Energy transfers in telecommunication-band region of \((\text{Sc,Er})_2\text{O}_3\) thin films grown on Si(111)

S. Adachi\(^1\), Y. Kawakami\(^1\), R. Kaji\(^1\), T. Tawara\(^{2,3}\), H. Omi\(^{2,3}\)

\(^1\) Department of Applied Physics, Hokkaido University, Sapporo 060-8628, Japan
\(^2\) NTT Basic Research Laboratories, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan
\(^3\) NTT Nanophotonics Center, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan

E-mail: adachi-s@eng.hokudai.ac.jp

Abstract. The energy transfer dynamics in 1.5-m\(\mu\)m region of \((\text{Er}_x\text{Sc}_{1-x})_2\text{O}_3\) epitaxial thin films grown on Si(111) were investigated via temperature-dependence of the time-resolved photoluminescence (TR-PL). In order to exclude the dissipation via the cooperative up-conversion, the low power and resonant excitation of the third crystal-field level \((^4I_{13/2} : Y'_4)\) of the Er\(^{3+}\) site with \(C_{3v}\) symmetry was employed. The TR-PL measurements of the \(Y'_1\)-\(Z'_1\) transition have proved the existence of two decay components having fast (10–100 \(\mu\)s) and slow (0.1–1 ms) relaxation times in the range of 4–60 K. The model calculation including the temperature-sensitive and -insensitive non-radiative relaxations could explain well all the observed results. Moreover, the long averaged inter-Er-ion distance by decreasing Er density was found to be very effective to reduce both non-radiative relaxation rates.

1. Introduction
In the subject of the manipulations of the quantum states, the exciting activities are currently grown in different solid-state systems such as the semiconductor quantum dots [1] and the nitrogen-vacancy center in diamond [2] based on the interplay of the solid-state nature of the material engineering and the atomic-like character of the sharp discrete energy levels. The rare-earth-doped solids are alternative attractive candidates to exploit the coherent quantum phenomena because the intra-4\(f\) transitions in rare-earth ions are weakly perturbed by the crystalline environments, and they exhibit the resonance with a very narrow linewidth. In the various rare-earth-doped solids, we focus on Sc-doped erbium oxide \(((\text{Er}_x\text{Sc}_{1-x})_2\text{O}_3)\) [3, 4] since the Er ions (Er\(^{3+}\)) can interact with a telecomm-band photon (\(\sim 1.54 \mu\)m) and can be grown on the Si(111) substrates. Therefore, the materials have a high possibility to be a platform for the coherent manipulations of the quantum information network using the existing fiber-optic network. However, for this purpose, the details of the energy transfers (ETs) have to be revealed.

2. Samples and Energy transfers in Er\(^{3+}\) levels
Er\(_2\)O\(_3\) crystals have the lattice constant \((a=10.54 \text{ Å})\) that is almost twice that of Si(111) \((a=5.43 \text{ Å})\). \((\text{Er}_x\text{Sc}_{1-x})_2\text{O}_3\) has the similar properties. Thus, the samples could be epitaxially grown on a Si(111) surface by MBE at 715°C, and were successful to be single-crystalline with very low density of defects [3]. Three \((\text{Er}_x\text{Sc}_{1-x})_2\text{O}_3\) samples with different Er density were used in this work, and hereafter the samples with \(x=1.000\), 0.054, and 0.012 (thickness~50 nm) are called
Various ETs that are observed in the transition between the Stark levels of $4I_{15/2}$ and $4I_{13/2}$ in $(Er_xSc_{1-x})_2O_3$ crystal. (b) Energy level diagram of Er$^{3+}$ in $C_2$ and $C_{3i}$ symmetry sites (right) and UC-PL transitions (left).

as A, B, and C, respectively. The composition of the grown films was determined by Rutherford backscattering. Note that a large number of Er$^{3+}$ ($\sim 3 \times 10^{20}$ cm$^{-3}$) are contained even in a sample C compared to a commercial Er-doped fiber amplifier material (typically <10$^{19}$ cm$^{-3}$).

