and $I(0)$ is the luminescence intensity at temperature T and 0 and E indicates the activation energy. A fit through the data in Figure S3, as indicated by the solid curve provides the activation energy $E = 0.05$ eV.

Figure 3a shows that the Ti^{4+} CT excitation bands shift to longer wavelength from $\text{La}_2\text{O}_2\text{S}$ (3.79 eV) to $\text{Lu}_2\text{O}_2\text{S}$ (3.44 eV). Here we take the CT excitation band maxima as the Ti^{4+} CT energy and the numbers are displayed on the figure legend (Figure 3a). For $\text{Lu}_2\text{O}_2\text{S}:\text{Ti}^{4+}$, we use the centroid of the band near 360 nm (3.44 eV) as the Ti^{4+} CT energy.

3.2. Thermoluminescence Emission Spectra. Thermoluminescence emission (TLEM) spectra were measured for $\text{RE}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ and $\text{RE}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ in order to identify the luminescence and recombination center during the TL readout. Figure 4 shows two typical TLEM spectra of $\text{Y}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ and $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$. Similar figures for RE = La, Gd and Lu can be found in Figure S4.

Two broad TL glow curves centered at ~ 350 and ~ 455 K can be observed for $\text{Y}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ (Figure 4a). The TL emission spectra centered at ~ 615 nm matches with the photoluminescence emission spectra shown in Figure 3b, indicating that Ti acts as the recombination center leading to Ti^{4+} charge transfer emission. The Ti^{4+} TL emission can also be observed in the $\text{Gd}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ (Figure S4a) and $\text{Lu}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ (Figure S4b) although the later one shows much weaker Ti^{4+} TL intensity

than the others. No Ti^{4+} TL emission was observed in $\text{La}_2\text{O}_2\text{S}:\text{Ti}^{4+}$, which is attributed to the almost complete thermal quenching of Ti^{4+} emission above room temperature (Figure S3). Characteristic red Eu^{3+} TL emission can be observed for $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ (Figure 4b), $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ (Figure S4c), $\text{Gd}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ (Figure S4d) and $\text{Lu}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ (Figure S4e). The observation of Eu^{3+} TL emission evidence that, like Ti^{4+} , Eu^{3+} acts as the recombination center.

3.3. Low-Temperature Thermoluminescence. Figure 5 displays the low-temperature TL glow curves of $\text{Y}_2\text{O}_2\text{S}$ single-doped with Tb^{3+} , Pr^{3+} , Ce^{3+} , Eu^{3+} , or Ti^{4+} .

Tb^{3+} , Pr^{3+} and Ce^{3+} single-doped $\text{Y}_2\text{O}_2\text{S}$ (Figure 5a) have the same glow peaks (herein referred to peaks 1 and 2) at ~ 115 K and ~ 182 K with different relative intensity. This implies that charge carriers are not released from Ce, Pr or Tb but from other trapping centers. The TL intensity of Ce^{3+} is around 3 orders of magnitude lower than that of Tb^{3+} which is due to the significant thermal quenching of Ce^{3+} emission at this temperature. Figure S5 shows that the temperature $T_{0.5}$ where Ce^{3+} emission intensity is quenched by 50% is at ~ 63 K. An Arrhenius fit of the quenching curve provides a 30 meV quenching energy barrier. The rising glow above 350 K in the $\text{Y}_2\text{O}_2\text{S}:\text{Pr}^{3+}$ and $\text{Y}_2\text{O}_2\text{S}:\text{Ce}^{3+}$ TL glow curves are due to blackbody radiation. No TL glow peaks are observed above 225 K in Figure 5a.

