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# Stimulated-emission cross-sections of trivalent erbium ions in the cubic sesquioxides $Y_2O_3$, $Lu_2O_3$, and $Sc_2O_3$

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**Abstract:** We report on a detailed revision of the spectroscopic properties of $Er^{3+}$ ions in the cubic sesquioxide host crystals $R_2O_3$ (R = Y, Lu and Sc). The 4f-4f transition probabilities are calculated by applying a modified Judd-Ofelt theory accounting for configuration interaction based on the measured absorption spectra. The stimulated-emission cross-sections for the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ (at ~2.8 µm) and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ (at ~1.6 µm) transitions of $Er^{3+}$ ions are determined and the luminescence dynamics from the $^4I_{11/2}$ and $^4I_{13/2}$ manifolds are studied at different temperatures. It is found that the luminescence lifetime of the $^4I_{11/2}$ state strongly depends on the host-forming $R^{3+}$ cation even at low temperatures due to a non-negligible non-radiative multiphonon decay channel. Er:$Y_2O_3$ exhibits the lowest phonon energies and consequently the longest $^4I_{11/2}$ luminescence lifetimes. A disagreement between the absorption and emission probabilities for the $^4I_{15/2} \leftrightarrow {}^4I_{11/2}$ transition of $Er^{3+}$ ions is observed at room temperature and explained considering the distribution of $Er^{3+}$ ions over two non-equivalent crystallographic sites, $C_2$ and $C_{3i}$.



## 1. Introduction

Trivalent erbium ions ($Er^{3+}$) possess the electronic configuration [Xe]$4f^{11}$ with the ground-state $^4I_{15/2}$. They feature a complex and dense energy level scheme allowing for multiple emission lines in the visible, near and mid-infrared spectral ranges, as well as efficient energy-transfer processes. As shown in Fig. 1, the two most commonly exploited laser transitions of $Er^{3+}$ ions are the transitions $^4I_{13/2} \rightarrow {}^4I_{15/2}$ at wavelengths around 1.55 µm and $^4I_{11/2} \rightarrow {}^4I_{13/2}$ at wavelengths around 2.85 µm. In particular the latter attracts attention for medical applications, driving sources for nonlinear processes or trace gas analysis in the molecular fingerprint region [1–3].

Among the host materials suitable for $Er^{3+}$ doping with the goal of achieving laser emission in the 3 µm range, the rare-earth sesquioxides $R_2O_3$, where R stands for the host cations Y, Lu or Sc attracted a lot of attention [4]. These compounds crystallize in the cubic space group $Ia\bar{3}$ adopting the body-centered bixbyite structure. Cubic sesquioxide crystals feature attractive thermo-physical properties such as a high thermal conductivity of more than 12 $Wm^{-1}K^{-1}$ for undoped $Lu_2O_3$ at room temperature, a weak thermal expansion coefficient as well as small and positive thermo-optic coefficients [5]. Moreover, their maximum phonon energies below 700 $cm^{-1}$

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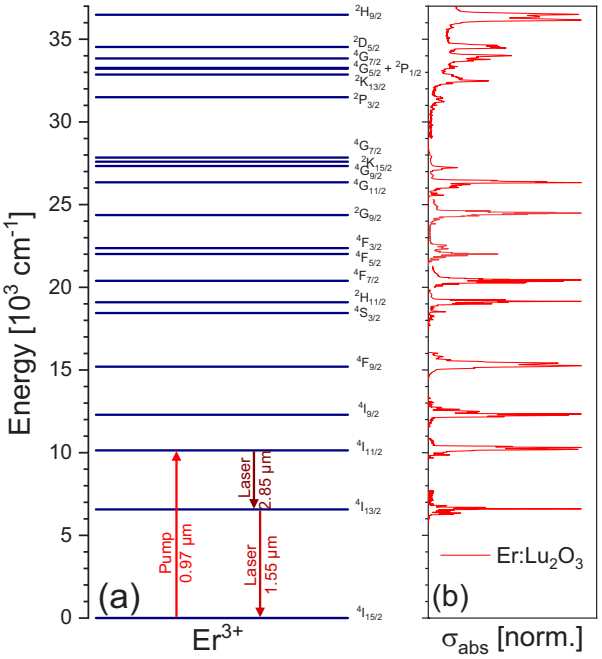


**Fig. 1.** (a) Energy level scheme [14] of $Er^{3+}$ ions showing laser transitions at 1.6 µm and 2.8 µm and the energy levels relevant for the absorption measurements and calculations within this work. (b) Absorption cross sections normalized for the highest peak in the respective range indicating that all expected energy levels were detected in the absorption measurements.

[6] are moderate for oxide materials leading to reduced non-radiative multiphonon relaxation [7] in particular for transitions from the $^4I_{11/2}$ manifold. Finally, they exhibit strong crystal-fields for the dopant $Er^{3+}$ ions leading to broad emission spectra. Isostructural substitutional solid-solutions are formed in the $R_2O_3 - Er_2O_3$ binary systems allowing for the formation of cubic sesquioxides even at $Er^{3+}$ high doping levels. The latter is relevant for the development of 2.8 µm lasers as high $Er^{3+}$ doping concentrations strongly increase the probability for energy-transfer upconversion from the metastable terminal laser level $^4I_{13/2}$, avoiding high population of this level which may otherwise lead to self-termination of lasers based on the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition [8].

Note that cubic sesquioxides in general and $Er^{3+}$-doped compounds in particular can be obtained in the form of transparent polycrystalline ceramics benefiting from lower synthesis temperatures of around 1800 °C as compared to sesquioxide single-crystals with melting points in excess of 2400 °C [9,10].

Highly-efficient and power-scalable crystalline and ceramic $Er^{3+}$-doped sesquioxide lasers operating on the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition are known. Li *et al.* reported on a crystalline Er:$Lu_2O_3$ laser pumped by an optically pumped semiconductor laser delivering 1.4 W at 2.85 µm with a slope efficiency as high as 36%. Under diode-pumping, the output was scaled up to 5.9 W at the expense of a reduced slope efficiency of 27% [11]. Yao *et al.* developed a diode-pumped Er:$Lu_2O_3$ ceramic laser generating 6.7 W at 2.85 µm with a slope efficiency of 30.2% [9] and more recently, a diode-pumped Er:$Y_2O_3$ ceramic laser enabled an output power of 13.4 W at 2.7 µm at room temperature [12]. By operation at cryogenic temperatures, even higher output power levels are feasible at 2.853 µm [13].

Despite their wide use in lasers, the spectroscopic properties of $Er^{3+}$-doped sesquioxides, and, in particular, the transition probabilities at 2.85 µm, remain not completely understood. There

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are two common methods to calculate the stimulated-emission cross-sections for rare-earth ions. The Füchtbauer-Ladenburg equation [15] relies on the directly measured luminescence spectrum and the radiative lifetime $\tau_{rad}$ of the emitting level. In cases where more than one terminal level for the emission exists, the luminescence branching ratio $B$(JJ') for each transition J → J' needs to be determined. $\tau_{rad}$ and $B$(JJ') are often obtained using theoretical calculations for f-f transition intensities known as Judd-Ofelt theory [16,17]. Another approach relies on the reciprocity method (RM) known as McCumber equation [18,19], using Einstein's theory of equal transition probabilities for absorption and emission between two Stark levels [20].

