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Quantum efficiency of 1.5 μm emission of Er^{3+} in ZBLAN and BiGaZYT fluoride glasses and in silica glass obtained by photoacoustic spectroscopy

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Abstract: In this work we present a comparison of the quantum efficiencies (QE) of the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} in ZBLAN (58 ZrF_4 -18 BaF_2 -5.5 LaF_3 -3 AlF_3 -15 NaF), BiGaZYT (30 BaF_2 -18 InF_3 -20 ZnF_2 -10 YF_3 -10 ThF_4 -12 GaF_3), and silica (67.7 SiO_2 -16.2 SiO -11.1 CaO -5 Al_2O_3) glasses obtained by photoacoustic spectroscopy. In the case of ZBLAN and BiGaZYT glasses, the method takes into account the $^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2}$ excited state absorption.

1. INTRODUCTION

The use of large bandwidth technologies in optical communication infrastructures requires high performance optical amplifiers. Erbium doped fiber amplifiers (EDFA) are being used extensively for the third transmission window at 1500 nm. Together with silica, fluoride glasses are the most important materials on which optical amplifiers are developed. Optimization of fiber design for improved amplifier performance can be achieved in two ways: by modifying the glass composition to improve the optical properties of the dopant and/or designing a more efficient waveguide. In order to improve our knowledge about the rare earth behaviour inside oxide and fluoride glasses, quantum efficiency (QE) measurements have been performed in the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} in ZBLAN and BiGaZYT fluoride glasses, and in a silica glass. QE measurements were carried out by photoacoustic spectroscopy taking into account the $^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2}$ excited state absorption.

2. THEORETICAL MODEL

2.1. Er^{3+} in ZBLAN and BiGaZYT glasses

The effective level scheme of Er^{3+} in ZBLAN and BiGaZYT glasses after excitation of the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ transition is represented in figure 1. After absorption of the incident photon of energy $\hbar\omega$, the electron in the $^4\text{I}_{15/2}$ (1) ground state reaches the $^4\text{I}_{11/2}$ (3) excited state. From this level, radiative or non-radiative deexcitation to the $^4\text{I}_{13/2}$ level (2), or radiative relaxation to the ground state can occur. Moreover, absorption to the $^4\text{F}_{7/2}$ excited state (4) can take place. From this level, non-radiative and radiative transitions to the $^4\text{I}_{11/2}$ and $^4\text{I}_{15/2}$ states are respectively considered. Finally radiative and non-radiative relaxation from the state $^4\text{I}_{13/2}$ can take place. Following this scheme, the heat H released in the sample per unit time per unit volume is

$$H = \frac{\sigma_1 n_1}{\hbar \omega} (\hbar\omega - E_{31}) + W_{43}^{nr} E_{43} n_4 + W_{32}^{nr} E_{32} n_3 + W_{21}^{nr} E_{21} n_2 + \frac{\sigma_3 n_3}{\hbar \omega} (\hbar\omega - E_{43})$$

where n_i is the population density of level i , I is the power density of the incident beam, σ_1 and σ_3 are the absorption cross-sections of transitions $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ and $^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2}$ respectively and E_{ij} the energy difference between levels i and j .

Figure1: Electronic level scheme of Er^{3+} ion in BIGaZYT and ZBLAN glasses. W_{ij} and W_{ij}^{nr} are the radiative and non-radiative transition probabilities from level i to level j respectively.

For continuous excitation at low chopping frequencies, the rate equations of the system in the steady state are

$$\begin{aligned} \frac{d n_1}{d t} &= - n_1 \frac{\sigma_1 I}{\hbar \omega} + n_3 W_{31} + \frac{n_2}{\tau_2} + n_4 W_{41} = 0 \\ \frac{d n_2}{d t} &= n_3 (W_{32} + W_{32}^{\text{nr}}) - \frac{n_2}{\tau_2} = 0 \\ \frac{d n_3}{d t} &= \frac{I}{\hbar \omega} (n_1 \sigma_1 - n_3 \sigma_3) - \frac{n_3}{\tau_3} + n_4 W_{43}^{\text{nr}} = 0 \\ \frac{d n_4}{d t} &= n_3 \frac{\sigma_3 I}{\hbar \omega} - \frac{n_4}{\tau_4} = 0 \end{aligned} \quad (1)$$

where τ_i is the experimental lifetime of level i . The solution of the last system gives the ratios between the populations of levels 2, 3, and 4 and the population of level 1. However, for laser power densities below 17 W/cm^2 , the ground state population can be taken equal to the number of ions per unit volume in the matrix; in the next, we shall assume this approximation. For optically thin samples the photoacoustic signal is proportional to $H^{(1)}$, giving