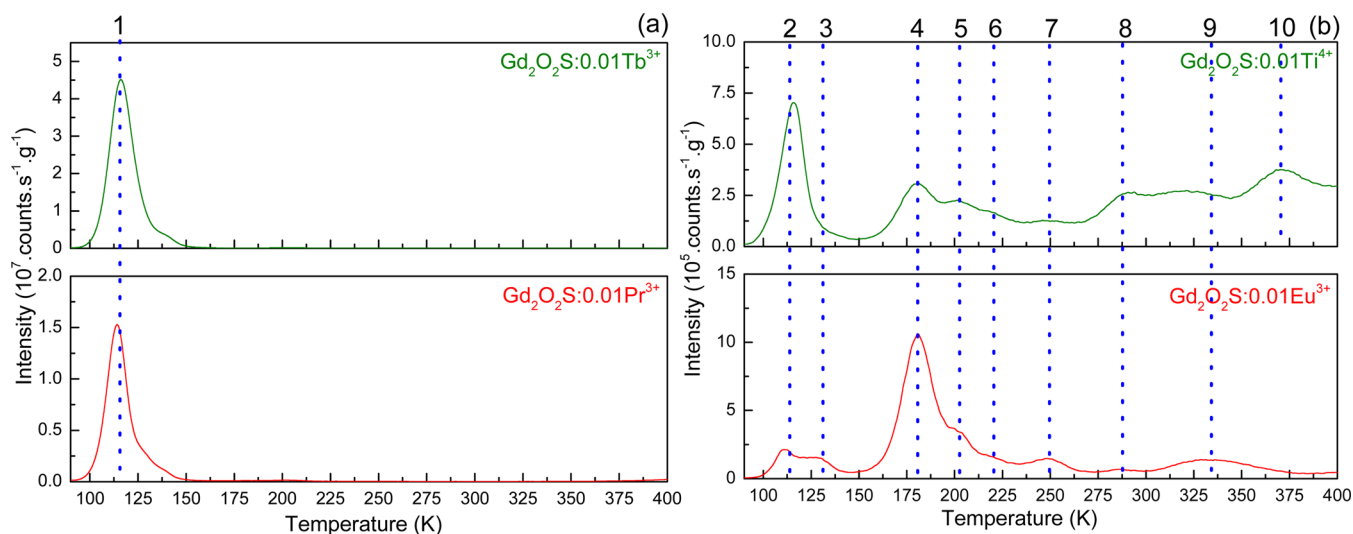


Figure 7. Low-temperature thermoluminescence glow curves of (a) $\text{Gd}_2\text{O}_2\text{S}:0.01\text{Tb}^{3+}$ and $\text{Gd}_2\text{O}_2\text{S}:0.01\text{Pr}^{3+}$, (b) $\text{Gd}_2\text{O}_2\text{S}:0.01\text{Ti}^{4+}$ and $\text{Gd}_2\text{O}_2\text{S}:0.01\text{Eu}^{3+}$. The heating rate was 1 K/s for all TL-recordings. The peak intensities are normalized by the mass of the sample.

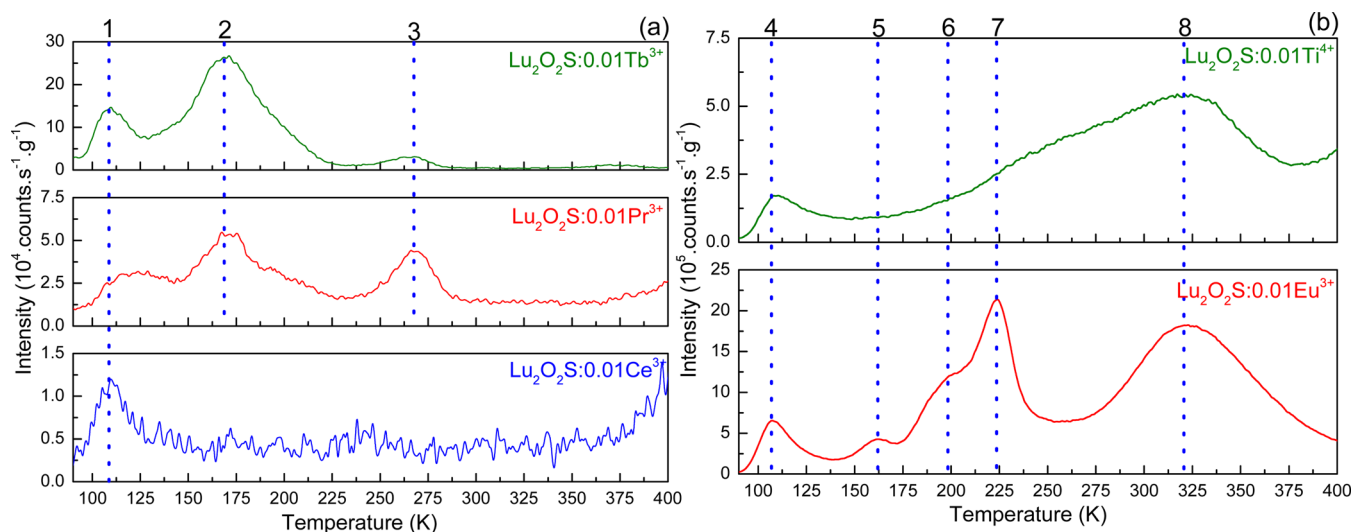


Figure 8. Low-temperature thermoluminescence glow curves of (a) $\text{Lu}_2\text{O}_2\text{S}:0.01\text{Tb}^{3+}$, $\text{Lu}_2\text{O}_2\text{S}:0.01\text{Pr}^{3+}$ and $\text{Lu}_2\text{O}_2\text{S}:0.01\text{Ce}^{3+}$ (b) $\text{Lu}_2\text{O}_2\text{S}:0.01\text{Ti}^{4+}$ and $\text{Lu}_2\text{O}_2\text{S}:0.01\text{Eu}^{3+}$. The heating rate was 1 K/s for all TL-recordings. The peak intensities are normalized by the mass of the sample.