One of the main challenges for determining the spectroscopic properties of rare-earth ions in cubic sesquioxides is a disagreement between the experimental absorption and emission probabilities for certain optical transitions. It was suggested that such a disagreement may originate from different oscillator strengths for rare-earth ions incorporated on two non-equivalent sites in the cubic bixbyite structure [21], having the symmetries $C_2$ and $C_{3i}$ (Wyckoff: 24$d$ and 8$b$, respectively) and a sixfold oxygen coordination. The unit-cell of cubic sesquioxide crystals contains 32 cation sites and for an ideal structure, 3/4 of the cations occupy $C_2$ sites and 1/4 occupies $C_{3i}$ sites. This proportion is expected to hold also for rare-earth doping ions. Theoretical models suggest a deviation from this behavior at room temperature for Er:$Sc_2O_3$ [22], but these models are not valid at the high growth temperatures of this material and due to the low mobility of cations at room temperature, the random distribution at high temperatures can be expected to be maintained at room temperature. Due to the presence of a center of inversion, electric dipole (ED) transitions are forbidden for rare-earth ions residing on $C_{3i}$ sites. Still, these ions can contribute to transition intensities with a magnetic dipole (MD) component, *i.e.*, J ↔ J' transitions with $\Delta J = 0, \pm 1$ (except for $0 \leftrightarrow 0'$). Note that both the $^4I_{11/2} \leftrightarrow {}^4I_{13/2}$ as well as the $^4I_{13/2} \leftrightarrow {}^4I_{15/2}$ transition are ED and MD allowed while the transition $^4I_{11/2} \leftrightarrow {}^4I_{15/2}$ is MD forbidden due to $\Delta J = 2$.

To determine the stimulated-emission cross-sections of $Er^{3+}$ ions in cubic sesquioxides, we performed a comparative study of the absorption and emission probabilities for the three cubic sesquioxides yttria ($Y_2O_3$), lutetia ($Lu_2O_3$) and scandia ($Sc_2O_3$). This study involved the Judd-Ofelt analysis, the measurement of the absorption and emission spectra, as well as the luminescence dynamics as a function of temperature. Even though the three studied compounds are isostructural, they exhibit significantly different properties in terms of the lattice parameter and phonon energies, which is explained by the different sizes and masses of the host-forming cations. This also leads to a strong variation of the spectroscopic parameters within this host crystal family.

## 2. Absorption spectra and Judd-Ofelt analysis

Figure 2 shows the absorption cross-section spectra for $Er^{3+}$ ions in $Y_2O_3$, $Lu_2O_3$ and $Sc_2O_3$ crystals. For the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition which is commonly used for pumping of mid-infrared $Er^{3+}$ lasers, the peak absorption cross sections amount to $0.35 \times 10^{-20}$ cm$^2$ at 974.2 nm, $0.30 \times 10^{-20}$ cm$^2$ at 980.7 nm, and $0.33 \times 10^{-20}$ cm$^2$ at 979.3 nm, respectively.

Based on these data, the transition intensities of $Er^{3+}$ ions in the three sesquioxide crystals were determined using the Judd-Ofelt formalism [16,17]. The experimental absorption oscillator strengths $f_{exp}$ were calculated as:

$$f_{exp}(JJ') = \frac{m_e c^2}{\pi e^2 \langle \lambda \rangle^2} \Gamma(JJ'), \tag{1}$$

where $m_e$ and $e$ are the electron mass and charge, respectively, $c$ is the speed of light, $\Gamma$(JJ') is the integrated absorption cross-section within the absorption band for the J → J' transition, and $\langle \lambda \rangle$ is the wavelength corresponding to the barycenter of the absorption band. The experimental

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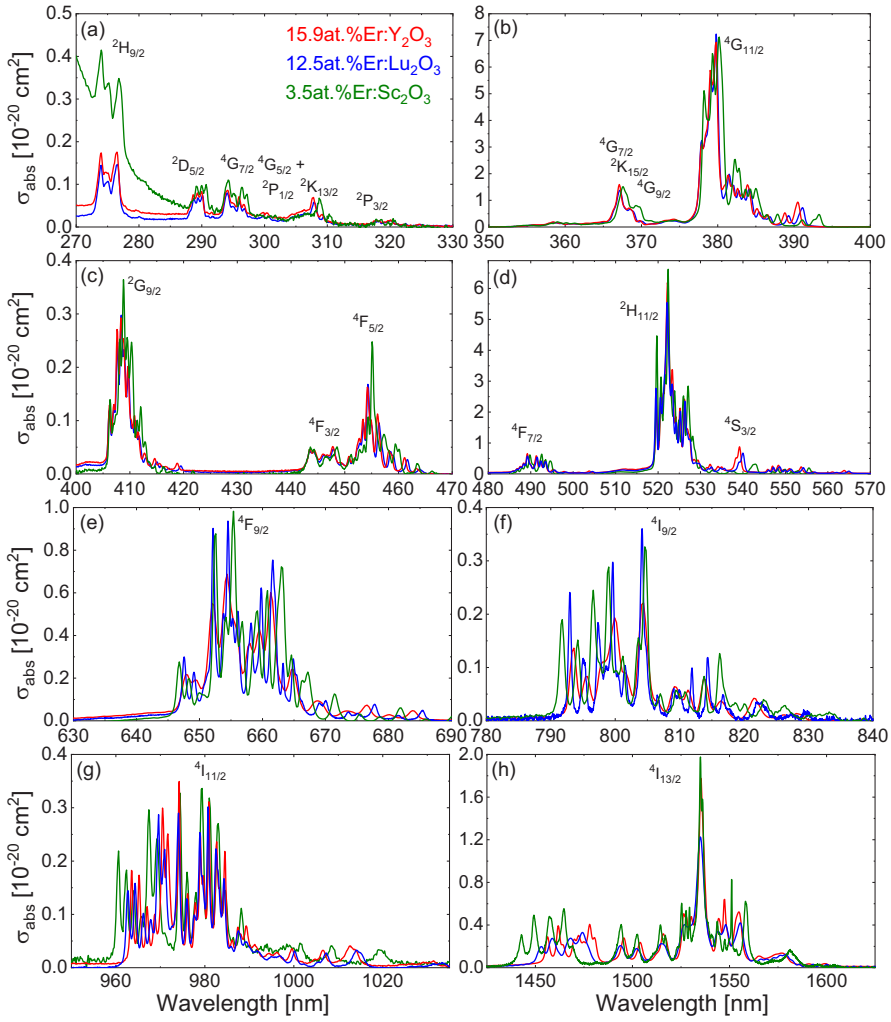


**Fig. 2.** (a-h) Ground-state absorption cross-sections $\sigma_{abs}$ of $Er^{3+}$ ions in $Y_2O_3$, $Lu_2O_3$ and $Sc_2O_3$ crystals for the energy levels shown in Fig. 1. The UV absorption background for Er:$Sc_2O_3$ in (a) is attributed to color centers and was subtracted for the J-O-calculations.

absorption oscillator strengths $f_{exp}$ and the values $f_{calc}$ calculated by three different approaches detailed below are given in Table 1 for the example of Er:$Lu_2O_3$.

The electric dipole (ED) contribution to the calculated absorption oscillator strengths $f_{calc}$ of a transition can be determined from the corresponding line strengths $S$(JJ'):

$$f_{calc}^{ED}(JJ') = \frac{8}{3h(2J'+1)\langle\lambda\rangle}\frac{\left(\langle n\rangle^2+2\right)^2}{9n}S_{calc}^{ED}(JJ'), \quad (2)$$

where $h$ is the Planck constant and $n$ is the refractive index calculated from the dispersion formulas for cubic sesquioxide crystals given in [23].

