



Upconversion fluorescence spectroscopy of Er ³⁺ /Yb ³⁺ - doped heavy metal Bi ₂ O ₃ –Na ₂ O–Nb ₂ O ₅ –GeO ₂ glass

A. S. Oliveira, M. T. de Araujo, A. S. Gouveia-Neto, A. S. B. Sombra, J. A. Medeiros Neto, and N. Aranha

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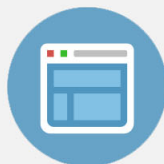
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Upconversion fluorescence spectroscopy of $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped heavy metal $\text{Bi}_2\text{O}_3\text{--Na}_2\text{O--Nb}_2\text{O}_5\text{--GeO}_2$ glass

A. S. Oliveira, M. T. de Araujo, and A. S. Gouveia-Neto^{a)}

Departamento de Física, Universidade Federal de Alagoas, Maceió-57072/970-AL-Brasil

A. S. B. Sombra

Departamento de Física, Universidade Federal do Ceará, Fortaleza-64450-CE-Brasil

J. A. Medeiros Neto

Departamento de Engenharia Mecânica, Universidade Federal do Ceará, Fortaleza-64450-CE-Brasil

N. Aranha

Instituto de Química-Departamento de Química Inorgânica, UNESP-Araraquara-SP-Brasil

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Upconversion fluorescence emission of $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped $\text{Bi}_2\text{O}_3\text{--Na}_2\text{O--Nb}_2\text{O}_5\text{--GeO}_2$ heavy metal glass samples excited at $1.06\text{ }\mu\text{m}$ is experimentally investigated. The results reveal the existence of intense emission bands centered around 520, 545, and 655 nm. The germano-niobate based host glass presents high transparency in the region of 400–2700 nm, the capability of incorporating high dopant concentrations, high melting temperature, and large resistance to atmospheric moisture. The observed intensity of the green fluorescence emission, suggested that the niobium based host glass material plays an important role in the efficiency of the upconversion process. Emission lines centered at 425, 483, 503, 608, and 628 nm were also observed. © 1997 American Institute of Physics. [S0021-8979(98)01401-7]

Considerable attention has recently been devoted to the conversion of near infrared radiation to visible light in rare-earth doped glass materials, for a wide range of applications, including color displays, optical data storage, biomedical diagnostics, sensors, and undersea optical communications. In general, the upconversion process is accomplished via the so-called frequency upconversion mechanism, first investigated by Auzel.¹ The frequency upconversion process involves stepwise excitation and energy transfer between rare-earth ions in solids. The researchers' effort has already led to the realization of rare-earth doped glass lasers,^{2,3} fiber lasers,^{4–8} and sensor devices.^{9,10}

A very important factor to be considered when developing a rare-earth doped optical device, is the host material. The host glass is desired to present a minimal absorption coefficient within the wavelength range of interest, ultrafast response times, compatibility with waveguide fabrication process, high optical damage threshold, and large nonlinearity. Particularly for temperature sensor devices, an important requirement for practical applications is that the material must yield a large upconversion signal when excited with powers comparable to commercially available diode lasers.^{9,10} Amongst many, fluorindate,¹⁰ fluorophosphate,¹¹ fluorozirconate,¹² and heavy metal silicate glasses,¹³ have already proven to satisfy the majority of the desired characteristics mentioned above. However, unlike for silicates, phos-

phates, and fluoride glasses, little attention has been directed to the study of nonlinear frequency conversion in niobate glasses.

In this work, we report on the experimental investigation of upconversion fluorescence spectroscopy of $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped heavy metal germano-niobate based glass samples excited at $1.06\text{ }\mu\text{m}$. The results show the generation of intense green and red signals centered around 520, 545, and 655 nm, respectively. The results also suggest that the glass niobate composition plays an important role in the upconversion efficiency.

