Influence of TiO₂ host crystallinity on Er³⁺ light emission

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Abstract: This work presents a study of the luminescence properties of Er³⁺ when included into two different TiO₂ hosts: a polycrystalline and an amorphous host. The two host environments were produced by depositing two thin films with different Er³⁺ concentration using radio-frequency magnetron sputtering. Structural analysis revealed the presence of the rutile and anatase phases in the polycrystalline film. Time-resolved and steady-state photoluminescence measurements evidenced the presence of two distinct local Er³⁺ environments in the polycrystalline host. For the amorphous TiO₂ host, only one Er³⁺ environment was observed, which differed from the two environments in the polycrystalline host. A method for extracting a fast and slow time-resolved emission spectrum from the two observed local environments in the polycrystalline host is also presented.

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OCIS codes: (310.6860) Thin films, optical properties; (250.5230) Photoluminescence; (300.6280) Spectroscopy, fluorescence and luminescence.

References and links

1. Introduction

The rare-earth erbium ions (Er$^{3+}$) has been studied extensively as a dopant in a host matrix, predominately due to its luminescent properties around 1540 nm, which makes it suitable as a fiber amplifier for telecommunications [1, 2]. In addition, due to its upconversion properties [3, 4], enabling conversion of near-infrared radiation into red/green light, it has applications in a wide variety of fields like display technologies [5], photovoltaics [6, 7], and medical diagnostics [8]. In order to utilize these luminescent properties of Er$^{3+}$ ions, they must be doped into appropriate hosts like fluorides, phosphates, or oxides. The energy levels of Er$^{3+}$ are only slightly affected by the host because the 4f electrons, which are responsible for the luminescence around 1540 nm and the upconversion properties, are shielded by the outer 5s and 5p electrons. Hence, the interaction between the local electric field of the host and the 4f electrons is weak. As a result, the local host structure around Er$^{3+}$ only results in minor splitting of the free-ion energy levels, 2$^I_{15/2}$ into multiplets. This splitting is called crystal-field (CF) splitting or Stark splitting, and the number of CF sublevels is determined by the symmetry of the surrounding crystal host, such that a reduction in the symmetry around the lanthanide ion will introduce a higher number of sub-levels.

In this paper, we study how the crystallinity of the TiO$_2$ host influences the splitting of the ground state ($^4I_{15/2}$) of Er$^{3+}$, and how this impacts the luminescence from Er$^{3+}$. TiO$_2$ is of interest as a host for Er$^{3+}$ due to its low phonon energy ($< 700$ cm$^{-1}$), which reduces multiphonon relaxation. Furthermore, TiO$_2$ is inexpensive and chemically stable. Other papers on the Er$^{3+}$ doped TiO$_2$ system have studied Er$^{3+}$ in either an anatase or a rutile phase [9–12]. The focus of these studies was primarily the local structure of the Er$^{3+}$ environment and how Er$^{3+}$ is incorporated into TiO$_2$. However, the influence of the host environment on the luminescent properties has only been investigated in few papers and only for crystalline phases [9, 11, 13]. The present paper studies the influence of a polycrystalline TiO$_2$ host with two crystalline phases (anatase and rutile), and an amorphous TiO$_2$ host on the light emission properties of Er$^{3+}$. In particular, the effect of the different host environments on the light emission, CF splitting, and lifetime of the lowest excited level $^4I_{15/2}$, are considered by time-resolved and steady-state photoluminescence spectroscopy (emission and excitation spectra).

2. Experimental details

Two types of Er$^{3+}$ doped TiO$_2$ thin films, with different doping concentrations, were deposited by a radio-frequency magnetron sputtering system from AJA Orion ATC, on n-type Si (100) substrates. The targets were commercially produced (Able Targets) by mixing powders of TiO$_2$ and Er$_2$O$_3$ in desired ratios to achieve Er$^{3+}$ doping concentrations of 1.3 at%...
and 6.1 at%. The sputtering power and the deposition temperature were 100 W and 350 °C for both film depositions. The pressure during deposition was 0.40 Pa. However, the deposition times were modified to ensure that the thin films had approximately the same thickness [3]. The thin films were fabricated with high reproducibility, and the percentage of the different phases could in principle be controlled by varying the deposition parameters, like sputtering power or substrate temperature. From a previous study [3], polycrystalline thin films were observed for Er³⁺ concentrations of 1.3 at%, however, the variation in the percentage of the different TiO₂ phases, and crystalline orientation was not that influenced by changes in the deposition parameters. Hence, our fabrication method do not allow for fabrication of the anatase and rutile phases separately. Anyway, understanding the optical properties of magnetron-sputtered mixed phase TiO₂ films with Er³⁺ doping remains an important topic due to their use in, e.g., upconversion processes for enhanced solar cell efficiency [3, 14].

