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Anastasia Uvarova, Pavel Loiko, Sascha Kalusniak, Elena Dunina, Liudmila Fomicheva, et al.. Stimulated-emission cross-sections of trivalent erbium ions in the cubic sesquioxides Y_2O_3 , Lu_2O_3 , and Sc_2O_3 . *Optical Materials Express*, 2023, 13 (5), pp.1385. 10.1364/OME.487909 . hal-04209395

HAL Id: hal-04209395

<https://hal.science/hal-04209395>

Submitted on 2 Nov 2023

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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 ($\text{R} = \text{Y}, \text{Lu}$ 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 ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{13/2}$ (at $\sim 2.8 \mu\text{m}$) and ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ (at $\sim 1.6 \mu\text{m}$) transitions of Er^{3+} ions are determined and the luminescence dynamics from the ${}^4\text{I}_{11/2}$ and ${}^4\text{I}_{13/2}$ manifolds are studied at different temperatures. It is found that the luminescence lifetime of the ${}^4\text{I}_{11/2}$ state strongly depends on the host-forming R^{3+} cation even at low temperatures due to a non-negligible non-radiative multiphonon decay channel. $\text{Er}:\text{Y}_2\text{O}_3$ exhibits the lowest phonon energies and consequently the longest ${}^4\text{I}_{11/2}$ luminescence lifetimes. A disagreement between the absorption and emission probabilities for the ${}^4\text{I}_{15/2} \leftrightarrow {}^4\text{I}_{11/2}$ 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} .

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1. Introduction

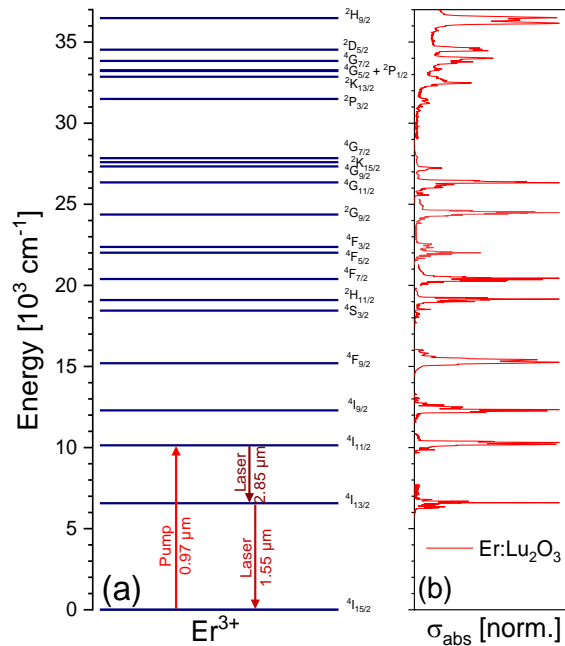
Trivalent erbium ions (Er^{3+}) possess the electronic configuration $[\text{Xe}]4f^{11}$ with the ground-state ${}^4\text{I}_{15/2}$. They feature a complex and dense energy level scheme allowing for multiple emission lines in the visible, near and mid-infrared spectral ranges, as well as efficient energy-transfer processes. As shown in Fig. 1, the two most commonly exploited laser transitions of Er^{3+} ions are the transitions ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ at wavelengths around $1.55 \mu\text{m}$ and ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{13/2}$ at wavelengths around $2.85 \mu\text{m}$. 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 $3 \mu\text{m}$ 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 $12 \text{ W m}^{-1}\text{K}^{-1}$ 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} [6] are moderate for oxide materials leading to reduced non-radiative multiphonon relaxation [7] in particular for transitions from the ${}^4\text{I}_{11/2}$ manifold. Finally, they exhibit strong

47 crystal-fields for the dopant Er^{3+} ions leading to broad emission spectra. Isostructural
 48 substitutional solid-solutions are formed in the $\text{R}_2\text{O}_3 - \text{Er}_2\text{O}_3$ binary systems allowing for the
 49 formation of cubic sesquioxides even at Er^{3+} high doping levels. The latter is relevant for the
 50 development of $2.8 \mu\text{m}$ lasers as high Er^{3+} doping concentrations strongly increase the
 51 probability for energy-transfer upconversion from the metastable terminal laser level $^4\text{I}_{13/2}$,
 52 avoiding high population of this level which may otherwise lead to self-termination of lasers
 53 based on the $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ transition [8].

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

58 Highly-efficient and power-scalable crystalline and ceramic Er^{3+} -doped sesquioxide lasers
 59 operating on the $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ transition are known. Li *et al.* reported on a crystalline $\text{Er}:\text{Lu}_2\text{O}_3$
 60 laser pumped by an optically pumped semiconductor laser delivering 1.4 W at $2.85 \mu\text{m}$ with a
 61 slope efficiency as high as 36% . Under diode-pumping, the output was scaled up to 5.9 W at
 62 the expense of a reduced slope efficiency of 27% [11]. Yao *et al.* developed a diode-pumped
 63 $\text{Er}:\text{Lu}_2\text{O}_3$ ceramic laser generating 6.7 W at $2.85 \mu\text{m}$ with a slope efficiency of 30.2% [9] and
 64 more recently, a diode-pumped $\text{Er}:\text{Y}_2\text{O}_3$ ceramic laser enabled an output power of 13.4 W at
 65 $2.7 \mu\text{m}$ at room temperature [12]. By operation at cryogenic temperatures, even higher output
 66 power levels are feasible at $2.85 \mu\text{m}$ [13].