In the experiment, the excitation source was a cw Nd:yttrium aluminum garnet (YAG) laser operated at $1.06\text{ }\mu\text{m}$. The excitation light was injected onto the samples by means of a 5-cm-focal length lens. The laser beam waist at the sample location was approximately $54\text{ }\mu\text{m}$. The signal light emitted from the sample was collected by a 10-cm-focal length lens and coupled to an optical fiber bundle which conveyed the signal light into a 0.34 m scanning spectrograph. The detection system comprised an S-20 uncooled photomultiplier tube, coupled to a lock-in amplifier and computer.

Glass samples were prepared from reagent-grade bismuth oxide (Bi_2O_3), sodium carbonate (Na_2CO_3), niobium oxide (Nb_2O_5), and germanium oxide (GeO_2), as starting materials. They were carefully mixed in appropriate proportions and melted in a platinum crucible in an electric furnace at temperatures between 1000 and 1100 °C. The samples had the two sides (faces) polished so that they had plate shapes with dimensions of 31×11 and 20×13 mm, and thickness of

^{a)}Electronic mail: artur@fis.ufal.br

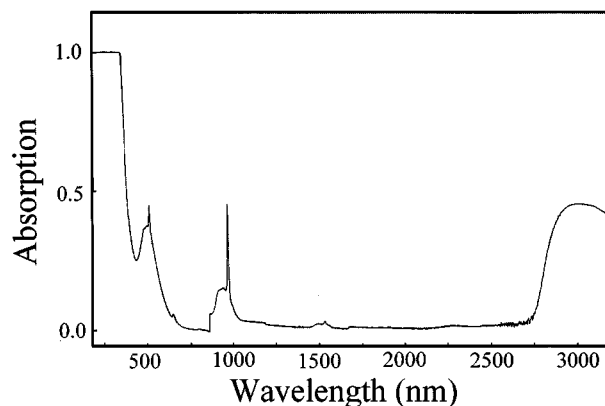


FIG. 1. Absorption spectrum of $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped $\text{Bi}_2\text{O}_3\text{-Na}_2\text{O-Nb}_2\text{O}_5\text{-GeO}_2$ glass.

3.4 and 2.6 mm, respectively. The dopants concentrations were 500 and 5000 ppm/wt for Er_2O_3 and Yb_2O_3 , respectively. Figure 1 illustrates a typical absorption spectrum of our samples. As can be seen, the material presents a wide transparency region extending from 400 nm to beyond 2700 nm. It is also shown in the spectrum, the three important absorption bands centered around 975 nm due to Yb^{3+} ions and 520 and 1530 nm owing to Er^{3+} ions.

Figure 2 shows a typical power spectrum of upconversion fluorescence visible radiation emanating from the glass sample. The intense green emission bands centered around 520, 545, and 655 nm, correspond, respectively, to the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ transitions to the $^4\text{I}_{15/2}$ ground state of Er^{3+} ions, as indicated in the simplified energy level diagram of Fig. 3. The excitation process for the $^4\text{S}_{3/2}$ - $^4\text{I}_{15/2}$ transition can be explained as follows.¹ In a first step, a $1.06\text{ }\mu\text{m}$ photon is absorbed by a Yb^{3+} which provokes the $^2\text{F}_{7/2}$ - $^2\text{F}_{5/2}$ transition. The second step involves the excitation of an Er^{3+} in the $^4\text{I}_{11/2}$, by means of the energy transfer mechanism¹ of excited Yb^{3+} to Er^{3+} . Finally, as the third step, either the same Yb^{3+} which absorbs a second $1.06\text{ }\mu\text{m}$ photon or another nearby Yb^{3+} being still in the $^2\text{F}_{5/2}$ state, transfers its energy to the same Er^{3+} , and the mechanism in

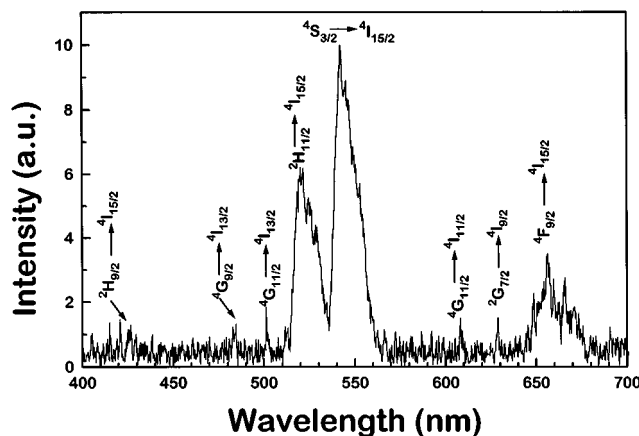


FIG. 2. Visible upconversion fluorescence spectrum for $1.06\text{ }\mu\text{m}$ pumping wavelength.

