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Citation: J. Appl. Phys. 108, 093514 (2010); doi: 10.1063/1.3493239
View online: http://dx.doi.org/10.1063/1.3493239
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v108/i9
Published by the AIP Publishing LLC.

Additional information on J. Appl. Phys.
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Stokes and anti-Stokes luminescence of Er$^{3+}$ doped Ga$_{10}$Ge$_{25}$S$_{65}$ glass excited at 980 and 532 nm

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(Received 24 May 2010; accepted 25 August 2010; published online 9 November 2010)

We report on photoluminescence (PL) properties of Er$^{3+}$ doped Ga$_{10}$Ge$_{25}$S$_{65}$ glass. Experiments were performed using 5 ns laser pulses at 980 nm (532 nm), in resonance with the $^4_{15/2} ightarrow ^2_{11/2}$ transition of the Er$^{3+}$ ions. PL bands were observed from the blue to the near-infrared and the dependence of their intensity as a function of the laser intensity was analyzed. The PL temporal behavior was analyzed through rate equations for the population densities and using the Inokuti–Hirayama model. The results allowed identification of the PL pathways and the characterization of energy transfer processes involving pairs of ions. © 2010 American Institute of Physics. [doi:10.1063/1.3493239]

I. INTRODUCTION

Glasses doped with trivalent rare-earth (RE) ions attract large interest due to their wide range of photonic applications that include optical amplifiers, lasers, sensors, and colored displays.1,2 The choice of appropriate glass hosts and optimum RE ions concentration is crucial to develop efficient devices. Among the glasses known, the chalcogenide glasses (based on S, Se, and Te) present ideal characteristics for RE ions based photonics, because they have low energy phonons, high stability against moisture, and devitrification, and may be doped by large RE ions concentrations.1–4 Moreover, they have a high refractive index, which contributes to increase local field on the hosted RE ions, leading to enhanced radiative transition probabilities. In particular the sulfides glasses deserve special attention because they can be fibered and laser action has been demonstrated in neodymium (Nd$^{3+}$) doped gallium–lanthanum-sulphide glass bulk5 and fiber.6 Another glass composition of interest is Ga$_{10}$Ge$_{25}$S$_{65}$ (GGS) that has wide transparency window from the infrared to the blue/green region and low phonon energy ($\approx$370 cm$^{-1}$).

Recently the optical properties of GGS glass doped with Nd$^{3+}$,7 Pr$^{3+}$,8 and Er$^{3+}$ ions9 were investigated. In the case of Nd$^{3+}$ doped GGS glass a study of the linear optical characteristics and the infrared-to-visible frequency upconversion (UC) was reported.7 Transition probabilities, radiative lifetimes, and branching ratios associated with the Nd$^{3+}$ levels were determined. Two-photon absorption by isolated Nd$^{3+}$ ions and energy transfer among pairs of Nd$^{3+}$ ions contribute for the UC emissions. The mechanisms leading to the UC luminescence as well as the dynamics of the process were studied.

The phenomenon of orange-to-blue UC in Pr$^{3+}$ doped GGS containing silver nanoparticles was also studied using pulsed lasers emitting in the orange region.8 Enhanced UC signals from Pr$^{3+}$ ions due to the presence of the metallic nanoparticles were observed and their origin was clearly identified.

The properties of Er$^{3+}$ doped GGS were studied under continuous wave and pulsed laser excitation at 800 nm. Infrared-to-visible upconversion was observed and mechanisms based on excited state absorption and energy transfer were discussed.9

In this paper we present a study of Stokes and anti-Stokes photoluminescence (PL), excited at 532 and at 980 nm, in Er$^{3+}$ doped GGS glass. Strong PL signals were observed for excitation at the two wavelengths. The mechanisms and energy pathways that lead to the PL signals were investigated as well as the dynamics of the processes.