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Fig. 1. (a) Energy level scheme [14] of Er^{3+} ions showing laser transitions at $1.6 \mu\text{m}$ and $2.8 \mu\text{m}$ 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.

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Despite their wide use in lasers, the spectroscopic properties of Er^{3+} -doped sesquioxides, and, in particular, the transition probabilities at $2.85 \mu\text{m}$, remain not completely understood. There 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 τ_{rad} of the emitting level. In cases where more

77 than one terminal level for the emission exists, the luminescence branching ratio $B(JJ')$ for each
 78 transition $J \rightarrow J'$ needs to be determined. τ_{rad} and $B(JJ')$ are often obtained using theoretical
 79 calculations for f-f transition intensities known as Judd-Ofelt theory [16, 17]. Another approach
 80 relies on the reciprocity method (RM) known as McCumber equation [18, 19], using Einstein's
 81 theory of equal transition probabilities for absorption and emission between two Stark levels
 82 [20].

83 One of the main challenges for determining the spectroscopic properties of rare-earth ions
 84 in cubic sesquioxides is a disagreement between the experimental absorption and emission
 85 probabilities for certain optical transitions. It was suggested that such a disagreement may
 86 originate from different oscillator strengths for rare-earth ions incorporated on two non-
 87 equivalent sites in the cubic bixbyite structure [21], having the symmetries C_2 and C_{3i}
 88 (Wyckoff: $24d$ and $8b$, respectively) and a sixfold oxygen coordination. The unit-cell of cubic
 89 sesquioxide crystals contains 32 cation sites and for an ideal structure, 3/4 of the cations occupy
 90 C_2 sites and 1/4 occupies C_{3i} sites. This proportion is expected to hold also for rare-earth doping
 91 ions. **Theoretical models suggest a deviation from this behavior at room-temperature for**
 92 **Er:Sc₂O₃ [22], but these models are not valid at the high growth temperatures of this material**
 93 **and due to the low mobility of cations at room temperature, the random distribution at high**
 94 **temperatures can be expected to be maintained at room temperature.** Due to the presence of a
 95 center of inversion, electric dipole (ED) transitions are forbidden for rare-earth ions residing on
 96 C_{3i} sites. Still, these ions can contribute to transition intensities with a magnetic dipole (MD)
 97 component, *i.e.*, $J \leftrightarrow J'$ transitions with $\Delta J = 0, \pm 1$ (except for $0 \leftrightarrow 0'$). Note that both the ${}^4I_{11/2}$
 98 $\leftrightarrow {}^4I_{13/2}$ as well as the ${}^4I_{13/2} \leftrightarrow {}^4I_{15/2}$ transition are ED and MD allowed while the transition ${}^4I_{11/2}$
 99 $\leftrightarrow {}^4I_{15/2}$ is MD forbidden due to $\Delta J = 2$.

100 To determine the stimulated-emission cross-sections of Er³⁺ ions in cubic sesquioxides, we
 101 performed a comparative study of the absorption and emission probabilities for the three cubic
 102 sesquioxides yttria (Y₂O₃), lutetia (Lu₂O₃) and scandia (Sc₂O₃). This study involved the Judd-
 103 Ofelt analysis, the measurement of the absorption and emission spectra, as well as the
 104 luminescence dynamics as a function of temperature. Even though the three studied compounds
 105 are isostructural, they exhibit significantly different properties in terms of the lattice parameter
 106 and phonon energies, which is explained by the different sizes and masses of the host-forming
 107 cations. This also leads to a strong variation of the spectroscopic parameters within this host
 108 crystal family.

109 2. Absorption spectra and Judd-Ofelt analysis

110 Figure 2 shows the absorption cross-section spectra for Er³⁺ ions in Y₂O₃, Lu₂O₃ and Sc₂O₃
 111 crystals. For the ${}^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition which is commonly used for pumping of mid-infrared
 112 Er³⁺ lasers, the peak absorption cross sections amount to $0.35 \times 10^{-20} \text{ cm}^2$ at 974.2 nm,
 113 $0.30 \times 10^{-20} \text{ cm}^2$ at 980.7 nm, and $0.33 \times 10^{-20} \text{ cm}^2$ at 979.3 nm, respectively.