The TiO₂ thin film with an Er³⁺ doping concentration of 1.3 at% had a resulting thickness of 161 ± 5 nm, while the TiO₂ with 6.1 at% Er³⁺ had a thickness of 150 ± 5 nm as determined by ellipsometry (Sentech SE 850 PV Spectroscopic Ellipsometer).

The thin films were characterized structurally by x-ray diffraction (XRD) using a Bruker D8 Discover diffractometer at a grazing angle of 3 degrees, and by transmission electron microscopy (TEM) using a Philips CM 20 and a FEI-Talos instrument. Furthermore, they were characterized by time-resolved photoluminescence spectroscopy at temperatures of 16 and 300 K, excited by a mode-locked femtosecond Ti:Sapphire laser system which delivers ~100 fs pulses with a central wavelength of 800 nm at a repetition rate of 1 kHz. The emitted light was spectrally dispersed by a monochromator and detected by a photomultiplier tube. By altering the detection wavelength, a time-resolved emission spectrum (TRES) was acquired. The samples were also characterized in another experimental setup by steady-state photoluminescence emission and excitation spectroscopy at a temperature of 12 K. The excitation source was a 450 W Xe arc lamp, which was split by a modular double grating. The emitted light was acquired with a spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Horiba Scientific) coupled to a photomultiplier tube. All emission spectra were corrected for the spectral response of the detection equipment, and the excitation spectra were also corrected for the spectral distribution of the lamp intensity.

3. Results and discussion

3.1 Structural characterization

Figure 1 shows the XRD spectrum measured on the TiO₂ thin films with 1.3 at% Er³⁺ and 6.1 at% Er³⁺. The former shows peaks corresponding to the anatase and rutile phases of TiO₂, whereas the latter shows no peaks indicating that the film is amorphous. This is expected as a high doping concentration will disturb the TiO₂ matrix and eventually result in the loss of the crystalline order [3, 15]. TEM diffraction patterns of the two samples confirm the polycrystalline structure of the TiO₂:Er 1.3 at% thin film, and the amorphous structure of the TiO₂:Er³⁺ 6.1 at% thin film; see insets in Fig. 1(b) and 1(c), respectively. Furthermore, a TEM cross section of TiO₂:Er 1.3 at% is shown in Fig. 1(b), where crystalline grains sitting at the Bragg condition are observed as dark areas. In Fig. 1(c) a STEM cross section of TiO₂:Er³⁺ 6.1 at% shows that there are no crystalline grains in this thin film. In the following sections, the TiO₂:Er³⁺ 1.3 at% thin film will be denoted as the polycrystalline sample and the TiO₂:Er³⁺ 6.1 at% thin film as the amorphous sample. They will be studied separately and then compared.
3.2 Time-resolved emission spectra from the polycrystalline host

Time-resolved emission spectra are obtained from the polycrystalline sample in order to investigate the influence of the polycrystalline environment on the light emission from Er\(^{3+}\), and on the lifetime of the \(^4I_{13/2}\) level, see inset in Fig. 2(a). The Er\(^{3+}\) ions are excited by a short 800 nm laser pulse, which results in population of the upper level \(^4I_{9/2}\). After excitation, the electrons relax to the ground state through several relaxation mechanisms such as radiative decay, or non-radiative decays like cross relaxation, energy transfer, or multi-phonon relaxation. Consequently, the \(^4I_{13/2}\) level is populated by decays from the higher-lying levels as indicated in the inset to Fig. 2(a). The time evolution of the electron populations \(N_N\) in the different levels, can be described by the following differential equations (for one environment type):

\[
\frac{dN_{9/2}}{dt} = -\Gamma_{9/2}N_{9/2}(t)
\]

\[
\frac{dN_{11/2}}{dt} = -\Gamma_{11/2}N_{11/2}(t) + b_{9/2}^0\Gamma_{9/2}N_{9/2}(t)
\]

\[
\frac{dN_{13/2}}{dt} = -\Gamma_{13/2}N_{13/2}(t) + b_{11/2}^0\Gamma_{9/2}N_{9/2}(t) + b_{11/2}^{1/2}\Gamma_{11/2}N_{11/2}(t)
\]
\[
\frac{dN_{15/2}(t)}{dt} = h_{35/2}^{9/2} \Gamma_{9/2} N_{9/2}(t) + h_{15/2}^{11/2} \Gamma_{11/2} N_{11/2}(t) + \Gamma_{13/2} N_{13/2}(t)
\]

(4)

