Enhancement of Er\textsuperscript{3+} 4I\textsubscript{13/2} population in Y\textsubscript{2}O\textsubscript{3} by energy transfer to Ce\textsuperscript{3+}

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Abstract

We report measurements of the energy transfer between Er\textsuperscript{3+} and Ce\textsuperscript{3+} in Y\textsubscript{2}O\textsubscript{3}. The transition between the Er\textsuperscript{3+} 4I\textsubscript{11/2} and 4I\textsubscript{13/2} excited states can be stimulated by energy transfer to Ce\textsuperscript{3+}, augmenting the population in the 4I\textsubscript{13/2} state at the expense of that in the 4I\textsubscript{11/2} state. Experiments were performed on Y\textsubscript{2}O\textsubscript{3} planar waveguides doped with 0.2 at.% erbium and 0–0.42 at.% cerium by ion implantation. From measurements of Er\textsuperscript{3+} decay rates as a function of cerium concentration we derive an energy transfer rate constant of 1.3 \times 10^{-18} \text{cm}^3/\text{s}. The efficiency of the energy transfer amounts to 0.47 at 0.42 at.% cerium. The energy transfer rate constant measured in Y\textsubscript{2}O\textsubscript{3} is two times smaller for Er\textsuperscript{3+} \rightarrow Ce\textsuperscript{3+} than that for Er\textsuperscript{3+} \rightarrow Eu\textsuperscript{3+} in the same material. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Optical amplifiers in telecommunication networks make use of population inversion between the first excited (4I\textsubscript{13/2}) and ground (4I\textsubscript{15/2}) states of Er\textsuperscript{3+} to achieve amplification around 1540 nm (cf. Fig. 1). Population inversion is obtained by exciting the second excited state 4I\textsubscript{11/2} with 980 nm radiation, from where the ion relaxes to the 4I\textsubscript{13/2} level by interactions with matrix vibrations. To attain high population of the 4I\textsubscript{13/2} state, this non-radiative de-excitation route has to be efficient compared to the radiative transitions from the 4I\textsubscript{11/2} and 4I\textsubscript{13/2} levels to the ground state.

In many promising amplifier and laser materials this is not the case. Their phonon energies are low, therefore multiple phonons are required to bridge the energy gap between the 4I\textsubscript{11/2} and 4I\textsubscript{13/2} levels, making the de-excitation inefficient. This means that when Er\textsuperscript{3+} is excited with 980 nm radiation, a considerable amount of energy is stored in the second excited state, and is not available for stimulated emission from the 4I\textsubscript{13/2} level. The efficiency of the transition from the 4I\textsubscript{11/2} to the 4I\textsubscript{13/2} state can be improved by transferring the energy difference between the two levels to a suitable acceptor ion. This process has been shown for Ce\textsuperscript{3+} [1–5] and Eu\textsuperscript{3+} [6,7] in glasses and crystalline materials. It is not known, however, which of these ions acts as the most efficient acceptor in a given material.

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known to lead to well controlled doping profiles and a homogeneous distribution of the implanted ions. These samples were implanted with erbium at energies between 200 and 500 keV to a total fluence of $1.34 \times 10^{14}$ cm$^{-2}$ to create a flat dopant profile at a concentration of $1.38 \times 10^{20}$ cm$^{-3}$ (0.21 at.%) over the depth from 30 to 130 nm from the surface. Cerium was then coimplanted into parts of the samples at energies between 185 and 425 keV. These energies were chosen such as to match the cerium and erbium dopant profiles. Nominal implantation fluences were $2.17 \times 10^{14}$, $6.9 \times 10^{14}$, $1.73 \times 10^{15}$, and $2.68 \times 10^{15}$ cm$^{-2}$. The cerium concentrations were obtained by RBS and amount to 0.05, 0.07, 0.25, and 0.42 at.%. The sample temperature was kept at 77 K during all implantations. After ion implantation, the samples were annealed at 700$^\circ$C for 1 h in a vacuum furnace at a base pressure below $10^{-4}$ Pa. The part of the samples not implanted with cerium serves as an on-wafer reference for the analysis. In this way slight differences in luminescent properties between the samples can be taken into account.