Figure 5b displays the TL glow curves for Ti^{4+} and Eu^{3+} single-doped $\text{Y}_2\text{O}_2\text{S}$. Between 90 and 260 K both samples share the same TL glow peaks (numbered 3, 4, 5, 6, 7 and 8) indicating that charge carriers are released from the same type of trapping centers not related to Eu or Ti. One observes a very broad TL glow starting from ~ 260 K and maximum at ~ 350 K in the Ti^{4+} -doped sample which matches with that in the TLEM spectra (Figure 4a), and it contributes to the Ti^{4+} CT-luminescence afterglow. The Eu^{3+} -doped sample shows like in Figure 4b the same glow at ~ 350 K that contributes to the afterglow although it is 1 order of magnitude less intense than that of the Ti^{4+} -doped sample.

The trap depth E corresponding with the TL glow peaks numbered in Figure 5 was roughly estimated using the temperature T_m at the maximum of the glow and employing the first order kinetics equation

$$\frac{\beta E}{kT_m^2} = s \exp\left(-\frac{E}{kT_m}\right) \quad (2)$$

where $\beta = 1 \text{ K s}^{-1}$ is the heating rate, k is the Boltzmann constant ($8.62 \times 10^{-5} \text{ eV/K}$), and s is the frequency factor (s^{-1}).³⁰ The frequency factor s , which is related to the host lattice vibrational mode, is estimated using the 444 cm^{-1} ($1.3 \times 10^{13} \text{ s}^{-1}$)³¹ R3 line from $\text{Y}_2\text{O}_2\text{S}$ Raman spectroscopy and assumed to be the same for all the $\text{Y}_2\text{O}_2\text{S}$ samples with different dopants. The TL parameters (frequency factor s , peak position T_m and trap depth E) are listed in Table 1.

Figure 6a, 7a, and 8a display the low-temperature TL for $\text{La}_2\text{O}_2\text{S}$, $\text{Gd}_2\text{O}_2\text{S}$, and $\text{Lu}_2\text{O}_2\text{S}$ with different dopants. As in Figure 5a, with Tb^{3+} and Pr^{3+} doping, TL glow peaks at the same temperature are observed. With Ce^{3+} doping, the same TL glow peak temperature as with Tb^{3+} and Pr^{3+} doping in $\text{Lu}_2\text{O}_2\text{S}$ is observed in Figure 8a. For Ce^{3+} doping in $\text{La}_2\text{O}_2\text{S}:\text{Ce}^{3+}$ and $\text{Gd}_2\text{O}_2\text{S}:\text{Ce}^{3+}$ the Ce^{3+} emission totally quenched²⁶ and no TL glow peaks were measured.

Figure 6b illustrates the low temperature TL for Ti^{4+} and Eu^{3+} single-doped $\text{La}_2\text{O}_2\text{S}$. We observe that between 90 to 400 K both samples share almost the same TL glow peaks except for peaks 7 and 11. The same TL peak position implies that

