Electronic and optical properties of Er-doped Y$_2$O$_2$S phosphors†

M. Pokhrel,a G. A. Kumar,*b C.-G. Ma,cd M. G. Brik,sdef Brian W. Langloss,g Ian N. Stanton,g Michael J. Therien,g D. K. Sardar*b and Yuanbing Mao*a

In this paper, we report a detailed computational and experimental investigation of the structural, electronic and dynamic properties of undoped and Er$^{3+}$-doped Y$_2$O$_2$S phosphors by using computational crystal field (CF) calculations and electronic density of states by density functional theory (DFT), combined with optical measurements including excitation spectra, emission spectra from X-ray, ultraviolet and near infrared (NIR) excitations, and quantum yield determination under ultraviolet and NIR excitations. Emission decays and quantum yields of the visible and NIR bands were measured for different Er$^{3+}$ doping concentrations in the Er$^{3+}$-doped Y$_2$O$_2$S phosphors. Results show that green (550 nm) and red (667 nm) emission intensity and the respective ratio of these emission intensities depend on both the excitation wavelength and the Er$^{3+}$ doping concentration. Although the total emission efficiency does not appreciably depend on the excitation wavelength, the excitation wavelength that provided the highest efficiency was found to be 250 nm in these Er$^{3+}$-doped Y$_2$O$_2$S phosphors with both 1% and 10% Er doping concentrations.

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Introduction

Rare earth doped metal oxysulphides M$_2$O$_2$S, e.g. M = Y, Gd, La, are well-known optical materials in the photonics industry, mainly due to their excellent chemical stability, low toxicity, and the economic feasibility of large scale production with a broad range of applications in lighting and displays.1–6 As in other rare earth doped wide band gap materials, the emission spectral properties of rare earth doped oxysulphides can be tuned over a very wide range of wavelengths for specific applications based on rare earth dopants and their doping concentrations in the host oxysulphide crystals.7–12 In addition to their excellent spectral emission properties, the metal cations can be selected to endow additional functionalities to the oxysulphide phosphors. For example, Gd$_2$O$_2$S:Er phosphor was found to have excellent upconversion (UC) efficiency, X-ray excitation and magnetic properties where the X-ray and magnetic features are due to the properties of Gd$^{3+}$.13 Recently, we explored the multifunctional features of several oxysulphide materials with their possible applications in medical imaging, with Gd$_2$O$_2$S:Yb/Er showing the most potential to replace existing halide based upconverting phosphors for infrared based biomedical imaging. These phosphors not only enable near-IR imaging but at the same time can be used as contrast agents in MRI imaging, thus making them effective bimodal imaging contrast agents.13,14 Furthermore, we explored the UC efficiency of M$_2$O$_2$S:Yb/Er under 980 and 1550 nm excitation in comparison with NaYF$_4$:Yb/Er.14–17 Under different pump power densities and a wide range of Yb$^{3+}$ and Er$^{3+}$ concentrations, we explored the static and dynamic spectral properties as well as the UC quantum yield (QY) to understand the optimum oxysulphide compositions for the highest UC efficiency.15 We found that UC QY in these M$_2$O$_2$S:Yb$^{3+}$/Er$^{3+}$ (M = Gd, La, Y) solid phosphors are 3–4 times higher than that of β-NaYF$_4$:20%Yb$^{3+}$/2%Er$^{3+}$ at lower excitation power densities, especially under 980 nm excitation.18 We also demonstrate the highest UC QY (6.20 ± 0.90)% in La$_2$O$_2$S:1%Yb$^{3+}$/1%Er$^{3+}$ at the excitation power density of 22 ± 3 W cm$^{-2}$.18 Moreover, the threshold excitation power density was found to be essential to generate the highest UC QY for these compositions. Due to the wide range of excitation and emission wavelengths...
available in $\text{M}_2\text{O}_3: \text{Yb/Er}$, a detailed study is still needed to explore their electronic and optical properties.

In this article, we present both the electronic and optical properties of $\text{Y}_2\text{O}_2\text{S}:\text{Er}^{3+}$ using various theoretical and experimental techniques for the first time. The structural, electronic, and dynamic properties of pure $\text{Y}_2\text{O}_3$ was calculated using density functional theory (DFT), and the low temperature absorption spectral data was fitted with a crystal field model to explore the crystal field parameters. We successfully predict the location of the lowest erbium states in the band gap of $\text{Y}_2\text{O}_2\text{S}$—estimated at 0.915 eV above the valence band. The static and dynamic emission spectral properties were also investigated under ultra-violet (UV), 980 nm near infrared (NIR) and X-ray excitation for $\text{Y}_2\text{O}_2\text{S:x%Er}$ ($x = 1, 7, 10$).