Three different models were applied to calculate the ED contributions to the line strengths of f-f transitions of $Er^{3+}$ ions, (i) the standard Judd-Ofelt (J-O) theory and two modifications accounting for configuration interaction, (ii) the modified Judd-Ofelt theory (mJ-O) and (iii) the

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**Table 1. Experimental and calculated absorption oscillator strengths for $Er^{3+}$ ions in $Lu_2O_3$[a]**

| $^4I_{15/2} \rightarrow {}^{2S+1}L_J$ | $E_J$, $cm^{-1}$ | $\Gamma$, $10^{-20}\,cm^{-2}nm$ | $f_{exp}$, $10^{-6}$ (ED + MD) | $f_{calc}$, $10^{-6}$ | | |
|---|---|---|---|---|---|---|
| | | | | J-O | mJ-O | ICI |
| $^4I_{13/2}$ | 6600 | 30.81 | 1.516 | $0.931^{ED} + 0.599^{MD}$ | $0.984^{ED} + 0.599^{MD}$ | $0.846^{ED} + 0.599^{MD}$ |
| $^4I_{11/2}$ | 10196 | 3.708 | 0.437 | $0.511^{ED}$ | $0.527^{ED}$ | $0.499^{ED}$ |
| $^4I_{9/2}$ | 12466 | 1.720 | 0.300 | $0.156^{ED}$ | $0.242^{ED}$ | $0.229^{ED}$ |
| $^4F_{9/2}$ | 15222 | 5.861 | 1.538 | $1.286^{ED}$ | $1.574^{ED}$ | $1.567^{ED}$ |
| $^4S_{3/2} + {}^2H_{11/2}$ | 18978 | 23.83 | 9.799 | $9.030^{ED}$ | $9.769^{ED}$ | $9.798^{ED}$ |
| $^4F_{7/2}$ | 20303 | 2.742 | 1.281 | $1.338^{ED}$ | $1.248^{ED}$ | $1.336^{ED}$ |
| $^4F_{5/2} + {}^4F_{3/2}$ | 22116 | 0.774 | 0.428 | $0.676^{ED}$ | $0.545^{ED}$ | $0.581^{ED}$ |
| $^2G_{9/2}$ | 24404 | 1.199 | 0.811 | $0.528^{ED}$ | $0.441^{ED}$ | $0.504^{ED}$ |
| $^4G_{11/2} + {}^2K_{15/2} + {}^4G_{9/2} + {}^2G_{7/2}$ | 26561 | 24.81 | 19.58 | $19.87^{ED} + 0.070^{MD}$ | $19.52^{ED} + 0.070^{MD}$ | $19.50^{ED} + 0.070^{MD}$ |
| r.m.s. dev. | | | | 0.369 | 0.168 | 0.184 |

[a]$E_J$ – experimental barycenter energy of the multiplet, $\Gamma$ – integrated absorption cross-section, $f_{exp}$ and $f_{calc}$ – experimental and calculated absorption oscillator strengths, respectively, ED – electric-dipole, MD – magnetic-dipole, r.m.s. dev. – root mean square deviation between $f_{exp}$ and $f_{calc}$.

approximation of an intermediate configuration interaction (ICI) [24,25]. The contributions of magnetic-dipole (MD) transitions were calculated independently within the Russell-Saunders approximation on wave functions of $Er^{3+}$ under the assumption of a free-ion.

For the standard J-O theory, the ED line strengths for a transition J → J' are:

$$S^{ED}_{calc}(JJ') = \sum_{k=2,4,6} U^{(k)}\Omega_k, \tag{3}$$

$$U^{(k)} = \langle (4f^n)SLJ||U^k||(4f^n)S'L'J'\rangle^2. \tag{4}$$

Here, $U^{(k)}$ ($k = 2, 4, 6$) are the reduced squared matrix elements calculated using the free-ion parameters reported in [26], and $\Omega_k$ are the three intensity (J–O) parameters.

In the ICI approximation, the ED line strengths become

$$S^{ED}_{calc}(JJ') = \sum_{k=2,4,6} U^{(k)}\tilde{\Omega}_k, \tag{5}$$

$$\tilde{\Omega}_k = \Omega_k[1 + 2R_k(E_J + E_{J'} - 2E^0_f)], \tag{6}$$

where the intensity parameters $\tilde{\Omega}_k$ depend linearly on the energies $E_J$ and $E_{J'}$ of the two multiplets involved in the transition, $E_f{}^\circ$ has the meaning of the average energy of the $4f^{11}$ $Er^{3+}$ configuration, and $R_k$ ($k = 2, 4, 6$) are the parameters representing the configuration interaction. Consequently, there are six free parameters, namely $\Omega_k$ and $R_k$ for $k = 2$, 4, and 6, each.

Assuming that only the excited configuration with opposite parity $4f^{10}5d^1$ contributes to the configuration interaction, $R_2 = R_4 = R_6 = \alpha \approx 1/(2\Delta)$ and Eq. (6) is simplified to

$$\tilde{\Omega}_k = \Omega_k[1 + 2\alpha(E_J + E_{J'} - 2E^0_f)]. \tag{7}$$

This approximation is referred to as the modified J-O (mJ-O) theory and it corresponds to only four free parameters, namely $\Omega_2$, $\Omega_4$, $\Omega_6$ and $\alpha$. In this model, $\Delta$ is the energy of the excited configuration $4f^{10}5d^1$ of $Er^{3+}$. It should be noted that for high $4f^{10}5d^1$ energies ($\Delta \rightarrow \infty$, $\alpha \rightarrow 0$), Eq. (7) yields the formula for the standard J-O model.

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The absorption oscillator strengths for $Er^{3+}$ ions in sesquioxides were calculated using all three above-mentioned models. The root mean square (r.m.s.) deviation between $f_{exp}$ and $f_{calc}$ (ED + MD) values was determined, as shown in Table 1 for the case of Er:$Lu_2O_3$. The ICI model provides the lowest r.m.s. deviation and the best agreement between the experimental and calculated transition intensities for the $^4I_{13/2}$ and $^4I_{11/2}$ excited states. Thus, it was selected for further calculations.

The resulting intensity parameters of the standard J-O and ICI models for $Er^{3+}$ ions for the three host materials under investigation here are listed in Table 2.

**Table 2. Intensity parameters for $Er^{3+}$ ions in cubic sesquioxide host materials (J-O and ICI models)**

| Parameter | $Y_2O_3$ | | $Lu_2O_3$ | | $Sc_2O_3$ | |
|---|---|---|---|---|---|---|
| | J-O | ICI | J-O | ICI | J-O | ICI |
| $\Omega_2$, $10^{-20}$ cm$^2$ | 4.520 | 4.478 | 4.933 | 5.115 | 4.626 | 4.309 |
| $\Omega_4$, $10^{-20}$ cm$^2$ | 1.313 | 1.511 | 0.635 | 1.042 | 2.306 | 1.721 |
| $\Omega_6$, $10^{-20}$ cm$^2$ | 0.511 | 0.479 | 0.667 | 0.570 | 0.516 | 0.671 |
| $R_2$, $10^{-4}$ cm | | -0.048 | | -0.106 | | 0.182 |
| $R_4$, $10^{-4}$ cm | | 0.092 | | 0.061 | | -0.035 |
| $R_6$, $10^{-4}$ cm | | 0.002 | | 0.011 | | 0.020 |

The probabilities of spontaneous radiative transitions (ED + MD) were calculated from the corresponding line strengths:

$$A_{\Sigma}^{calc}(JJ') = \frac{64\pi^4 e^2}{3h(2J'+1)\langle\lambda\rangle^3} n\left(\frac{n^2+2}{3}\right)^2 S_{ED}^{calc}(JJ') + A_{MD}(JJ'). \tag{8}$$

The $A_{MD}$(JJ') contributions are calculated separately as explained above for the transitions in absorption. Then, the radiative lifetimes of the excited states $\tau_{rad}$ and the luminescence branching ratios for the particular emission channels $B$(JJ') were derived:

$$\tau_{rad} = \frac{1}{A_{tot}^{calc}}, \text{where } A_{tot}^{calc} = \sum_{J'} A_{\Sigma}^{calc}(JJ'), \text{ and } B(JJ') = \frac{A_{\Sigma}^{calc}(JJ')}{\sum_{J'} A_{\Sigma}^{calc}(JJ')}. \tag{9}$$

The results on the transition probabilities in emission for $Er^{3+}$:$Lu_2O_3$ are shown in Table 3.

