

Blue Cooperative Emission in Yb³⁺ - Doped GeO₂ - PbO Glasses

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Investigation of the blue cooperative luminescence in a binary composition of GeO₂-PbO glasses with different Yb³⁺ concentrations is reported. High refractive index (1.96) and large transmission window (0.4 up to 5.0 μm) are characteristics of this vitreous system. Luminescence and lifetime measurements in the visible and near infrared regions were performed to investigate the spectroscopic characteristics of the glasses. Visible emission around 507 nm was detected in all samples. The visible emission intensity increases with the Yb₂O₃ content at least up to 2.0 wt. (%), that represents the maximum Yb₂O₃ concentration possible for this glass system. The visible lifetimes are about half of their respective near infrared ones, and the blue luminescence comes from a cooperative process. A rate equation was used to describe the behavior of the cooperative emission intensity as a function of Yb₂O₃ concentration; a good agreement with the calculated and measured cooperative luminescence was achieved.

Keywords: glasses, ytterbium, cooperative luminescence

1. Introduction

The heavy metal oxide glasses^{1,2}, in which the usual vitrifying elements³ are oxides of germanium, gallium and tellurium, have attracted interest for photonics applications because of their optical properties such as high refractive index, optical non-linearity and infrared transmittance providing the possibility to develop efficient lasers and amplifiers at longer wavelengths than available from other oxide glasses^{4,5}.

Regarding the Yb-doped materials, several investigations have revealed the technological potentiality of these systems since they may generate tunable lasers in the infrared region from 920 to 1060 nm and visible emission at about 500 nm^{6,7}, by means of a cooperative effect. There are only two manifolds in the Yb³⁺ energy level scheme in the 4fⁿ configuration, the ²F_{7/2} ground state and the ²F_{5/2} excited state. The lack of intermediate levels and the large separation between the excited state and the ground state manifolds reduces nonradiative decay. The cooperative luminescence is an upconversion process in which two interacting ions in the excited state decay simultaneously to the ground state, emitting one photon at twice the energy of single-ion-transitions. 3-D displays⁸, intrinsic bistability for optical switching^{9,10} and planar lasers for optical devices in telecommunications¹¹ are some applications for cooperative emission in systems doped with Yb ions.

In this work we present a study of the cooperative luminescence in a binary composition of Yb³⁺ - doped GeO₂ - PbO glasses prepared at the Laboratory of Glasses and Datation at FATEC-SP. The measured emission spectra and lifetimes in the visible region as a function of Yb³⁺ concentration are presented. From the luminescence spectra and lifetime measurements in the near infrared region, the mechanism responsible by the visible emission in this glass system was identified.

2. Experimental

Different concentrations of Yb₂O₃ varying from 0.1 to 2.0 wt. (%), were added to the binary composition 59GeO₂ - 41 PbO (mol%), henceforth named GP¹². The powders were melted in an alumina crucible (with impurities of 0.01%) at 1323 K during 1 hour in air

and poured into a brass mold previously heated. During the melting the powders were stirred by a mechanical system, developed in our laboratory, to enhance the optical quality. The stirring is performed during the last 10 minutes of the melting. Annealing treatments were performed on each sample for 3 hours at 693 K (considering the glass transition temperature) and then cooled to room temperature inside the furnace. The samples produced are transparent, homogeneous and stable against crystallization. For concentrations greater than 2.0 wt. (%) of Yb₂O₃ we observe a loss of transparency. Therefore, the solubility limit of Yb₂O₃ in this heavy metal oxide glass, considering the current melting scheme employed, is approximately 2.0 wt. (%) of Yb₂O₃. The density of (6.21 ± 0.1) g/cm³ was measured using the Archimedes method. The samples were polished for refractive index, absorption, luminescence and lifetime measurements. The refractive index of (1.96 ± 0.05) was determined by means of the "apparent depth method" that relates the physical thickness of the samples to their optical thickness (apparent thickness). The optical thickness was measured with a 10 x objective lens of a microscope (Carl Zeiss). The absorption spectra were obtained using a spectrophotometer (Cary 500). Infrared luminescence measurements were performed by optically pumping the samples with laser diode operating at 808 nm. The signal was dispersed by a monochromator (Jarrel-Ash) and detected by an InGaAs detector connected to a lock-in amplifier. The excitation was performed close to the sample edge¹³ to minimize re-absorption due to radiation trapping effect. The radiation trapping effect¹⁴ arises from the spectral overlap of the emission and absorption bands of Yb³⁺. This effect normally deforms the Yb³⁺ emission band and increases with sample size, refractive index and Yb³⁺ concentration.