In this study, these compositions were selected to study the effect of low and high doping concentration of $\text{Er}^{3+}$ in the $\text{Y}_2\text{O}_2\text{S}$ host on downconversion QY. We limited our study within the optimum $\text{Er}^{3+}$ doping concentration (10%) because this $\text{Er}^{3+}$ doping level demonstrated the highest UC luminescence intensity compared to other doping levels. An analysis of red (640–690 nm), green (510–570 nm) and NIR (900–1600 nm) emissions under UV excitation (250, 258, 264, 296 and 380 nm) is unprecedentedly reported for the $\text{Er}^{3+}$-doped $\text{Y}_2\text{O}_3$ at different $\text{Er}^{3+}$ doping concentrations. We found that the emission intensity and the ratio of emission intensities are functions of excitation wavelength and $\text{Er}^{3+}$ doping concentration. We further measured the QY of the visible emission under various UV excitations and NIR 980 nm excitation to explore the most desirable pumping wavelength for efficient light output. The measured QY showed that these $\text{Er}$-doped $\text{Y}_2\text{O}_3$ phosphors possess 3–4 times higher QYs under UV excitations compared to that of 980 nm excitation.

**Experimental section**

**Synthesis**

A high temperature solid state flux fusion method was used for the syntheses of the undoped and $\text{Er}^{3+}$-doped $\text{Y}_2\text{O}_3$ phosphors. The starting materials are $\text{Y}_2\text{O}_3$, $\text{Er}_2\text{O}_3$ (Sigma Aldrich, all 99.99%), both $\text{Na}_2\text{CO}_3$ (30–50 wt%) and $\text{K}_3\text{PO}_4$ (20 wt%) (Sigma Aldrich, 99.99%) salts were used with S as flux. More details regarding the synthesis was reported in our earlier work. The $\text{Er}^{3+}$ doping concentration was varied from 0 to 10 mol% of $\text{Y}_2\text{O}_3$. The starting chemicals were thoroughly mixed using an agate mortar and then heated in a muffle furnace at 1150 °C for 60 min. When the furnace was cooled down, the samples were taken out and washed 6 times with distilled water, and finally with dilute hydrochloric acid. The washed powder was subsequently dried and sieved.

**Characterization**

Powder X-ray diffraction (XRD) of the prepared undoped and $\text{Er}^{3+}$-doped $\text{Y}_2\text{O}_3$ samples was measured by a Rigaku-Miniflex™ II X-ray diffractometer with CuKα radiation ($\lambda = 0.15406$ nm). The morphologies of these samples were observed using a field emission scanning electron microscope (Carl Zeiss Sigma VP FE-SEM) equipped with a field emission gun operated at 5 kV. Absorption spectra were measured in the 300–1700 nm range using a UV-VIS-NIR spectrophotometer (Cary, Model 14R) in transmission mode. Electronic absorption spectral samples were prepared by pressing the synthesized undoped and $\text{Er}^{3+}$-doped $\text{Y}_2\text{O}_3$ phosphor powders to form pellets. For low temperature ($T = 8$ K) absorption measurements, the formed pellets were mounted in a closed-cycle helium cryostat (Janis, Wilmington, MA) with fused silica. The excitation and emission spectra of the as-prepared $\text{Y}_2\text{O}_2\text{S:x%Er}$ ($x = 1, 7, 10$) micron sized powders were measured using an Edinburgh Instruments FLS980 fluorometer system. For absolute QY measurements and emission intensity comparisons, a BenFlect coated integrating sphere was employed in the Edinburgh Instruments FLS980 fluorometer. Details of the UC QY measurement setup can also be found in our earlier publications and is further detailed in the ESI.1

**X-ray excited luminescence**

To characterize the X-ray induced luminescence, the $\text{Y}_2\text{O}_2\text{S:x%Er}$ samples ($x = 1, 7$ and 10) were irradiated in a Faxitron X-ray Cabinet System (Model RX-650). The X-ray induced luminescence was collected in a coaxial transmission irradiation configuration with the sample centered under the X-ray source. Samples were made by pressing 10 mg of the synthesized powder materials using a 7 mm diameter mold in a hand-pellet press with consistent pressure. Pellet samples were then mounted on a piece of angled teflon using double sided tape and placed ~2 mm in front of an optical fiber in the Faxitron system. The emitted light was collected with an optical fiber attached to the Edinburgh Instruments FLS920 spectrometer. All samples were excited over an X-ray range of 20 to 130 kVp (5 mA). In addition, photostability of our samples was tested after X-ray irradiation for different time periods (up to 60 minutes) at 130 kVp (5 mA). Pellet samples were made and mounted in the X-ray cabinet. An initial spectrum was obtained under X-ray irradiation. The sample was then irradiated for a total of 60 minutes in the same X-ray cabinet. Spectral data were collected every 10 minutes. The area of each emission peak was calculated in the same X-ray cabinet. Spectral data were collected every 10 minutes. The area of each emission peak was calculated in the same X-ray cabinet. Spectral data were collected every 10 minutes. The area of each emission peak was calculated in the same X-ray cabinet. Spectral data were collected every 10 minutes. The area of each emission peak was calculated in the same X-ray cabinet. Spectral data were collected every 10 minutes. The area of each emission peak was calculated in the same X-ray cabinet. Spectral data were collected every 10 minutes. The area of each emission peak was calculated in the same X-ray cabinet. Spectral data were collected every 10 minutes. 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**Theoretical method**