II. EXPERIMENTAL DETAILS

Glass samples with composition Ga$_{10}$Ge$_{25}$S$_{65}$:(Er$_2$S$_3$)$_{0.25}$ were prepared for the present study by the classical melting mixture of highly pure raw materials (Ga$_2$S$_3$, Ge, S: 99.999% and Er$_2$S$_3$: 99.9%) in a silica ampoule sealed under vacuum (10$^{-4}$ mbar), as described in Ref. 10 The sealed ampoule of 9 mm inner diameter was placed in a rocking furnace, slowly heated up to 900 °C and maintained at this temperature for 12 h. The silica tube was quenched in water at room temperature, annealed at a temperature near the glass transition temperature for 3 h to minimize inner constraints, and finally, slowly cooled down to room temperature. The glass rods obtained were cut into slices of 2 mm thickness and polished for different measurements. The glass transition temperature, $T_g$=430 °C, and the onset crystallization temperature, $T_s$ =540 °C, of the prepared glasses were determined by differential scanning calorimetry, with a heating rate of 10 °C/min.

Linear optical absorption measurements were made using a commercial spectrophotometer operating from 300 to 3300 nm.

PL experiments were performed using lasers operating at 532 and 980 nm (pulses of 5 ns at 20 Hz) as the excitation.
sources. In both cases, the linearly polarized beam was focused onto the sample with a lens of 15 cm focal-length; the PL signal was collected by a 5 cm focal-length lens along a direction perpendicular to the incident beam direction. The PL was dispersed by a 0.5 m monochromator and detected by a photomultiplier. The signals were recorded using a digital oscilloscope connected to a computer. All measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

Figure 1 presents the absorption spectrum of the sample from ~5500 to 21 500 cm⁻¹. The features correspond to 4f–4f transitions originating from the Er³⁺ ions ground state, 4I₁₅/₂, to excited states, as indicated in Fig. 1.

The experimental oscillator strength, F_{exp}, of each absorption band is determined by the expression F_{exp} = \frac{mc^2}{\pi \varepsilon_0^2 \rho} f(E) dE, where m and e are the electron mass and charge, respectively, c is the speed of light in vacuum, and ρ is the number of Er³⁺ ions per cm³. The factor f(E) dE is the integrated absorbance with E in per centimeter and can be determined from the absorption spectrum.

According to the Judd–Olfelt theory, the oscillator strength, F_{theo}, for an electric-dipole transition between the manifolds (S, L, J) and (S', L', J') is given by F_{theo} = \chi^2 \sum_{\lambda=2,4,6} \Omega_{\lambda} \frac{|\langle (S, L, J)|U^{(\lambda)}|(S', L', J')\rangle|^2}{9n}, where \chi = (n^2 + 2)/9n is the local field correction factor, n is the refractive index, J is the total angular momentum of the ground state, h is Planck’s constant, and |\langle (S, L, J)|U^{(\lambda)}|(S', L', J')\rangle| is the reduced dipole matrix element that is independent of the host material. \Omega_{\lambda} (\lambda = 2, 4, 6) are parameters that are dependent on the radial electronic eigenfunctions, the host environment, and the closest electronic configuration having opposite parity. These parameters were calculated with the least-squares method using the experimentally determined oscillator strength for the different transitions. The values obtained are: \Omega_{2} = 11 \times 10^{-20} \text{ cm}^², \Omega_{4} = 2.9 \times 10^{-20} \text{ cm}^², and \Omega_{6} = 1.6 \times 10^{-20} \text{ cm}^². Table I shows the experimental and theoretical values of the oscillator strengths, with \delta_{rms} = 0.66 \times 10^{-6}.

The spontaneous emission probability, A_{J'J}, between the manifolds (S, L, J) and (S', L', J') is given by

\begin{equation}
A_{J'J} = \frac{64\pi^4 e^2 \nu^3}{3 hc^3(2J+1)} \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle (S, L, J)|U^{(\lambda)}|(S', L', J')\rangle|^2 \times |\langle (S', L', J')\rangle|^2.
\end{equation}

The radiative lifetimes of the excited states are calculated by \tau_{R} = (\Sigma_{J'}A_{J'J})^{-1} and Table II gives the values of A_{J'J} and \tau_{R}.