The lifetimes of the ⁴F_{5/2} → ⁴F_{7/2} transition were measured using a modulated laser working at 980 nm. The infrared lifetimes were recorded using a germanium detector connected to a Tektronix oscilloscope. Cooperative luminescence was obtained with laser excitation at 980 nm. The emission was dispersed by a monochromator and collected by a standard photomultiplier coupled to a lock-in amplifier. Cooperative lifetimes were obtained using a modulated diode laser (980 nm), the signal emitted from the samples were collected by a photomultiplier

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connected to a digital oscilloscope. As will be shown Yb^{3+} ions have a strong absorption at 980 nm. So this is the most adequate wavelength for the measurement of the cooperative luminescence: more ions are excited favoring the cooperative luminescence. All measurements were performed at room temperature; errors of luminescence and lifetime measurements are estimated to be of $\pm 5\%$.

3. Results and Discussion

The transmission in the infrared region is presented in Figure 1 for the undoped sample. The band positioned around $3.4 \mu\text{m}$ is related to the presence of OH^- radicals into the glass. The broad infrared transmission (up to $5.0 \mu\text{m}$) observed is a consequence of the small field strengths and relatively large masses of the components of these glasses that present more than 50% of heavy metal oxides, such as PbO^4 .

Figure 2 shows the absorption spectrum of the sample doped with 1.0 wt. (%) of Yb_2O_3 . The transition observed is related to the ${}^2\text{F}_{7/2} \rightarrow$

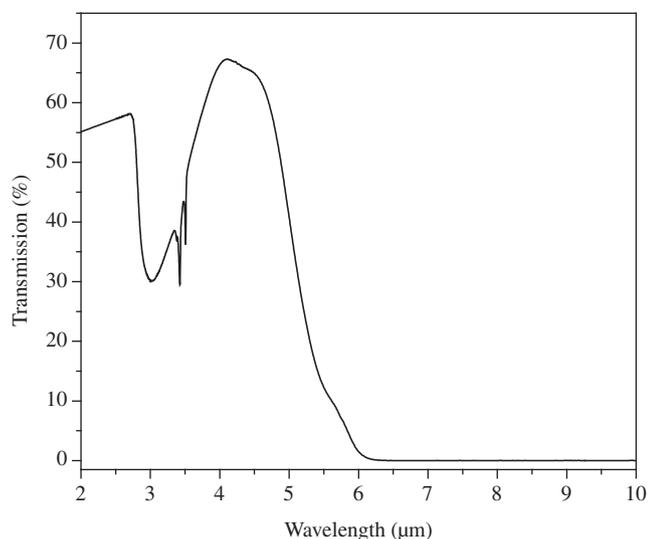


Figure 1. Infrared transmission spectrum of the GP glass with 2 mm thickness.