Table 4 summarizes the radiative lifetimes of the $^4I_{13/2}$ and $^4I_{11/2}$ excited states and the luminescence branching ratios $B$(JJ') for the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition for all three studied sesquioxides. These values are relevant for further calculations of the stimulated-emission cross-sections for the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions of $Er^{3+}$ ions in these hosts as well as the interpretation of the results of the measurements of the luminescence dynamics.

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**Table 3. Probabilities of spontaneous radiative transitions of $Er^{3+}$ ions in $Lu_2O_3$ (ICI model)[a]**

| Emitting state | Terminal state | $<\lambda_{em}>$, nm | $A$(JJ'), $s^{-1}$ | $B$(JJ') | $A_{tot}$, $s^{-1}$ | $\tau_{rad}$,ms |
|---|---|---|---|---|---|---|
| $^4I_{13/2}\rightarrow$ | $^4I_{15/2}$ | 1515 | $101.98^{ED} + 72.15^{MD}$ | 1 | 174.1 | 5.74 |
| $^4I_{11/2}\rightarrow$ | $^4I_{13/2}$ | 2781 | $18.41^{ED} + 15.19^{MD}$ | 0.167 | 201.5 | 4.96 |
| | $^4I_{15/2}$ | 980.8 | $167.86^{ED}$ | 0.833 | | |
| $^4I_{9/2}\rightarrow$ | $^4I_{11/2}$ | 4405 | $1.00^{ED} + 2.42^{MD}$ | 0.019 | 182.9 | 5.47 |
| | $^4I_{13/2}$ | 1705 | $39.16^{ED}$ | 0.214 | | |
| | $^4I_{15/2}$ | 802.2 | $140.28^{ED}$ | 0.767 | | |
| $^4F_{9/2}\rightarrow$ | $^4I_{9/2}$ | 3628 | $5.32^{ED} + 4.24^{MD}$ | 0.006 | 1613 | 0.619 |
| | $^4I_{11/2}$ | 1990 | $63.85^{ED} + 10.44^{MD}$ | 0.046 | | |
| | $^4I_{13/2}$ | 1160 | $81.51^{ED}$ | 0.050 | | |
| | $^4I_{15/2}$ | 656.9 | $1447.83^{ED}$ | 0.898 | | |
| $^4S_{3/2} + {}^2H_{11/2}\rightarrow$ | $^4F_{9/2}$ | 2662 | $28.72^{ED} + 0.26^{MD}$ | 0.002 | 13407 | 0.075 |
| | $^4I_{9/2}$ | 1536 | $165.99^{ED} + 1.13^{MD}$ | 0.012 | | |
| | $^4I_{11/2}$ | 1139 | $117.13^{ED} + 14.11^{MD}$ | 0.011 | | |
| | $^4I_{13/2}$ | 807.9 | $544.87^{ED} + 117.77^{MD}$ | 0.049 | | |
| | $^4I_{15/2}$ | 526.9 | $12417.1^{ED}$ | 0.926 | | |
| $^4F_{7/2}\rightarrow$ | $^4S_{3/2} + {}^2H_{11/2}$ | 7547 | $0.91^{ED}$ | 0.000 | 3817 | 0.262 |
| | $^4F_{9/2}$ | 1968 | $7.53^{ED} + 19.60^{MD}$ | 0.007 | | |
| | $^4I_{9/2}$ | 1276 | $122.24^{ED} + 17.94^{MD}$ | 0.037 | | |
| | $^4I_{11/2}$ | 989.4 | $258.44^{ED}$ | 0.068 | | |
| | $^4I_{13/2}$ | 729.8 | $621.27^{ED}$ | 0.163 | | |
| | $^4I_{15/2}$ | 492.5 | $2769.2^{ED}$ | 0.725 | | |

[a] $<\lambda_{em}>$ – mean emission wavelength, ED – electric-dipole, MD – magnetic-dipole, $A$(JJ') – probability of spontaneous radiative transition, $B$(JJ') – luminescence branching ratio, $\tau_{rad}$ – radiative lifetime of an excited state. The $^4S_{3/2} + {}^2H_{11/2}$ levels are considered as thermally coupled.

**Table 4. Selected radiative lifetimes and luminescence branching ratios for $Er^{3+}$ Ions in cubic sesquioxide crystals (ICI model)**

| Crystal | $^4I_{13/2}$ $\tau_{rad}$, ms | $^4I_{11/2}$ $\tau_{rad}$, ms | $^4I_{11/2} \rightarrow {}^4I_{13/2}$ $B$(JJ'), % | $^4I_{13/2}$ (MD) $\tau_{rad}$, ms |
|---|---|---|---|---|
| Er:$Y_2O_3$ | 5.79 | 5.39 | 18.3 | 13.22 |
| Er:$Lu_2O_3$ | 5.74 | 4.96 | 16.7 | 13.86 |
| Er:$Sc_2O_3$ | 5.64 | 5.57 | 21.2 | 14.73 |

## 3. Experimental verification of the results of the Judd-Ofelt analysis

One possibility to estimate the ratio of $B$(JJ') and $\tau_{rad}$ by experimental methods, is to simultaneously use two independent methods for calculating the stimulated-emission cross-sections $\sigma_{SE}$, namely the Füchtbauer-Ladenburg (F-L) equation [15] and the reciprocity method (RM). This approach can be applied to any transition occurring between the ground-state and an excited-state, but for the particular case of sesquioxides, the presence of doping ions on the two sites $C_2$ and $C_{3i}$ may lead to wrong results. However, as explained above, for ions on $C_{3i}$ sites, only MD transitions are allowed. The MD-forbidden $^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition leading to emission around 1 μm is thus a good candidate to widely exclude the influence of ions on $C_{3i}$ sites. The

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Füchtbauer-Ladenburg equation is:

$$\sigma_{SE}(\lambda) = \frac{\lambda^5}{8\pi <n>^2 \tau_{rad} c} \frac{B(JJ')W'(\lambda)}{\int \lambda W'(\lambda) d\lambda}, \tag{10}$$

where, $\lambda$ is the light wavelength, $<n>$ is the refractive index at the mean emission wavelength $<\lambda_{em}>$, $\tau_{rad}$ is the radiative lifetime of the emitting state, $B$(JJ') is the luminescence branching ratio for the considered transition, and $W'(\lambda)$ is the luminescence spectrum corrected for the apparatus function of the set-up.

The SE cross-sections are calculated via the reciprocity method as:

$$\sigma_{SE}(\lambda) = \sigma_{abs}(\lambda) \frac{Z_1}{Z_2} \exp\left(-\frac{(hc/\lambda) - E_{ZPL}}{kT}\right), \tag{11}$$

$$Z_m = \sum_k g_k^m \exp(-E_k^m/kT). \tag{12}$$

Here, $k$ is the Boltzmann constant, $T$ is the temperature, $E_{ZPL}$ is the energy of the zero-phonon- line (ZPL) transition between the lowest Stark sub-levels of the involved multiplets (10192 $cm^{-1}$ [27]), $Z_m$ are the partition functions of the lower ($m = 1$) and upper ($m = 2$) manifold ($Z_1/Z_2 = 1.046$ [27]), and $g_k^m$ is the degeneracy of the Stark sub-level $k$ and energy $E_k^m$ relative to the lowest sub-level of each multiplet.

By comparing Eq. (10) and (11), one can estimate $B$(JJ')/$\tau_{rad}$. Such an analysis was performed for the $^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition of $Er^{3+}$ ions in $Lu_2O_3$, as shown in Fig. 3. Note that in the spectral range of strong overlap between absorption and emission, the luminescence intensity can decrease owing to reabsorption. This was widely avoided by applying the pinhole-method for the luminescence measurements [28–30]. For photon energies well above the ZPL energy, the reciprocity method yields strong noise due to the exponential term in Eq. (11). The best matching between the areas under the $\sigma_{SE}$ curves obtained using both methods was achieved for $B$(JJ')/$\tau_{rad} = 155 \pm 5$ $s^{-1}$.