\(\Gamma \) denotes the total decay rate including both the radiative and non-radiative decay rates from a level \(4I_J\). The quantity \(b\) is the branching ratio, for example \(h_{11/2}^{9/2} + h_{35/2}^{9/2} + h_{11/2}^{11/2} = 1\). Solving Eq. (1) yields

\[
N_{9/2}(t) = N_{9/2}(0) \cdot e^{-\Gamma t}
\]

(5)

Inserting this into Eq. (2) and assuming that \(\Gamma_{9/2}\) is fast compared to the subsequent decays, we can obtain the following approximate solution

\[
N_{11/2}(t) = \left[ N_{11/2}(0) + h_{11/2}^{9/2} N_{9/2}(0) \right] \cdot e^{-\Gamma_{9/2} t} \equiv \tilde{N}_{11/2}(0) \cdot e^{-\Gamma_{9/2} t}
\]

(6)

Thus, in addition to the original \(N_{11/2}(0)\) population, the \(4I_{11/2}\)-level is immediately filled with the \(h_{11/2}^{9/2} N_{9/2}(0)\) contribution from \(4I_{9/2}\). This common initial population is denoted \(\tilde{N}_{11/2}(0)\). If the same approximation is used to solve Eq. (3), we get

\[
N_{13/2}(t) = \tilde{N}_{13/2}(0) \cdot e^{-\Gamma_{9/2} t} \frac{1 - a_{\text{rise}} e^{-\Gamma_{13/2} t}}{1 - a_{\text{rise}}}
\]

(7)

Where

\[
a_{\text{rise}} = \frac{1}{1 + \frac{\tilde{N}_{13/2}(0)}{N_{11/2}(0) \cdot \Gamma_{11/2} - \Gamma_{13/2} \cdot h_{13/2}^{11/2}}}
\]

(8)

\[
\Gamma_{\text{rise}} = \Gamma_{11/2} - \Gamma_{13/2}
\]

\[
\tilde{N}_{13/2}(0) = N_{13/2}(0) + h_{13/2}^{9/2} N_{9/2}(0)
\]

The time evolution of the emission corresponding to a transition from level \(4I_{13/2}\) to level \(4I_{15/2}\) is measured, and the resulting decay curve is fitted by Eq. (7). In Fig. 2(a) a typical decay curve is seen. It has a small rise \((\Gamma_{\text{rise}})\) followed by an exponential decay \((\Gamma_{13/2})\), as expected from the solution of the differential equation for level \(4I_{13/2}\) (Eq. (7)). For the fitting procedure the factor \(\tilde{N}_{13/2}(0) / (1 - a_{\text{rise}})\) is used as the amplitude. Hence we arrive at the following fitting function

\[
N_{13/2}(t) = A \cdot e^{-\Gamma_{13/2} t} \cdot \left(1 - a_{\text{rise}} e^{-\Gamma_{13/2} t}\right)
\]

(9)

where

\[
A = \frac{\tilde{N}_{13/2}(0)}{1 - a_{\text{rise}}}
\]
Decay curves are measured for several emission wavelengths in the range of 1450 – 1650 nm, at temperatures of 16 and 300 K and each with an integration time of 5 ms. To allow for identification of any time-dependent spectral features, the decay curves are divided into five time intervals, during which the spectra are integrated, as indicated in Fig. 2(a). The results at 16 K, shown in Fig. 2(b), present the time-resolved emission spectra (TRES) at these time intervals. The spectrum changes as a function of time; in particular the relative significance of the 1532 nm peak changes. Some emission wavelengths (1528, 1532, 1542, 1553, 1557, 1573 nm) are studied further by measuring additional decay curves with longer integration times and hence a better signal-to-noise ratio, as exemplified in Fig. 2(a). The decay curves were tentatively fitted using Eq. (9), but fitting with a single exponential decay did not yield an appropriate fit. However, good fits are obtained by fitting with a double-exponential function instead, see Fig. 3 and Eq. (10). Consequently, the decay curves are, at first, only fitted with a double exponential decay without the rise factor to avoid too many free parameters. The acquired two decay rates (lifetimes) as function of the emission wavelength are seen in the inset on Fig. 3. The two lifetimes obtained at the different emission wavelengths are similar, and as a result, only the average lifetimes are reported (Table 1). The same behavior is observed at 300 K, and the obtained average lifetimes are likewise shown in Table 1. The measured lifetimes are similar at 16 and 300 K. For both temperatures it is apparent that one decay component is faster than the other, and consequently this is denoted as the fast decay or the short-lifetime component. The observation of two distinct lifetimes for the same optical transition in Er$^{3+}$ indicates that the Er$^{3+}$ ions are sitting in two different environments. Due to the presence of two crystalline phases, anatase and rutile, as observed in the structural measurements, we suggest that the two distinguishable environments are precisely these two phases. Furthermore, since both components are present at all the investigated wavelength intervals – and even exhibit similar lifetimes at all emission wavelengths – the two environments must have quite similar CF splitting. This will be discussed in more detail in the next section.
Fig. 3. Typical decay curve (black) at 16 K with a double exponential-function fit with rise (red). Insert: Lifetimes as a function of emission wavelength (16 K).