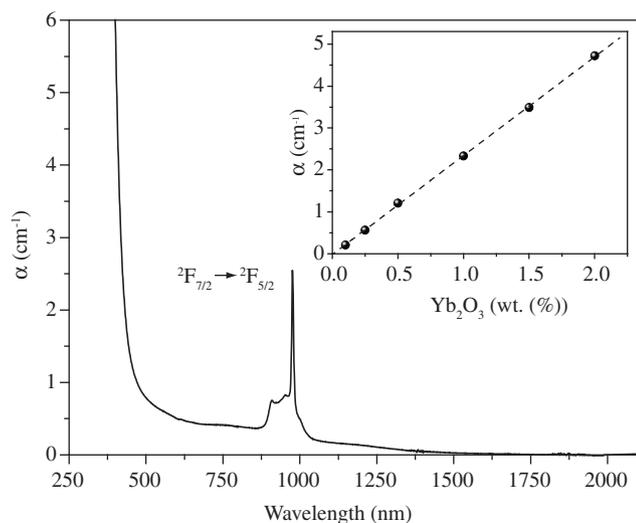


Figure 2. Absorption spectrum of the GP glass doped with 1.0 wt. (%) of Yb_2O_3 . The inset shows the absorption coefficient as a function of Yb_2O_3 concentration.

${}^2\text{F}_{5/2}$ Yb^{3+} transition. The inset shows that the absorption coefficient increases linearly with Yb^{3+} concentration, indicating a systematic incorporation of Yb ions by the vitreous matrix. So the relative concentrations of Yb^{3+} are in agreement with the nominal values. In addition, we also can observe that the absorption edge starts at 400 nm in the GP glass; no absorption related to impurities was observed.

Yb^{3+} ions absorb and emit in the near infrared spectral range when excited by radiation of the near infrared region. However, some materials containing Yb^{3+} can exhibit visible luminescence at twice the energy of the ${}^2\text{F}_{5/2}$ levels. The upconverted emission involves Yb^{3+} ion pairs excited by radiation in the near infrared spectral region; so a simultaneous de-excitation of two excited Yb^{3+} ions, in the ${}^2\text{F}_{5/2}$ level, results in the emission of one visible photon around 500 nm. Yb^{3+} ions not only emit in the near infrared from their ${}^2\text{F}_{5/2}$ excited-state multiplet, but can also undergo visible emission at the blue-green spectral region from the doubly excited ${}^2\text{F}_{5/2}, {}^2\text{F}_{5/2}$ pair state: this is known as cooperative process. The cooperative luminescence depends on the inter-ionic distances, phonon energy, edge of the transmission window in the visible region and laser power employed for the excitation of Yb^{3+} . The investigations reported in the literature show that the visible lifetime value related to the cooperative mechanism is half of its respective near infrared one^{6,7}.

The near-infrared luminescence from the ${}^2\text{F}_{5/2}$ excited level of the sample doped with 2.0 wt. (%) Yb_2O_3 is displayed in the Figure 3. The emission around 1000 nm is attributed to ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition. It is interesting to mention that the near infrared emission intensity increases with Yb_2O_3 concentration; this indicates that no fluorescence quenching related to nonradiative transitions is observed for this range of concentration.

The visible luminescence spectrum of the samples is shown in Figure 4. The band at 507 nm may be ascribed to the combination of electronic energies associated to the Stark components of the ${}^2\text{F}_{5/2}$ level of isolated Yb^{3+} ions. A strong blue emission can be easily observed by naked eyes focusing the laser beam in the glasses. Then the broad and strong visible emission observed around 507 nm from GP glasses under near infrared excitation is attributed to the cooperative process involving Yb^{3+} ions and, as predicted by the literature, the peak value corresponds approximately to half of the near infrared one (around 1000 nm). In the inset of the same figure the intensity of the lumi-

