Red up-conversion dynamics in Er$^{3+}$-doped TeO$_2$–ZnO glasses

ABDELFATTEH CHERIF*, ABDELAZIZ KANOUN, NEJEH JABA

Laboratoire de Physique des Semi-conducteurs, Département de Physique, Faculté des Sciences, 5019 Monastir, Tunisie

*Corresponding author: cherif_af@yahoo.fr

Red fluorescence has been obtained under 980 nm excitation in Er$^{3+}$-doped TeO$_2$–ZnO glasses. The dynamics of the red up-conversion is well explained with the proposed model. The energy transfer processes are predominant.

Keywords: tellurite glasses, erbium: Er$^{3+}$, dynamics of up-conversion.

1. Introduction

Rare earth-activated fluoride and oxide glasses are very attractive materials for many applications, such as optical amplifiers in the second and third telecommunications windows (at 1.3 and 1.53 μm, respectively) and frequency up-converters [1, 2]. One of the most used oxide glasses is tellurite thanks to its good compromise between high refractive index and low oxide phonon energy [3, 4]. Rare-earth doped solids materials have been studied by the up-conversion [5]. In addition, this phenomenon (up-conversion) has been used to explain laser processes [6]. In the rare-earth doped glasses, the emission always occurs at 4$f$ electron level. Their up-conversion can be understood by the well-known mechanisms [6–14]: excited-state absorption (ESA), energy transfer up-conversion (ETU) and photon avalanche (PA).

The up-conversion fluorescence has already been studied in Er$^{3+}$-doped TeO$_2$–Na$_2$O [15], TeO$_2$–PbO [16], TeO$_2$–ZnO [17] and TeO$_2$–Nb$_2$O$_5$ [18].

In this paper, we present an analysis of Er$^{3+}$ optical transitions behavior in the visible range. We have focused our study details on the red emission centered on 670 nm. Finally, we have investigated the dynamics of the $^4F_{9/2}$ state and explained it based on the relative efficiency of the different mechanisms.

2. Experimental details

Glasses were prepared from oxide powders of TeO$_2$, ZnO and Er$_2$O$_3$ as starting materials using the conventional melt-quenching method. The amount of dopant was
varied between 0.2 and 3 mol% Er₂O₃. A continuous wave infrared Ti:sapphire laser tuned to 980 nm was used for up-conversion excitation in the 400–700 nm regions. The intrinsic lifetimes of the levels were obtained by exciting the samples with a laser analytical systems dye laser pumped by a pulsed frequency doubled Nd:YAG laser from BM Industries. The duration of pulses was 8 ns. The emitted light has been focused on a Jobin–Yvon HR S2 spectrophotometer. The detection has been performed using an R 1767 Hammamatsu photomultiplier and a Lecroy 9410 averager oscilloscope. All experiments were performed at room temperature.

3. Up-conversion results and mechanisms

Figure 1 shows the up-conversion spectra of Er³⁺-doped samples (0.2 and 3 mol%) excited at 980 nm. As we can note, the luminescence intensities increase with increasing Er³⁺ content. The emission bands associated with Er³⁺ transitions are centered at 410 nm (²H₉/₂ → ⁴I₁₅/₂), 530 nm (⁴H₁₁/₂ → ⁴I₁₅/₂), 555 nm (⁴S₃/₂ → ⁴I₁₅/₂) and 670 nm (⁴F₉/₂ → ⁴I₁₅/₂). The green emission at 555 nm is more efficient than the red one at 670 nm. The blue ²H₉/₂ → ⁴I₁₅/₂ up-conversion transition around 410 nm has been barely observed.

![Up-conversion spectra](image)

Fig. 1. Up-conversion spectra for 0.2 and 3 mol% Er³⁺ in the 70TeO₂–30ZnO tellurite glass at T = 300 K, of the blue, green and red emissions.

In our study, we focus our investigation on the emission line in the red region of the spectrum at 670 nm. As we can observe in Fig. 1, the intensity of the red up-conversion emission in the heavily doped sample remains much stronger than in the sample with low erbium concentration. If we consider that the excite-state absorption (ESA) is the only process responsible for the up-conversion in the case of the weak concentrations of dopant, this result means that ESA cannot explain the weaker signal obtained for 0.2 mol% erbium (at 670 nm). Also, the red up-conversion for 3 mol% erbium is not explained by ESA, since this process does not depend on the concentration.
In order to confirm this assumption, we have recorded the luminescence decays of the transition $^{4}F_{9/2}$ after direct ($\lambda_{\text{exc}} = 670\,\text{nm}$) and under two selective laser pulse excitations (at $\lambda_{\text{exc}} = 980\,\text{nm}$ and $\lambda_{\text{exc}} = 550\,\text{nm}$), for 0.2 mol% concentration. Figure 2a shows a difference in decay profiles of the red emission (at $\lambda_{\text{exc}} = 670\,\text{nm}$ and $\lambda_{\text{exc}} = 550\,\text{nm}$). This result means that the $^{4}F_{9/2}$ level cannot be populated via a non-radiative relaxation through the $^{4}S_{3/2}$ excited state.