First principle calculations, based on CASTEP module of Materials Studio, were implemented for the structural, electronic, optical properties of $\text{Y}_2\text{O}_3$. The generalized gradient approximation (GGE) with the Perdew–Burke–Ernzerhof exchange model was applied to treat the exchange–correlation effects. The Monkhorst–Pack $k$-points grid was chosen as $4 \times 4 \times 2$ for geometry optimization and $8 \times 8 \times 4$ for the optical properties calculations in the case of $\text{Y}_2\text{O}_3$. The cut-off energy, which determines the size of the plane-wave basis set, was 500 eV. The electronic configurations were as follows: $4d^{5}5s^{2}$ for $\text{Y}$, $2s^{2}2p^{6}$ for $\text{O}$, $3s^{2}3p^{4}$ for $\text{S}$, and the norm-conserving pseudopotentials were used for all chemical elements.
Results & discussion

Phase and morphology

Powder XRD and SEM were used to characterize the crystalline phase, size and morphology of the Y2O2S:Er phosphor particles. A typical XRD pattern of the prepared samples is shown in Fig. 1a along with the JCPDS standard data (JCPDS Card No. 26-1422) for the hexagonal phase Y2O2S as vertical lines. The intense and sharp diffraction peaks correlate well with the standard suggesting that the as-synthesized phosphors were well-crystallized in a single phase. Within the detection limit of the X-ray diffractometer, no additional lines were observed for either low or high Er3+-doped Y2O2S samples. FE-SEM micrographs (Fig. 1b–d) obtained from different locations of the same sample also show that the as-synthesized Er3+-doped Y2O2S mostly crystallized in hexagonal plates. The average size of the hexagonal plates was about 3.5 μm and the size distribution was within a 1 μm range of 3.5 ± 1 μm.

Summary of structural data and details of ab initio calculations

Initial structural data was taken from the literature as an input for optimizing the crystal structure with subsequent calculations of the structural, electronic and optical properties of the Y2O2S:Er phosphor particles. A typical XRD pattern of the prepared samples is shown in Fig. 1a along with the JCPDS standard data (JCPDS Card No. 26-1422) for the hexagonal phase Y2O2S as vertical lines. The intense and sharp diffraction peaks correlate well with the standard suggesting that the as-synthesized phosphors were well-crystallized in a single phase. Within the detection limit of the X-ray diffractometer, no additional lines were observed for either low or high Er3+-doped Y2O2S samples. FE-SEM micrographs (Fig. 1b–d) obtained from different locations of the same sample also show that the as-synthesized Er3+-doped Y2O2S mostly crystallized in hexagonal plates. The average size of the hexagonal plates was about 3.5 μm and the size distribution was within a 1 μm range of 3.5 ± 1 μm.

Calculated structural, electronic, and dynamic properties of pure Y2O2S

As shown in Table 1, there is a good agreement between the results of the optimized crystal structure obtained in the present study and those available in the literature. The calculated band gap was underestimated (Table 1), as always happens with DFT-based methods. To overcome such an underestimation, a 1.6 eV scissor operator, which simply shifts the conduction band upward to make it match with the experimental findings, was applied. The calculated band gap is of an indirect character (Fig. 2b).

The electronic states in both valence and conduction bands exhibit well-pronounced dispersion, thus indicating a high mobility of the hole and electron charge carriers. The conduction band is 7–8 eV wide, and the valence band has a width of 4 eV. The composition of the calculated electronic bands is shown in Fig. 2c: the valence band is mainly composed of the O 2p and S 3p states in which the former produces a peak at about −4 eV and the latter has a maximum contribution closer to the top of the valence band at about −2 eV. The conduction band is formed mainly by the 4d (5d) states of Y (La) atoms. It is worthwhile noting that the 4d (5d) states of Y (La) are more strongly hybridized with the 2p states of O, than with the 3p states of S, since the Y–O (La–O) bonds are considerably shorter.

Finally, we also show the cross-sections of the electron density distributions in the space between atoms in Y2O2S crystal lattice (Fig. 2d). The difference in the interaction between the Y (La) atoms from one side and O and S atoms from the...
other side is clearly seen in Fig. 2d. The calculated effective Mulliken charges (in the units of the proton charge) are as follows: −0.75 for oxygen, −0.70 for sulfur, and +1.11 for yttrium ions. This data shows that the effective electric charges on all ions are different from what might be expected from the chemical formula. This circumstance stresses the importance of the covalent and chemical bond formation effects in the present material.

