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COMMUNICATIONS

Blue upconversion enhancement by a factor of 200 in Tm³⁺-doped tellurite glass by codoping with Nd³⁺ ions

N. Rakov, G. S. Maciel,[a)] M. L. Sundheimer, L. de S. Menezes, and A. S. L. Gomes
Departamento de Física, Universidade Federal de Pernambuco, 50670-901 Recife-PE, Brazil

Y. Messaddeq, F. C. Cassanjes, G. Poirier, and S. J. L. Ribeiro
*Instituto de Química, Universidade do Estado de São Paulo, P.O. Box 355,
14801-970 Araraquara-SP, Brazil*

We investigated near-infrared-to-blue upconversion from thulium (Tm^{3+}) doped in tellurite glasses upon continuous wave excitation near 800 nm. We observed an enhancement of over two orders of magnitude of the upconverted emission at ~ 480 nm when neodymium (Nd^{3+}) ions were codoped with Tm^{3+} ions. For comparison, using a $Tm^{3+}:Nd^{3+}$ codoped fluorozirconate glass as a reference material we observed a 40-fold enhancement of the blue emission. Analysis of the blue emission for samples with different doping levels of Nd^{3+} ions showed that energy transfer between Nd^{3+} and Tm^{3+} is the mechanism responsible for the enhancement in upconversion. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1515376]

The need for short wavelength laser sources in the compact disc industry and optical data storage systems has led to the development of a great number of solid state violet and blue emitters such as semiconductor diodes, organic compounds and rare-earth doped materials.[1–5] Besides being a promising candidate for optical communication amplification in the *S* band, thulium (Tm^{3+}) is one of the most studied rare-earth ions for violet and blue laser operation based upon upconversion.[6–11] One approach to improve the luminescence efficiency of Tm^{3+} is to codope it with other rare-earth ions.[12,13] The choice of host material is also an important issue when one deals with improving the efficiency of the emission process. In this case, the main goal is to increase the luminescence (radiative emission) efficiency by quenching nonradiative channels (multiphonon relaxation). This is possible using matrices with low cut-off phonon energies such as fluoride glasses, but these present poor mechanical and chemical stability. Therefore, there must be a compromise between low cut-off phonon energy and good environmental stability for device operation purposes.

Tellurite glass has a wide transmission window (typically $0.4–5.0$ μm), high linear and nonlinear refractive indices, good corrosion resistance and mechanical stability, and the lowest cut-off phonon energy among oxide materials (800 cm^{-1}). Although infrared laser operation has been demonstrated in neodymium[14] and erbium[15]-doped tellurite fibers, the blue lasing potential of this material has yet to be carefully investigated. Previous results have shown that tellurite glass doped with Tm^{3+} is a good infrared-to-blue upconverter.[16] Here we show that the upconverted blue emis-

sion of Tm^{3+}-doped tellurite glasses is improved by over two orders of magnitude when codoped with neodymium (Nd^{3+}) ions. Furthermore, the upconversion enhancement is approximately five times larger than that of a $Tm^{3+}:Nd^{3+}$-codoped fluorozirconate (ZBLAN) glass, thus demonstrating that $Tm^{3+}:Nd^{3+}$ tellurite glass is an excellent candidate for blue lasing.

The samples used were tellurite and ZBLAN glasses obtained by conventional melting/casting procedures. Base compositions were (in mol %) $(69.8 - x)TeO_2 - 10GeO_2 - 10NbO_2 - 5K_2O - 5Li_2O - 0.2TmO_{1.5} - xNdO_{1.5}$ and $(52.8 - x)ZrF_4 - 20NaF - 20BaF_2 - 4LaF_3 - 3AlF_3 - 0.2TmF_3 - xNdF_3$ $(x = 0.5, 1, $ and $2)$. The samples were cut and polished to the same dimensions ($4 \times 2 \times 7$ mm^3) to guarantee the same excitation (illumination) area. The excitation source for the luminescence measurements was a homemade continuous wave (cw) tunable Ti:sapphire laser pumped by an Ar$^+$ laser. The excitation power was 350 mW and the laser spot size at the sample was ~ 30 μm. The upconverted luminescence emission was collected perpendicular to the excitation direction and the signal was spectrally resolved using a monochromator and detected by a photomultiplier tube (1P28). All the measurements were made at room temperature.