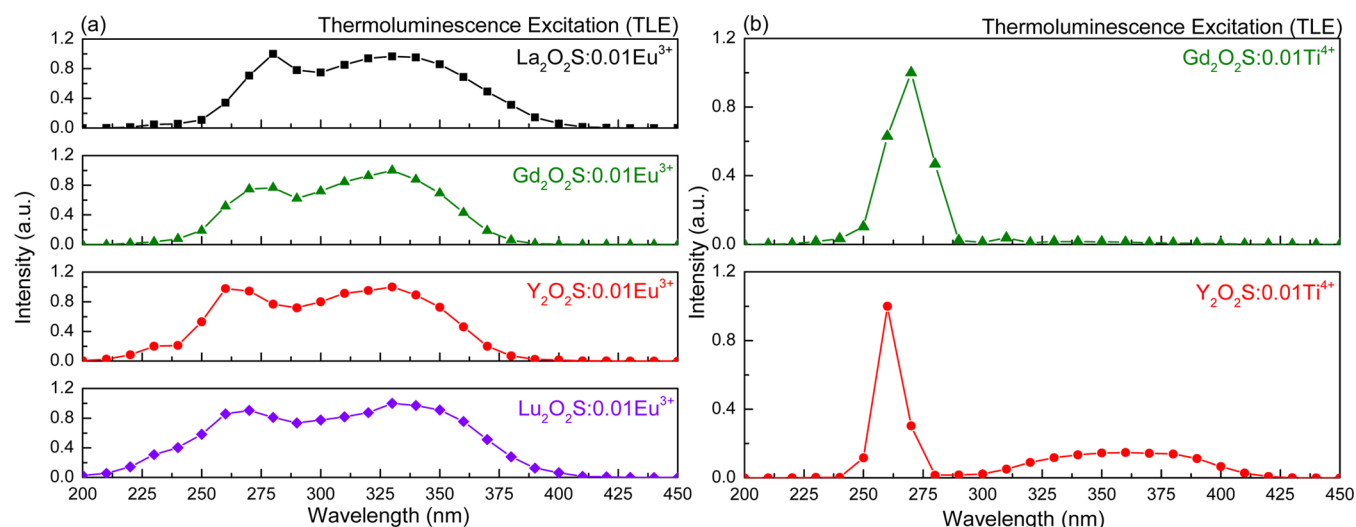


Figure 9. Thermoluminescence excitation (TLE) spectra of (a) $\text{RE}_2\text{O}_2\text{S}:0.01\text{Eu}^{3+}$, (b) $\text{Gd}_2\text{O}_2\text{S}:0.01\text{Ti}^{4+}$ and $\text{Y}_2\text{O}_2\text{S}:0.01\text{Ti}^{4+}$. The samples have been excited by an Xe lamp with wavelengths ranging from 200 to 450 nm during 600 s before TL glow curve recording. The slit width was set at 1 mm leading to a spectrum resolution of 8 nm. The thermoluminescence excitation spectra were obtained by plotting the integrated TL from 300 to 600 K as a function of the excitation wavelength. The heating rate for TL readout is 1 K/s, and the wavelength step is 10 nm. The sample was excited at room temperature.

charge carriers are released from the same type of trapping centers not related to Eu or Ti. The absence of TL glow above 325 K in $\text{La}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ is probably due to the almost complete thermal quenching of Ti^{4+} emission above room temperature (Figure S3).

Almost the same TL glow peak positions are observed for $\text{Gd}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ and $\text{Gd}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ shown in Figure 7b with peak numbers 2, 3, 4, 5, 6, 7, 8, and 9. An extra peak (peak 10) is observed at ~ 375 K for $\text{Gd}_2\text{O}_2\text{S}:\text{Ti}^{4+}$.

$\text{Lu}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ in Figure 8b shows an extremely broad Ti^{4+} TL glow curve that begins at ~ 135 K and reaches maximum glow at ~ 320 K. It appears that Ti^{4+} -doped $\text{RE}_2\text{O}_2\text{S}$ shows broader TL glow peaks than when Eu^{3+} is the dopant. This may indicate a trap depth distribution³² caused by the need for charge compensating defects.

Table 1 lists all thermoluminescence parameters. All the frequency factors s are from the R3 line of $\text{RE}_2\text{O}_2\text{S}$ Raman spectroscopy,³¹ which is 1.1×10^{13} (365 cm^{-1}) for $\text{La}_2\text{O}_2\text{S}$, 1.3×10^{13} (428 cm^{-1}) for $\text{Gd}_2\text{O}_2\text{S}$, 1.3×10^{13} (444 cm^{-1}) for $\text{Y}_2\text{O}_2\text{S}$ and 1.4×10^{13} (472 cm^{-1}) for $\text{Lu}_2\text{O}_2\text{S}$ and all the trap depths (E) were calculated by eq 2.

So far, we found that in Tb^{3+} , Pr^{3+} , and Ce^{3+} single-doped $\text{RE}_2\text{O}_2\text{S}$, the charge carriers are not released from Ce, Pr, or Tb but from other trapping centers. The same applies for Ti^{4+} and Eu^{3+} single-doped $\text{RE}_2\text{O}_2\text{S}$. Here we conclude that for Tb^{3+} , Pr^{3+} - and Ce^{3+} -doped $\text{RE}_2\text{O}_2\text{S}$ the TL glow curves are from host related electron traps while for Ti^{4+} - and Eu^{3+} -doped samples the TL bands are from host related hole trapping centers. The reasons will be discussed in detail in the Discussion.