114 Based on these data, the transition intensities of Er³⁺ ions in the three sesquioxide crystals
 115 were determined using the Judd-Ofelt formalism [16, 17]. The experimental absorption
 116 oscillator strengths f_{exp} were calculated as:

$$117 \quad f_{\text{exp}}(JJ') = \frac{m_e c^2}{\pi e^2 \langle \lambda \rangle^2} \Gamma(JJ'), \quad (1)$$

118 where m_e and e are the electron mass and charge, respectively, c is the speed of light, $\Gamma(JJ')$ is
 119 the integrated absorption cross-section within the absorption band for the $J \rightarrow J'$ transition, and
 120 $\langle \lambda \rangle$ is the wavelength corresponding to the barycenter of the absorption band. The experimental
 121 absorption oscillator strengths f_{exp} and the values f_{calc} calculated by three different approaches
 122 detailed below are given in Table 1 for the example of Er:Lu₂O₃.

123

Table 1. Experimental and calculated absorption oscillator strengths for Er³⁺ ions in Lu₂O₃

$^4I_{15/2} \rightarrow ^{2S+1}L_J$	E_J , cm ⁻¹	Γ , 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}
$^4G_{11/2} + ^2K_{15/2}$	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

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E_J – experimental barycenter energy of the multiplet, Γ – 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} .

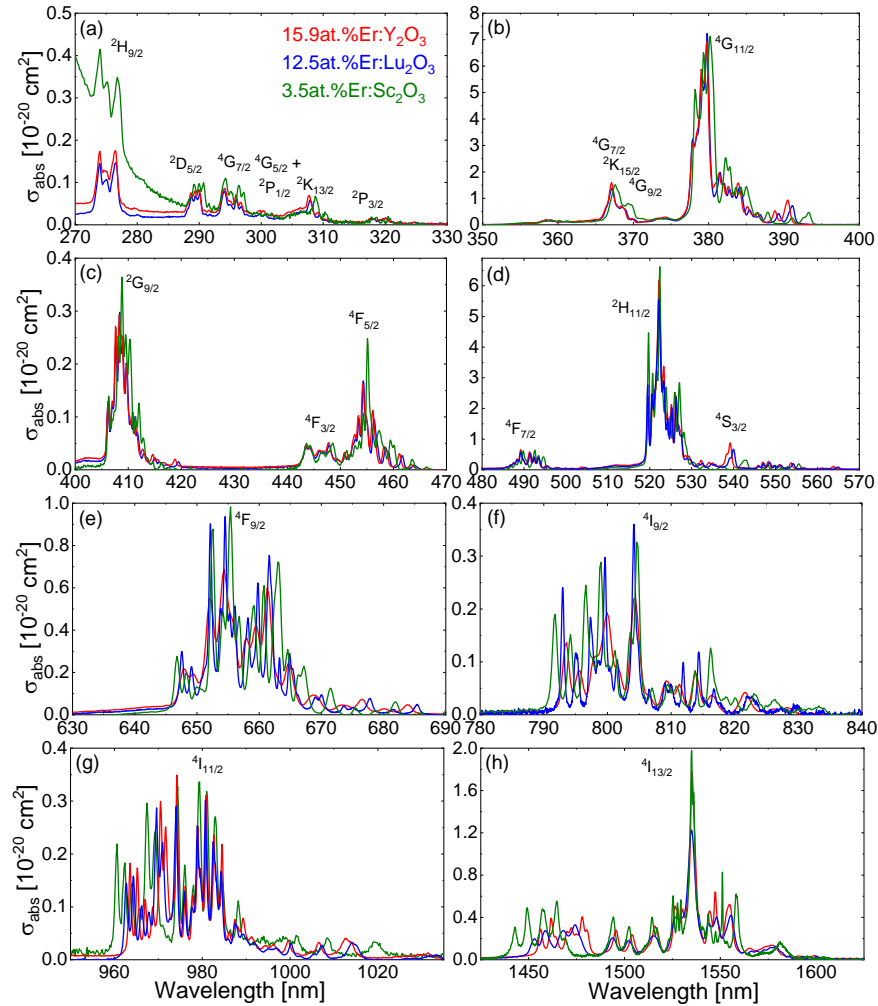
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Fig. 2. (a-h) Ground-state absorption cross-sections σ_{abs} of Er³⁺ ions in Y₂O₃, Lu₂O₃ and Sc₂O₃ crystals for the energy levels shown in Fig. 1. The UV absorption background for Er:Sc₂O₃ in (a) is attributed to color centers and was subtracted for the J-O-calculations.

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

$$135 \quad f_{\text{calc}}^{\text{ED}}(JJ') = \frac{8}{3h(2J'+1)\langle\lambda\rangle} \frac{(\langle n \rangle^2 + 2)^2}{9n} S_{\text{calc}}^{\text{ED}}(JJ'), \quad (2)$$

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

138 Three different models were applied to calculate the ED contributions to the line strengths
 139 of f-f transitions of Er^{3+} ions, (i) the standard Judd-Ofelt (J-O) theory and two modifications
 140 accounting for configuration interaction, (ii) the modified Judd-Ofelt theory (mJ-O) and (iii)
 141 the approximation of an intermediate configuration interaction (ICI) [24, 25]. The contributions
 142 of magnetic-dipole (MD) transitions were calculated independently within the Russell-
 143 Saunders approximation on wave functions of Er^{3+} under the assumption of a free-ion.