Table 1. Lifetimes and rise times of level $I_{13/2}$ for TiO$_2$:Er$^{3+}$ 1.3 at% (polycrystalline fast and slow decay), and TiO$_2$:Er$^{3+}$ 6.1 at% (amorphous) at 16 and 300 K. The stated uncertainty was calculated as the standard deviation of the individual lifetimes measured at each emission wavelength as shown in the inset of Fig. 3.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>TiO$_2$ host</th>
<th>Lifetime (ms)</th>
<th>Rise time (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 K</td>
<td>Polycrystalline fast</td>
<td>0.8 ± 0.3</td>
<td>170 ± 24</td>
</tr>
<tr>
<td></td>
<td>Polycrystalline slow</td>
<td>2.1 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Amorphous</td>
<td>0.74 ± 0.03</td>
<td>118 ± 15</td>
</tr>
<tr>
<td>300 K</td>
<td>Polycrystalline fast</td>
<td>0.9 ± 0.1</td>
<td>143 ± 9</td>
</tr>
<tr>
<td></td>
<td>Polycrystalline slow</td>
<td>2.4 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Amorphous</td>
<td>0.37 ± 0.02</td>
<td>74 ± 11</td>
</tr>
</tbody>
</table>

As Eq. (9) did not yield a satisfactory fit to the observed decay curves with rise, an additional decay term is added to Eq. (9) to accommodate the two different decay rates.

$$N_{I_{13/2}}(t) = \left( A_1 \cdot e^{-\tau_{1}} + A_2 \cdot e^{-\tau_{2}} \right) \left( 1 - a_{rise} \cdot e^{-\tau_{rise}} \right)$$  (10)

However, in order to avoid too many free parameters in fitting with Eq. (10), the lifetime parameters in Table 1 are used as fixed input parameters. Then, by fitting the measured decay curves with Eq. (10), information on the relative strength of the fast and slow components is obtained from the amplitudes $A_1$ and $A_2$. As suggested above, we attribute these two components to light emission from Er$^{3+}$ in the two different sites. Furthermore, also the rise time is acquired which is found to be comparable, within the uncertainties, for all emission wavelengths and the average rise time at 16 and 300 K is shown in Table 1.

It is clear that the majority of the excited ions, which decay with the short lifetime, have decayed to the ground state at late time periods. Consequently, if the decays are studied at a late time, most of the detected signal arises from the long-lifetime ions, and the corresponding TRES spectrum primarily contains spectral features from the long-lifetime environment. Furthermore, because the decay is exponential with parameters obtained from fitting using Eq. (10), it is possible to extrapolate the TRES of the long-lifetime environment from late times back to earlier (all) times. Subtracting this derived long-lifetime TRES from the total...
TRES, we obtain the TRES for the short-lifetime environment. The result of this procedure is seen in Fig. 4 (solid curves). The short-lifetime environment primarily exhibits light emission at ~1532 nm, whereas the long-lifetime environment shows a broader spectrum with more emission in the entire detection range. The same trends are observed if the areas under the fast and slow decay curves are calculated from the fitted exponential decay functions, see the triangles in Fig. 4. Hence the two approaches yield the same result, and consequently the approach to divide the TRES spectra in a fast and slow decay is reasonable. In particular, the fact that the slow and fast components of the light emission have different spectra proves that the two time scales indeed correspond to different local environments for the Er\(^{3+}\) ions. The two TRES curves and the area of the decay curves both indicate that the two environments emit light at the same wavelengths, however the relative intensity of the light is different, although of same order of magnitude.

