Infrared-to-visible upconversion of Er^{3+} ions in GeO_2–PbO–Nb_2O_5 glass fibers

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Abstract

Infrared to visible upconversion of Er^{3+} is observed in the GeO_2–PbO–Nb_2O_5 fibers. The visible emissions are related to the upconverted green emissions at about 530 nm ($^2H_{11/2} \rightarrow {}^4I_{15/2}$) and 550 nm ($^4S_{3/2} \rightarrow {}^4I_{15/2}$), and red emission at 668nm ($^4F_{9/2} \rightarrow {}^4 I_{15/2}$) under 980 nm excitation. The results obtained suggest that the fibers exhibit the same structure of the parent glasses and can be used in upconversion fiber optical devices.

Introduction

Recently, interest in upconversion emission in rare-earth doped materials has increased because of the search for all-solid compact laser devices operating in the visible region and the availability of powerful near-infrared) laser diodes. The potential applications include detection of IR radiation by conversion of the IR signal into the visible range and upconversion lasers [1-2] Among rare-earth-doped glass materials, erbium-doped glasses are promising host materials because of their important optical properties, which make them suitable for applications in photonics such as lasers, optical amplifiers, and frequency upconverters.

Among the heavy metal oxide (HMO) glasses, germanate based glasses are potential candidates for applications in optical devices because of their low transmission loss in the mid-infrared region [3-4]; recently these glasses have been drawn into optical fibers due to their good mechanical strength, high thermal stability, good chemical durability and high refractive index (~2) [5]. The heavy metal germanate (HMG) and the heavy metal fluoride (HMFG) glass fibers are two infrared (IR) transmitting glass fiber systems that are relatively similar to the most popular silica glass fibers. Because of these characteristics, HMOG fibers based on undoped GeO_2 glasses have recently shown great promise as an alternative to HMFG fibers for high power laser delivery at Er:YAG wavelength used in many medical and odontological applications [6-7].

Experimental Setup

Glass preparation

The glass was prepared by adding 1.0 wt % of Er_2O_3 to the following composition: (60GeO_2–25PbO–15Nb_2O_5), in mol%. A mixture of high purity (Aldrich 99.999%) raw materials (batches of 15 g) was melted for one hour in a platinum crucible at 1050°C, poured onto a heated brass mold and then annealed at 420°C during 3

hours. Care was taken during the preparation in order to reduce the OH^- contamination; one of the main sources of OH^- impurities may be from the starting materials. So we performed a treatment of the raw materials, during 1hour at 300°C. A glass block (20 x 20 x 2 mm^3) was obtained that was further used in the fiber drawing process.

Fiber Fabrication

Fibers were produced from Er-doped germanate glass using the composition mentioned above (GPN). The glass block was initially grounded in a planetary ball mill (Pulverisette–Fritsch) and melted in an platinum crucible at 800°C for 1 hour using a vertical electrical furnace. The temperature was then slowly decreased to 750°C when the liquid viscosity became appropriate for pulling glass fibers manually. At this temperature the liquid viscosity is within the working range making the pulling process possible. Fibers were pulled continuously by touching the liquid surface with the tip of a silica rod and moving upwards using constant speed. Fibers with diameter of 150 μm and length varying from 1 to 5 m were produced and selected afterwards according to the best uniformity and homogeneity. Previously, GP and GPB fibers were produce through this technique.

Upconversion Measurement

The visible upconversion spectra, was measured by optically pumping the sample with a high power diode laser emitting an average power of 5 W at 960 nm (50% duty cycle), dispersing the sample's luminescence with a 30 cm monocromator and collecting the signal with a S-20 photomultiplier. In order to enhance the signal from the small fibers, an imaging system was used that imaged the fibers onto the slit of the monocromator with the exact dimensions of the slit (0.1 x 10) mm^2. Data were analyzed using a lockin amplifier (EGG) coupled to a computer. This system is shown in the Figure 1.

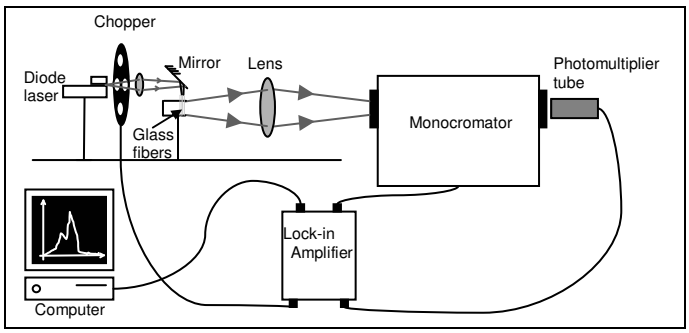

Figure 1: System used to measure visible emission of the GPN fiber.

Results and Discussions

We can observe the incorporation of Er^{3+} in the GPN glass through the absorption spectra (Figure 2) measured at room temperature; it showed the typical bands of Er^{3+} related to the transitions from the $^4I_{15/2}$ ground state to the excited sates. Figure 2 shows the absorption spectrum for GPN glass doped with 0.5 wt % of Er_2O_3.

Figure 3 presents the broad infrared transmission of GPN glass. The band positioned around 3.3 μm is related to the presence of OH^- radicals in the glass. It is normally difficult to eliminate the incorporation of OH^- and care must be taken during the preparation in order to reduce it. However, as will be shown, the presence of OH^- is not significant in our case as it did not affect the results.