144 For the standard J-O theory, the ED line strengths for a transition $J \rightarrow J'$ are:

$$145 \quad S_{\text{calc}}^{\text{ED}}(JJ') = \sum_{k=2,4,6} U^{(k)} \Omega_k, \quad (3a)$$

$$146 \quad U^{(k)} = \langle (4f^n)SLJ || U^{(k)} || (4f^n)S'L'J' \rangle^2. \quad (3b)$$

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

149 In the ICI approximation, the ED line strengths become

$$150 \quad S_{\text{calc}}^{\text{ED}}(JJ') = \sum_{k=2,4,6} U^{(k)} \tilde{\Omega}_k, \quad (4a)$$

$$151 \quad \tilde{\Omega}_k = \Omega_k [1 + 2R_k(E_J + E_{J'} - 2E_f^0)], \quad (4b)$$

152 where the intensity parameters $\tilde{\Omega}_k$ depend linearly on the energies E_J and $E_{J'}$ of the two
 153 multiplets involved in the transition, E_f^0 has the meaning of the average energy of the $4f^{11} \text{Er}^{3+}$
 154 configuration, and R_k ($k = 2, 4, 6$) are the parameters representing the configuration interaction.
 155 Consequently, there are six free parameters, namely Ω_k and R_k for $k = 2, 4,$ and 6 , each.

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

$$158 \quad \tilde{\Omega}_k = \Omega_k [1 + 2\alpha(E_J + E_{J'} - 2E_f^0)]. \quad (5)$$

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

163 The absorption oscillator strengths for Er^{3+} ions in sesquioxides were calculated using all
 164 three above-mentioned models. The root mean square (r.m.s.) deviation between f_{exp} and f_{calc}
 165 (ED + MD) values was determined, as shown in Table 1 for the case of $\text{Er}:\text{Lu}_2\text{O}_3$. The ICI
 166 model provides the lowest r.m.s. deviation and the best agreement between the experimental
 167 and calculated transition intensities for the $^4I_{13/2}$ and $^4I_{11/2}$ excited states. Thus, it was selected
 168 for further calculations.

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

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173 **Table 2. Intensity parameters for Er³⁺ ions in cubic sesquioxide host materials (J-O and ICI models)**

Parameter	Y ₂ O ₃		Lu ₂ O ₃		Sc ₂ O ₃	
	J-O	ICI	J-O	ICI	J-O	ICI
Ω ₂ , 10 ⁻²⁰ cm ²	4.520	4.478	4.933	5.115	4.626	4.309
Ω ₄ , 10 ⁻²⁰ cm ²	1.313	1.511	0.635	1.042	2.306	1.721
Ω 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

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

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$$A_{\Sigma}^{calc}(JJ') = \frac{64\pi^4 e^2}{3h(2J'+1)\langle\lambda\rangle^3} n \left(\frac{n^2+2}{3} \right)^2 S_{ED}^{calc}(JJ') + A_{MD}(JJ'). \quad (6)$$

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

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$$\tau_{rad} = \frac{1}{A_{tot}^{calc}}, \text{ where } A_{tot}^{calc} = \sum_{J'} A_{\Sigma}^{calc}(JJ'), \text{ and } B(JJ') = \frac{A_{\Sigma}^{calc}(JJ')}{\sum_{J'} A_{\Sigma}^{calc}(JJ')}. \quad (7)$$

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The results on the transition probabilities in emission for Er³⁺:Lu₂O₃ are shown in Table 3.

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Table 3. Probabilities of spontaneous radiative transitions of Er³⁺ ions in Lu₂O₃ (ICI model)

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

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

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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} → 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} → ⁴I_{13/2} and ⁴I_{13/2} → ⁴I_{15/2} transitions of Er³⁺ ions in these hosts as well as the interpretation of the results of the measurements of the luminescence dynamics.

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Table 4. Selected radiative lifetimes and luminescence branching ratios for Er³⁺ ions in cubic sesquioxide crystals (ICI model)

Crystal	⁴ I _{13/2} τ _{rad} , ms	⁴ I _{11/2} τ _{rad} , ms	⁴ I _{11/2} → ⁴ I _{13/2} B(JJ'), %	⁴ I _{13/2} (MD) τ _{rad} , ms
Er:Y ₂ O ₃	5.79	5.39	18.3	13.22
Er:Lu ₂ O ₃	5.74	4.96	16.7	13.86
Er:Sc ₂ O ₃	5.64	5.57	21.2	14.73

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

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

$$205 \sigma_{\text{SE}}(\lambda) = \frac{\lambda^5}{8\pi \langle n \rangle^2 \tau_{\text{rad}} c} \frac{B(JJ')W'(\lambda)}{\int \lambda W(\lambda) d\lambda}, \quad (8)$$

206 where, λ is the light wavelength, $\langle n \rangle$ is the refractive index at the mean emission wavelength
207 $\langle \lambda_{\text{em}} \rangle$, τ_{rad} is the radiative lifetime of the emitting state, $B(JJ')$ is the luminescence branching
208 ratio for the considered transition, and $W(\lambda)$ is the luminescence spectrum corrected for the
209 apparatus function of the set-up.