Furthermore, Fig. 2b shows that luminescence decay is different for both $\lambda_{\text{exc}} = 980\,\text{nm}$ and $\lambda_{\text{exc}} = 670\,\text{nm}$. These results imply that the excite-state absorption is not responsible for red up-conversion. The dominant mechanism is then the energy transfer up-conversion (ETU).

To better understand the up-conversion mechanism, we have measured the luminescence intensity of red emission as a function of the pump power. Figure 3 exhibits

![Graph showing luminescence intensity vs pump power](image)

Fig. 3. Intensity of the up-converted red emission from Er$^{3+}$ versus laser power excitation, for 3 mol% Er$^{3+}$ in tellurite glass using 980 nm excitation. Measurements were performed at 300 K. The value 1.84 is the slope of the line.
a log–log plot of $I_{\text{upc}}$ versus $I_{\text{IR}}$ intensities. As we can note, we have obtained a linear behavior. The extracted slope is about 1.84. This indicates that the red emission arises from a two-step up-conversion process.

Figure 4 illustrates the energy level diagram. In this figure, the possible mechanisms leading to the observed red luminescence after infrared excitation are also shown. The excited $^4F_{9/2}$ state can be populated by two possible mechanisms, ESA and/or energy transfer (ETU). In the first process (ESA), one Er$^{3+}$ ion, initially in the ground state, absorbs one IR photon and is excited to the $^4I_{11/2}$ state from where the $^4I_{13/2}$ state is populated by multiphonon relaxation. This is followed by the absorption of a second IR photon from the $^4I_{13/2}$ excited state to the $^4F_{9/2}$ state. In the second process (ETU), we can explain the up-conversion of the red emitting $^4F_{9/2}$ state by three mechanisms:

- The first one is the energy transfer up-conversion ETU-1: $^4I_{11/2} + ^4I_{11/2} \rightarrow ^4I_{13/2} + ^4F_{9/2}$.
- The second one is the energy transfer up-conversion ETU-2: $^4I_{13/2} + ^4I_{11/2} \rightarrow ^4I_{15/2} + ^4F_{9/2}$.
- The third one is the ESA: $^4I_{13/2} \rightarrow ^4F_{9/2}$.

And of the cross-relaxation (RC): $^4I_{15/2} + ^4F_{9/2} \rightarrow ^4I_{13/2} + ^4I_{11/2}$.

### 3.1. Decay times investigation

The evidence of excitation-density-dependent decay is most easily presented through the use of luminescence decay measurements.

Lifetimes of $^4I_{11/2}$ and $^4F_{9/2}$ transitions, into direct excitations, show non-exponential behaviors which can be fitted by a mean decay lifetime given by:

$$\tau_m = \int_0^\infty \frac{I(t)}{I_0} \, dt$$
In case of $^4I_{13/2}$ the decay transient was fitted with the dual exponential decay function:

$$\frac{I(t)}{I(0)} = \exp\left(-\frac{t}{\tau_1}\right) - \exp\left(-\frac{t}{\tau_2}\right)$$

where $\tau_1$ and $\tau_2$ are the decay times of $^4I_{11/2}$ and $^4I_{13/2}$, respectively.

The values of measured lifetimes for different Er$^{3+}$ ion concentrations ranging from 0.5 to 3 mol% are gathered in Tab. 1.

The cross-relaxation energy transfer efficiency $\eta_{CR}$ for an active ion concentration of $c\%$ may be derived from the fluorescence decays using the following equation:

$$\eta_{CR} = 1 - \frac{\int_0^\infty I(t)\,dt}{\tau(0\%)}$$

The integral determines the area under the fluorescence decay curves. The results given in Tab. 1 show really high cross-relaxation energy transfer efficiencies in the 3 mol% Er$^{3+}$ doped TeO$_2$–ZnO glass. Several articles use this definition to determine the quantum yield of the cross-relaxation mechanism [19–21].