Room temperature photoluminescence from Er$^{3+}$ was measured by exploiting the planar waveguide geometry of the samples. Light from an Ar$^+$ ion laser operating at 488 nm was mechanically chopped and butt-coupled into the samples using an optical fibre. The photo-luminescence emission from the different energy levels of Er$^{3+}$ was collected perpendicular to the waveguide plane with an optical fibre of core diameter 0.8 mm. The light was dispersed in a 96 cm monochromator and detected with an AgOCS photomultiplier tube in the wavelength region between 500 and 1100 nm, and a germanium detector cooled to 77 K in the region around 1500 nm.

Photoluminescence decay traces of the Er$^{3+}$ $^4I_{15/2}$ energy level at 1538 nm were recorded on a digital oscilloscope, averaging typically 2500 single traces for each measurement. The decay traces of the $^4I_{11/2}$ level at 980 nm as well as of the higher lying energy levels were measured using a photon counting system and a multichannel scaler. The decay traces were fitted by single exponential functions to obtain the decay rates. Only the decay of the $^4I_{11/2}$ level in the sample with the highest cerium concentration was not single exponential.

Fig. 1. Energy levels of Er$^{3+}$ and Ce$^{3+}$. The arrows indicate the relevant transitions for the rate equation model.

2. Experimental

The yttrium oxide planar waveguides were fabricated by sputter deposition on thermally oxidised silicon wafers [8]. The SiO$_2$ and Y$_2$O$_3$ layer thicknesses are 3 μm and 750 nm, respectively, as determined with Rutherford backscattering spectrometry (RBS). To dope the Y$_2$O$_3$ with the rare earth ions we have used ion implantation, as it is
In this case the first e-folding time has been used to define the decay rate.

Values for the ratio of intensities emitted from the $^4I_{13/2}$ and $^4I_{11/2}$ states were obtained by measuring photoluminescence spectra of the corresponding emission lines under identical experimental conditions, using the Ge detector. The spectral resolution was set to 3 nm, the Er$^{3+}$ was excited with 488 nm radiation. Standard lock-in techniques were employed to reduce the noise level. The spectra were corrected for the detector response and integrated in the frequency domain to obtain the emission intensity in each line.

For all the measurements reported in this article, care has been taken to keep the excitation power so low as to ensure a linear relationship between excitation and emission intensities. In this way, power and population dependent effects, like cooperative upconversion and excited state absorption, can be excluded and do not have to be taken into account for the analysis.

3. Results and discussion

3.1. Rate equation model

In Fig. 1 we show a schematic of the mechanism that accelerates the transition between the Er$^{3+}$, $^4I_{11/2}$ and $^4I_{13/2}$ states. The transition rates $W_1$, $W_{20}$, and $W_{21}$ are defined as the intrinsic Er$^{3+}$ rates in Y$_2$O$_3$. $W_1$ is the decay rate of the $^4I_{13/2}$ level and can be written as the sum of a radiative rate $W_{1r}$ and a non-radiative rate $W_{1nr}$. $W_{21}$ and $W_{20}$ are the rates of the transitions from the $^4I_{11/2}$ level to the $^4I_{13/2}$ and $^4I_{15/2}$ states, respectively. We define $W_{21}$ as the sum of the relevant radiative and non-radiative transition rates, while we assume $W_{20}$ to be purely radiative. The sum of $W_{21}$ and $W_{20}$, $W_2$, is the total decay rate of the $^4I_{11/2}$ level.

The coupling of the $^4I_{11/2} \rightarrow ^4I_{13/2}$ transition with Ce$^{3+}$ depends on cerium concentration and is described by the rate constant $C_2$. We assume the population in the $^2F_{7/2}$ state of Ce$^{3+}$ to be negligible at all times. This presumption is plausible at room temperature, considering that the Stark levels of both the $^2F_{7/2}$ and $^2F_{5/2}$ energy levels are split widely in Y$_2$O$_3$ [10] and all energy gaps can be bridged by two to three phonons of the Y$_2$O$_3$ host (highest phonon density of states at 400 cm$^{-1}$ [11]).