![Fig. 4. Left scale and solid lines: TRES spectrum of the two environments, fast and slow decay, for the polycrystalline host, and the TRES spectrum for the amorphous host. Right scale and triangles: Area of the decay curves for the fast and the slow decay at different emission wavelengths. All data are obtained at 16 K.](image)

### 3.3 Low-temperature emission and excitation spectra from the polycrystalline host

Figure 5(a) presents the low-temperature NIR emission spectra of the polycrystalline sample under distinct excitation wavelengths revealing the Er\(^{3+}\) intra-\(4f^{11}\) transition, \(^4I_{13/2} \rightarrow ^4I_{15/2}\). The spectra show, at least, 8 clearly express Stark components (marked in Fig. 5(a) with vertical lines) whose energy and full-width-at-half-maximum (FWHM) is almost independent of the excitation wavelength. However, the intensity of the Stark peaks changes with the excitation wavelength. The energy peak position is around 6588 \(\pm\) 3 cm\(^{-1}\), 6557 \(\pm\) 3 cm\(^{-1}\), 6540 \(\pm\) 3 cm\(^{-1}\), 6523 \(\pm\) 3 cm\(^{-1}\), 6498 \(\pm\) 3 cm\(^{-1}\), 6460 \(\pm\) 3 cm\(^{-1}\), 6439 \(\pm\) 3 cm\(^{-1}\) and 6369 \(\pm\) 3 cm\(^{-1}\) (1518 nm, 1525 nm, 1529 nm, 1533 nm, 1539 nm, 1548 nm, 1553 nm and 1570 nm, respectively). We note that the FWHM is smaller (approx. 30 cm\(^{-1}\)) than those observed in the time-resolved photoluminescence. We believe that the broader peaks observed in the time-resolved spectra are related to the short-pulse excitation process, since the steady-state photoluminescence spectra are acquired using a Xe arc lamp as excitation source.
To determine the main excitation paths for populating the excited states of Er$^{3+}$, the excitation spectra are monitored around the $^4I_{13/2} \rightarrow ^4I_{15/2}$ Stark components, see Fig. 5(b). The excitation spectra are formed of a broad band between 250 and 400 nm, with a shoulder around 305 nm and whose peak position depends on the monitoring wavelength (vertical lines), namely, peaks around 326 nm (monitoring wavelength around 1529 nm and 1533 nm) and 340 nm (1518 nm, 1539 nm, 1548 nm and 1553 nm). We note the presence of a low-relative intensity line around 520 nm ascribed to the $^4I_{15/2} \rightarrow ^4H_{11/2}$ transition. The dependence of the excitation spectra on the monitoring wavelength is an experimental evidence of the presence of more than one local Er$^{3+}$ environment, supporting the observations from the time-resolved measurements, which demonstrate that the Er$^{3+}$ ions occupy, at least, two distinct average local environments. For the sake of simplicity, the two Er$^{3+}$ local sites will hereafter be labeled as Site 1 and Site 2 corresponding to the excitation spectra peaking at 326 and 340 nm, respectively. At the higher monitoring wavelength (1570 nm) the spectrum reveals both components at 326 and 340 nm. These two components are attributed to the contribution of the anatase [16] and rutile [17] phases, respectively. The shoulder at around 305 nm may be attributed to the presence of smaller anatase nanocrystallites located in amorphous titania walls [18], or to defects assigned to unsaturated titanium ions at the crystal surface, or at the interface between nanocrystallites and an amorphous matrix [13].

Another observation from the excitation spectra is the fact that the TiO$_2$-related components at 326 and 340 nm dominates the excitation spectra of Site 1 and Site 2 (compared with the low-relative intensity of the $^4I_{15/2} \rightarrow ^4H_{11/2}$ transition at 520 nm), which indicates that the main excitation path for the Er$^{3+}$ excited states arises from energy transfer from the polycrystalline TiO$_2$ host [13].