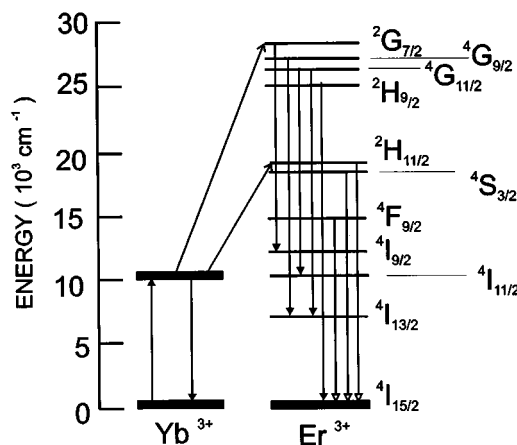


FIG. 3. Simplified energy-level diagram of the Er^{3+} and Yb^{3+} ions. Upwards arrows indicate excitation photons and downwards stand for fluorescence emission.

which the Er^{3+} in the excited state $^4\text{I}_{11/2}$ absorbs a $1.06\text{ }\mu\text{m}$ photon is also possible. The Er^{3+} reaches $^4\text{S}_{3/2}$ with phonon assistance. It is very important to point out the intense peak centered around 520 nm corresponding to the $^2\text{H}_{11/2}$ - $^4\text{I}_{15/2}$ transition. The emission can be obtained whenever the $^4\text{S}_{3/2}$ level is excited. The $^4\text{H}_{11/2}$ level is populated from $^4\text{S}_{3/2}$ via a fast thermal equilibrium between the levels.^{9,14,15} There exist two main possible pumping mechanisms for the red emission in $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped glass. The first pumping mechanism comprises the population of the $^4\text{S}_{3/2}$ level, by means of the process described previously, followed by a fast nonradiative decay through multiphonon interaction from the populated $^4\text{S}_{3/2}$ to $^4\text{F}_{9/2}$ and then to the $^4\text{I}_{15/2}$ ground state. In the other possible mechanism, the excited-state $^4\text{I}_{11/2}$ level populated via energy transfer between Er^{3+} and Yb^{3+} ions, relaxes to $^4\text{I}_{13/2}$ through a multiphonon interaction from where $^4\text{F}_{9/2}$ is populated by an excited-state absorption. This pumping mechanism also involves two $1.06\text{ }\mu\text{m}$ photons.

The pump power dependence of the three main upconversion fluorescence bands was analyzed and the results are depicted in the log-log plot of Fig. 4. As can be inferred

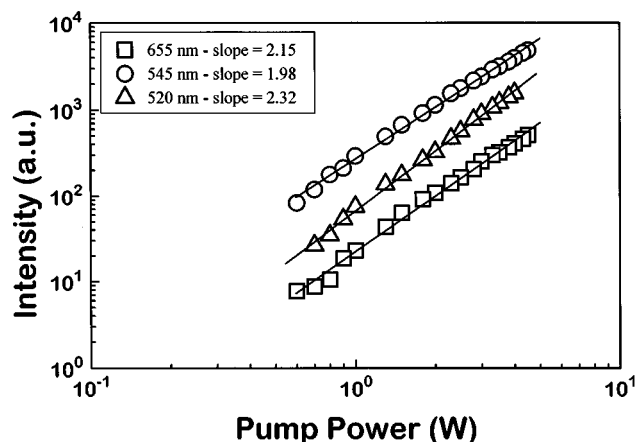


FIG. 4. Log-log plot of upconversion fluorescence emission as a function of pump power at $1.06\text{ }\mu\text{m}$.