Figure 2 shows the UC spectrum obtained by excitation at 980 nm, and Fig. 3 shows the PL spectrum under excitation at 532 nm. The observed emissions from the Er³⁺ ions excited states to the lower energy states correspond to the transitions: 4S_{3/2} \rightarrow 4I_{15/2} (~549 nm), 4F_{9/2} \rightarrow 4I_{15/2} (~663 nm), 4I_{9/2} \rightarrow 4I_{15/2} (~806 and 824 nm), and 4S_{3/2} \rightarrow 4I_{13/2} (~855 nm). The emissions originating from the 4F_{7/2} state appear only for excitation at 980 nm [4F_{7/2} \rightarrow 4I_{15/2} (~949 nm) and 4F_{7/2} \rightarrow 4I_{13/2} (~727 nm)]. We also observed emission from the 2H_{11/2} to the ground state for excitation with both wavelengths but in the 532 nm experiment the signal is overlapped with the scattered laser light. Therefore, Fig. 3(a) exhibits only a fraction of the 2H_{11/2} to 4I_{15/2} band because the main part of the signal was suppressed by the notch filter used to reject the scattered laser.

The energy level scheme shown in Fig. 4 indicates the states involved in the PL process and the relevant transitions.

Assuming that the UC process is not saturated, the UC intensity, I_{UC}, is proportional to some power, m, of the excitation intensity, I_{L}, such that I_{UC} \propto I_{L}^{m}, where m is the number of laser photons absorbed per upconverted photon. Then, to determine the number of photons participating in the UC process, the upconverted PL intensity was measured as a function of the laser intensity. The data are shown in Figs. 5

<table>
<thead>
<tr>
<th>Transition</th>
<th>ΔE (cm⁻¹)</th>
<th>A \left(\times 10^2 \text{ s}^{-1}\right)</th>
<th>\tau_{R} (\mu s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4F_{7/2} \rightarrow 4I_{15/2}</td>
<td>20 243</td>
<td>148.2 ± 2.7</td>
<td>67.5 ± 1.2</td>
</tr>
<tr>
<td>4F_{7/2} \rightarrow 4I_{13/2}</td>
<td>13 755</td>
<td>413.1 ± 1.4</td>
<td>24.2 ± 0.1</td>
</tr>
<tr>
<td>2H_{11/2} \rightarrow 4I_{15/2}</td>
<td>18 726</td>
<td>62.8 ± 1.0</td>
<td>159.3 ± 2.4</td>
</tr>
<tr>
<td>4S_{2/2} \rightarrow 4I_{13/2}</td>
<td>11 682</td>
<td>64.8 ± 1.3</td>
<td>154.2 ± 3.1</td>
</tr>
<tr>
<td>4I_{9/2} \rightarrow 4I_{15/2}</td>
<td>12 392</td>
<td>7.3 ± 0.2</td>
<td>1378.1 ± 30.8</td>
</tr>
<tr>
<td>4I_{11/2} \rightarrow 4I_{15/2}</td>
<td>10 173</td>
<td>6.7 ± 0.1</td>
<td>1489.5 ± 15.6</td>
</tr>
<tr>
<td>4I_{13/2} \rightarrow 4I_{15/2}</td>
<td>650 6</td>
<td>4.7 ± 0.1</td>
<td>2134.0 ± 32.1</td>
</tr>
</tbody>
</table>
For excitation at 980 nm we obtained $m=2.1$ for the emission centered at $\approx 549$ nm; $m=1.9$ for the $\approx 534$, 663, and 855 nm bands, and $m=1.8$ for the $\approx 727$ and 806 nm emissions. These results indicate that two laser photons contribute to the emission of each UC photon and the data are shown in Fig. 5. For excitation at 532 nm we found $m=1.0$ for the emission at $\approx 549$ nm and $m=1.1$ for the $\approx 663$ and 855 nm bands. The results, shown in Fig. 6, indicate that one photon is emitted for each laser photon absorbed.

To obtain more information about the UC process, the temporal behavior of the transitions $^4F_{7/2} \rightarrow ^4I_{13/2}$, $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$, and $^4F_{9/2} \rightarrow ^4I_{15/2}$ was studied for excitation at 980 and 532 nm. Figure 7 shows the signal behavior for transitions $^4F_{7/2} \rightarrow ^4I_{13/2}$, $^2H_{11/2} \rightarrow ^4I_{15/2}$, and $^4F_{9/2} \rightarrow ^4I_{15/2}$ for excitation at 980 nm. We observed that the rise time of the emission corresponding to $^4F_{7/2} \rightarrow ^4I_{13/2}$ follows the laser pulse; the decay signal from the $^4F_{7/2}$ state showed exponential behavior with decay time of $\approx 179$ ns which is of the same order of magnitude as the nonradiative decay time between states $^4F_{7/2}$ and $^2H_{11/2}$, estimated using the energy-gap law. This indicates that the dominant relaxation process related to the $^4F_{7/2}$ state is the nonradiative decay to lower energy levels. The rise time corresponding to transition $^2H_{11/2} \rightarrow ^4I_{15/2}$ is $\approx 188$ ns, which is understood considering that the $^2H_{11/2}$ state is fed by decay from state $^4F_{7/2}$.