We note that the large overlap between the contribution from the anatase and rutile phases in the excitation spectra disable a selective excitation of the emission spectra arising from Site 1 and Site 2. Nevertheless, further insight into the excitation and emission from the apparent two Er$^{3+}$ environments is gained by studying the emission line with the highest intensity in each environment. The most intense emission lines are at 1529 and 1539 nm. The emission and excitation spectra at these wavelengths are fitted with Gaussian curves. From this fitting procedure it is possible to obtain quantitative information on the position and CF splitting of the energy levels in Er$^{3+}$ which are used for excitation. We assume that the emission spectra are dominated by the transitions from the lowest level of the $^4I_{13/2}$ multiplet to the ground state multiplets ($^4I_{15/2}$). As a result, the emission spectra contain information on the CF splitting of the ground state. According to Luo et al. [11], Er$^{3+}$ is probably sitting in a C$_2v$ symmetry site (low symmetry site) in the anatase TiO$_2$ host. Consequently, if Er$^{3+}$ is sitting in the anatase phase a CF splitting of level $^4I_{15/2}$ into 8 sublevels is expected [11, 19]. Hence, in the emission spectra only 8 emission peaks should be visible. However, an 8-Gauss fit does not capture all the observed peaks in the emission spectrum, Fig. 6(a). The presence of more than 8 Stark components may arise from: i) hot bands arising from transitions from the $^4I_{15/2}$ Stark sublevels, or ii) the presence of, at least, two distinct average Er$^{3+}$-local sites as already pointed out. We remind that the structural characterization showed the presence of both the anatase and the rutile phases of TiO$_2$ in the thin film, Fig. 1(a). Hence, we expect the additional peaks to arise from Er$^{3+}$ sitting in the rutile phase. Regardless of which site Er$^{3+}$ occupies (interstitial or replacing Ti$^{4+}$) in rutile we expect it to be a low symmetry site, because the Ti$^{4+}$ site in rutile has the D$_{2h}$ symmetry which is of low symmetry [16, 19]. Consequently, a splitting of level $^4I_{15/2}$ into 16 (8 + 8) sublevels is anticipated. Accordingly 16 Gauss curves are fitted to the emission spectrum obtained at 326 nm excitation, and each curve along with the cumulative fit are shown in Fig. 6(a). However, some Gauss curves do overlap (6400 – 6450 cm$^{-1}$) which makes them difficult to distinguish and therefore the fit is not perfect. 16 Gauss curves are also fitted to the emission spectrum at 340 nm excitation. The positions and areas of the 16 Gauss curves obtained for both excitations are plotted in Fig. 6(b). Generally, the energy and peak area are similar for all
the Gauss peaks, however for the peaks at ~6540 cm$^{-1}$ (~1529 nm) the 326 nm excitation dominates. Thus one Er$^{3+}$ environment emits more light at this excitation wavelength than the other environment, and consequently, it is possible to distinguish between the two types of Er$^{3+}$ environments at this wavelength.

Fig. 5. (a) Emission spectra from TiO$_2$:Er$^{3+}$ 1.3 at% at 12 K. The excitation wavelengths are indicated in the legend, while the vertical dashed lines indicate the location of the emission peaks. (b) Normalized excitation spectra from TiO$_2$:Er$^{3+}$ 1.3 at% at 12 K. The studied emission wavelengths are indicated in the legend, and the vertical dashed lines indicate the excitation wavelengths used in panel (a).
In the TRES data, the emission intensity from the fast decaying environment is generally lower than that from the slow decay, however, at 1532 nm the intensity of the emission from the fast decay increases abruptly (Fig. 4). The same trend is seen when analyzing the areas of the exponential decay curves. Comparing the results from the TRES measurements with the emission spectra, we find that one of the environments suddenly emits more light at ~1530 nm. Hence the environment which is preferentially excited at 326 nm could correspond to the fast decaying environment because there is an observed change in light emission.

Fig. 6. (a) Emission spectrum at 326 nm excitation (12 K) with Gaussian curves fitted to the spectrum. Shown are the cumulative fits with 8 or 16 Gauss curves respectively, and the 16 individual Gauss curves. (b) Peak area of the Gaussian curves fitted to the emission spectrum at 326 and 340 nm excitation, as a function of the energy of the peak.
Fig. 7. (a) Excitation spectrum (12 K) monitored at 1539 nm with three Gauss curves fitted to the spectrum. The cumulative fit is also included. (b) Energy level diagram at 12 K for the two types of Er$^{3+}$ sitting in the TiO$_2$:Er$^{3+}$ 1.3 at% thin film. The two types are in the diagram denoted by 1529 and 1539 according to the studied emission line used for the excitation spectra. The left side of the diagram is constructed from the Gauss peak positions (thick black lines) and widths (spacing between thin gray lines) obtained from the excitation spectra at 1539 and 1529 nm emission, respectively. Thus the left side shows the excitation to higher energy levels. The A is short for anatase and the R for rutile. The right side show the Er$^{3+}$ energy levels obtain from ref [11] for Er$^{3+}$ in an anatase TiO$_2$ host (ground state to $^4G_{11/2}$). The higher energy levels are found in ref [20], however this is for a LaF$_3$ host because the data are not available for TiO$_2$. Hence only the central position of the energy level are indicated and not the CF splitting.