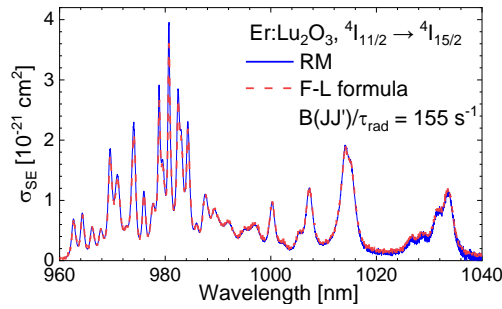
210 The SE cross-sections are calculated via the reciprocity method as:

$$211 \sigma_{\text{SE}}(\lambda) = \sigma_{\text{abs}}(\lambda) \frac{Z_1}{Z_2} \exp\left(-\frac{(hc/\lambda) - E_{\text{ZPL}}}{kT}\right), \quad (9a)$$

$$212 Z_m = \sum_k g_k^m \exp(-E_k^m / kT). \quad (9b)$$

213 Here, k is the Boltzmann constant, T is the temperature, E_{ZPL} is the energy of the zero-phonon-
214 line (ZPL) transition between the lowest Stark sub-levels of the involved multiplets (10192 cm^{-1}
215 [27]), Z_m are the partition functions of the lower ($m = 1$) and upper ($m = 2$) manifold ($Z_1/Z_2 =$
216 1.046 [27]), and g_k^m is the degeneracy of the Stark sub-level k and energy E_k^m relative to the
217 lowest sub-level of each multiplet.

218 By comparing Eq. (8) and (9a), one can estimate $B(JJ')/\tau_{\text{rad}}$. Such an analysis was performed
219 for the ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition of Er³⁺ ions in Lu₂O₃, as shown in Fig. 3. Note that in the spectral
220 range of strong overlap between absorption and emission, the luminescence intensity can
221 decrease owing to reabsorption. This was widely avoided by applying the pinhole-method for
222 the luminescence measurements [28-30]. For photon energies well above the ZPL energy, the
223 reciprocity method yields strong noise due to the exponential term in Eq. (9a). The best
224 matching between the areas under the σ_{SE} curves obtained using both methods was achieved
225 for $B(JJ')/\tau_{\text{rad}} = 155 \pm 5 \text{ s}^{-1}$.



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Fig. 3. Comparison of the stimulated-emission cross-sections σ_{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).

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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.

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

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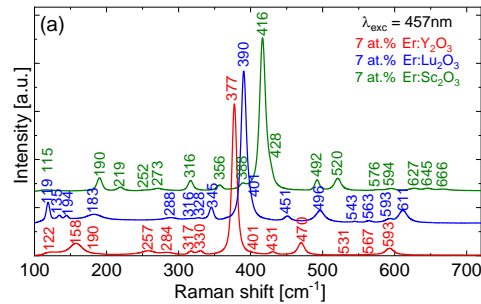
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Prior to the lifetime studies, we measured the Raman spectra of $Er:R_2O_3$ crystals. For the cubic sesquioxide crystals under investigation, the set of irreducible representations for the optical modes at the center of the Brillouin zone Γ ($\mathbf{k} = 0$) 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].



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

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The room-temperature (RT) luminescence lifetimes τ_{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

258 energy-transfer upconversion (ETU) process ${}^4I_{13/2} + {}^4I_{13/2} \rightarrow {}^4I_{15/2} + {}^4I_{11/2}$. The resulting
 259 improved ratio of the nearly constant ${}^4I_{11/2}$ lifetime and the quenched ${}^4I_{13/2}$ is favorable for
 260 2.85 μm lasers based on the transition between these multiplets.

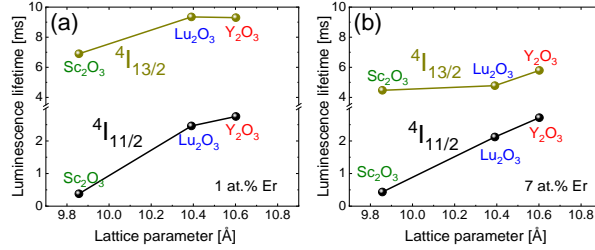


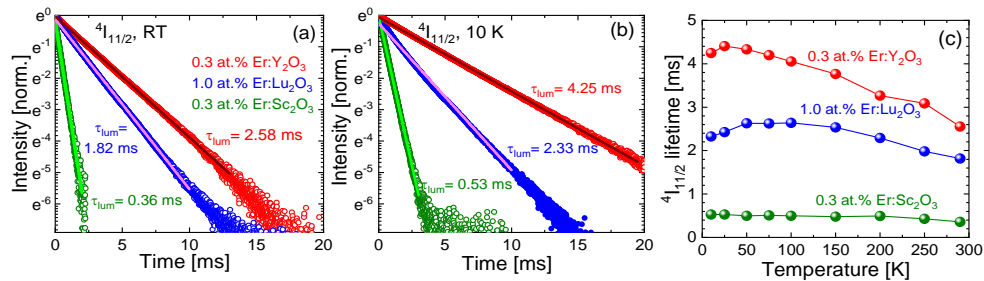
Fig. 5. Room temperature luminescence lifetimes of the ${}^4I_{11/2}$ and ${}^4I_{13/2}$ multiplets of (a) 1 at.% and (b) 7 at.% Er^{3+} -doped sesquioxides. The solid lines are guides to the eye with no physical meaning.