As described in detail in [7], to account for effects due to the ion implantation, we have to introduce an additional phenomenological decay rate of the Er$^{3+}$ $^4I_{13/2}$ state, $S_1$. The interaction causing this decay can either be due to the presence of energy levels of Ce$^{3+}$ (e.g., via phonon-assisted energy transfer) or to implantation defects. Taking further into account that the excitation of the Er$^{3+}$ takes place into the $^4F_{7/2}$ state at 488 nm, the rate equations for the $^4I_{11/2}$ and $^4I_{13/2}$ levels can be written as

$$\frac{dN_2}{dt} = R_2 - W_2 N_2 - C_2 N_q N_2,$$

$$\frac{dN_1}{dt} = R_1 - W_1 N_1 + W_{21} N_2 + C_2 N_q N_2 - S_1 N_1.$$

The symbols $R_1$ and $R_2$ refer to the excitation rate per unit volume into the first and second excited states of Er$^{3+}$ (as indicated by the subscripts). They depend on the branching ratio of the $^4F_{7/2}$ level and possibly lower states. $N_1$, $N_2$ are the population densities in the first and second excited states of Er$^{3+}$, and $N_q$ refers to the codopant concentration. Implicit in these equations is the assumption that the excitation density is small enough to preclude bleaching of the ground state and non-linear processes such as upconversion by energy transfer. These equations are easily adapted to describe excitation of the $^4I_{11/2}$ state by radiation around 980 nm. The only change necessary is setting $R_1 = 0$.

We can now define the fraction of the population in the $^4I_{11/2}$ level that is de-excited via energy transfer to Ce$^{3+}$ as

$$Q_2 = \frac{C_2 N_q}{W_2 + C_2 N_q}.$$

The choice of this function, namely the linear dependence of the energy transfer rate $C_2 N_q$ on cerium concentration, is justified by experiment (cf. Section 3.2). Similarly we can write the fraction of population in the $^4I_{13/2}$ level that is de-excited due to the interaction $S_1$ as
\[ Q_1 = \frac{S_1}{W_1 + S_1}. \] (3)

These branching ratios serve as a measure for the efficiency of the de-excitation processes acting on the two energy levels and are determined by means of decay rate measurements.

To obtain an expression for the ratio of the emission intensities of the \( ^4I_{13/2} \) and \( ^4I_{11/2} \) levels, we substitute the expressions for \( Q_1 \) and \( Q_2 \) into the rate equation, Eq. (1). Expressing the emission intensities in terms of the population in each level, \( I_1 = W_{1r}h\nu_1N_1 \) and \( I_2 = W_{20}h\nu_2N_2 \), the intensity ratio can be written as

\[ \frac{I_1}{I_2} = \frac{1 - Q_1 I_0}{1 - Q_2 I_0} = \frac{W_{1r} Q_2(1 - Q_1)}{W_1} \frac{\nu_1}{1 - Q_2} \frac{\nu_2}{\nu_1}, \] (4)

where \( I_1 \) and \( I_2 \) are the integrated emission intensities pertaining to transitions from first and second excited state of \( \text{Er}^{3+} \) to its ground state in the presence of cerium, and \( I_0 \) and \( I_0 \) the intensities in the limit of zero cerium concentration. \( \nu_1 \) and \( \nu_2 \) are the corresponding emission frequencies. We assume that \( W_{20} \) is purely radiative.