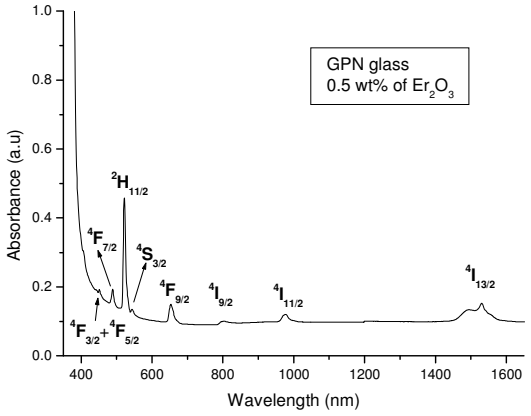

Figure 2: Absorption spectrum of GPN glass.

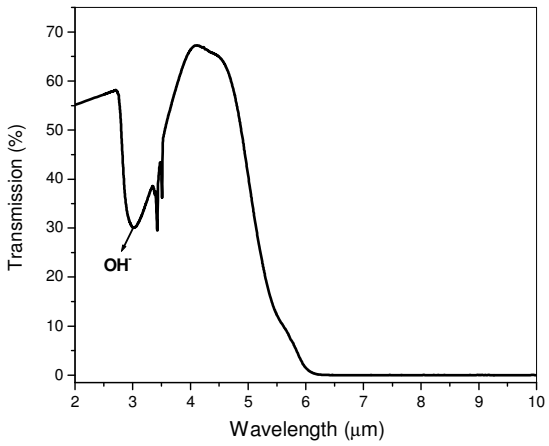

Figure 3: Infrared transmission.

The green luminescence with maxima around 530 nm and 550 nm is assigned to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions, respectivelly; the signal, at 668 nm is ascribed to the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. The most intense emission (easily seen by the naked eye) correspond to the green emission from $^4S_{3/2}$ level. The good agreement with the results of GPN bulk glasses indicates the glassy state of the GeO_2–PbO–Nb_2O_5 fiber. Besides, these emissions are in agreement with previous investigations on erbium doped GPN [8]. The visible spectra of the GPN fiber and the GPN glass are observed in Figure 3.

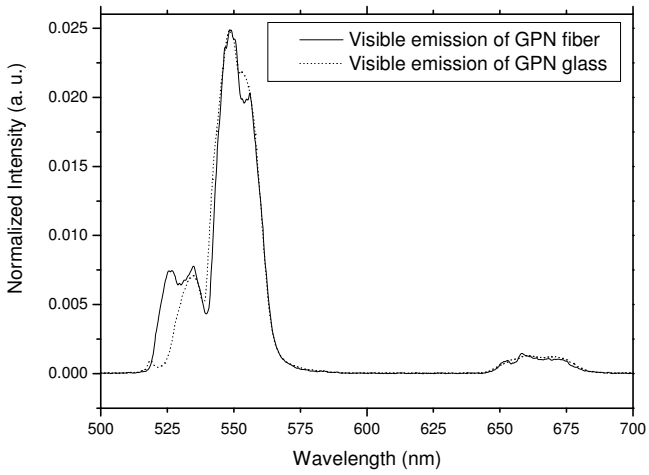

Figure 4: Visible spectra (upconversion) of GPN fiber (1wt%) and GPN glass (1wt%).

The mechanism responsible for the emissions in the visible region is indicated in Fig. 4; it describes the upconversion mechanism based on the excited state absorption in which one pump photon is absorbed and induces the transition $^4I_{15/2} \rightarrow {}^4I_{11/2}$; then a second pump photon promotes the transition $^4I_{11/2} \rightarrow {}^4F_{7/2}$ (solid upwards arrows in Fig. 4). The population of the excited state $^4F_{7/2}$, decays nonradiatively by multiphonon emission (dotted downwards arrow in Fig. 4) to the excited states $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$. These levels emit photons that originate the emissions shown in figures 3 at 530, 550 and 668 nm (solid downwards arrows in figure 4).

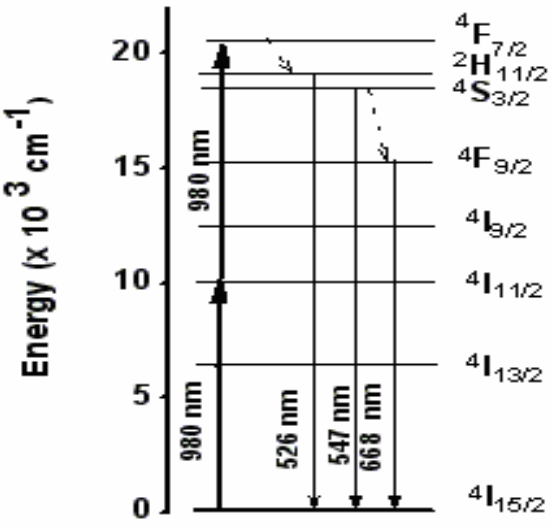

Figure 5: Energy level diagram and the mechanism of infrared to visible upconversion for Er^{3+} doped glass, under 980 nm excitation.

Conclusions

In this work we present results concerning the upconversion effect in GeO_2–PbO–Nb_2O_5 glass fibers doped with Er^{3+}. The glassy state of the fibers was confirmed by observation of the identical fluorescence signals in the visible, between the glass and the fiber. The results indicate that this glass fiber is a good candidate for applications in upconversion fiber optical devices.

Acknowledgements

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