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265 To explain the obvious difference between the luminescence and the radiative lifetimes of
 266 the ${}^4I_{11/2}$ and ${}^4I_{13/2}$ Er^{3+} states in sesquioxides, we studied the luminescence dynamics at different
 267 temperatures from room temperature down to 10 K. To minimize the influence of reabsorption
 268 and concentration quenching, we used samples with the lowest available Er^{3+} doping levels,
 269 *i.e.*, 0.3 at.% $\text{Er}:\text{Y}_2\text{O}_3$, 1.0 at.% $\text{Er}:\text{Lu}_2\text{O}_3$ and 0.3 at.% $\text{Er}:\text{Sc}_2\text{O}_3$.

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

281 The temperature dependence of the ${}^4I_{11/2}$ luminescence lifetimes τ_{lum} for low-doped
 282 sesquioxides shown in Fig. 6 (c) shows a maximum reached at different temperatures,
 283 depending on the host matrix. For $\text{Er}:\text{Y}_2\text{O}_3$ featuring the lowest phonon energies, the
 284 luminescence lifetime increases from 2.58 ms at RT to 4.25 ms at 10 K with a maximum at
 285 25 K. The 10-K value is approaching the corresponding RT radiative lifetime of 5.39 ms (cf.
 286 Table 4). For $\text{Er}:\text{Lu}_2\text{O}_3$ and $\text{Er}:\text{Sc}_2\text{O}_3$, the longest lifetimes of 2.64 ms and 0.53 ms achieved at
 287 50 K and 10 K, respectively remain well below the radiative lifetimes of around 5 ms in Table 4,
 288 indicating significant non-radiative decay even at 10 K.



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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, $\lambda_{\text{exc}} = 960$ nm, $\lambda_{\text{lum}} = 1015$ nm; the solid lines represent single exponential fits. (c) Temperature dependence of the luminescence lifetimes.

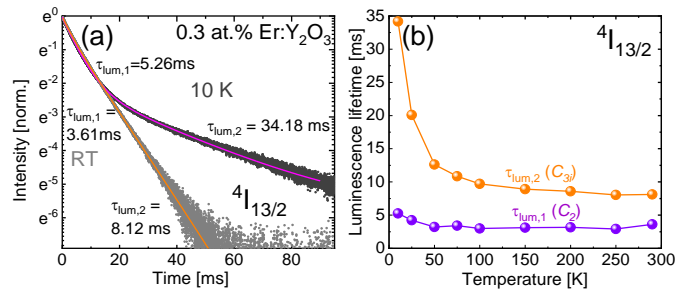


Fig. 7. Luminescence dynamics from the ${}^4I_{13/2}$ state of Er^{3+} ions in 0.3 at.% $\text{Er}:\text{Y}_2\text{O}_3$: (a) luminescence decay curves at RT and 10 K, the solid lines represent biexponential fits to the data, $\lambda_{\text{exc}} = 1461$ nm, $\lambda_{\text{lum}} = 1543$ nm; (b) temperature dependence of the ‘fast’ and ‘slow’ component of the biexponential fit.

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 see Table 3. Thus, Er^{3+} ions on both sites, C_2 and C_{3i} contribute to the corresponding emission at $1.55 \mu\text{m}$. 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 Tab. 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.

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 $\tau_{\text{rad}} = 1/A(\text{JJ})^{\text{MD}}$ 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 $\text{Er}:\text{Y}_2\text{O}_3$, 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.% $\text{Er}:\text{Y}_2\text{O}_3$ 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 in absorption are MD forbidden and not influenced by ions on C_{3i} sites. Thus, assuming $3/4$ of the Er^{3+} ions being on C_2 sites and $1/4$ on C_{3i} sites allows to calculate the ‘effective’ transition probability as $\langle A \rangle = 3/4 A_{\text{ED+MD}}(C_2) + 1/4 A_{\text{MD}}(C_{3i})$, and the corresponding ‘effective’ radiative lifetime to be $\langle \tau_{\text{rad}} \rangle = 1/\langle A \rangle$. The resulting values are shown in Table 5 and are in good agreement with the measured room temperature luminescence lifetimes $\langle \tau_{\text{lum}} \rangle$.