Therefore, the dynamical behavior corresponding to transition $^2H_{11/2} \rightarrow ^4I_{15/2}$ can be described by

$$n_1 = - \left( W_{12} + \gamma_1 \right) n_1$$

and

FIG. 2. (Color online) Upconverted luminescence spectrum for excitation wavelength at 980 nm, in resonance with the $^4I_{15/2} \rightarrow ^2H_{11/2}$ transition. The signal amplitude in (b) was multiplied by 50, to be presented in the same scale as in (a).

FIG. 3. (Color online) Upconverted luminescence spectrum for excitation wavelength at 532 nm, in resonance with the $^4I_{15/2} \rightarrow ^2H_{11/2}$ transition. The signal amplitude in (b) and (c) were multiplied by 20 and 100, respectively, to be presented in the same scale as in (a).

FIG. 4. (Color online) Simplified energy levels of Er$^{3+}$ ions. Solid arrows represent radiative transitions. Dashed line arrows indicate nonradiative transitions.
\[ n_2 = W_{12}n_1 - \gamma_2 n_2, \]  

where \( n_1 \) and \( n_2 \) are the population densities of the \(^4F_{7/2}\) (state \( |1\rangle \)) and \(^2H_{11/2}\) (state \( |2\rangle \)) multiplets, respectively. \( \gamma_1 \) represents the relaxation rate of state \( |1\rangle \) due to all possible mechanisms except transition to state \( |2\rangle \), \( \gamma_2 \) is the total radiative rate of state \( |2\rangle \), and \( W_{12} \) is the nonradiative decay rate from state \( |1\rangle \) to state \( |2\rangle \). Hence, the UC intensity from state \(^2H_{11/2}\), proportional to \( n_2 \), is described by

\[ I_{UC} \propto \frac{n_1(t=0)}{(W_{12} + \gamma_1) - \gamma_2} \left[ e^{-\gamma_2 t} - e^{-(W_{12}+\gamma_1)t} \right]. \]  

A fitting of Eq. (4) to the experimental result of Fig. 7(b) gives a rise time of 188 ns and decay time of 24 \( \mu s \), which is in agreement with the predictions of Judd–Ofelt theory (Table II).

To describe the PL signal shown in Fig. 7(c) for transition \(^4F_{9/2} \rightarrow ^4I_{15/2}\) we considered the following rate equations:

\[ \dot{n}_1 = -(W_{12} + \gamma_1)n_1, \]  
\[ \dot{n}_2 = W_{12}n_1 - (W_{23} + \gamma_2)n_2, \]

where \( n_1 \), \( n_2 \), and \( n_3 \) are the population densities of the \(^4F_{7/2}\) (state \( |1\rangle \)), \(^4S_{3/2}\) (state \( |2\rangle \)) and \(^4F_{9/2}\) (state \( |3\rangle \)) multiplets, respectively. \( \gamma_3 \) is the total radiative rate of state \( |3\rangle \), \( W_{23} \) is the nonradiative decay rate from state \( |2\rangle \) to state \( |3\rangle \), and the other parameters have the same meaning given before. Then the UC intensity, proportional to \( n_3 \), is described by

\[ I_{UC} \propto \left[ A e^{-\gamma_3 t} + B e^{-(W_{23}+\gamma_3)t} + C e^{-(W_{12}+\gamma_1)t} \right], \]  

where \( A, B, \) and \( C \) are related to \( \gamma_i(i=1, 2, 3) \), \( W_{12} \), and \( W_{23} \). In this case, the data fitting gives the lifetime of \( \approx 76 \) \( \mu s \) for state \(^4F_{9/2}\), which is smaller than the radiative lifetime predicted by the Judd–Ofelt theory indicating that interaction between \( \text{Er}^{3+} \) ions should be considered.