3.4. Thermoluminescence Excitation Spectra. Figure 9a shows the thermoluminescence excitation (TLE) spectra of Eu^{3+} single-doped $\text{RE}_2\text{O}_2\text{S}$. A comparison with the Eu^{3+} excitation spectra (PLE) from Figure 2a can be seen in Figures S7–S10 in the Supporting Information. For each sample two broad bands centered near 260 and 330 nm can be observed that matches with the host exciton creation bands and Eu^{3+} CT-bands, respectively.

Figure 9b shows the TLE spectra of $\text{Gd}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ and $\text{Y}_2\text{O}_2\text{S}:\text{Ti}^{4+}$. Comparison with the PLE spectra from Figure 3a can be seen in Figures S8 and S9. The TLE band between 260 to 280 nm is the host exciton creation band and the one between 300 to 400 nm is the Ti^{4+} CT-band, similar to the Ti^{4+} PLE spectra shown in Figure 3a. $\text{Gd}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ shows a very weak TLE band near 350 nm with intensity much lower than in the PLE spectrum. However, the band still exists indicating that this sample can be charged by 350 nm UV light. No TLE spectra could be recorded for $\text{La}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ and $\text{Lu}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ which is probably related to the very weak excitation efficiency of Ti^{4+} CT-luminescence in Figure 3.

4. DISCUSSION

4.1. Vacuum Referred Binding Energy (VRBE) Diagram of $\text{RE}_2\text{O}_2\text{S}$ and Ti^{4+} Charge Transfer Bands. To discuss the trapping and detrapping processes of electrons and holes in $\text{RE}_2\text{O}_2\text{S}$, we will first construct and exploit the VRBE diagram. The VRBE stands for vacuum referred binding energy that is defined as the energy needed to bring an electron from a level in the diagram to the vacuum outside the sample. The energy at rest in vacuum or vacuum level is then defined as energy zero. The reason to choose the VRBE diagram is because the binding energy of an electron in a lanthanide defect (both divalent and trivalent) states within the bandgap can be compared in different materials with respect to the same energy reference. Further details about how to construct the VRBE diagrams from spectroscopic data can be found in refs 33 and 34.

Figure 10 shows the stacked VRBE diagrams of $\text{RE}_2\text{O}_2\text{S}$ with location of Pr^{3+} , Tb^{3+} , Eu^{2+} and Ti^{3+} levels. The detailed VRBE diagrams with all lanthanide impurities level locations can be found in Figure S11. All the data needed and used to construct the VRBE diagrams are listed in Table 2. We adopted for all four samples a value of 6.37 eV for the so-called U-parameter of the chemical shift model. The reason for adopting the same U-parameter is due to the similar chemical environment surrounding Eu^{3+} in $\text{RE}_2\text{O}_2\text{S}$. This value defines within the chemical shift model a VRBE of -3.77 eV in the ground state of Eu^{2+} in the four $\text{RE}_2\text{O}_2\text{S}$ samples. The Pr^{3+} and Tb^{3+} grounds

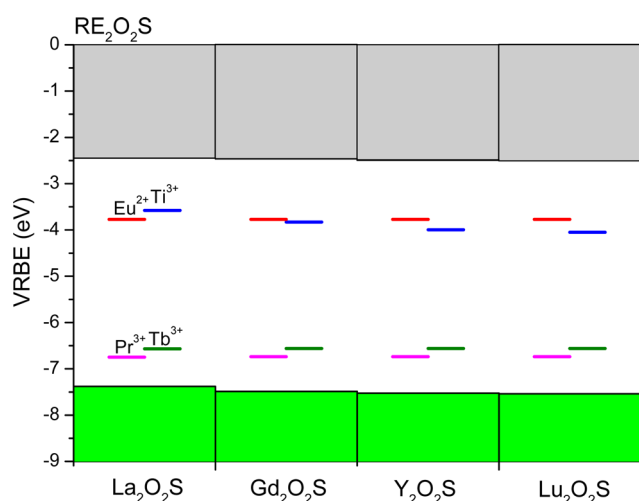


Figure 10. Stacked VRBE diagrams of $\text{RE}_2\text{O}_2\text{S}$ (RE = La, Gd, Y, and Lu) with the VRBE in the ground states of Pr^{3+} , Tb^{3+} , Eu^{2+} , and Ti^{3+} .

states are then fixed at the same energy for all of the samples, with the values of -6.76 eV and -6.57 eV, respectively.