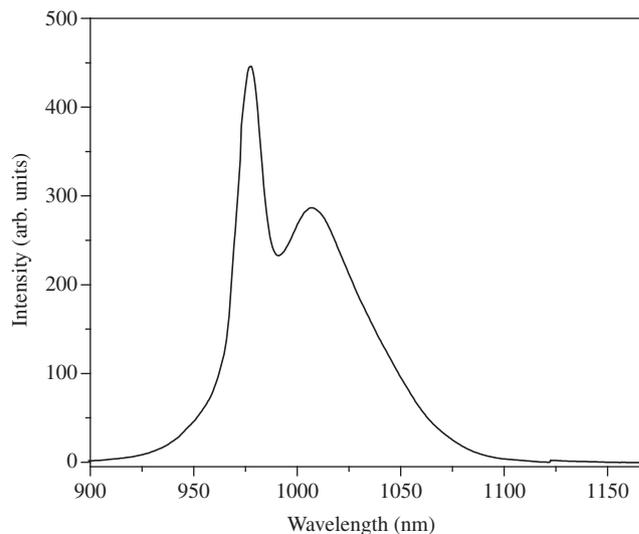


Figure 3. Near infrared luminescence spectrum for GP glass with 2.0 wt. (%) of Yb_2O_3 .

nescence in the visible region (~ 507 nm) is plotted as a function of Yb₂O₃ concentration. The blue emission intensity increases with the Yb₂O₃ concentration indicating that no quenching of the luminescence is observed at least up to 2.0 wt. (%). Therefore, unfavorable non-radiative de-excitation mechanisms such as multiphonon relaxation and quenching due to OH- radicals can be neglected. A continuous line was achieved from a rate equation explained below; the points in Figure 4 represent the experimental values.

The dependence of the cooperative and near-infrared intensities on Yb₂O₃ concentration can be determined by means of a rate equation that considers the nonradiative and radiative decays as done in references^{15,16}.

$$\dot{N}_2 = RN_1 - (W_{rad} + W_{nr})N_2 \quad (1)$$

where N_i ($i = 1, 2$) represents the populations of the ${}^2F_{7/2}$ and ${}^2F_{5/2}$ Yb³⁺ levels, respectively. $N_{yb} = N_1 + N_2$ gives the total concentration of Yb³⁺ ions, W_{rad} is the radiative rate from the ${}^2F_{5/2}$ level. Equation 1 means that the population of the ${}^2F_{5/2}$ level is increased by a pumping term RN_1 that depends on the laser intensity (I) according to $R = \sigma_{abs} I/h\nu$, where R is the pumping rate, σ_{abs} is the absorption cross section at the pumping energy $h\nu$. All other terms are responsible for losses from the ${}^2F_{5/2}$ level; $W_{rad}N_2$ represents the radiative decay, $W_{nr}N_2$ accounts for nonradiative losses, such as multiphonon relaxation and energy transfer from Yb ions to OH groups. The cooperative effect was neglected in the equation because it contributes very little for the emptying of the state ${}^2F_{5/2}$ when compared to term $(W_{rad} + W_{nr})N_2$. Considering the sample under low excitation density (N_1 can be approximated to the total concentration N_{yb}) and in the stationary condition ($\dot{N}_2 = 0$), N_2 is given by $N_2 = RN_{yb} \tau_{IR}$, where $\tau_{IR} = (W_{rad} + W_{nr})^{-1}$ is the experimental lifetime of the ${}^2F_{5/2}$ level. Starting from that, the near infrared and cooperative luminescence intensity can be determined from this expression because they are proportional to N_2 and $(N_2)^2$, respectively¹⁶. The square dependence of the cooperative luminescence intensity with respect to Yb³⁺ concentration is expected for an upconversion process due to pair interaction. The inset of Figure 4 indicates a good agreement between the normalized cooperative luminescence intensity predicted by the above rate equation (continuous line) and the normalized experimental results (points).

Figure 5 exhibits the near infrared and the cooperative lifetimes as a function of Yb₂O₃ concentration in GP glasses. The alterations of the fluorescence lifetime as a function of Yb content in both near infrared and visible regions are of the order of the experimental errors. The slight decrease of the fluorescence lifetime corroborates that the nonradiative decay is not serious in this system. The other aspect that has to be added is that cooperative lifetimes are about half of their respective near infrared ones, as predicted in the literature^{6,7} for systems in which the visible emission is caused by the cooperative process.