Calculated structural and electronic properties of Er-doped Y₂O₂S

After doping, Er³⁺ ions occupy the Y sites in the Y₂O₂S crystal lattice. Since the ionic radius of Er³⁺ (1.03 Å) is slightly smaller than that of Y³⁺ (1.04 Å), one may expect a slight decrease of the lattice constant of the doped compound in comparison with the pure Y₂O₂S. Indeed, optimization of the crystal lattice with 5% of yttrium sites occupied by erbium gave the following lattice parameter values: a = b = 3.68912 Å and c = 6.27642 Å. The main influence of an impurity ion on the electronic properties of a host is related to the formation of the electronic energy levels of this impurity in the host’s band gap. Eventually, these energy levels would be responsible for modification, often quite considerable, of the optical properties of a doped material.

Fig. 3 presents the details of the calculated DOS diagrams in the energy region covering the top of the valence band and band gap. The 4f unfilled shell of the Er³⁺ ions gives rise to a maximum of the electron density distribution in the band gap. Taking the difference between the maxima of the Er³⁺ 4f states and the O 2p and S 3p states, the location of the lowest erbium state in the band gap was estimated as 0.915 eV. This value will be further used when linking the results of the ab initio and crystal field studies together. Unfortunately, it is not possible to give a proper treatment to the multiplet effects in the unfilled shells of impurity ions using the CASTEP program since the calculations are essentially one-electron. Therefore, to analyze the experimental absorption spectra of Y₂O₂S:Er³⁺ and the erbium energy levels in details, crystal field theory was used as described in the next section.

Energy level calculation and crystal field analysis

The model Hamiltonian that was used to study the energy level structure of rare earth ions is written as:

\[
H = E_{\text{avg}} + \sum_{k=2,4,6} F^{\alpha}p_k + \zeta\gamma A_{so} + \alpha L(L+1) + \beta G(G_z) + \gamma G(R_z)
+ \sum_{i=0.2,4} T^i T_i + \sum_{b=0.2,4} M^b m_b + \sum_{k=2,4,6} P^k p_k + \sum_{b,q} B_q^b C^{(k)}_{bq},
\]

where the first term \(E_{\text{avg}}\) is the barycenter of the 4f⁴ electronic configuration (in our case \(N = 11\) for Er³⁺ ions), the second term \((F^{\alpha}p_k)\) describes the Coulomb interaction between the 4f⁴ electrons, which forms the set of the so-called LS terms of a free ion (there are 17 LS terms for Er³⁺ ions). In addition, \(\alpha, \beta\) and \(\gamma\) represent the two-body configuration interactions, \(T^i\) the three-body interactions, and \(M^b\) and \(P^k\) the magnetically and electrostatically correlated interactions respectively. More precisely, the third term \((\gamma A_{so})\) is related to the spin–orbit (SO) interaction which results in the set of the free ion 3S¹L₄ multiplets (41 3S¹L₄ multiplets in our case of erbium), the next four terms are the effective two- \((\alpha, \beta, \gamma)\) and three- \((T^i)\) electron Coulomb correlation contributions from higher configuration with the same parity, the two-body magnetically correlated interactions described by the Marvin integrals \(M^b\) represent the spin–spin and spin-other-orbit relativistic corrections, and the electrostatically correlated SO contributions of the two-body interactions represented by the \(P^k\) entries. Following Carnall et al., the ratios of \(M^b\) \((k = 2\) and \(4))\) to \(M^a\) and \(P^k\) \((k = 4\) and \(6))\) to \(P^a\) are usually constrained to minimize the number of fitting parameters. For the 4f⁴ and 4f⁴₋₋ configurations \((N \leq 7)\), the two- and three-body parameters exist only if \(N > 1\) and \(N > 2\). All these terms represent the “free-" ion" Hamiltonian, whose parameters vary slightly from one host to another due to nephelauxetic effects. The last term describes the anisotropic components of the crystal field (CF) interactions, where the \(B^{(k)}_{pq}\) entries are referred to as the crystal field parameters (CFPs), and \(C^{(k)}_{pq}\) are the spherical operators (here the Wybourne notation is adopted). In total, for the rare-earth elements there can be in up to 27 non-zero CFPs in the case of the C₁ symmetry. The number of non-zero CFPs depends on the local site symmetry of the position occupied by the rare earth ion and considerably decreases when going to the sites of higher symmetry. Since the site symmetry of the doped Er³⁺ ions, which occupy the Y³⁺ sites in the Y₂O₂S host, is C₃ᵥ point-group symmetry, the CF Hamiltonian, i.e., the last term in the above equation, can be further expanded as:

\[
H_{\text{CF}} = B_0^2 C^{(3)}_{00} + B_4^2 C^{(3)}_{40} + B_6^2 C^{(3)}_{60} - C^{(3)}_{50} + B_0^0 C^{(6)}_{00} + B_3^6 C^{(6)}_{30} + B_6^6 C^{(6)}_{60} + C^{(6)}_{50},
\]

where all CFPs are real.