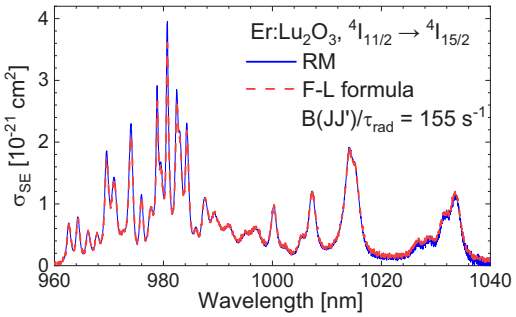


**Fig. 3.** Comparison of the stimulated-emission cross-sections $\sigma_{SE}$, for the $^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition of $Er^{3+}$ ions in $Lu_2O_3$, obtained using two methods (F-L and RM).

Considering the values of $\tau_{rad}(^4I_{11/2})$ of 4.96 ms and $B(^4I_{11/2} \rightarrow {}^4I_{15/2})$ of 0.833 obtained using the ICI model (see Table 4) for Er:$Lu_2O_3$, we achieve a $B$(JJ')/$\tau_{rad}$ of 169 $s^{-1}$, yielding a good agreement between the two approaches.

## 4. Luminescence lifetimes of $^4I_{11/2}$ and $^4I_{13/2}$ states of $Er^{3+}$ ions

Prior to the lifetime studies, we measured the Raman spectra of Er:$R_2O_3$ crystals. For the cubic sesquioxide crystals under investigation, the set of irreducible representations for the optical modes

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at the center of the Brillouin zone Γ ($\boldsymbol{k} = 0$) is $\Gamma_{op} = 4A_g + 4E_g + 14F_g + 5A_{2u} + 5E_u + 16F_u$, of which 22 modes ($A_g$, $E_g$ and $F_g$) are Raman-active, 16 modes ($F_u$) are IR-active and the rest are silent [31]. The dominant Raman peak seen in Fig. 4 is assigned to $A_g + F_g$ vibrations. Its peak energy depends on the cation in the sesquioxide matrix. While it is found at 377 $cm^{-1}$ in Er:$Y_2O_3$ its value increases to 390 $cm^{-1}$ in Er:$Lu_2O_3$ and 416 $cm^{-1}$ in Er:$Sc_2O_3$. The maximum phonon energy follows a similar trend: 593 $cm^{-1}$ (Er:$Y_2O_3$), 611 $cm^{-1}$ (Er:$Lu_2O_3$) and 666 $cm^{-1}$ (Er:$Sc_2O_3$). These values are in good agreement with the values reported for undoped cubic rare-earth sesquioxide crystals [31].

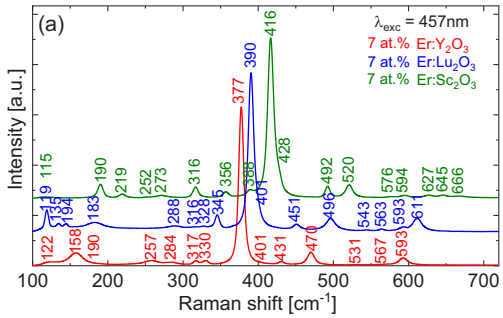


**Fig. 4.** Room-temperature unpolarized Raman spectra of 7 at.% $Er^{3+}$-doped sesquioxides, *numbers* – Raman peak energies in $cm^{-1}$, $\lambda_{exc} = 457$ nm.

The room-temperature (RT) luminescence lifetimes $\tau_{lum}$ of the $^4I_{11/2}$ and $^4I_{13/2}$ $Er^{3+}$ states in yttria, scandia and lutetia for two reference doping levels (1 at.% and 7 at.% $Er^{3+}$) are compared in Fig. 5. The values presented here were measured under resonant excitation using finely powdered ceramic samples to avoid the effect of reabsorption. For both considered multiplets, the luminescence lifetime values tend to increase from Er:$Sc_2O_3$ to Er:$Lu_2O_3$ and further to Er:$Y_2O_3$, and this trend is more evident for the $^4I_{11/2}$ level. Considering the difference in the phonon spectra of sesquioxides as depicted in Fig. 4, as well as the relatively similar radiative transition probabilities as derived by the J-O theory for these compounds, this variation is assigned to the effect of non-radiative multiphonon relaxation. Increasing the $Er^{3+}$ doping level from 1 at.% to 7 at.%, the $^4I_{13/2}$ luminescence lifetime is reduced while the $^4I_{11/2}$ lifetime remains almost unchanged. This is attributed to the previously mentioned concentration dependent energy-transfer upconversion (ETU) process $^4I_{13/2} + {}^4I_{13/2} \rightarrow {}^4I_{15/2} + {}^4I_{11/2}$. The resulting improved ratio of the nearly constant $^4I_{11/2}$ lifetime and the quenched $^4I_{13/2}$ is favorable for 2.85 µm lasers based on the transition between these multiplets.

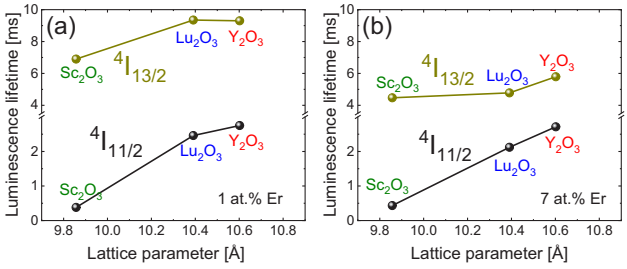


**Fig. 5.** Room-temperature luminescence lifetimes of the $^4I_{11/2}$ and $^4I_{13/2}$ multiplets of (a) 1 at.% and (b) 7 at.% $Er^{3+}$-doped sesquioxides. The solid lines are guides to the eye with no physical meaning.

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To explain the obvious difference between the luminescence and the radiative lifetimes of the $^4I_{11/2}$ and $^4I_{13/2}$ $Er^{3+}$ states in sesquioxides, we studied the luminescence dynamics at different temperatures from room temperature down to 10 K. To minimize the influence of reabsorption and concentration quenching, we used samples with the lowest available $Er^{3+}$ doping levels, *i.e.*, 0.3 at.% Er:$Y_2O_3$, 1.0 at.% Er:$Lu_2O_3$ and 0.3 at.% Er:$Sc_2O_3$.

First, we focused on the $^4I_{11/2}$ luminescence lifetimes. There are two emission channels from this state, the purely ED transition around 1 µm corresponding to the transition $^4I_{11/2} \rightarrow {}^4I_{15/2}$ and the 2.85 µm transition $^4I_{11/2} \rightarrow {}^4I_{13/2}$, which is ED and MD allowed with a strong MD component (see Table 3 and Table 4). Still, owing to the low luminescence branching ratio of the latter transition, the total MD contribution to the $^4I_{11/2}$ luminescence is very low. Thus, by looking at the $^4I_{11/2} \rightarrow {}^4I_{15/2}$ emission, we observe nearly exclusively the contribution of $Er^{3+}$ ions on $C_2$ sites. Consequently, the luminescence decay curves measured under resonant excitation have a nearly single-exponential nature at 10 K and RT, as shown in Fig. 6(a,b). Note the significant difference of the corresponding luminescence lifetimes between the different host materials attributed to the different rates of non-radiative multiphonon relaxation (see above). This behavior is preserved even at 10 K.

