Comparative Study of Cooperative Luminescence in Tellurite Glasses and Fibers Doped with Yb^{3+}

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Abstract

This work presents the results of cooperative luminescence in seven different compositions of Yb_2O_3 doped tellurite glasses. High refractive index (~2.0) and large transmission window (360-6000 nm) are characteristics of the glasses studied. The emission measured in the visible region, centered at 500 nm, is a strong indication of the presence of the cooperative luminescence; The cooperative luminescence was also measured in glass fibers prepared by manual pulling in one of the compositions studied (TeO_2-ZnO).

Introduction

Tellurite glasses are promising materials for laser applications because of their spectroscopic properties, chemical and mechanical stability. The glasses studied in this work have transmission window ranging from 0.36 μm to 6.5 μm, low phonon energy around 800 cm^{-1} [1], similar to germanate glasses but lower than silicate (1100 cm^{-1}) and phosphate (1200 cm^{-1}) [2] and high refractive index (~2.0).

The rare-earth ytterbium presents many applications for infrared lasers with ultra-short amplified pulses. There are only two manifolds in the Yb^{3+} energy level scheme, 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 non-radiative decay. Another interesting characteristic is the fact that Yb^{3+} presents a phenomenon named cooperative effect. Since the first observation by Nakazawa and Shionoya in $YbPO_4$ [3] cooperative luminescence of ytterbium has been reported in several hosts, mainly in crystals [4]; it is an up-conversion 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 (at about 500 nm). The cooperative luminescence depends on inter-ionic distances, the phonon energy, edge of the transmission window in the visible region and laser power employed for the excitation of Yb^{3+}.

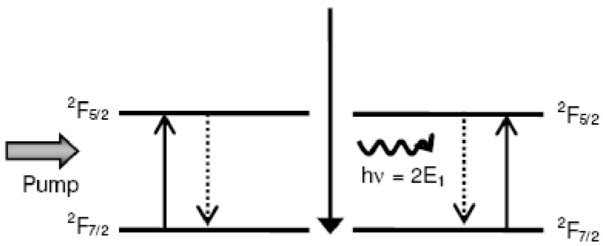

Figure 1: Simplified energy level diagram of Yb^{3+} cooperative luminescence.

In this work, we present a comparative study of the cooperative luminescence in seven glasses based on TeO_2 doped with Yb_2O_3 and prepared at the Laboratory of Glasses and Datation at FATEC-SP. Some spectroscopic properties in the infrared region are also shown in order to corroborate the cooperative luminescence effect. The presence of cooperative luminescence was also observed in glass fibers produced using one of the seven compositions studied.

Experimental Setup

The glasses (bulk) were prepared adding 1.0 wt% of Yb_2O_3 to seven different compositions presented in Table 1.

Composition	Sample	Refractive Index
TeO_2 - ZnO	B1	2.10
TeO_2 - BaO	B3	2.06
TeO_2 - Nb_2O_5	B4	2.14
TeO_2 - GeO_2 - PbO	T1	1.96
TeO_2 - ZnO - Na_2O - PbO	Q1	2.06
TeO_2 - ZnO - Na_2O - GeO_2	Q2	1.98
TeO_2 - BaO - GeO_2 - Nb_2O_5	Q3	1.89

Table 1: The seven tellurite glasses compositions studied.

The powders were melted in a platinum crucible at 750-1050 °C, for one hour, quenched in heated brass molds, in air, annealed with different temperatures (270-400 ºC, 1-2 hours) and then cooled to room temperature, inside the furnace. The glasses were prepared with high purity (99.999 %) oxides; special care was taken during the preparation in order to reduce the incorporation of OH^- and to avoid the contamination of other rare-earth than ytterbium itself. The samples produced are yellowish, homogeneous, stable against crystallization and nonhygroscopic. Finally, the samples were polished for absorption and emission measurements. The absorption spectra were measured using a spectrometer (Cary Zeiss 500), in the range of 800-1200 nm. Luminescence measurements in the near- infrared region were performed by optically pumping the samples with a laser diode of 808 nm; the luminescence was dispersed by a Jarrel-Ash monochromator and analysed using an InGaAs detector connected to a lock-in amplifier. Cooperative luminescence was obtained with 16 W of pulsed (50 % duty cycle) diode laser excitation at 980nm, dispersed by a monochromator and collected by a S-20 photomultiplier. All measurements were made at room temperature. The same procedure (laser excitation at 980 nm) was employed for the measurement of the cooperative luminescence in GeO_2-PbO-Bi_2O_3 glasses [5]. For the measurements of the luminescence in the visible and near infrared region the excitation was performed close to the sample edge to minimize re-absorption due to the radiation trapping effect. The radiation trapping effect arises from the spectral overlap of the emission and absorption bands of Yb^{3+}. This effect normally deforms the Yb^{3+} emission band and increases with sample size, refractive index and Yb^{3+} concentration [6]. The refractive index (Table 1) 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 is measured with a 10 x objective lens of a microscope (Carl Zeiss). The density, around 5.0 g/cm^3, was measured with the Archimedes method. The infrared transmission in the infrared region was measured with a FT-IR spectrometer (Nicolet).