$$\frac{P}{\sigma_1 I} = C \frac{\frac{(\hbar\omega - E_{31})}{\hbar\omega} (\hbar\omega + \tau_3 \sigma_3 I \frac{\tau_4}{\tau_4^R}) + \frac{I}{\hbar\omega} \tau_3 \sigma_3 (\hbar\omega - \frac{\tau_4}{\tau_4^R} E_{43}) + (\frac{1}{\tau_3} - \frac{1}{\tau_3^R}) \tau_3 E_{32} + (1 - \eta_2) (1 - \frac{\tau_3}{\tau_3^R} (1 - \beta_{32})) E_{21}}{\hbar\omega + \tau_3 \sigma_3 I \tau_4 / \tau_4^R}$$

where P is the photoacoustic signal amplitude, C is a factor depending on the experimental conditions, τ_1^R is the radiative lifetime of level i , β_{32} is the branching ratio for the $4I_{11/2} \rightarrow 4I_{13/2}$ transition and η_2 is the unknown QE. The optical parameters involved in the equation can be obtained from theoretical calculations or luminescence measurements, and measurements of the photoacoustic signal and absorption coefficient at different wavelengths give the values of C and η_2 . As can be seen, the knowledge of the absolute incident power density is necessary. However, for low pumping power densities the term $\tau_3 \sigma_3 I \tau_4 / \tau_4^R$ can be neglected if compared with the photon energy $\hbar\omega$. Within this approximation, the above relation can be written as follows,

$$\frac{P}{\sigma_1 I} = C \frac{\hbar\omega - E_{31} + (\frac{1}{\tau_3} - \frac{1}{\tau_3^R}) \tau_3 E_{32} + (1 - \eta_2) (1 - \frac{\tau_3}{\tau_3^R} (1 - \beta_{32})) E_{21}}{\hbar\omega}$$

From the slope of the straight line obtained by the fit of the experimental $P/\sigma_1 I$ values versus the excitation wavelength, a reliable value of η_2 can be obtained.

2.2. Er^{3+} in silica glass

In the case of Er^{3+} in silica glass the effective electronic level scheme is a three level system as shown in figure 2.

Figure 2: Electronic level scheme of Er^{3+} ion in silica glass. W_{ij} and W_{ij}^{nr} are the radiative and non-radiative transition probabilities from level i to level j respectively.

In our case, excitation takes place from the $4I_{15/2}$ ground state to the $4I_{11/2}$ (3) level. This subsequently deexcites to the $4I_{13/2}$ (2) level and then fluoresces to the ground state with radiative and non-radiative decay rates W_2 and W_2^{nr} respectively. In this case, the heat H released in the sample per unit time per unit volume is,

$$H = n_1 \frac{\sigma I}{\hbar \omega} (\hbar \omega - E_{31}) + n_2 W_{21}^{nr} E_{31} + n_2 W_{21} (E_{31} - \hbar \omega_F)$$

where σ is the $4I_{15/2} \rightarrow 4I_{11/2}$ transition absorption cross section, ω_F is the fluorescence photon frequency and the rest of the symbols have the same meaning than before. The rate equation for the second-level population is now

$$\frac{dn_2}{dt} = -\frac{n_2}{\tau_2} + \frac{n_1 \sigma I}{\hbar \omega}$$

For low chopping frequencies, the in-phase photoacoustic signal is given by ⁽²⁾

$$\frac{P}{\sigma I} = C (1 - \eta \frac{\omega_F}{\omega})$$

The QE can be obtained from the slope of $P/\sigma I$ versus $1/\omega$.

3. EXPERIMENTAL

Fluoride ZBLAN and BIGaZYT glasses, and the silica glass were doped with Er^{3+} (2 mol%).

Conventional absorption spectra were performed with a CARY 5 spectrophotometer.

In the photoacoustic measurements the samples were excited using a continuous wave 15 W Argon-ion pumped Sapphire:Ti laser in the long-wave tuning range (950-1050 nm) with a linewidth of 6 GHz. The incident beam was chopped at 20 Hz and split to record its energy on a Moletron P3-01 pyroelectric detector

inside a piezoelectric photoacoustic cell, the signal received by a piezoelectric PZT membrane, amplified with a EG&G PAR 115 preamplifier and finally recorded on an EG&G PAR 5302 lock-in amplifier. The ratio of the two signals was carried out by this instrument.

4. RESULTS AND DISCUSSION

Figure 3 shows the absorption and photoacoustic spectra of the three samples. As described before, QE of Er^{3+} in these samples was obtained from the ratio of photoacoustic and absorption spectra. This gave the following values of η :

ZBLAN: Er^{3+} (2%)	$\eta=1.0$
BIGaZYT: Er^{3+} (2%)	$\eta=0.94$
Silica glass: Er^{3+} (2%)	$\eta=0.69$

Figure 3: Photoacoustic and absorption spectra of Er^{3+} in ZBLAN BIGaZYT and Silica glasses.

As can be observed, fluoride glasses are more efficient than silica glass. This is a reasonable result because fluoride glasses have lower phonon frequencies. Nevertheless, results do not behave as expected for BIGaZYT with respect to ZBLAN because the former is known to have lower phonon frequencies. This discrepancy could be related to the existence of clustering of rare-earth ions in BIGaZYT glass.

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