### 3.2. Experimental results

Fig. 1 shows the energy levels for \( \text{Er}^{3+} \) and \( \text{Ce}^{3+} \) in \( \text{Y}_2\text{O}_3 \) as reported by Chang et al. [10]. The Stark levels of the \( \text{Ce}^{3+} \) \(^2\text{F}_{7/2} \) and \(^2\text{F}_{5/2} \) states are split widely and therefore provide for efficient de-excitation of the upper levels via vibrational interactions with the \( \text{Y}_2\text{O}_3 \) lattice. The transition between the lowest energy Stark level of the ground state and the highest energy Stark level of the excited state is resonant with the transition between the \( ^4I_{11/2} \) and \( ^4I_{13/2} \) levels of \( \text{Er}^{3+} \). This is the condition necessary for active transfer of population from the \( ^4I_{11/2} \) to the \( ^4I_{13/2} \) state of \( \text{Er}^{3+} \) and thus for an increased transition rate between the \( ^4I_{11/2} \) and \( ^4I_{13/2} \) levels of \( \text{Er}^{3+} \).

The interaction between \( \text{Er}^{3+} \) and \( \text{Ce}^{3+} \) manifests itself by an increased decay rate of the \( \text{Er}^{3+} \) \(^4I_{11/2} \) level. The difference between the \(^4I_{11/2} \) decay rates for cerium concentrations \( N_g \) and zero can be interpreted as the energy transfer rate from the \( \text{Er}^{3+} \) \(^4I_{11/2} \) state to cerium.

\[ W_{1r}^{N_g} = W_{981}^{N_g} - W_{981}^0 \] (5)

with \( W_{981}^{N_g} \), the measured decay rates at cerium concentrations of zero and \( N_g \). As shown in the inset of Fig. 2, a double logarithmic plot of \( W_{1r} \) against \( N_g \), the transfer rate depends linearly on cerium concentration. This result justifies the definition of Eq. (2) as the efficiency of de-excitation via \( \text{Ce}^{3+} \).

The energy transfer efficiency between \( \text{Er}^{3+} \) and \( \text{Ce}^{3+} \) can be derived from experimental data as

\[ Q_{981}^{N_g} = 1 - \frac{W_{981}^0}{W_{981}^{N_g}} \] (6)

and a similar definition can be given for the energy transfer efficiency from the \( \text{Er}^{3+} \) \(^4I_{13/2} \) state, \( Q_{958}^{N_g} \).

The values obtained for both \( Q_{981}^{N_g} \) and \( Q_{958}^{N_g} \) at different cerium concentrations are plotted in Fig. 2. \( Q_{981} \) rises monotonically over the full concentration range, reaching a value of 0.47 for 0.42 at.\% cerium. This behaviour is expected when energy transfer from the \( \text{Er}^{3+} \) \(^4I_{11/2} \) level to \( \text{Ce}^{3+} \) takes place. By fitting the data for \( Q_{981} \) with the function given by Eq. (2), we determine the energy transfer coefficient.

![Fig. 2. Efficiency of the Er	extsuperscript{3+} \((^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2})\) to Ce	extsuperscript{3+} energy transfer (\( Q_{981} \)) and the fraction of energy lost from the Er\textsuperscript{3+} \(^4\text{I}_{13/2} \) state due to cerium implantation (\( Q_{958} \)). The line is a fit of Eq. (2) to the data for \( Q_{981} \). The inset shows a double logarithmic plot of the transfer rate \( W_{1r} \) from the Er\textsuperscript{3+} \(^4\text{I}_{11/2} \) state to cerium vs cerium concentration. The linear dependence justifies the definition of \( W_{1r} = C_P N_g \) in Eq. (2).](image)
C₂ to be (1.3 ± 0.1) × 10⁻¹⁸ cm³/s. Q₁₅₃₈ also increases with cerium concentration. The data cannot be described, however, by a function of the form of Eq. (2) and therefore by an energy transfer to cerium. Similar behaviour has been observed in previous work on the same system using Eu³⁺ as the codopant [7]. It is attributed to defects induced by the ion implantation that are not removed during the anneal of the samples.