from data, both green and red emissions intensities presented a quadratic dependence upon excitation intensity. This behavior indeed corroborates with the proposed routes for the excitation mechanism involving two 1.06 μm photons to reach the upper emitting levels. It is important to mention that differently from reports of Ref. 16, we have observed no saturation behavior in any of the three curves of Fig. 4, even for pump powers as high as 3 W. It is also important to point out that the upconversion process in this glass was so efficient that the green emission could readily be seen with the naked eye, at pump powers as low as a few tens of milliwatts. For 100 mW absorbed power, as much as 10 μW of visible upconversion fluorescence was generated, giving rise to a conversion efficiency $\eta \approx 10^{-4}$ ($\eta = I_{\text{out}}/I_{\text{abs}}$). The excitation Gaussian beam waist at the sample location was $\sim 54 \mu\text{m}$, yielding an excitation power density in the sample of $\sim 1.1 \text{ kW/cm}^2$ for the 100 mW cw power used in this measurement. This is to be compared with results reported in Refs. 16 and 17 where a maximum room temperature upconversion efficiency of $\sim 10^{-5}$ was measured for Er/Yb-doped heavy metal fluoride glasses. We believe that the relatively high efficiency of frequency upconversion in our $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped $\text{Bi}_2\text{O}_3\text{--Na}_2\text{O--Nb}_2\text{O}_5\text{--GeO}_2$ samples, is attributed to the presence of niobium in the host glass matrix. The addition of cations such as niobium has already been proven to increase both linear and nonlinear refractive indices of glass materials by over 15% (Ref. 13 and references therein) depending upon the Nb concentration. The radiative emission cross section of rare-earth energy levels varies as $\sim n^3$, n being the linear refractive index. The higher linear refractive index of niobate glasses gives rise to a much higher radiative emission rate for rare-earth energy levels. As a result, a substantial improvement by an order of magnitude in the unconversion efficiency, as compared to results reported in Refs. 16 and 17, is obtained from niobate glass hosts.

The spectrum illustrated in Fig. 2, also revealed the existence of five less intense emission peaks in the region of the blue-green and orange-red, which were accounted for as three-photon excited emission levels. The blue-green emission lines at 425, 483, and 503 nm, correspond to $^2\text{H}_{9/2}\text{--}^4\text{I}_{15/2}$, $^4\text{G}_{9/2}\text{--}^4\text{I}_{13/2}$, and $^4\text{G}_{11/2}\text{--}^4\text{I}_{13/2}$ transitions, respectively. The orange-red emission peaks at 608 and 628 nm are associated with the transitions $^4\text{G}_{11/2}\text{--}^4\text{I}_{11/2}$ and $^2\text{G}_{7/2}\text{--}^4\text{I}_{9/2}$, respectively. The main route to populate the ^4G levels is through a two-photon absorption of Er^{3+} , connecting $^4\text{I}_{15/2}$ ground state to $^2\text{H}_{11/2}$ excited state, followed by a one-photon excited state absorption connecting $^4\text{S}_{3/2}$ to $^2\text{G}_{7/2}$. The population of ^4G lower energy levels is obtained via phonon assisted nonradiative decay. Another

possible route is through a one-photon excited state absorption from $^4\text{S}_{3/2}$, or energy transfer processes (Yb^{3+} in $^2\text{F}_{5/2}$ to Er^{3+} in $^4\text{S}_{3/2}$).

In conclusion, we have experimentally investigated, frequency upconversion fluorescence spectroscopy in $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped niobium based heavy metal glass excited at 1.06 μm . The results showed the emission of three intense visible fluorescence bands centered around 520, 545, and 655 nm. The observed intensity of the green fluorescence emission suggested that the presence of the niobium in the host glass material plays a major role in the efficiency of the upconversion process. This characteristic, added to the wide transparency region (400–2700 nm), high vitreous transition and melting point temperatures, the possibility to incorporate high dopant concentrations and large resistance to atmospheric moisture, makes the material an alternative contender to optical temperature sensors.

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