In this study, various types of ET shown in Fig. 1(a) are observed from one of the Stark levels in $4I_{13/2}$ manifold of Er$^{3+}$, where the ETs between Er ions with same symmetry sites (intra-site ET) and with different symmetry sites (inter-site ET) are separated clearly. Er$^{3+}$ has many optical transitions between $4I_{13/2}$ manifold (Stark levels $Y_i^{(i)}$, $i=1-7$, Fig. 1(b)) and $4I_{15/2}$ (Stark levels $Z_j^{(j)}$, $j=1-8$), which exhibits the photon emission and absorption at around 1.54 $\mu$m. The (forced) electric-dipole transitions between the Stark levels are allowed for Er$^{3+}$ in $C_2$ symmetry sites ($Y_i^{(i)} \leftrightarrow Z_j^{(j)}$) and only magnetic dipole transitions are possible for Er$^{3+}$ in $C_{3i}$ sites ($Y_i^{(i)} \leftrightarrow Z_j^{(j)}$).

Since $Sc_2O_3$ is transparent in visible to 1.5-2 $\mu$m region, the emission and absorption at 1.54 $\mu$m in $(Er_xSc_{1-x})_2O_3$ originate from Er$^{3+}$. In the experiments, the micro-PL setup with a streak camera (Hamamatsu Photonics C11293S) was used.

3. Results and Discussion

One of the important ETs is known as up-conversion process (UC in Fig. 1(a)) in the Er-doped materials. The UC-PL means the photon emission with shorter wavelength than the excitation one, and comes from the excited-state absorption and/or the cooperative UC (Auger process). [5] The UC process makes the ET dynamics complicated, and therefore avoiding the UC effect is preferable in this work. As an example of UC-PL, Fig. 2(a) summarizes the UC-PL spectra in the sample A at 4 K and $Y_3^{(3)}$ resonant excitation with $P_{exc}=1$ mW (upper panel) and $P_{exc}=30$ mW (lower panel). While the observed UC-PLs were negligible at $P_{exc}=1$ mW, the UC-PLs were significant in the high power excitation. Especially, the UC-PLs from $4F_{9/2}$ and $4S_{3/2}$ manifolds were much stronger than other UC-PLs and these UC-PLs become a severe population dissipation from a target state. Figure 2(b) shows the excitation power dependence of the integrated UC-PLs from $4F_{9/2}$, $4S_{3/2}$ and $4I_{11/2}$ to the $4I_{15/2}$, which indicates clearly that the appearance of the UC-PL needs a given critical excitation power and the UC-PLs become remarkable in high power excitation. The similar power dependence of the UC-PLs was observed in the samples B and C. Consequently, the influence of the UC-PL is considered to be negligible in the low power excitation region of 0.1-a few mW, and therefore, in the following experiments, all the measurements were carried out under $P_{exc}=1$ mW. Considering that the observed UC-PL peaks correspond to the predicted transitions between Stark levels only in the $C_2$ site, the UC-PLs are found to emit only from Er$^{3+}$ in $C_2$ site. This is supported also by the fact that the optical transitions between the higher-lying states and the ground states in $C_{3i}$.

Figure 1. (a) Various ETs that are observed in the transition between the Stark levels of $4I_{15/2}$ and $4I_{13/2}$ in $(Er_xSc_{1-x})_2O_3$ crystal. (b) Energy level diagram of Er$^{3+}$ in $C_2$ and $C_{3i}$ symmetry sites (right) and UC-PL transitions (left).

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Figure 2. (a) The UC-PLs from various manifolds in the sample A with $P_{exc}=30$ mW (lower panel, red) and $P_{exc}=1$ mW (upper panel, black) at the $Y'_3$ resonant excitation ($\lambda_{exc}=1530.5$ nm) and 4 K. (b) Excitation power dependence of the UC-PL intensities of three manifolds. (c) 2D plot of the PLE spectra of $4I_{13/2}$ manifold in the sample A at 4 K with $P_{exc}=1$ mW. The PLs below 1540 nm shown by a gray square are blocked by a low-pass filter. The central saturated region is due to the excitation laser stray.

Figure 3. (a) TR-PL signals of the $Y'_1 - Z'_1$ transition at 6 K. The signal for the sample B is shifted down for easy view. (b), (c) Temperature dependence of the fast and slow relaxation components, $\tau_{fast}$ and $\tau_{slow}$ for the samples A and C. The solid curves in (a)-(c) are the calculated results based on the model shown in (d), but not the simple fitting curves.