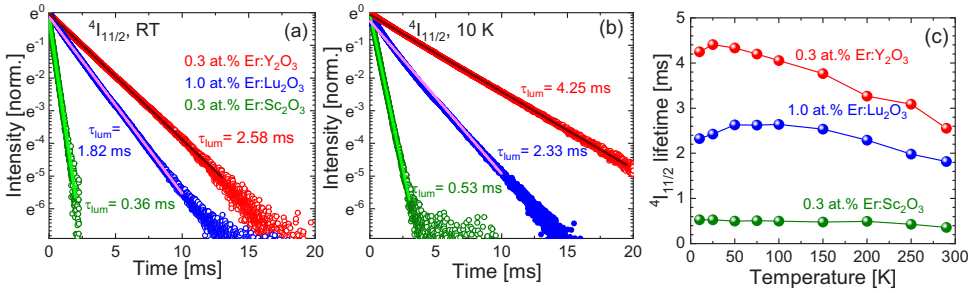


**Fig. 6.** (a,b) Luminescence decay curves of the $^4I_{11/2}$ multiplet of $Er^{3+}$-doped sesquioxides (a) at RT (290 K) and (b) 10 K, $\lambda_{exc}$ = 960 nm, $\lambda_{lum}$ = 1015 nm; the solid lines represent single exponential fits. (c) Temperature dependence of the luminescence lifetimes.

The temperature dependence of the $^4I_{11/2}$ luminescence lifetimes $\tau_{lum}$ for low-doped sesquioxides shown in Fig. 6 (c) shows a maximum reached at different temperatures, depending on the host matrix. For Er:$Y_2O_3$ featuring the lowest phonon energies, the luminescence lifetime increases from 2.58 ms at RT to 4.25 ms at 10 K with a maximum at 25 K. The 10-K value is approaching the corresponding RT radiative lifetime of 5.39 ms (cf. Table 4). For Er:$Lu_2O_3$ and Er:$Sc_2O_3$, the longest lifetimes of 2.64 ms and 0.53 ms achieved at 50 K and 10 K, respectively remain well below the radiative lifetimes of around 5 ms in Table 4, indicating significant non-radiative decay even at 10 K.

For luminescence starting from the lowest excited multiplet $^4I_{13/2}$, the only emission channel is $^4I_{13/2} \rightarrow {}^4I_{15/2}$. The corresponding transition is ED and MD allowed with a strong MD contribution as seen in Table 3. Thus, $Er^{3+}$ ions on both sites, $C_2$ and $C_{3i}$ contribute to the corresponding emission at 1.55 µm. With this in mind, we selected the excitation and emission wavelengths for the temperature dependent lifetime experiments to cover absorption and emission lines of $Er^{3+}$ ions on $C_2$ and $C_{3i}$ sites according to the crystal-field data given in [32] and applied a biexponential fit to the decay curves of this manifold, as shown in Fig. 7. As seen in Fig. 7 (a), the RT decay curve is hardly recognized as biexponential due to energy migration between the two sites at RT. In fact a biexponential fit would not yield reasonable results for the other two materials. Therefore, the values stated in Table 5 for the RT fluorescence lifetimes of the $^4I_{13/2}$ multiplet are based on single-exponential fits and thus averaged over both sites. Consequently, the corresponding decay curves were single exponential and are not shown here for brevity.

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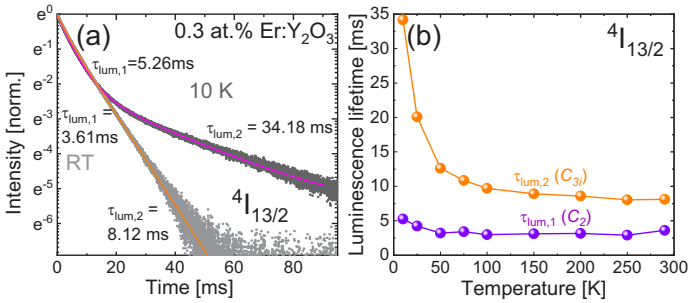


**Fig. 7.** Luminescence dynamics from the $^4I_{13/2}$ state of $Er^{3+}$ ions in 0.3 at.% Er:$Y_2O_3$: (a) luminescence decay curves at RT and 10 K, the solid lines represent biexponential fits to the data, $\lambda_{exc}$ = 1461 nm, $\lambda_{lum}$ = 1543 nm; (b) temperature dependence of the 'fast' and 'slow' component of the biexponential fit.

**Table 5. Luminescence and radiative lifetimes of the $^4I_{11/2}$ and $^4I_{13/2}$ $Er^{3+}$ energy levels in sesquioxides**

| $T$ | $^{2S+1}L_J$ | Method | Lifetime, ms | | |
|---|---|---|---|---|---|
| | | | Er:$Y_2O_3$ | Er:$Lu_2O_3$ | Er:$Sc_2O_3$ |
| RT | $^4I_{11/2}$ | $\tau_{lum}$ | 2.58 | 1.82 | 0.36 |
| | | $\tau_{rad}$, J-O | 5.39 | 4.96 | 5.57 |
| | $^4I_{13/2}$ | $<\tau_{lum}>$ | 7.08 | 7.07 | 6.27 |
| | | $\tau_{rad}$, J-O ($C_2$) | 5.79 | 5.74 | 5.64 |
| | | $\tau_{rad}$(MD), J-O ($C_{3i}$) | 13.22 | 13.86 | 14.73 |
| | | $<\tau_{rad}>$, J-O (¾:¼) | 6.73 | 6.72 | 6.67 |
| 10 K | $^4I_{11/2}$ | $\tau_{lum}$ | 4.25 | 2.33 | 0.53 |
| | $^4I_{13/2}$ | $\tau_{lum,1}$ ($C_2$) | 5.26 | - | - |
| | | $\tau_{lum,2}$ ($C_{3i}$) | 34.18 | - | - |

ED transitions are forbidden for ions on $C_{3i}$ sites. The corresponding radiative lifetime was thus calculated accounting only for the MD component of the transition probability. The corresponding radiative lifetime $\tau_{rad} = 1/A(JJ')^{MD}$ is shown in the last column of Table 4. Consequently, different radiative lifetimes for ions on $C_2$ sites exhibiting both ED and MD contributions and ions on $C_{3i}$ sites exhibiting pure MD transitions, are achieved. As expected, these values differ significantly; for Er:$Y_2O_3$, they amount to 5.79 ms and 13.2 ms, respectively. Consequently, the short and long component of the bi-exponential fits of the decay curves from the $^4I_{13/2}$ state can be assigned to $Er^{3+}$ ions on $C_2$ and $C_{3i}$ sites, respectively. For the case of 0.3 at.% Er:$Y_2O_3$ shown in Fig. 7(a,b) at RT, the fit yields 3.61 ms for the $C_2$ sites and 8.12 ms for the $C_{3i}$ sites, while at 10 K values of 5.26 ms for $C_2$ sites and 34.18 ms for $C_{3i}$ sites are obtained. It should be noted that the low temperature lifetime is mainly determined by transitions from the lower-lying Stark sub-levels of the $^4I_{13/2}$ multiplet, which can significantly differ from the radiative lifetime [33]. The value of 34 ms for the $C_{3i}$ site is thus not in contradiction to the value of 13 ms listed in Tab. 4.

Table 5 summarizes the luminescence and radiative lifetimes of the $^4I_{11/2}$ and $^4I_{13/2}$ multiplets of $Er^{3+}$ in low-doped sesquioxides. Our analysis reveals that the significant difference between the measured luminescence lifetime and the radiative lifetime derived from the absorption spectra originates from the presence of $Er^{3+}$ ions on $C_2$ and $C_{3i}$ sites, both significantly contributing to the ED and MD allowed $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission. Note that the Judd-Ofelt analysis for $Er^{3+}$ has a low sensitivity to the contribution of ions on $C_{3i}$ sites, because most of the considered transitions

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in absorption are MD forbidden and not influenced by ions on $C_{3i}$ sites. Thus, assuming ¾ of the $Er^{3+}$ ions being on $C_2$ sites and ¼ on $C_{3i}$ sites allows to calculate the 'effective' transition probability as $<A> = ¾A_{ED+MD}(C_2) + ¼A_{MD}(C_{3i})$, and the corresponding 'effective' radiative lifetime to be $<\tau_{rad}> = 1/<A>$. The resulting values are shown in Table 5 and are in good agreement with the measured room-temperature luminescence lifetimes $<\tau_{lum}>$.