The top of the valence band is obtained from the $\text{VB} \rightarrow \text{Eu}^{3+}$ CT energy in Figure 2a and Table 2. The increase of that CT energy with smaller RE implies that the valence band maximum moves downward. The conduction band bottom is obtained from the exciton creation energy (Figure 2a) plus 8% of that to account for the electron–hole binding energy.

The Ti^{4+} -doped oxysulfides show very broad excitation (fwhm ~ 0.8 eV) and emission (fwhm ~ 0.5 eV) bands in Figure 3. The broad excitation band between 320 and 380 nm is due to the $\text{VB} \rightarrow \text{Ti}^{4+}$ charge transfer, which means that electrons in the anions are excited to Ti^{4+} forming Ti^{3+} in its lowest $3d_1$ state. Here we assume that the energy at the maximum of the CT-band corresponds with the location of the $\text{Ti}^{3+/4+}$ level above the VB-top. Therefore, the VRBE in the ground states of Ti^{3+} can be obtained as shown in Figure 10.

Rogers et al. compiled the VRBE in the Ti^{3+} ground state levels derived from different Ti^{4+} -doped materials. They found that the VRBE in the Ti^{3+} lowest $3d_1$ state (E_{3d1}) appears always near -4 ± 1 eV and the compound to compound variation of VRBE is attributed to the crystal field splitting (CFS).³⁵ Figure 10 shows that the Ti^{3+} $3d_1$ states are near -4 eV and decrease from $\text{La}_2\text{O}_2\text{S}$ to $\text{Lu}_2\text{O}_2\text{S}$. It was empirically found that the size of the CFS for the $5d$ -levels of the lanthanides is inversely proportional to the square of the bond length.³⁶ Ti^{3+} has one electron in the d -orbital like the $5d$ excited states of the lanthanides that shows the same CFS tendency as the $5d$ -levels of lanthanides.^{35,37} Table S1 shows that the RE-(O,S) bond lengths decrease from $\text{La}_2\text{O}_2\text{S}$ to $\text{Lu}_2\text{O}_2\text{S}$.^{38–41} Therefore, the CFS of the Ti^{3+} $3d$ -levels is expected to increase from $\text{La}_2\text{O}_2\text{S}$ to $\text{Lu}_2\text{O}_2\text{S}$. Such increased CFS will then reduce the VRBE in the lowest $3d_1$ state of Ti^{3+} .

This forms then our explanation for the red-shift from 327 nm (3.79 eV) in $\text{La}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ to 360 nm (3.44 eV) in $\text{Lu}_2\text{O}_2\text{S}:\text{Ti}^{4+}$ of the $\text{VB} \rightarrow \text{Ti}^{4+}$ charge transfer excitation and the red-shift of the Ti^{4+} CT-luminescence in Figure 3b.

4.2. Trapping and Detrapping. The stacked VRBE diagrams of Figure 10 show that the divalent Eu ground state is about 1.3 eV below the CB in $\text{RE}_2\text{O}_2\text{S}$ which implies that the corresponding trivalent Eu can act as an electron trapping center. The same applies to Ti which has Ti^{3+} ground state location about 1.2 to 1.5 eV below the CB as illustrated in Figure 10 which means that Ti^{4+} also acts as the electron trapping center.

During γ -ray irradiation in the TLEM spectra and β -ray irradiation in the low temperature TL spectra, the free charge carriers are generated that can move freely through the CB and the VB. For the Eu^{3+} or Ti^{4+} single-doped $\text{RE}_2\text{O}_2\text{S}$, the electrons will be trapped in either Eu^{3+} or Ti^{4+} forming Eu^{2+} or Ti^{3+} , and the holes must be trapped somewhere else. In Figure 5b–8b, some common TL glow peaks at the same temperature can be observed. The temperatures at the maxima of glow peaks 3, 4, 5, 6, 7, and 9 listed in Table 1 are about the same but with different relative intensities in $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}/\text{Ti}^{4+}$, $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}/\text{Ti}^{4+}$, $\text{Gd}_2\text{O}_2\text{S}:\text{Eu}^{3+}/\text{Ti}^{4+}$, and $\text{Lu}_2\text{O}_2\text{S}:\text{Eu}^{3+}/\text{Ti}^{4+}$ also show the common TL glow peaks at the same temperature. These suggest that the Eu^{3+} or Ti^{4+} single-doped samples have the same type of hole trapping centers.