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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 ₂ O ₃	Er:Lu ₂ O ₃	Er:Sc ₂ O ₃
RT	$^4I_{11/2}$	τ_{lum}	2.58	1.82	0.36
		τ_{rad} , J-O	5.39	4.96	5.57
	$^4I_{13/2}$	$\langle\tau_{lum}\rangle$	7.08	7.07	6.27
		τ_{rad} , J-O (C_2)	5.79	5.74	5.64
		τ_{rad} (MD), J-O (C_{3i})	13.22	13.86	14.73
	$\langle\tau_{rad}\rangle$, J-O ($3/4; 1/4$)	6.73	6.72	6.67	
10 K	$^4I_{11/2}$	τ_{lum}	4.25	2.33	0.53
	$^4I_{13/2}$	$\tau_{lum,1}$ (C_2)	5.26	-	-
		$\tau_{lum,2}$ (C_{3i})	34.18	-	-

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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 $\langle\tau_{rad}\rangle$ 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 Lu₂O₃ and Sc₂O₃, 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.

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5. Stimulated emission cross-sections

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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 stimulated-emission cross-sections, we used two complementary methods: the reciprocity method (Eq. 8) [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. 9) [34] based on the measured luminescence spectra. Using the effective luminescence lifetime $\langle\tau_{rad}\rangle$ 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 $1.61 \times 10^{-21} \text{ cm}^2$ at 1641 nm for Er:Y₂O₃, $1.60 \times 10^{-21} \text{ cm}^2$ at 1647 nm for Er:Lu₂O₃, and $1.58 \times 10^{-21} \text{ cm}^2$ at 1667 nm for Er:Sc₂O₃.

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For the $^4I_{11/2} \rightarrow ^4I_{13/2}$ transition at 2.85 μm , only the F-L formula was applied using the τ_{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 $5.36 \times 10^{-21} \text{ cm}^2$ at 2842 nm for Er:Y₂O₃, $5.67 \times 10^{-21} \text{ cm}^2$ at 2845 nm Er:Lu₂O₃, and $3.57 \times 10^{-21} \text{ cm}^2$ at 2857 nm for Er:Sc₂O₃. The emission of Er:Sc₂O₃ covers a wider wavelength range than those of Er^{3+} ions in Lu₂O₃ and Y₂O₃, 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.

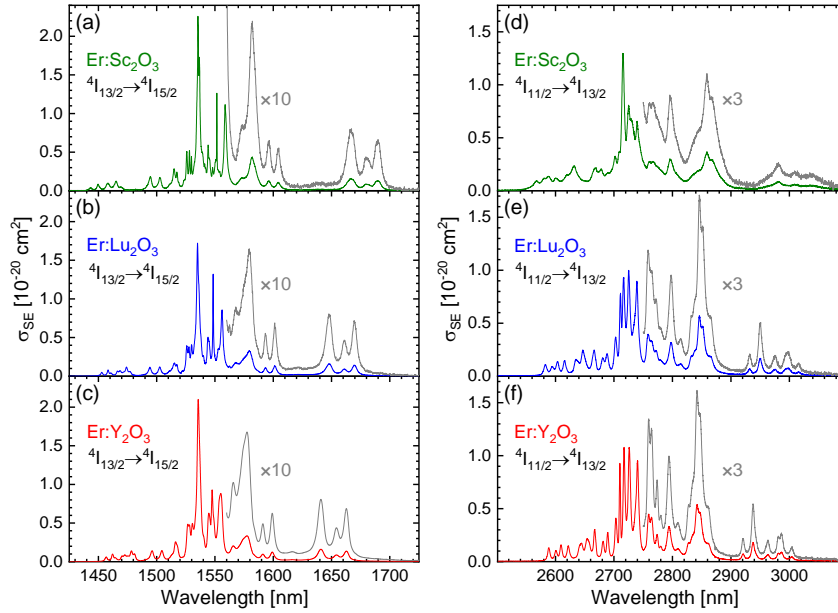


Fig. 8. Stimulated-emission (SE) cross-sections, σ_{SE} , for Er^{3+} ion in sesquioxide crystals: (a-c) the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition; (d-f) the ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{13/2}$ transition.

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378 6. Conclusion

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

385 For the ${}^4\text{I}_{11/2}$ state, the luminescence lifetime both at RT and even at 10 K strongly depends
386 on the host-forming cation in the sesquioxide matrix owing to a different rate of non-radiative
387 multiphonon relaxation associated to a difference in the phonon spectra of sesquioxides. Y_2O_3
388 features the lowest phonon energies leading to the longest ${}^4\text{I}_{11/2}$ luminescence lifetime. The
389 radiative lifetime of this level obtained via the Judd-Ofelt theory is assigned to Er^{3+} ions on C_2
390 sites. Consequently, the radiative lifetimes and branching ratios calculated by the J-O-theory
391 enabled to calculate reliable emission cross sections in the wavelength range of 2.85 μm for the
392 first time for $\text{Er}:\text{Y}_2\text{O}_3$, $\text{Er}:\text{Lu}_2\text{O}_3$ and $\text{Er}:\text{Sc}_2\text{O}_3$.

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

406 in excellent agreement with those obtained from the absorption spectra by the reciprocity
407 method.