In Fig. 7(a) the excitation spectrum monitored at 1539 nm is fitted with three Gauss curves. The position of the Gauss peak corresponds to the energy of the given energy level that is populated, and the FWHM corresponds to the width of the given level due to CF splitting. Consequently, from the fitting of the two excitation spectra monitored at 1529 and 1539 nm, it is possible to study the difference in the energy levels of the two environments (fitting results from the excitation spectrum monitored at 1529 nm is not shown). The energy levels, which are populated upon excitation, are marked on an energy diagram in Fig. 7(b) (left side). The central position of the energy level is represented by a thick black line, and the FWHM from the Gauss fits are indicated with gray lines. A small shift in the position of the energy levels is observed as the monitoring wavelength is moved from 1529 to 1539 nm. Figure 7(b) also contains the 4f energy levels of Er$^{3+}$ obtained from the literature [11, 20], which allows for a comparison and determination of which levels are populated. The levels at ~26500 cm$^{-1}$ (377 nm) could correspond to population of level $^4G_{11/2}$. However, there is a small shift in the center position when the monitoring wavelength is changed. The shift could be a result of a different CF splitting depending on Er$^{3+}$ sitting in either Site 1 or 2.
The levels at 29600 cm$^{-1}$ (338 nm), 30100 cm$^{-1}$ (332 nm) and ~32400 cm$^{-1}$ (309 nm) do not correspond to any of the energy levels of Er$^{3+}$, and furthermore the levels are very broad. As mentioned previously the level at ~340 nm is attributed to rutile [17] and the level at ~326 nm to anatase [16]. Whereas the level at ~305 nm could arise from smaller anatase crystallites in an amorphous TiO$_2$ matrix [18], interfacial states or defect states in TiO$_2$ [13].

Referring to the structural characterization, only crystalline phases are present in the polycrystalline sample, and the number of Er$^{3+}$ ions sitting at interfaces/defects must be much less than the number of ions sitting within the crystalline environment, as judged by the grain size in Fig. 1(b). We also note that the content of the anatase and rutile phases in the polycrystalline sample is comparable, judging by the area of the anatase and rutile peaks in the XRD spectrum in Fig. 1(a). Now, considering the emission spectra of the fast and slowly decaying environments in Fig. 4, we observe that the strength of the light emissions from the two sites is of the same order of magnitude, which strongly supports our attribution of the two local environments to the anatase and rutile phases. One could speculate whether the two sites could instead be attributed to an interfacial/defect environment and a crystalline environment. However, the similarity of the emission strengths of the two environments would then either require the much fewer Er$^{3+}$ ions located at interfaces to have a much larger quantum efficiency, or require that the Er$^{3+}$ ions at interfaces to actually be much higher in concentration without affecting (quenching) the quantum efficiency of light emission. Both of these possibilities seem very unlikely, again supporting our attribution of the two sites to the anatase and rutile phases.

3.4 Time-resolved emission spectra from the amorphous host

The TRES of Er$^{3+}$ in the amorphous host is shown in Fig. 8(a). The light emission is measured in the same wavelength range as for the polycrystalline sample. The TRES spectra are similar to those observed for the polycrystalline sample. In order to compare the TRES from the polycrystalline and the amorphous sample, the acquired results from both the amorphous and the two polycrystalline local environments are shown in Fig. 4. It can be seen that Er$^{3+}$ in the amorphous host emits light over a broader light spectrum than Er$^{3+}$ in the polycrystalline host. However, some emission peaks are easier to identify in the polycrystalline TRES than in the TRES for the amorphous host.

Decay curves at 16 and 300 K with a better signal-to-noise ratio are collected at the same emission wavelengths as for the polycrystalline sample. The decay curves are fitted well by a single exponential decaying function with rise (Eq. (9)). This indicates that there is only one environment in the amorphous host. The obtained average lifetime and rise time from the fitting of the decay curves at the different emission wavelength is seen in Table 1. The lifetime of $^4I_{13/2}$ is lower for the amorphous host than for either of the two polycrystalline hosts at 300 K. If, by analogy, the lifetime of level $^4I_{11/2}$ is also lower, the rise time would also be expected to be shorter in the amorphous host because it depends primarily on the lifetime of level $^4I_{11/2}$. However, the rise time is longer for the amorphous host, which indicates that the lifetime of level $^4I_{11/2}$ has increased. At 16 K the lifetime of the amorphous sample is longer than the lifetime measured at 300 K, resulting in the lifetime of Er$^{3+}$ in the fast-decay polycrystalline host and in the amorphous host being similar.

The area of the decay curves obtained from the amorphous and polycrystalline sample is plotted in Fig. 8(b) as a function of the emission wavelength. From this plot it is possible to gain information on the amount of light emitted at the different wavelengths. It is observe that the area of the decay curve of both environments in the polycrystalline host is smaller than the decay curve area of the amorphous host. Thus generally more light is emitted from Er$^{3+}$ in the amorphous host compared to the amount of light emitted from Er$^{3+}$ in the polycrystalline host. As the Er$^{3+}$ concentration is four times higher in the amorphous sample than in the polycrystalline sample, it is expected that approximately 4 times more light will be emitted from the amorphous sample (if no quenching occurs). However, only approximately 2 times...
more light is emitted from the amorphous sample, indicating that alternative decay routes to light emission from the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition are slightly more dominant in the amorphous environment.