### Table 1. Values of measured lifetimes $\tau_{mes}$ of different levels and the cross-relaxation energy transfer efficiency $\eta_{CR}$ of $^4F_{9/2}$ state for 0.5, 1 and 3 mol% Er$^{3+}$.

<table>
<thead>
<tr>
<th>Er$_2$O$_3$ [mol%]</th>
<th>0</th>
<th>0.5</th>
<th>1</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{^4I_{13/2}}$ [µs]</td>
<td>2600</td>
<td>2488</td>
<td>1666</td>
<td>1499</td>
</tr>
<tr>
<td>$\tau_{^4I_{11/2}}$ [µs]</td>
<td>145</td>
<td>132</td>
<td>114</td>
<td>86</td>
</tr>
<tr>
<td>$\tau_{^4F_{9/2}}$ [µs]</td>
<td>28</td>
<td>25</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>$\eta_{CR}$ ($^4F_{9/2}$)</td>
<td>0.00</td>
<td>0.11</td>
<td>0.51</td>
<td>0.64</td>
</tr>
</tbody>
</table>

3.2. Up-conversion investigation

The evaluations of the radiative lifetimes are indeed required to understand deexcitation mechanisms. To evaluate the radiative decay rate of the different transitions, the intensity parameters $\Omega_i = 2, 4, 6$ have been calculated using the Judd–Ofelt formulae [22, 23]. The relevant values are $\Omega_2 = 5.93\times10^{-20}$ cm$^2$, $\Omega_4 = 1.50\times10^{-20}$ cm$^2$, and $\Omega_6 = 1.07\times10^{-20}$ cm$^2$ [24]. From these parameters, the branching ratio $\beta_{ij}$ of the $(ij)$ transition and the radiative lifetimes can be evaluated.

The corresponding radiative lifetimes (Tab. 2) were compared with the measured lifetimes of the $^4F_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ levels. The $^4F_{9/2} \rightarrow ^4I_{9/2} \rightarrow ^4I_{11/2}$ transitions are mainly non-radiative and their quantum yields are almost 100%, so the $^4I_{9/2}$ level is not retained in the model.
The ground state absorption from the $^4I_{15/2}$ level to the $^4I_{11/2}$ level is represented by arrow $R_1$ ($1 \rightarrow 3$) and the transition $^4I_{13/2} \rightarrow ^4F_{9/2}$ is represented by the arrow $R_2$ ($2 \rightarrow 4$). The parameters of the model are gathered in Tab. 3.

ESA process is a single ion process and is independent of Er$^{3+}$ ions concentration, while ETU process involves two ions. Therefore the up-converted luminescence intensity in the ETU process usually varies quadratically with the dopant rare-earth ions concentration [6, 19, 25–30].

We are ready to exhibit a model, to describe the dynamics of the red up-conversion. Discussions of different models are presented in the literature [31–40].

Theoretically, the system can be easily described by a four levels scheme (at $\lambda_{\text{exc}} = 980$ nm). Our model is expressed by the following population rate equations:

$$\frac{dn_2}{dt} = R_2 n_2 - n_2 \frac{1}{\tau_2} + \frac{n_2}{\tau_2} + \frac{\eta_{\text{CR}} n_1 n_4}{(1 - \eta_{\text{CR}}) \tau_4} + \frac{\beta_{32} n_3}{(1 - \eta_{\text{CR}}) \tau_4} +$$

$$+ \frac{\beta_{42} n_4}{(1 - \eta_{\text{CR}}) \tau_4} - Q_2 n_3 n_2 + Q_1 n_3^2$$  \hspace{1cm} (1a)

$$\frac{dn_3}{dt} = R_1 n_1 - n_3 \frac{1}{\tau_3} - Q_2 n_3 n_2 + \frac{\beta_{43} n_4}{(1 - \eta_{\text{CR}}) \tau_4} - 2 Q_1 n_3^2 + \frac{\eta_{\text{CR}} n_1 n_4}{(1 - \eta_{\text{CR}}) \tau_4}$$  \hspace{1cm} (1b)

$$\frac{dn_4}{dt} = R_2 n_2 - n_4 \frac{1}{\tau_4} - \eta_{\text{CR}} n_1 n_4 \frac{1}{(1 - \eta_{\text{CR}}) \tau_4} + Q_2 n_3 n_2 + Q_1 n_3^2$$  \hspace{1cm} (1c)

$$n_1 + n_2 + n_3 + n_4 = 1$$  \hspace{1cm} (1d)

where $n_1$, $n_2$, $n_3$ and $n_4$ are the populations of $^4I_{15/2}$, $^4I_{13/2}$, $^4I_{11/2}$ and $^4F_{9/2}$ levels, respectively; $R_1$ is the GSA probability and $R_2$ is the ESA probability; $Q_1$ and $Q_2$ are the ETU up-conversion coefficients; $\beta_{ij}$ is the branching ratio of the ($ij$) transition, and $\eta_{\text{CR}}$ is the cross relaxation rate according to Fig. 4. We have measured all these parameters and their following values are returned in Tab. 4.