The increase of the decay rate of the Er³⁺ ⁴I₁₁/₂ state due to cerium codoping does of course also have an influence on the shape of the decay curves of the ⁴I₁₃/₂ state. The ⁴I₁₃/₂ state receives excitation from the ⁴I₁₁/₂ state on the time scale of the ⁴I₁₁/₂ decay rate W₉₈₁. This can be discerned in the ⁴I₁₃/₂ decay rate at short times [12]. Fig. 3 compares the decay traces doped with 0 and 0.25 at.% cerium. While both traces approach the same decay rate at long times, initially there is a clear difference between them. When no codoping with cerium has taken place, the decay is clearly non-exponential at short times. It becomes more single exponential when cerium is introduced as codopant. Solving the rate Eq. (1), we obtain the decay function of the ⁴I₁₃/₂ state as

\[ N₁(t) = \left( N₁₀ + \frac{W₁ N₁₀}{W₂ - W₁} \right) e^{-W₁ t} - \frac{W₁ N₁₀}{W₂ - W₁} e^{-W₂ t}, \]

(7)

where \( N₁₀ \) and \( N₁₀ \) represent the initial population of the ⁴I₁₃/₂ and ⁴I₁₁/₂ manifolds.

It is clear that all information on the decay rates of the ⁴I₁₁/₂ state is contained in the decay traces of the ⁴I₁₃/₂ state. Fitting Eq. (7) to the decay trace without cerium (for data and fit cf. Fig. 3), we obtain a value of 392 ± 50 s⁻¹ for \( W₂ \). It is in reasonable agreement with the one measured by direct observation of the decay of the ⁴I₁₁/₂ level (428 ± 8 s⁻¹). The accuracy is however lower than for the direct measurement, and decreases even further when the decay rate \( W₂ \) increases.

Evidence that the population from the ⁴I₁₁/₂ state of Er³⁺ is indeed transferred to the ⁴I₁₃/₂ state is provided by measurements of the ratio between the photoluminescence intensities emitted from these two levels. These are plotted in Fig. 4. As expected from considerations of the model outlined in Fig. 1, the data show an increase of the intensity ratio of the ⁴I₁₃/₂ and ⁴I₁₁/₂ levels with increasing cerium concentration. This indicates that the population in the first excited state of Er³⁺ is growing with respect to the population in its

![Fig. 3. Decay of the ⁴I₁₃/₂ emission at 1538 nm for a sample containing only erbium and a sample codoped with 0.25 at.% cerium, excited at 488 nm. The decay at short times is slower than at long times, reflecting the de-excitation of the ⁴I₁₁/₂ to the ⁴I₁₃/₂ manifold. The drawn line is a fit of Eq. (7) to the data. Note that the effect decreases with cerium codoping, an indication of the increase in decay rate of the ⁴I₁₁/₂ state.](image)

![Fig. 4. Ratio of emission intensity from the Er³⁺ ⁴I₁₁/₂ and ⁴I₁₃/₂ energy levels. Overlaid is a calculation according to Eq. (4) with \( W₉₈₁ = 89 \) s⁻¹, using the data from Fig. 2. Direct de-excitation of the Er³⁺ ⁴I₁₁/₂ state to the ground state (\( W₉₈₁ = 0 \)) does not reproduce the data.](image)
second excited state. Making use of the values for the $Q_i$’s obtained from decay rate measurements (cf. Fig. 2), we can calculate the expected behaviour of the $^{4}I_{13/2}/^{4}I_{11/2}$ intensity ratio according to Eq. (4). The only free parameter in the calculation is the radiative decay rate of the $^{4}I_{13/2}$ level. The minimal mean squared deviation between data and calculation is achieved for $W_{\text{sr}} = 89 \text{ s}^{-1}$. Note that correspondence between calculation and experiment cannot be obtained assuming direct de-excitation of the $^{4}I_{11/2}$ level to the ground state. In this case the intensity ratio is determined completely by the measured decay rates, without any adjustable parameters. Mathematically this is equivalent to setting $W_{\text{sr}} = 0$ in Eq. (4). The values of the intensity ratio under this condition are also shown in Fig. 4.