We also measured the cooperative luminescence in glass fibers doped with 1.0, 3.0 and 5.0 wt% of Yb_2O_3 using B1 composition. These fibers were obtained by a manual pulling process. The glass (bulk) was melted again in a platinum crucible at 800°C, for 20 minutes. The temperature was slowly decreased and the viscosity of the melt became appropriate for pulling glass fibers manually. Fibers were pulled continuously by touching the liquid surface with the tip of a silica rod moving upwards using constant speed.

Results and Discussions

Figure 2 presents the absorption spectra of the sample B1 doped with 1.0 wt% of Yb_2O_3 related to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. We observe three peaks centered around 925, 960 and 978 nm that correspond to the transitions from the lowest Stark level of the $^2F_{7/2}$ multiplet into the various Stark levels of the $^2F_{5/2}$ excited multiplet. No absorption related to impurities was observed. The strong absorption at 978 nm indicates that the glass is suitable for laser pumping at this wavelength.

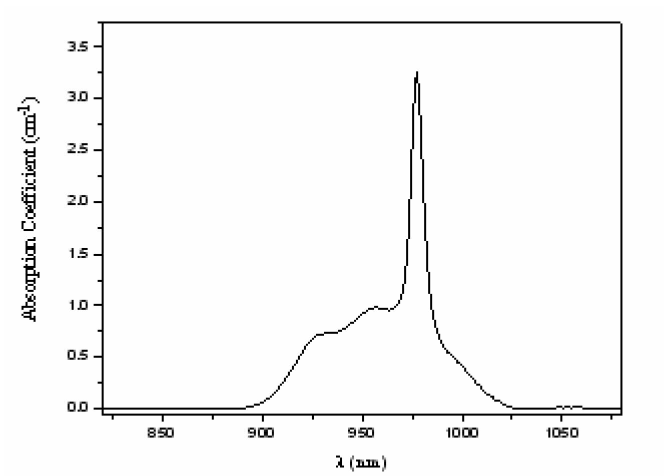

Figure 2: Absorption spectra of the TeO_2-ZnO (B1) glass doped with 1.0 wt% of Yb_2O_3.

Figure 3 shows the absorption spectra of the undoped sample B1 in the UV and visible (on the left) and its transmission in the infrared region (on the right). We observe that the transmission window starts around 0.36 μm. The band in 3.0 μm is attributed to the presence of OH^- radicals and the one around 4.5 μm is related to CO_2. We also observe that the IR cut-off is situated at 6.5 μm.

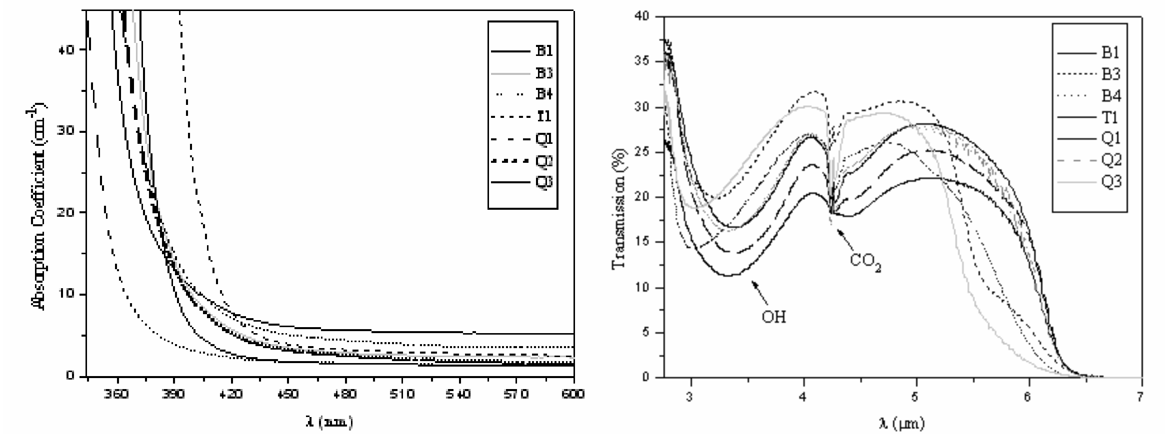

Figure 3: Absorption in the UV and visible (left) and transmission in the infrared region (right) of the glasses.