In our fitting calculation, the quasi-free ion interactions, i.e., the two-body configuration interactions \(\alpha, \beta,\) and \(\gamma,\) three-body interactions \(T^i,\) and magnetically \(M^b\) and electrostatically \(P^k\) correlated interactions,
are all fixed and taken from literature. Only the CFPs, Slater parameters $F^k$ ($k = 2$, 4 and 6), SO coupling parameter $\zeta_{4f}$, and the configuration barycenter parameter $E_{av}$ were freely varied to obtain the ultimate optimization results. Using the Hamiltonians (1) and (2) and the experimental low temperature absorption spectra shown in Fig. 4a, we performed the calculations of the Er$^{3+}$ energy levels in Y$_2$O$_2$S. All the energy parameters we employed are given in Table 2. The calculated Er$^{3+}$ energy levels in comparison with the experimental ones are collected in Table 3. It is seen from Table 3 and Fig. 4a that a good agreement between experiment and theory is obtained. In addition, the calculated Er$^{3+}$ energy levels are superimposed onto the experimental absorption spectrum of Y$_2$O$_2$S:Er$^{3+}$ in Fig. 4a to visualize agreement between the experimental data and results of the crystal field calculations.

Finally, it is possible to combine the results from the \textit{ab initio} calculations of the electronic structure of Y$_2$O$_2$S:Er$^{3+}$ with those from the crystal field calculations. Since the separation between the 4f states of erbium and the O 2p and S 3p states is 0.915 eV, taking this value as the ground state of Er$^{3+}$ in the band gap, we can plot all higher calculated Er$^{3+}$ levels from Table 3, as presented in Fig. 4b. Such a diagram gives complete description of the energetic properties of the host itself and impurity ions.

Excitation and emission properties under UV excitation

The excitation spectra of these Er$^{3+}$-doped Y$_2$O$_2$S samples (Fig. 5a) consist of two broad bands at 264 and 296 nm, corresponding to the charge transfer bands (CTBs) of Er$^{3+}$–O$^{2–}$ and Er$^{3+}$–S$^{2–}$ bonding, respectively. Most of the other narrow bands in the excitation spectra are identical to the absorption spectra (Fig. 5a vs. Fig. S1, ESI†) and correspond to the f–f transitions of Er$^{3+}$ ions. The intensity of both the CTB and Er$^{3+}$ (f–f) transitions are found to be dependent on the Er$^{3+}$ concentrations. We observed the weak Er$^{3+}$ emission at 410 nm overlapped with broad emission centered at 400 nm for Y$_2$O$_2$S:1%Er as shown in Fig. 5b for above host band (250 nm), band edge (258 nm) and CTB (Er$^{3+}$–O$^{2–}$, 264 nm) excitations (Fig. S2, ESI†), indicating that the Y$_2$O$_2$S host to Er$^{3+}$ energy transfer is a combination of radiative and nonradiative energy transfers at low Er$^{3+}$ doping levels. However, at 296 nm excitation corresponding to (Er$^{3+}$–S$^{2–}$) CTB, the broad emission at 400 nm was absent confirming that this broad emission was related to bandgap emission (Fig. S2, ESI†). In addition, with higher Er$^{3+}$ doping (above 3%), we were able to suppress the bandgap related emission (Fig. 5b and Fig. S3, ESI†). This confirms that the energy transfer from the Y$_2$O$_2$S host to Er$^{3+}$ dopants is nonradiative at higher Er$^{3+}$ doping concentrations.

Furthermore, the broad excitation spectra monitoring the red emission (Fig. 5a) shows asymmetric CT bands corresponding to Er$^{3+}$–O$^{2–}$ at 264 nm and Er$^{3+}$–S$^{2–}$ at 296 nm lying below the band gap (4.6–4.8 eV) of the Y$_2$O$_2$S host. The asymmetric excitation CT bands further indicate that either there exists excitation bands in the high energy side beyond the detection limit of the spectrophotometer or that the tail extends to that side, which could be the band edge of the host as estimated above by the band structure calculation.