Figures 1(a)–1(d) show the upconversion signal of tellurite and ZBLAN glasses doped with Tm^{3+} (0.2 mol %) and codoped with Tm^{3+} (0.2 mol %) and Nd^{3+} (0.5 mol %) under cw excitation at 795 nm. This excitation wavelength is resonant with transitions $^3H_6 \rightarrow ^3H_4$ of Tm^{3+} and $^4I_{9/2} \rightarrow (^4F_{5/2}, ^2H_{9/2})$ of Nd^{3+}. The bands peaked at ~ 463 and at ~ 480 nm correspond, respectively, to transitions $^1D_2 \rightarrow ^3F_4$ and $^1G_4 \rightarrow ^3H_6$ of Tm^{3+}. An additional line is observed at

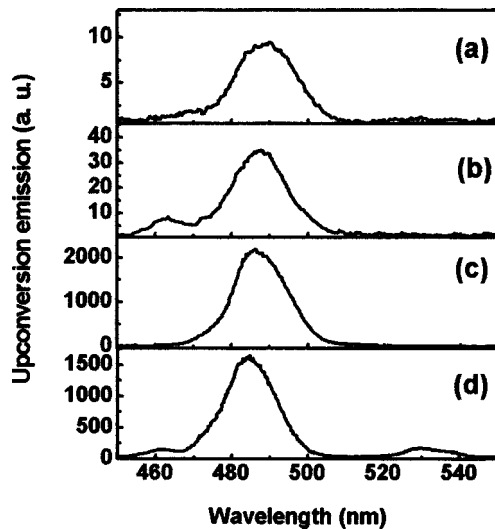a)Corresponding author; electronic mail: glauco@df.ufpe.br

FIG. 1. Upconverted signal for (a) tellurite glass doped with Tm^{3+} (0.2 mol %); (b) ZBLAN glass doped with Tm^{3+} (0.2 mol %); (c) tellurite glass codoped with Tm^{3+} (0.2 mol %) and Nd^{3+} (0.5 mol %); (d) ZBLAN glass codoped with Tm^{3+} (0.2 mol %) and Nd^{3+} (0.5 mol %); upon near-infrared (795 nm) excitation.

~530 nm that represents the transition $^2G_{9/2}\rightarrow^4I_{9/2}$ of Nd^{3+}. Other lines (not shown here) were detected in ZBLAN glass corresponding to Nd^{3+} emissions at ~371 nm ($^4D_{3/2}\rightarrow^4I_{11/2}, ^2P_{3/2}\rightarrow^4I_{9/2}$), ~396 nm ($^4D_{3/2}\rightarrow^4I_{13/2}, ^2P_{3/2}\rightarrow^4I_{11/2}$), ~425 nm ($^2P_{1/2}\rightarrow^4I_{9/2}, ^4D_{3/2}\rightarrow^4I_{15/2}$), and ~580 nm ($^2H_{11/2}\rightarrow^4I_{9/2}$) and Tm^{3+} transition at ~376 nm ($^1D_2\rightarrow^3H_6$). We did not observe upconversion luminescence from level $^1D_2$ of Tm^{3+} in our tellurite glasses. This is because the absorption edge of our tellurite glass has a lower energy than level $^1D_2$, causing luminescence quenching.[9] The same reasoning applies to the absence of upconversion luminescence originating from level $^2P_{1/2}$ and higher lying levels of Nd^{3+} in our tellurite glasses. Using an InGaAs photodetector, lines in the red and infrared were also observed in both tellurite and ZBLAN samples but analysis of these lines will not be addressed here.

Figure 2(a) shows the integrated intensity of the blue luminescence (~480 nm) and Fig. 2(b) shows the enhancement of the blue intensity for the samples studied. The enhancement of the blue intensity is defined as the ratio of the integrated intensity (the area below the line peaked at ~480 nm) between codoped samples and the samples doped only with Tm^{3+}. Note that the enhancement of the blue signal for Tm^{3+}:Nd^{3+} tellurite glass is very high (over two orders of magnitude). Moreover the enhancement of the Tm^{3+}:Nd^{3+} tellurite glass is approximately five times larger than that of Tm^{3+}:Nd^{3+} ZBLAN glass. Figure 2 also indicates that the optimum Nd^{3+} concentration for the samples studied is 0.5 mol %.

The energy level diagram for the blue upconversion (~480 nm) process involving Tm^{3+} and Nd^{3+} is shown in Fig. 3. Two mechanisms may lead to the blue upconversion: excited state absorption ($^3H_5\rightarrow^1G_4$) and energy transfer from Nd^{3+} to Tm^{3+}. The observation of enhancement of the luminescence at ~480 nm from Tm^{3+} due to the presence of Nd^{3+} ions shown in Fig. 2 indicates that energy transfer is
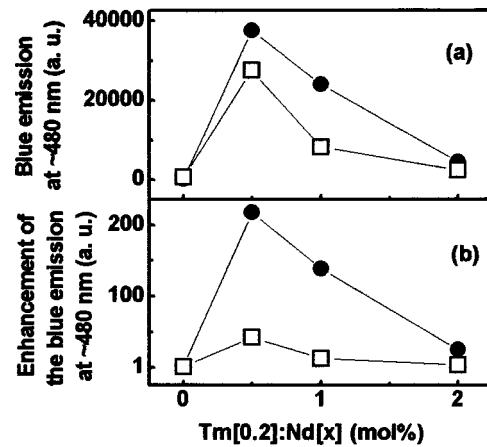