Figure 4, left side, presents the near-infrared luminescence of the sample B1 (with 1.0 wt% of Yb_2O_3). The peaks around 977 and 1000 nm are due to the transitions from the lowest Stark level of the excited multiplet $^2F_{5/2}$ to the $^2F_{7/2}$ ground-state multiplet. The luminescence peak in the visible region (Figure 4, right side) is centered at 500 nm and corresponds to half of the wavelength value of the near infrared luminescence, as predicted in the literature [7] for the cooperative effect.

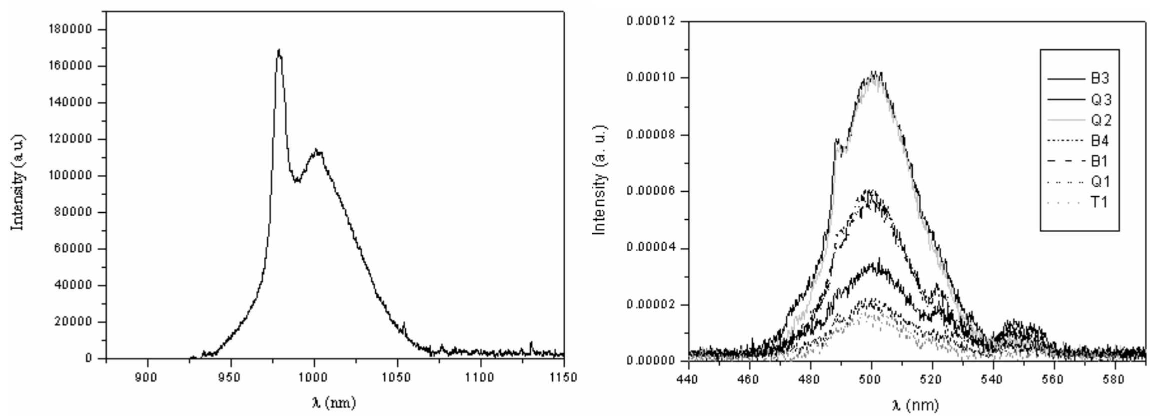

Figure 4: Emission spectrum in the infrared region of B1 glass (left) and Cooperative luminescence spectra of all glasses (right)

The highest cooperative luminescence is observed in Q2 and Q3 samples.

Figure 5, left side, presents a comparison of the cooperative luminescence between the glass (bulk) and the glass fiber for sample B1, both doped with 1.0 wt% of Yb_2O_3. The right spectra show the cooperative luminescence for glass fibers with different concentrations of Yb_2O_3. The highest luminescence is observed for 5 wt% of Yb_2O_3.

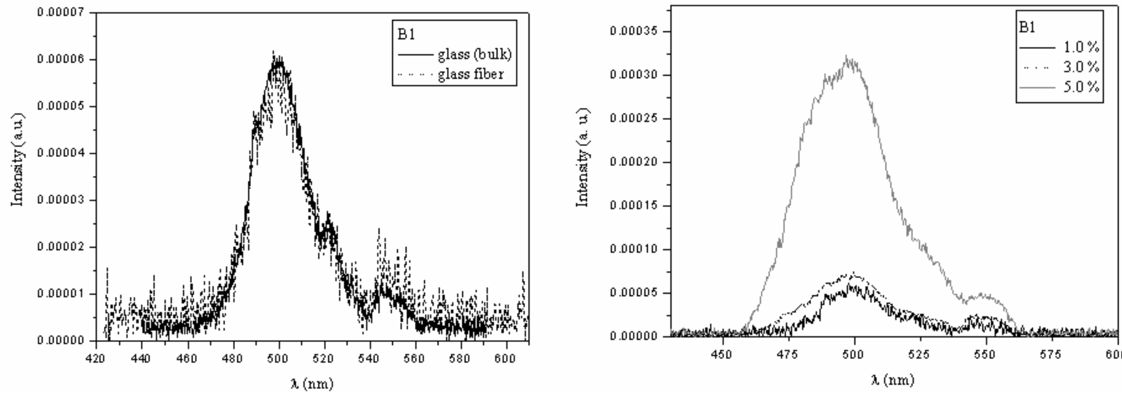

Figure 5: Comparison of the cooperative luminescence between the glass (bulk) and the glass fiber of B1 sample (left) and glass fibers with different concentrations of Yb_2O_3 (right)

Conclusions

We show in this work, a comparison of seven different tellurite hosts doped with Yb3+. We obtained the most intense cooperative emission in Q2 and Q3 compositions. Future studies with the cooperative effect in tellurite based glasses and fibers will use these results, mainly in the research of nanophotonic devices, like nanostructured glasses and fibers.

Acknowledgements

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