For excitation at 532 nm, the PL signal from state \(^4S_{3/2}\) shows a decay time of \( \approx 25 \) \( \mu s \), which is smaller than the lifetime calculated using the Judd–Ofelt theory (Table II). This behavior indicates that energy transfer among \( \text{Er}^{3+} \) ions is an efficient process when state \(^4S_{3/2}\) is populated. This
its the results for the signals that are originated from state \(4S_{3/2}/H_9253\) plot are equal to 0.52

\[ P_{\text{citation at 980 nm}, \text{slope}} = 0.52 \]

for excitation at 980 nm; the slopes determined from the PL signal can be described by

\[ I_t = I_0 \exp(-t/\tau_R - P(t)) \]

where \(P(t) = \gamma t^{3/2}\) is a function that depends on the interaction potential between donors and acceptors and \(s=6, 8, 10\) corresponds to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interaction, respectively.16

To infer the kind of interaction potential between donors and acceptors, we examined the behavior of \(P(t)\) versus \(t\), in a log-log plot. The graph is obtained by extracting the exponential part \(\exp(-t/\tau_R)\) from the recorded PL signal. For excitation at 980 nm, the slopes determined from the \(P(t)\times t\) plot are equal to 0.52 (0.48) for the PL signal originated from the \(4S_{3/2}/4F_{9/2}\) state that corresponds to \(s=5.77\) (6.25). These results are corroborated by the results for excitation at 532 nm, that gives \(s=5.56\) and \(s=6.00\) for the \(4S_{3/2}\) and the \(4F_{9/2}\) state, respectively. The results indicate a dominant dipole–dipole interaction between Er3+ ions. Figure 8 exhibits the results for the signals that are originated from state \(4S_{3/2}\).

With basis on the results described above we understand the UC process in the following way. The laser photons at 980 nm induce a two-step transition \(4I_{13/2}/H_9270 \rightarrow 4I_{11/2}/H_9270 \rightarrow 4F_{7/2}/H_9270\) such that two photons are simultaneously absorbed from the same laser pulse. A small number of the excited ions decays directly to state \(4I_{13/2}/H_9270\), emitting radiation at 727 nm, and to the ground state, emitting radiation centered at 494 nm. Most of the ions in the state \(4F_{9/2}/H_9270\) decay nonradiatively to the lower energy states \(3H_{11/2}\) and \(S_{3/2}\). From there, emissions to the ground state give rise to the UC luminescence at \(=534\) and 549 nm. On the other hand, nonradiative decay from the state \(4S_{3/2}/H_9253\) to the \(4F_{9/2}/H_9253\) state followed by radiative decay to the ground state originates the emission at \(=663\) nm. The emission at \(=855\) nm is due to transition from the \(4S_{3/2}/H_9253\) to level \(4I_{13/2}/H_9253\), while the emissions at \(=806\) and 824 nm correspond to the transition from state \(4I_{9/2}/H_9253\) to the ground state.

In summary, we fabricated Er3+ doped GGS glasses and investigated some of their optical properties. Radiative transition rates for the excited Er3+ ions and intensity parameters were determined from the absorption spectrum using the Judd–Ofelt theory. Stokes and anti-Stokes luminescence were studied by exciting the samples with lasers operating at 980 and 532 nm. The dependence of the luminescence intensity on the excitation power and its time behavior were investigated. The measurements allowed understanding the energy pathway for both excitation wavelengths.

**ACKNOWLEDGMENTS**

We acknowledge financial support from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Amparo à Ciência e Tecnologia do Estado de Pernambuco (FACEPE). The work was performed under the Photonics National Institute (INCT de Fotônica) Project and the Nanophotonics Network, supported by CNPq.

2*Rare-Earth-Doped Fiber Lasers and Amplifiers*, edited by M. J. F. Digonnet (Dekker, New York, 1993) and references therein.

**FIG. 8.** (Color online) Log–log plot of \(P(t)\) vs \(t\) for the \(4S_{3/2}\) state: (a) with slope 0.52 for excitation at 980 nm; (b) with slope 0.54, for excitation at 532 nm.