The inter-site and intra-site ETs avoiding the UC process can be reflected more directly to the TR-PL signals under the weak excitation condition ($P_{exc}=1$ mW). The TR-PL measurements were carried out varying the temperature in the range of 4-60 K under the resonant excitation of $Y'_3$ level. The resonantly excited electrons to $Y'_3$ level relax quickly to the lowest energy level $Y'_1$ as mentioned above. Figure 3(a) shows the TR-PL signals of the $Y'_1 \rightarrow Z'_1$ transition in the three samples at 6 K in one instance. Though the signal decay in the sample A occurs in a different time scale, all the TR-PL signals for each sample and each temperature could be dissolved to two components by the double exponential fitting: fast decay and slow decay components with
the relaxation times of $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$. Note that the solid lines in the figures are the calculated results based on the model (Fig. 3(d)) but not the simple double exponential fitting curves. Temperature dependences of $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$ for the samples A and C are shown in Fig. 3(b) and (c). Both $\tau_{\text{fast}}$ and $\tau_{\text{slow}}$ are found to have the dependence on Er density. In addition, the $\tau_{\text{fast}}$ in all samples is insensitive to the temperature and is almost constant. Then the fast decay component is considered to be the temperature-insensitive non-radiative relaxation from $Y_1$ level due to the multi-phonon (MP) emissions ($W_d$ in Fig. 3(d)). The temperature dependence of the MP relaxation time $\tau_{\text{MP}}(T)$ is expressed as $\tau_{\text{MP}}(T)/\tau_{\text{MP}}(0) = [1 - \exp(-E_p/k_B T)]^m$ in the single frequency model, where $E_p$ is the phonon energy and $m$ is the number of phonons. Since $E_p$ is $\approx 74$ meV in Sc$_2$O$_3$ [3], the MP relaxation for $m=1$ to 15 has no temperature dependence till 100 K according to the above equation. On the other hand, $\tau_{\text{slow}}$ shows the rapid reduction with increasing the sample temperature, particularly in the sample A. Since the radiative relaxation rate $A_\lambda$ is determined quantum-mechanically and is considered to be independent of the temperature, these results suggest strongly that the slow decay component includes the temperature-sensitive process such as a thermally-activation-type non-radiative relaxation: 

$$1/\tau_{\text{slow}} = A_\lambda + W_{nr}^0 \exp \left(-E_A/k_B T\right),$$

where $W_{nr}^0$ are the non-radiative relaxation rate at 0 K and $E_A$ is the activation energy. From the results, $A_\lambda$ and $W_{nr}^0$ were estimated to be 3.92 and 122 ms$^{-1}$, 0.88 and 8.08 ms$^{-1}$, and 0.56 and 2.70 ms$^{-1}$ for the sample A, B, and C, respectively. The large $A_\lambda$ for the sample A indicates the increase of the effective transition dipole moment due to the increase of the coherence volume. The smaller inter-Er distance (3.3, 8.8, 14.5 Å for the sample A, B, and C) enhances the Er-Er interaction and induces the larger coherence volume, and therefore, it may lead to the larger effective dipole moment and the larger $A_\lambda$.

To reproduce the TR-PL signals and their temperature dependences by the model calculation, the ET model shown in Fig. 3(d) is considered and the rate equations based on the model were solved. The calculated results indicated by the solid lines in Fig. 3(a), (b), and (c) agree well with the experimental results. The coincidence supports the validity of our model and assumption. From these analyzes, the temperature-insensitive non-radiative relaxation rate can be estimated to be 100, 3.3, and 1.4 ms$^{-1}$ for the sample A, B, and C. It is found that the reduction of Er density is effective to suppress both non-radiative rates. This is because the longer inter-Er$^{3+}$ distance suppresses the ETs in the same sites, and consequently the capturing events of the excited electrons by quenching centers are reduced.

4. Summary
We have investigated the ETs via the temperature dependence of the PL intensity and lifetime in (Er,Sc)$_2$O$_3$ epitaxial thin films grown on Si(111). The TR-PL measurements have proved the existence of two kinds of the decay component having fast and slow relaxation times in the range of 4–60 K. The model calculation introducing the inter-site ET, the temperature-sensitive and -insensitive non-radiative relaxations were found to explain all the experimental results. Thermal quenching could be suppressed greatly with decreasing Er density. The obtained results can contribute to realize the highly efficient optical devices based on Er-related materials for Si photonics and quantum-state manipulation devices in quantum information networks.

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