![Graph](image1)

**Fig. 8.** (a) Time-resolved emission spectrum for the TiO$_2$:Er$^{3+}$ 6.1 at% thin film at 16 K. The different time intervals are indicated in the legend. (b) Area of the decay curve for the amorphous host and polycrystalline (poly) host at 16 K.

### 3.5 Low-temperature emission and excitation spectra from the amorphous thin film

![Graph](image2)

**Fig. 9.** (a) Normalized emission spectra of TiO$_2$:Er$^{3+}$ 6.1 at% at 12 K. The excitation wavelengths are indicated in the legend. (b) Normalized excitation spectra of TiO$_2$:Er$^{3+}$ at 12 K. The emission wavelengths are indicated in the legend.

The emission and excitation spectra measured on Er$^{3+}$ in the amorphous host are shown in Fig. 9(a) and (b), respectively. In the emission spectra, the same peaks are observed...
independently on the applied excitation wavelength at 325, 377 and 520 nm. Fewer peaks are observed as compared to the polycrystalline host; they are positioned at 1520, 1529, 1537, 1580 and 1600 nm. However, the peaks are very broad and some are difficult to distinguish. The broadening of the peaks occurs because the amorphous host environment does not possess crystalline order, and thus the Er\(^{3+}\) ions experience an inhomogeneous environment which is slightly different for each Er\(^{3+}\) ion. The same broadening is observed in the TRES on Fig. 4.

The excitation spectra are also similar at all the measured emission wavelengths, and consequently both the excitation and the emission spectra confirm the results from the time-resolved photoluminescence: Er\(^{3+}\) is sitting in one inhomogenous environment in the amorphous host.

4. Discussion and conclusion

In this study it is observed that the crystallinity of TiO\(_2\) affects the light emission from Er\(^{3+}\), and the CF splitting of the energy levels of Er\(^{3+}\). Er\(^{3+}\) is studied in a polycrystalline phase consisting of rutile and anatase, and in an amorphous phase. In the polycrystalline TiO\(_2\) thin film, light emission from two different Er\(^{3+}\) environments is observed. Both steady-state and time-resolved photoluminescence spectroscopy are consistent with this observation. From the time-resolved photoluminescence spectroscopy, two decay rates, a fast and a slow, are observed for the polycrystalline sample. The two Er\(^{3+}\) environments are further confirmed by emission and excitation spectra. In the emission spectra (Fig. 6), more emission lines due to CF splitting are observed than expected for level \(^7I_{15/2}\) in a single TiO\(_2\) environment. In the excitation spectra, a shift in the excitation wavelength, and hence a shift in the energy levels, is observed for some emission wavelengths (Figs. 5 and 7).

The light emission from the two Er\(^{3+}\) environments in the polycrystalline host can arise from Er\(^{3+}\) ions populating an anatase and a rutile crystalline environment. It could also arise from Er\(^{3+}\) populating a crystalline and an amorphous environment, however, the structural analysis of the polycrystalline host indicated that the thin film is purely polycrystalline, and does not contain an amorphous phase. If the lifetimes of level \(^7I_{13/2}\) in the amorphous and the polycrystalline hosts are compared, we find that the two lifetimes in the polycrystalline host are different from the lifetime in the amorphous host at 300 K (Table 1). Consequently, the two environments in the polycrystalline host are different from the environment in the amorphous host. It is therefore likely that the different light emitting behaviors of Er\(^{3+}\) in the polycrystalline host can be ascribed to Er\(^{3+}\) ions populating both a rutile and an anatase phase of TiO\(_2\).

We were able to divide the time-resolved emission spectrum obtained from the polycrystalline sample into a fast decay spectrum and a slow decay spectrum, which yielded some spectral features from the two environments. The obtained fast and slow decay time-resolved emission spectra were confirmed by analyzing the area of the decay curves. As a result, it seems like a good approach to gain information on light emission from the two environments.

Acknowledgments

This work was supported by the Danish Strategic Research Council under the project named “Thin-film solar cell based on nanocrystalline silicon and structured backside reflectors—THINC.” This work has also been partially developed in the scope of the project CICECO Aveiro Institute of Materials (Ref. FCT UID/CTM/50011/2013), financed by Portuguese funds through FCT/MEC and when applicable co-financed by FEDER under the PT2020 Partnership Agreement. AVT Freitas from University of Aveiro is gratefully acknowledged for the help during the low-temperature steady-state photoluminescence measurements.

Received 22 Feb 2016; revised 10 Apr 2016; accepted 12 Apr 2016; published 19 Apr 2016