The thermoluminescence excitation (TLE) spectra for each Eu^{3+} -doped sample in Figure 9a shows a broad band that coincides with the $\text{VB} \rightarrow \text{Eu}^{3+}$ CT excitation in Figure 2a. During CT-band excitation electrons are excited from the valence band to the $\text{Eu}^{2+8}\text{S}_{7/2}$ ground state leaving a hole in the valence band. It was demonstrated by Struck et al. that during the Eu^{3+} CT excitation a hole can dissociate from the CT-state.⁴² Also p-type photoconductivity was observed by Dobrov et al. in $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ during $\text{VB} \rightarrow \text{Eu}^{3+}$ CT excitation.⁴³ So, during CT-band excitation, part of the holes are released and trapped in the hole trapping centers. Then during the TL readout, the captured holes release again to recombine with Eu^{2+} producing Eu^{3+} characteristic emission as shown in Figure 4 and Figure S4. The same conclusion was also suggested by Forest et al.²⁵ and Fonger et al.^{44,45} by studying the thermoluminescence after CT excitation in $\text{La}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ and $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$.

The TLE spectra for Ti^{4+} -doped $\text{Y}_2\text{O}_2\text{S}$ and $\text{Gd}_2\text{O}_2\text{S}$ in Figure 9b again shows a broad band that coincides with the $\text{VB} \rightarrow \text{Ti}^{4+}$ CT-bands in Figure 3a. During the CT-band excitation, Ti^{3+} is formed and holes are released to the VB to be captured by the hole trapping center. Similar as for Eu doping, during the TL readout, the captured holes are released again and recombine at Ti^{3+} producing Ti^{4+} CT-luminescence as shown in Figure 4 and Figure S4.

Figure 5a and Table 1 show that the Ce^{3+} , Pr^{3+} , and Tb^{3+} single-doped $\text{Y}_2\text{O}_2\text{S}$ all have the same glow peaks. From the

Table 2. Parameters Used to Construct the VRBE Diagram for $\text{RE}_2\text{O}_2\text{S}$ with $U = 6.37$ eV^a

sample	E^{ex}	$E^{\text{CT}}(\text{Eu}^{3+})$	$E^{\text{CT}}(\text{Ti}^{4+})$	E_{V}	E_{C}	$E_{\text{Tb}^{3+}}$	$E_{\text{Pr}^{3+}}$
$\text{La}_2\text{O}_2\text{S}$	4.57	3.61	3.79	−7.38	−2.44	−6.57	−6.75
$\text{Gd}_2\text{O}_2\text{S}$	4.66	3.72	3.65	−7.49	−2.46	−6.57	−6.75
$\text{Y}_2\text{O}_2\text{S}$	4.67	3.75	3.53	−7.52	−2.48	−6.57	−6.75
$\text{Lu}_2\text{O}_2\text{S}$	4.66	3.77	3.44	−7.54	−2.51	−6.57	−6.75

^aAll numbers are in eV.

stacked VRBE diagrams in Figure 10 and Figure S11, we observe that the trivalent Ce, Pr, and Tb ground states are 2.6, 0.77, and 0.95 eV above the VB and these trivalent ions can act as hole trapping center during β irradiation. Then the electrons must be captured by the host lattice itself. Now the question turns to whether the captured electrons release earlier or the trapped holes release earlier.

If the holes from Ce^{4+} , Pr^{4+} , or Tb^{4+} release earlier than electrons, one can estimate according to eq 2 with a heating rate of 1K/s that the TL peak positions (T_m) due to hole release from Ce^{4+} , Pr^{4+} and Tb^{4+} to the VB in $\text{Y}_2\text{O}_3\text{S}$ are expected at ~ 900 , 276, and 339 K, respectively. This means that the TL peak temperature for $\text{Y}_2\text{O}_3\text{S}:\text{Ce}^{3+}$, $\text{Y}_2\text{O}_3\text{S}:\text{Pr}^{3+}$ and $\text{Y}_2\text{O}_3\text{S}:\text{Tb}^{3+}$ should be different and much higher than the observed TL temperature shown in Figure 5a. Similarly, one observes that with Pr^{3+} and Tb^{3+} doping in $\text{La}_2\text{O}_3\text{S}$, $\text{Gd}_2\text{O}_3\text{S}$ and $\text{Lu}_2\text{O}_3\text{S}$, the TL glow peaks for each sample are at the same temperature shown in Figure 6a, 7a and 8a, respectively. Therefore, in Ce^{3+} , Pr^{3+} , and Tb^{3+} single-doped $\text{RE}_2\text{O}_3\text{S}$, the TL glow curves originate from electrons released from host lattice related trapping centers and recombine at the Ce^{4+} , Pr^{4+} or Tb^{4+} hole trapping center providing Ce^{3+} , Pr^{3+} , and Tb^{3+} emission.