The studies presented in this work will be used in the future to produce glass fibers and thin films viewing applications with waveguides.

4. Conclusion

An investigation of cooperative luminescence in Yb³⁺-doped GeO₂ - PbO glasses is presented. Emission in the visible region, at about 507 nm was measured and no quenching luminescence was observed. The near infrared fluorescence lifetimes slightly change with Yb₂O₃ concentration indicating that the nonradiative decay is not serious in this vitreous system. The visible lifetimes are about half of their respective near infrared ones, corroborating the hypothesis that the blue luminescence comes from a cooperative effect involving Yb ions. The behavior of the cooperative luminescence as a function

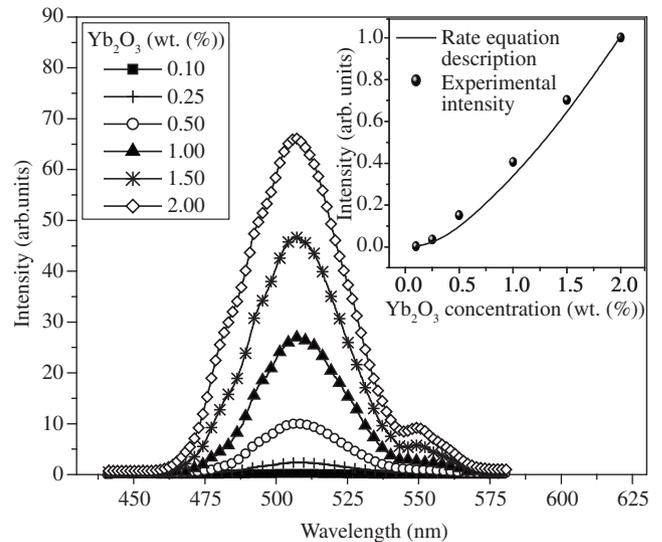


Figure 4. The cooperative luminescence for GP glass doped with different concentrations of Yb₂O₃. The inset shows the experimental (points) and calculated (continuous line) cooperative emission intensity as a function of Yb₂O₃ concentration.

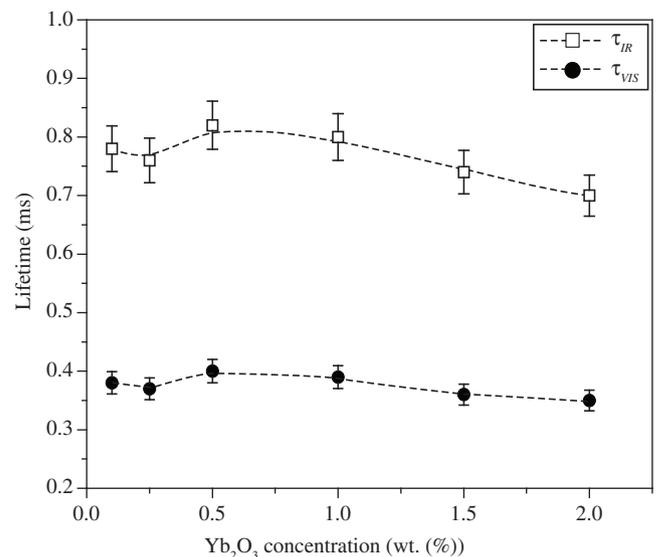


Figure 5. Cooperative (τ_{vis}) and near infrared lifetime (τ_{IR}) in Yb³⁺ doped GP glasses.

of Yb₂O₃ concentration was determined using a rate equation that considers the experimental near infrared lifetimes; a good agreement with the measured cooperative luminescence experimental was observed. The achieved results suggest the Yb-doped GP glasses as an interesting material to be used in the development of photonic devices operating in the visible region.

Acknowledgments

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