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

410 **Appendix A. Sample preparation and experimental methods**

411 *Synthesis of samples*

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

420 For the absorption measurements, we used three Er^{3+} -doped single-crystals, Y_2O_3 , Lu_2O_3
421 and Sc_2O_3 . The actual Er^{3+} doping levels were determined by the X-ray fluorescence (XRF)
422 method using a Bruker M4 Tornado spectrometer, to be 15.9 at.% $\text{Er}:\text{Y}_2\text{O}_3$, 12.5 at.% $\text{Er}:\text{Lu}_2\text{O}_3$
423 and 3.5 at.% $\text{Er}:\text{Sc}_2\text{O}_3$. The corresponding Er^{3+} ion densities N_{Er} were $0.427 \times 10^{22} \text{ cm}^{-3}$,
424 $0.428 \times 10^{22} \text{ cm}^{-3}$ and $0.117 \times 10^{22} \text{ cm}^{-3}$, respectively.

425 In addition, for luminescence lifetime studies, we used two low-doped crystals, 0.3 at.%
426 $\text{Er}:\text{Y}_2\text{O}_3$ and 0.3 at.% $\text{Er}:\text{Sc}_2\text{O}_3$ and a 1 at.% $\text{Er}:\text{Lu}_2\text{O}_3$ ceramic sample.

427 For measuring the concentration-dependent luminescence lifetimes of Er^{3+} ions, we used a
428 set of transparent sesquioxide ceramics with 1 at.% and 7 at.% Er^{3+} doping. The ceramics were
429 prepared by hot pressing of nanopowders. Commercial rare-earth oxide powders (4N purity)
430 were dissolved in nitric acid (6N) and mixed in the given ratios. We added glycine (3N) in a
431 molar ratio of 1:1 with respect to the nitrate groups and 1 wt.% of LiF (3N) with respect to the
432 oxide powder acting as a sintering aid. The precursors were placed in a furnace preheated to
433 500 °C, resulting in the synthesis of Er^{3+} -doped sesquioxide nanopowders. These were placed
434 in a graphite mold and hot pressed under 50 MPa at a temperature of 1500 °C for $\text{Er}:\text{Y}_2\text{O}_3$ or
435 1600 °C for $\text{Er}:\text{Sc}_2\text{O}_3$ and $\text{Er}:\text{Lu}_2\text{O}_3$ for 1 h under a vacuum of about 10 Pa. The ceramics were
436 then annealed in air at 900 °C for 5 h.

437 *Experimental methods*

438 The room temperature (RT, 290 K) transmission spectra of Er^{3+} -doped sesquioxide crystals
439 were measured in the wavelength range between 270 and 1700 nm using a Perkin Elmer
440 Lambda 1050 spectrometer. The spectral bandwidth (SBW) was 0.04 – 0.1 nm, depending on
441 the spectral range and required resolution. The absorption cross-sections were calculated as
442 $\sigma_{\text{abs}} = \alpha_{\text{abs}}/N_{\text{Er}}$, where α_{abs} is the absorption coefficient calculated via the Beer-Lambert law.

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

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

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

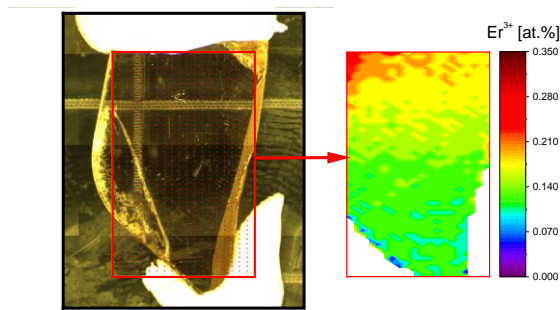


Fig. A1. Spatial distribution of dopant Er^{3+} ions across a 0.3 at.% $\text{Er}:\text{Sc}_2\text{O}_3$ crystal (doping level in the melt) determined by XRF analysis: the left image shows a photograph of the sample; the grid shows the points on which the high resolution compositional analysis was performed and the red rectangle marks the full analyzed area of $8.37 \times 12.87 \text{ mm}^2$; the right side shows the results of the Er^{3+} element mapping.

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For $\text{Er}:\text{Y}_2\text{O}_3$ and $\text{Er}:\text{Lu}_2\text{O}_3$ crystals, the gradient of Er^{3+} doping across the studied samples was found to be low and the segregation coefficient $K_{\text{Er}} = C_{\text{crystal}}/C_{\text{melt}}$ 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 the sixfold oxygen coordination. Figure A1 shows a photograph of a 0.3 at.% $\text{Er}:\text{Sc}_2\text{O}_3$ 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 $\text{Er}:\text{Sc}_2\text{O}_3$ 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.

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Acknowledgment. We acknowledge the help of Stefan Püschel in determining the XRF-measurements.

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Funding. French Agence Nationale de la Recherche (ANR) SPLENDID2 (ANR-19-CE08-0028). "RELANCE" Chair of Excellence project funded by the Normandy Region. Russian Science Foundation (research project No. 21-13-00397).

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Disclosures. The authors declare no conflicts of interest.

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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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