Table 2 Optimized energy parameters for Er$^{3+}$ ions in Y$_2$O$_2$S (unit: cm$^{-1}$)

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<th>Parameter</th>
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<tr>
<td>$B_{0e}$</td>
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</table>

Notes: those parameter values given in the square brackets are fixed. $M^0$/$M^0 = 0.56, M^0$/$M^0 = 0.38, P^0$/$P^0 = 0.75$, and $P^0$/$P^0 = 0.5$ were used to constrain those corresponding parameters not listed in the table.
These spectra demonstrate identical emission features, where the Er\(^{3+}\) emission bands were in the spectral ranges of 390–415 nm (\(^{2}G_{9/2} \rightarrow ^{4}I_{15/2}\), 515–532 nm (\(^{2}H_{11/2} \rightarrow ^{4}I_{15/2}\), 532–570 nm (\(^{2}S_{1/2} \rightarrow ^{4}I_{15/2}\)), 640–685 nm (\(^{2}F_{5/2} \rightarrow ^{4}I_{15/2}\)), and 780–840 nm (\(^{4}I_{9/2} \rightarrow ^{4}I_{15/2}\)). Emission intensity analysis clearly shows that the Er\(^{3+}\) (f–f) excitation band at 380 nm is the least efficient one. This also indicates that the Y\(_{2}\)O\(_{2}\)S host to Er\(^{3+}\) (f–f) energy transfer is more efficient compared to that of Er\(^{3+}\) (f–f) to Er\(^{3+}\) (f–f). This is mainly due to the narrow excitation or smaller absorption at 380 nm for Er\(^{3+}\) (f–f) band compared to those of CTB and band edge excitations of the Y\(_{2}\)O\(_{2}\)S host. Moreover, Er\(^{3+}\) concentration dependent emissions under 250 nm excitation (Fig. 6b) were observed in the ranges of 950–1050 and 1450–1650 nm, corresponding to \(^{4}I_{15/2} \rightarrow ^{4}I_{13/2}\) and \(^{4}I_{15/2} \rightarrow ^{4}I_{13/2}\) manifolds, respectively. Intensity analysis indicates that the NIR emission intensity also increases with increasing doping concentration and does not quench up to 10% Er\(^{3+}\) doping.

We measured the QYs of these Er\(^{3+}\)-doped Y\(_{2}\)O\(_{2}\)S solid phosphors from the green (510–570 nm) and red (640–690 nm) emissions under 250, 258, 264 and 296 nm excitations and the results and methods are summarized in Fig. 7, Fig. S4 and Table S1 (ESI†). These results clearly show the influence of Er\(^{3+}\) concentration in the efficiency of green (510–570 nm) and red (640–690 nm) emission bands. At low Er\(^{3+}\) doping concentrations, the green emission is prominent, while at high Er\(^{3+}\) doping concentrations, the red emission becomes stronger (Fig. S2 vs. Fig. S5, ESI†). This phenomenon mainly causes by the change in the population dynamics of corresponding manifolds due to the Er\(^{3+}\)–Er\(^{3+}\) interaction at different Er\(^{3+}\) doping concentrations. The excitation wavelength does not influence the total efficiency appreciably, except under 296 nm excitation where the total efficiency is less compared to other UV excitation wavelengths. These results indicate that 250 nm is the most appropriate excitation wavelength to achieve the highest efficiency in the Y\(_{2}\)O\(_{2}\)S:x%Er\(^{3+}\) phosphors with x = 1, 7 and 10. This is mainly due to efficient energy transfer between the Y\(_{2}\)O\(_{2}\)S host and Er\(^{3+}\) ions at the host band edge excitation compared to that of CTB excitation, or direct energy migration of the excitation along a chain of Er\(^{3+}\) ions under the host band edge excitation.

We also measured the QYs of these Er\(^{3+}\)-doped Y\(_{2}\)O\(_{2}\)S phosphors from the green (510–570 nm) and red (640–690 nm) emissions under 980 nm excitation (Fig. 8). Comparing the spectra under 980 nm excitation with those obtained under UV excitations at 250, 258, 264 and 296 nm (Fig. 8 vs. Fig. 7), we noticed that the red (640–690 nm) to green (510–570 nm) emission ratio is higher under NIR excitation than under UV excitations (Fig. S6, ESI†). In addition, the upconversion QY for red (640–690 nm) emission was found to be stronger for all Er\(^{3+}\) concentrations under 980 excitation, and the QY for both the red (640–690 nm) and green (510–570 nm) was found to increase up to 10% Er doping concentration as shown in Fig. 8. At 10% Er doping concentration, a maximum UC QY of 3.60 ± 0.36% was measured from these solid phosphors at an excitation power density of 19 W cm\(^{-2}\), which is almost 3 times less than the UV excited QY. The lower QYs under UC excitation conditions are obviously due to the less efficient nonlinear multiphoton process involved in emission process compared to that of single

<table>
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<th>Difference</th>
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Note: only the energy levels located at the experimentally-detected energy range are given for the sake of brevity, and the complete calculated energy level scheme is available from the authors upon request.
photon process involved in the downconversion emissions where a maximum of 100% efficiency can be achieved.