FIG. 2. (a) Intensity of the upconverted blue emission. (b) Intensity of the upconverted blue emission normalized by the data from a Tm^{3+} single doped sample. Closed circles represent the data for tellurite glass and open squares represent the data for ZBLAN glass.

the most relevant upconversion channel: after promotion of population to levels $^3H_4$ of Tm^{3+} and ($^2H_{9/2}, ^4F_{5/2}$) of Nd^{3+}, fast nonradiative relaxation takes place from levels ($^2H_{9/2}, ^4F_{5/2}$) to level $^4F_{3/2}$ of Nd^{3+}. Then, energy transfer may take place from Nd^{3+} to Tm^{3+}.[12] This energy transfer channel is shown by the dotted lines labeled by (I) in Fig. 3. Furthermore, we observed luminescence quenching of the signal at $\sim1.47\,\mu$m ($^3H_4\rightarrow^3F_4$) for the codoped samples which is another indication of the importance of channel (I). Figure 2 shows that the blue emission also decreases with an increase in Nd^{3+} concentration for both tellurite and ZBLAN hosts and quenching of the luminescence may be due to two different energy transfer processes: (a) energy transfer between neighboring excited Nd^{3+} ions and (b) energy transfer from excited Tm^{3+} ions to Nd^{3+} ions in the ground state, shown by the dotted lines labeled (II) in Fig. 3. The difference is that in case (b) the lifetime of level $^1G_4$ is modified (shortened) due to channel (II).

To clarify this point the dynamics of the population at level $^1G_4$ were studied by monitoring the temporal evolution of the blue signals using an electronically modulated diode laser as the pump source. The time resolution of the mea-
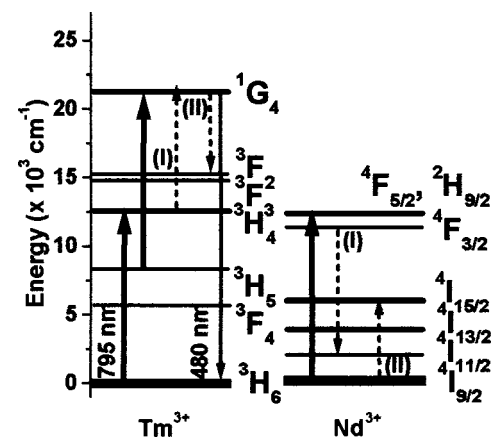

FIG. 3. Energy level schematic and the relevant channels responsible for the blue upconversion at 480 nm.

TABLE I. Rise (τ_r) and decay time (τ_d) of the upconverted blue emission at $\sim$480 nm for the samples studied. The results are shown for the samples doped with 0.2 mol % of Tm^{3+} and x mol % of Nd^{3+}. The measurement time resolution is $\sim$0.02 ms. The excitation wavelength is 809 nm. The excitation power is 225 mW.

Sample	$x=0.5$		$x=1.0$		$x=2.0$	
	τ_r (ms)	τ_d (ms)	τ_r (ms)	τ_d (ms)	τ_r (ms)	τ_d (ms)
Tellurite	0.22	0.18	0.20	0.13	0.13	0.08
ZBLAN	0.69	0.52	0.54	0.40	0.35	0.36

surement system is $\sim$0.02 ms. The results found for the rise and decay times of the blue luminescence for tellurite and ZBLAN glasses are shown in Table I. First, we must recall that the rise time is a function of the lifetimes of intermediate states participating in the upconversion process, mainly level $^3H_4$ which has a lifetime of $\sim$0.31 ms for tellurite and $\sim$0.74 ms for ZBLAN glasses.[17] The decay time of the signals is about the same order of magnitude of the lifetime of level $^1G_4$ which was estimated to be $\sim$0.33 ms for tellurite and $\sim$0.68 ms for ZBLAN glasses using Judd–Ofelt theory.[18] Note also that Table I shows that the rise and decay times of the blue emissions decrease with an increasing concentration of Nd^{3+} for the glasses studied. This is favorable evidence for the relevance of the energy transfer mechanisms shown in Fig. 3.

In summary, a significant increase (over two orders of magnitude) of the blue upconversion intensity in Tm^{3+}-doped tellurite glass was observed due to the presence of Nd^{3+}. The mechanism responsible for the upconversion enhancement is energy transfer from Nd^{3+} to Tm^{3+}. The enhancement of the signal was approximately five times larger than that observed in Tm^{3+}:Nd^{3+} ZBLAN glass, demonstrating the high potential of Tm^{3+}:Nd^{3+} codoped tellurite glass for photonic applications in the blue region of the spectrum, particularly for a diode pumped compact blue laser.

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