3.3. Comparison of the effects of cerium and europium codoping

Let us briefly compare two results of this work with our previous measurements on Er$^{3+}$ in Y$_2$O$_3$ codoped with europium [7]. For the case of codoping with europium we determined the energy transfer coefficient $C_2$ to be $2.9 \times 10^{-18} \text{ cm}^3/\text{s}$, more than a factor of two higher than for codoping with cerium. According to Dexter [13], multipolar energy transfer depends on the overlap integral between donor emission and acceptor absorption. Comparing the energy level structure of Ce$^{3+}$ and Eu$^{3+}$ in Y$_2$O$_3$ [10,14] shows that the higher transfer efficiency towards Eu$^{3+}$ is due to the better spectral overlap between the Er$^{3+}$ $^{4}I_{11/2} \rightarrow ^{4}I_{13/2}$ transition and the Eu$^{3+}$ energy levels. Measurements in glasses of different compositions [4,5] suggest that energy transfer between Er$^{3+}$ and Ce$^{3+}$ contains a phonon-assisted contribution. A similar process is suggested by decay rate measurements at different temperatures on our samples. These are shown in Fig. 5. Plotted are the decay rates of the Er$^{3+}$ $^{4}I_{11/2}$ state for a sample codoped with 0.25 at.% cerium and a reference without cerium. Both sets of decay rate measurements show an increase with temperature, due to phonon-assisted de-excitation to the $^{4}I_{13/2}$ state. The energy transfer rate $W_{\text{tr}}$, also drawn in Fig. 5, increases with temperature as well, by 60% over the temperature range between 13 and 300 K. Since the energy transfer rate does not vanish at 13 K we can conclude that some direct energy transfer from Er$^{3+}$ to Ce$^{3+}$ takes place. Although the accuracy of these measurements is limited, the temperature dependence of $W_{\text{tr}}$ suggests a considerable phonon-mediated component at room temperature. The poor overlap together with this phonon-assisted contribution can explain the lower efficiency for energy transfer between Er$^{3+}$ and Ce$^{3+}$.

It is interesting to note the correspondence of the values for the adjustable parameter ($W_{\text{tr}}$) in the fit of Eq. (4) to the intensity ratio data for experiments involving different acceptor ions. It amounts to $89 \text{ s}^{-1}$ for both energy transfer between Er$^{3+}$ and Eu$^{3+}$ presented earlier [7] and energy transfer between Er$^{3+}$ and Ce$^{3+}$ described in this article. This fact supports the claim that all transitions from the $^{4}I_{11/2}$ state induced by the codopants have the $^{4}I_{13/2}$ level as their final state: if an interaction were present de-exciting part of the excitation in the $^{4}I_{11/2}$ state directly to the ground state, the value for the adjustable parameter obtained from the ratio of the $^{4}I_{13/2}/^{4}I_{11/2}$ intensities would depend on the strength of this interaction. The interaction strength in turn depends on the energy level structure of the codopant, and treat-
ment conditions. Both are different for the two sample series and should therefore lead to different values of $W_1$. Since this is not the case, the dominant de-excitation of the $^4I_{11/2}$ state induced by the codopant must be to the $^4I_{13/2}$ level.

### 4. Conclusion

In this article we have shown that in a Y$_2$O$_3$ host the $^4I_{11/2} \rightarrow ^4I_{13/2}$ transition in Er$^{3+}$ can be accelerated by energy transfer to Ce$^{3+}$. In the process the population in the first excited state increases at the expense of the population in the second excited state. In this way the population inversion for amplification around 1540 nm is enhanced. This method is especially interesting for host materials with low phonon energies, whose steady-state population in the second excited state of Er$^{3+}$ is high when excited with 980 nm radiation. In our experiments an energy transfer efficiency of 0.47 was measured for a cerium concentration of 0.42 at.%. The energy transfer coefficient was determined to be $1.3 \times 10^{-18}$ cm$^3$/s.

The energy transfer between the $^4I_{11/2}$ state of Er$^{3+}$ and Ce$^{3+}$ in Y$_2$O$_3$ is less efficient than that between Er$^{3+}$ and Eu$^{3+}$. This is attributed to the smaller spectral overlap of the Er$^{3+}$ $^4I_{11/2} \rightarrow ^4I_{13/2}$ transition with the absorption of the $^2F_{7/2}$ state of Ce$^{3+}$.

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