**Lifetimes under UV (258 nm) and UC (980 nm) excitations**

Fig. 9 shows the decays of emissive transitions of the Y$_2$O$_2$S: x%Er$^{3+}$ (x = 1, 7 and 10) phosphors under pulsed excitations at 258 nm and 980 nm. The temporal evolution of the luminescence intensity as a function of time at these emission bands was obtained after the microsecond excitation pulse, and the decay curve was fitted by the single multieponential function as shown in eqn (3):

$$I(t) = I_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right)$$  \hspace{1cm} (3)
where $A_1$ is the fitting parameters and $\tau_1$ is the emission decay time. All the fitted decay times are shown in Fig. S6 (ESI†).

From Fig. 9 and Fig. S7 (ESI†), decay curves exhibited Er$^{3+}$ doping concentration dependence in the Y$_2$O$_2$S host. At low Er$^{3+}$ doping concentration, temporal evolution of the excited ion was happening at a slower rate compared to that of high Er$^{3+}$ doped samples. However, decay times were longer under 980 nm excitation compared to those of UV excitation at 258 nm for high Er$^{3+}$ doped samples as shown in Fig. 9 and Fig. S7 (ESI†), confirming that the energy transfer upconversion (ETU) processes play a significant role in populating excited states versus cooperative sensitization. In addition, lifetime lengthening of the $^4I_{13/2}$ (1550 nm) level under 980 nm excitation (3.88 ms vs. 2.56 ms under UV excitation) from the Y$_2$O$_2$S:1%Er$^{3+}$ (Fig. 9d and Fig. S7, ESI†) clearly indicates that UC emission is affected by the longer lifetime of the metastable state $^4I_{13/2}$ as proposed in the energy level diagram shown below.

Emission properties under X-ray excitation

Besides optically excited luminescence, these Er$^{3+}$-doped Y$_2$O$_2$S also shows luminescence under X-ray irradiation. Fig. 10a, c and e show the X-ray excited luminescence spectra for 1, 7 and 10% Er-doped Y$_2$O$_2$S. From the evaluation of the optical and X-ray excited spectra, it is apparent that the X-ray induced luminescence also originates from the same Er$^{3+}$ levels as in UV excitations at 250, 258, 264 and 296 nm. We also observed a broad emission band centered at 400 nm for the Y$_2$O$_2$S:1%Er sample as shown in Fig. 10a, confirming that the broad emission at 400 nm is a band gap related emission.

The emission profiles of the Y$_2$O$_2$S:x%Er (1, 7 and 10) phosphors under X-ray excitation do not differ from those obtained under UV/UC excitations but display clear differences in the relative intensities among the various transitions. The most obvious difference is the relative emission intensity of the red emission (640–690 nm) compared to that of the green emission (510–570 nm) as it is strongly decreased under X-ray excitation compared to UV and NIR excitations. As the X-ray emission intensity is proportional to the tube current and the tube voltage, we can conclude that good linearity in the emission intensity has been preserved for UV (400–420 nm), red (640–690 nm) and green (510–570 nm) emissions over a wide range of X-ray excitation energies (Fig. 10b, d and f). This clearly shows that corresponding Er$^{3+}$ levels of the Y$_2$O$_2$S:x%Er ($x = 1, 7$ and $10$) phosphors do not saturate at incident X-ray irradiance as high as 130 keV·5 mA (2.28 Gy min$^{-1}$) and X-ray induced visible light yield in the Y$_2$O$_2$S:x%Er ($x = 1, 7$ and $10$) phosphors is linearly correlated with the X-ray intensity. The linear response of scintillation intensity underscores the potential utility of these Y$_2$O$_2$S:x%Er ($x = 1, 7$ and $10$) nanomaterials for dosimetry. Furthermore, insignificant PL intensity variations over X-ray irradiation time ensures that the Y$_2$O$_2$S:x%Er phosphors are stable under X-ray irradiation exposure (Fig. S8, ESI†).

In addition, different optical response in the Y$_2$O$_2$S:x%Er ($x = 1, 7$ and $10$) phosphors under X-ray excitation compared to those obtained under optical downconversion excitation could
be due to the two different measurement conditions (pellet vs. powder). We anticipate that the X-ray attenuation length in Y$_2$O$_2$S pellet is relatively large, and the emitted photons may require traveling longer distance in the pellet layers, which ultimately induces a slight variation of the red to green emission intensities due to the wavelength dependent absorption/scattering process. We also anticipate the wavelength dependent process is added up due to the optical fiber used to collect the emitted photons under X-ray excitation. Nevertheless, the red emission intensity is increasing with the increase of the Er$^{3+}$ doping concentration and observed intensity variations is too small to account for the large difference between the red to green emission ratio measured with downconversion excitations. Further optical and X-ray excitation studies with additional experiments are needed to explain this effect.