<table>
<thead>
<tr>
<th>Level</th>
<th>$\tau_{4I_{13/2}}$ [μs]</th>
<th>$\tau_{4I_{11/2}}$ [μs]</th>
<th>$\tau_{4F_{9/2}}$ [μs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiative lifetime</td>
<td>3535</td>
<td>2850</td>
<td>325</td>
</tr>
</tbody>
</table>

| Table 3. Values of the parameters used in our model. |
|---|---|---|---|---|---|---|
| $\tau_2$ [μs] | $\tau_3$ [μs] | $\tau_4$ [μs] | $\beta_{32}$ [%] | $\beta_{42}$ [%] | $\beta_{43}$ [%] | $\eta_{\text{CR}}$ [%] |
| 2600 | 145 | 28 | 16.0 | 4.9 | 5.0 | 64 |
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Table 4. Values of fitting parameters: $R_1$, $R_2$, $Q_1$ and $Q_2$.

<table>
<thead>
<tr>
<th>$R_1$ [s$^{-1}$]</th>
<th>$R_2$ [s$^{-1}$]</th>
<th>$Q_1$ [s$^{-1}$]</th>
<th>$Q_2$ [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>258</td>
<td>0.12</td>
<td>0.6</td>
<td>28345</td>
</tr>
</tbody>
</table>

Fig. 5. Time evolution of the red fluorescence originating from the $^4F_{9/2}$ level at 980 nm excitation wavelength. The squares are the experimental data; the solid curve is the prediction of our model.

Fig. 6. Energy transfer and up-conversion processes considered in the simplified model.

System (1) leads to the fit of the time evolution of the red fluorescence represented by the line in Fig. 5 (at 980 nm). The fit was performed with four fitting parameters: $R_1$, $R_2$, $Q_1$ and $Q_2$.

Table 4 compares the numerical values for Er$^{3+}$-doped tellurite glass, and it can be seen that ASE and ETU-I are insignificant. Therefore, we can simplify our model as presented in Fig. 6. In this situation, the population rate Eqs. (1) become:
Equation (2c) suggests that change population of level 4 is similar to that population of levels 2 and 3 \( \frac{dn_4}{dt} \propto n_2n_3 \). Figure 7 confirms this idea.

\[ \begin{align*}
\frac{dn_2}{dt} &= -\frac{n_2}{\tau_2} + \frac{n_4}{\tau_4 (1 - \eta_{CR})} + \frac{\beta_{32} n_3}{\tau_4 (1 - \eta_{CR})} + \frac{\beta_{42} n_4}{\tau_4 (1 - \eta_{CR})} - Q_2 n_3 n_2 \tag{2a} \\
\frac{dn_3}{dt} &= R_1 n_1 - \frac{n_3}{\tau_3} - Q_2 n_3 n_2 + \frac{\beta_{43} n_4}{\tau_4 (1 - \eta_{CR})} + \frac{\eta_{CR} n_1 n_4}{\tau_4 (1 - \eta_{CR})} \tag{2b} \\
\frac{dn_4}{dt} &= -\frac{n_4}{\tau_4} - \frac{n_1}{\tau_4 (1 - \eta_{CR})} + Q_2 n_3 n_2 \tag{2c} \\
\end{align*} \]

\[ n_1 + n_2 + n_3 + n_4 = 1 \tag{2d} \]

Equation (2c) suggests that change population of level 4 is similar to that population of levels 2 and 3 \( \frac{dn_4}{dt} \propto n_2n_3 \). Figure 7 confirms this idea.

4. Conclusions

Up-conversion emission at 670 nm has been obtained in tellurite glasses doped with 3 mol% by excitation with 980 nm. The dynamics of the red up-conversion is well explained with the proposed model; from the results it is possible to distinguish the contribution of two ETU processes and tell which one is predominant. The 670 nm up-conversion emission presents maximum for the up-conversion efficiency at high concentration and at room temperature.

References

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