We thus conclude, that despite the presence of two different sites for $Er^{3+}$ ions in cubic sesquioxides, the radiative lifetime of the $^4I_{11/2}$ state calculated via the Judd-Ofelt theory can be taken as a reliable value for further calculations of the effective stimulated-emission cross-sections. This is because most of the relevant transitions in $Er^{3+}$ ions are forbidden for ions on $C_{3i}$ sites and the $C_2$ sites considered by the J-O-theory mainly contribute also to emission from the $^4I_{11/2}$ multiplet. As for the $^4I_{13/2}$ level, we suggest that the 'effective' radiative lifetime $<\tau_{rad}>$ accounting for $Er^{3+}$ ions located in both the $C_2$ and $C_{3i}$ sites should be taken for calculating the stimulated-emission cross-sections at room temperature, where a strong energy exchange between the two ion ensembles prohibits the presence of emission from only one class of ions.

It is worth to note that at low temperatures the decay characteristics may strongly depend on the chosen excitation and detection wavelength. For $Er^{3+}$ ions in $Lu_2O_3$ and $Sc_2O_3$, no information about the Stark level energies for $C_{3i}$ sites is available. Thus, we were not yet successful in obtaining a full analysis of the temperature dependent luminescence dynamics starting from the $^4I_{13/2}$ multiplet for these materials.

## 5. Stimulated emission cross-sections

The $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition terminates at the ground state and as a consequence the corresponding emission at 1.55 µm is subject to reabsorption. Thus, for the calculation of the

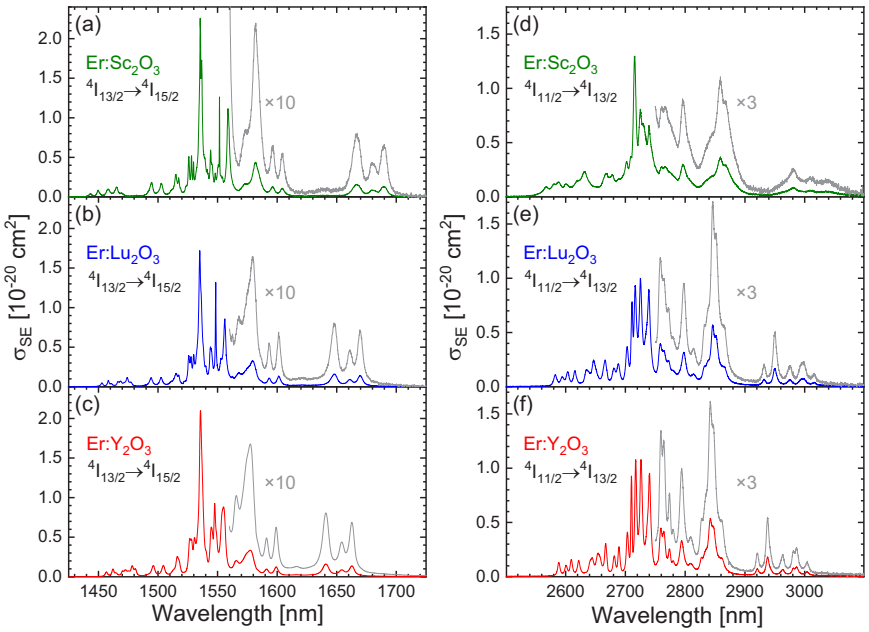


**Fig. 8.** Stimulated-emission (SE) cross-sections, $\sigma_{SE}$, for $Er^{3+}$ in sesquioxide crystals: (a-c) the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition; (d-f) the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition. For better visibility the cross sections in the longer wavelength range are also shown multiplied by a factor of 10 (a-c) and 3 (d-e).

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stimulated-emission cross-sections, we used two complementary methods: the reciprocity method (Eq. (10) [18]) based on the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ absorption cross-sections shown in Fig. 2(h), and the experimental crystal-field splitting of $Er^{3+}$ ions on $C_2$ sites, and the F-L equation (Eq. (11), (12)) [34] based on the measured luminescence spectra. Using the effective luminescence lifetime $<\tau_{rad}>$ stated in Table 5 in the F-L equation, we get an excellent agreement of both methods. The results are shown in Fig. 8(a) for the three studied $Er^{3+}$-doped sesquioxide crystals. The stimulated-emission cross-sections in the long wavelength spectral range, where laser operation is expected due to the quasi-three-level laser scheme with reabsorption, peak at $1.61 \times 10^{-21}$ cm$^2$ at 1641 nm for Er:$Y_2O_3$, $1.60 \times 10^{-21}$ cm$^2$ at 1647 nm for Er:$Lu_2O_3$, and $1.58 \times 10^{-21}$ cm$^2$ at 1667 nm for Er:$Sc_2O_3$.

For the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition at 2.85 µm, only the F-L formula was applied using the $\tau_{rad}$ and B(JJ') values obtained from the J-O analysis. In the range of expected laser wavelengths, we found stimulated-emission cross-sections of $5.36 \times 10^{-21}$ cm$^2$ at 2842 nm for Er:$Y_2O_3$, $5.67 \times 10^{-21}$ cm$^2$ at 2845 nm Er:$Lu_2O_3$, and $3.57 \times 10^{-21}$ cm$^2$ at 2857 nm for Er:$Sc_2O_3$. The emission of Er:$Sc_2O_3$ covers a wider wavelength range than those of $Er^{3+}$ ions in $Lu_2O_3$ and $Y_2O_3$, due to a stronger crystal field which is resulting in a larger Stark splitting of the manifolds. This allows for lasing on longer wavelengths in comparison to materials with lower crystal field strengths.

## 6. Conclusion

In this work, we revisited the spectroscopic properties of three $Er^{3+}$-doped cubic sesquioxides, $Y_2O_3$, $Lu_2O_3$, and $Sc_2O_3$. The transition probabilities for $Er^{3+}$ ions were calculated using the Judd-Ofelt theory accounting for the intermediate configuration interaction (ICI) based on the measured absorption cross-sections. To justify the obtained data on the radiative lifetimes of the $^4I_{11/2}$ and $^4I_{13/2}$ $Er^{3+}$ states, we performed a detailed study of luminescence dynamics from these manifolds at different temperatures.

For the $^4I_{11/2}$ state, the luminescence lifetime both at RT and even at 10 K strongly depends on the host-forming cation in the sesquioxide matrix owing to a different rate of non-radiative multiphonon relaxation associated to a difference in the phonon spectra of sesquioxides. $Y_2O_3$ features the lowest phonon energies leading to the longest $^4I_{11/2}$ luminescence lifetime. The radiative lifetime of this level obtained via the Judd-Ofelt theory is assigned to $Er^{3+}$ ions on $C_2$ sites. Consequently, the radiative lifetimes and branching ratios calculated by the J-O-theory enabled to calculate reliable emission cross sections in the wavelength range of 2.85 µm for the first time for Er:$Y_2O_3$, Er:$Lu_2O_3$ and Er:$Sc_2O_3$.