4.3. The Afterglow Mechanism of $\text{Y}_2\text{O}_3\text{S}:\text{Ti}^{4+},\text{Eu}^{3+}$. On the basis of the above discussion, the afterglow mechanism of $\text{Y}_2\text{O}_3\text{S}:\text{Ti}^{4+},\text{Eu}^{3+}$ can be proposed as illustrated in Figure 11.

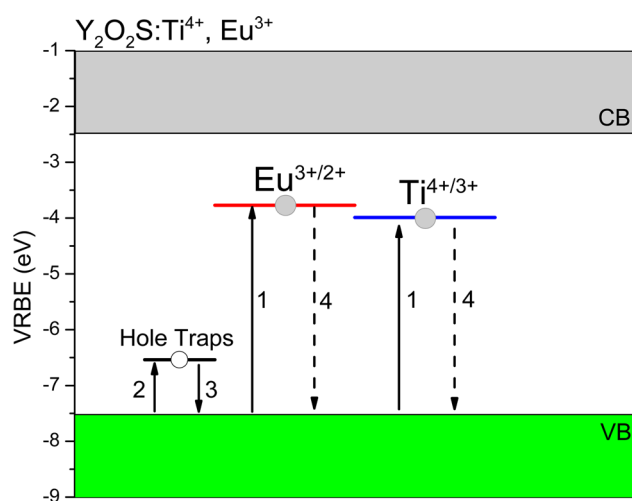


Figure 11. Proposed afterglow mechanism for $\text{Y}_2\text{O}_3\text{S}:\text{Ti}^{4+},\text{Eu}^{3+}$. The filled circle stands for electrons and the open circle stands for hole.

Upon UV excitation by day light, electrons are excited from the VB to Ti^{4+} and Eu^{3+} forming Ti^{3+} and Eu^{2+} in the ground states (arrows 1). The holes released to the VB are captured by the hole trapping centers (arrow 2) although it is still not clear what are those hole trapping centers. Then, the hole trapping center with a shallow trap depth enables spontaneously release of holes at the room temperature (arrow 3). It travels as a free hole via the VB or as a self-trapped hole or V_k center to recombine with Ti^{3+} and Eu^{2+} producing Ti^{4+} CT emission and Eu^{3+} 4f–4f emission (arrows 4). We conclude that the afterglow of $\text{Y}_2\text{O}_3\text{S}:\text{Ti}^{4+},\text{Eu}^{3+}$ is due to the hole release instead of the more common electron release. However, further research needs to be performed to identify the nature of the hole trapping centers.

5. CONCLUSION

Photoluminescence spectroscopy, thermoluminescence and the chemical shift model have been combined to study the trapping and detrapping processes of the charge carriers in $\text{RE}_2\text{O}_3\text{S}$. Photoluminescence spectroscopy shows that Ti^{4+} CT-luminescence provides the orange-red emission in $\text{RE}_2\text{O}_3\text{S}:\text{Ti}^{4+}$. The red-shift of the Ti^{4+} CT-excitation and emission from $\text{La}_2\text{O}_3\text{S}:\text{Ti}^{4+}$ to $\text{Lu}_2\text{O}_3\text{S}:\text{Ti}^{4+}$ is attributed to the increased crystal field splitting of the Ti^{3+} 3d levels with smaller size of the site occupied. The TLEM spectra confirm that Ti^{4+} and Eu^{3+} act as the recombination center. The low temperature TL measurements reveal that for Tb^{3+} , Pr^{3+} , and Ce^{3+} -doped $\text{RE}_2\text{O}_3\text{S}$ the TL glow curves are from host related electron traps while for Ti^{4+} - and Eu^{3+} -doped $\text{RE}_2\text{O}_3\text{S}$ the TL bands are from the host related hole trapping centers. The TL excitation spectra show that the electrons captured by Ti^{4+} and Eu^{3+} originate from the VB. Finally, the afterglow mechanism of $\text{Y}_2\text{O}_3\text{S}:\text{Ti}^{4+},\text{Eu}^{3+}$ were derived that is due to the hole release instead of the more common electron release based on the above information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b01577.

Photoluminescence emission spectra measured by PMT and CCD, the thermal-quenching spectra, the low-temperature (10 K) photoluminescence emission spectra, the thermoluminescence emission spectra, the thermoluminescence excitation spectra, and the energy level diagrams and a table of lattice parameters (PDF)

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Notes

The authors declare no competing financial interest.

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