**Plausible luminescence mechanisms under different excitations**

Based on all above measurements and analysis, the excitation and de-excitation mechanisms of the Er$^{3+}$-doped Y$_2$O$_2$S phosphors under these excitations are proposed (Fig. 11). According to our experimental results, the involved intermediate levels populating the red level ($^4$F$_{9/2}$) is via the following energy transfer of Er$^{3+}$: $^4$I$_{13/2}$ → $^4$I$_{11/2} + ^4$I$_{13/2}$ → $^4$I$_{11/2} + ^4$F$_{9/2}$. Note that the $^4$I$_{11/2}$ level is populated by nonradiative relaxation from the upper lying $^4$I$_{13/2}$ level. The lifetime of the $^4$I$_{13/2}$ level of Er$^{3+}$ is much longer than that of other levels, which makes the energy transfer of $^4$I$_{11/2} + ^4$I$_{13/2}$ → $^4$I$_{11/2} + ^4$F$_{9/2}$ (populating directly the red emitting level $^4$F$_{9/2}$ of Er$^{3+}$) more favorable than that of the $^4$I$_{11/2} + ^4$I$_{13/2}$ → $^4$I$_{13/2} + ^4$F$_{7/2}$ (populating the green emitting level $^4$F$_{7/2}$ → $^4$S$_{3/2}$, $^2$H$_{11/2}$ of Er$^{3+}$), and finally populate $^4$F$_{9/2}$ through the multiphonon relaxation. This clearly explains the higher QY for red emission compared to green emission observed in these highly Er$^{3+}$ doped Y$_2$O$_2$S samples when excited at NIR wavelengths. However, the fast decay time observed for $^4$F$_{9/2}$ reflects the slow feeding of the higher excited state $^4$G$_{9/2}$ by energy transfer between two Er$^{3+}$ ions, which brings one ion to a higher excited state responsible for the UC emission at UV (410 nm) and the other ion to the ground state. In addition, the increase of Er$^{3+}$ concentrations shortens the distance between neighboring Er$^{3+}$ ions and leads to increasing intensity ratio of red to green emission under UV excitations, which can be attributed to cross-relaxation (CR), in agreement with the experimental results shown in Fig. 5 and 7.

**Fig. 10** The X-ray induced luminescence and UV, green and red emission intensity vs. applied voltage in X-ray tube for samples of (a and b) Y$_2$O$_2$S:1%Er$^{3+}$, (c and d) Y$_2$O$_2$S:7%Er$^{3+}$, and (e and f) Y$_2$O$_2$S:10%Er$^{3+}$.

**Fig. 11** Energy level diagram of the Er$^{3+}$-doped Y$_2$O$_2$S system showing possible excitation and de-excitation mechanism at UV, X-ray and 980 nm excitations. BG: bandgap; CTB: charge transfer band.
In the X-ray excitation scheme (Fig. 11), the higher energy states of the Y₂O₂S host conduction band are excited with the subsequent formation of a great number of e–h pairs that migrate within its structure. The migration stage is strongly affected by defects, surfaces and interfaces that can introduce energy levels into the forbidden gap of the material. The luminescence occurs when these e–h pairs recombine at the Er³⁺ sites with the net luminescence intensity being determined by the competition between radiative recombination at the Er³⁺ sites versus nonradiative recombination at quenching centers and trapping of the carriers. Although different excitation mechanisms (optical and X-ray) may be responsible for the different photoluminescence responses, emission even at 40 keV-5 mA (less than 0.80 Gy min⁻¹) from Y₂O₂S:1%Er indicates that Y₂O₂S can be an excellent X-ray excited scintillating host. Due to the ultraviolet downconversion, upconversion luminescence, and X-ray induced luminescence properties of the Er³⁺-doped Y₂O₂S phosphors, they can act as a promising, single composition based platform for synergistic optical/X-ray applications.

Conclusions

The first principle calculation performed in the Y₂O₂S and Y₂O₂S:Er³⁺ enables us to understand the nature of the indirect band gap, and the co-existence of covalent (Y–O) and less covalent (Y–S) bonds in the system. By combining the results of the DFT and crystal field calculations, we succeeded in estimating the Er³⁺ energy levels in the host band gap, placing the Er³⁺ ground state at 0.915 eV above the top of the valence band. The theoretically calculated Er³⁺ energy levels are consistent with the experimental absorption spectrum of the Y₂O₂S:Er³⁺, including the asymmetric excitation CT bands. Also we have used a scissor parameter to correct the underestimation of the band gap in the DFT approach. These above mentioned observations assure the consistency between the corrected band gap and experimental observation. Quantum yield measurements under UV and NIR excitations show drastic differences in terms of efficiency which are attributed to the difference in the excitation and de-excitation mechanisms under the two different excitation processes as well as the consecutive energy transfer processes of upconversion. Based on the present study, these Y₂O₂S:Er crystals are comparatively efficient phosphors under UV, X-ray and NIR excitations and thus may find various potential applications in photonics.

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