For the $^4I_{13/2}$ state, the transitions in absorption and emission are both ED and MD allowed and thus $Er^{3+}$ ions residing on both $C_2$ and $C_{3i}$ sites contribute to these processes. This is indeed confirmed in the present work by observing a biexponential decay from the $^4I_{13/2}$ manifold at different temperatures. The fast and slow time components of this decay are assigned to ions in $C_2$ and $C_{3i}$ sites, respectively. The calculation of the radiative lifetime of the $^4I_{13/2}$ manifold by the Judd-Ofelt theory based on the measured absorption spectra yields a value being much shorter than the measured intrinsic luminescence lifetime at RT for samples doped with 1 at.% $Er^{3+}$ or less. It is also shorter than the estimated radiative lifetime achieved from the comparison of the stimulated-emission cross-sections calculated by two different methods (F-L and RM). This difference is resolved by considering the contributions of $Er^{3+}$ ions on $C_2$ and $C_{3i}$ sites, *i.e.*, by calculating an 'effective' average radiative lifetime weighted by the occurrence of these sites. The use of this 'effective' radiative lifetime enabled to calculate stimulated-emission cross-sections for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition by the Füchtbauer-Ladenburg method, which are in excellent agreement with those obtained from the absorption spectra by the reciprocity method.

The results obtained in this work will be of high relevance for the design, operation and further power scaling of 2.85-µm lasers based on $Er^{3+}$-doped sesquioxide gain materials.

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## Appendix A. Sample preparation and experimental methods

### Synthesis of samples

The single-crystals of $Er^{3+}$-doped sesquioxides $R_2O_3$ (R = Y, Lu, Sc) used in the experiments performed for this work were grown by the heat exchanger method (HEM) employing rhenium (Re) crucibles in a closed setup. The starting materials (rare-earth oxides, 5N purity) were thoroughly mixed and filled into a crucible on top of a seed crystal placed in the Re crucible's appendix. The inductively heated crucible was kept in an isothermal insulation setup. The required temperature gradient for directed crystallization was ensured by a controlled flow of the cooling gas from the bottom of the crucible. By slowly reducing the heating power, the whole melt crystallized successively. More details can be found in [35].

For the absorption measurements, we used three $Er^{3+}$-doped single-crystals, $Y_2O_3$, $Lu_2O_3$ and $Sc_2O_3$. The actual $Er^{3+}$ doping levels were determined by the X-ray fluorescence (XRF) method using a Bruker M4 Tornado spectrometer, to be 15.9 at.% Er:$Y_2O_3$, 12.5 at.% Er:$Lu_2O_3$ and 3.5 at.% Er:$Sc_2O_3$. The corresponding $Er^{3+}$ ion densities $N_{Er}$ were $0.427 \times 10^{22}\,cm^{-3}$, $0.428 \times 10^{22}\,cm^{-3}$ and $0.117 \times 10^{22}\,cm^{-3}$, respectively.

In addition, for luminescence lifetime studies, we used two low-doped crystals, 0.3 at.% Er:$Y_2O_3$ and 0.3 at.% Er:$Sc_2O_3$ and a 1 at.% Er:$Lu_2O_3$ ceramic sample.

For measuring the concentration-dependent luminescence lifetimes of $Er^{3+}$ ions, we used a set of transparent sesquioxide ceramics with 1 at.% and 7 at.% $Er^{3+}$ doping. The ceramics were prepared by hot pressing of nanopowders. Commercial rare-earth oxide powders (4N purity) were dissolved in nitric acid (6N) and mixed in the given ratios. We added glycine (3N) in a molar ratio of 1:1 with respect to the nitrate groups and 1 wt.% of LiF (3N) with respect to the oxide powder acting as a sintering aid. The precursors were placed in a furnace preheated to 500 °C, resulting in the synthesis of $Er^{3+}$-doped sesquioxide nanopowders. These were placed in a graphite mold and hot pressed under 50 MPa at a temperature of 1500 °C for Er:$Y_2O_3$ or 1600 °C for Er:$Sc_2O_3$ and Er:$Lu_2O_3$ for 1 h under a vacuum of about 10 Pa. The ceramics were then annealed in air at 900 °C for 5 h.

### Experimental methods

The room-temperature (RT, 290 K) transmission spectra of $Er^{3+}$-doped sesquioxide crystals were measured in the wavelength range between 270 and 1700nm using a Perkin Elmer Lambda 1050 spectrometer. The spectral bandwidth (SBW) was 0.04–0.1 nm, depending on the spectral range and required resolution. The absorption cross-sections were calculated as $\sigma_{abs} = \alpha_{abs}/N_{Er}$, where $\alpha_{abs}$ is the absorption coefficient calculated via the Beer-Lambert law.

The RT Raman spectra were measured using a Renishaw InVia confocal laser microscope equipped with an $Ar^+$ ion laser (458 nm) and a 50× Leica objective.

The luminescence dynamics were studied by employing an optical parametric oscillator (GWU versaScan) pumped by a frequency tripled 10-Hz, 5-ns $Nd^{3+}$-laser (Spectra-Physics Quanta-Ray) as the excitation source, a 1 m monochromator (Horiba 1000 M Series II) and a near-infrared photomultiplier module (Hamamatsu NIR-PMT H10330A-75) as well as a 2 GHz digital oscilloscope (Rohde&Schwarz RTE 1204). For low-temperature studies, the samples were mounted in a closed-cycle helium cryostat (Advanced Research Systems DE-204P).

The luminescence spectra were measured using a cw Ti:sapphire laser (3900S, Spectra Physics) as an excitation source and optical spectrum analyzers (Yokogawa AQ6376 and AQ6375B) using a $ZrF_4$ fiber for light collection.

For Er:$Y_2O_3$ and Er:$Lu_2O_3$ crystals, the gradient of $Er^{3+}$ doping across the studied samples was found to be low and the segregation coefficient $K_{Er} = C_{crystal}/C_{melt}$ was close to unity. In contrast, for $Sc_2O_3$, we observed a strong gradient of the dopant ion concentration, which is explained by the large difference of the ionic radii of $Er^{3+}$ (0.89 Å) and $Sc^{3+}$ (0.75 Å) [36] in

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the sixfold oxygen coordination. Figure 9 shows a photograph of a 0.3 at.% Er:$Sc_2O_3$ sample (doping level in the melt) used for the low temperature luminescence lifetime studies and the corresponding spatial distribution of the $Er^{3+}$ doping ions determined by XRF. The bottom part of the sample shown in this figure corresponds to the beginning of crystallization during the crystal growth and its upper part to the end of the crystal growth. A strong gradient of the actual $Er^{3+}$ doping level from less than 0.1 at.% in the bottom part up to 0.35 at.% in the upper part is observed. By fitting these data with the Scheil equation [37], we estimated the segregation coefficient $K_{Er}$ of about 0.35 in good agreement with the previous data [38]. A similar analysis was performed for the Er:$Sc_2O_3$ sample used for absorption studies resulting in a nearly identical $K_{Er}$ value. For calculating the absorption cross-sections for $Er^{3+}$ ions in $Sc_2O_3$, the average $Er^{3+}$ doping level in the region of the transmitted light beam was then used.

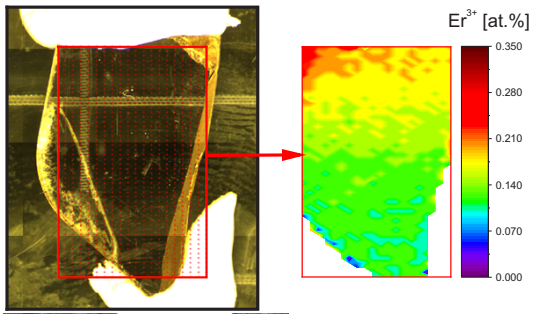


**Fig. A1.** Spatial distribution of dopant $Er^{3+}$ ions across a 0.3 at.% Er:$Sc_2O_3$ crystal (doping level in the melt) determined by XRF analysis: the left image shows a photography of the sample; the grid shows the points on which the high resolution compositional analysis was performed and the red rectangle marks the full analyzed area of $8.37 \times 12.87$ mm$^2$; the right side shows the results of the $Er^{3+}$ element mapping.

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**Disclosures.** The authors declare no conflicts of interest.

**Data availability.** Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

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