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Efficient energy upconversion of cw radiation at 1.064 μm into blue, red, and near infrared emission in Tm^{3+}-doped Yb^{3+}-sensitized $60TeO_2$-$10GeO_2$-$10K_2O$-$10Li_2O$-$10Nb_2O_5$ glasses is reported. Intense blue upconversion luminescence at 485 nm corresponding to the Tm^{3+} $^1G_4 \rightarrow {}^3H_6$ transition with a measured absolute power of 0.1 μW for 800 mW excitation power at room temperature is observed. The experimental results also revealed a sevenfold enhancement in the upconversion efficiency when the sample was heated from room temperature to 235 °C yielding 0.7 μW of blue absolute fluorescence power for 800 mW pump power. High brightness emission around 800 nm ($^3F_4 \rightarrow {}^3H_6$) in addition to a less intense 655 nm ($^1G_4 \rightarrow {}^3H_4$ and $^3F_{2,3} \rightarrow {}^3H_6$) fluorescence is also recorded. The energy upconversion excitation mechanism for thulium emitting levels is assigned to multiphonon-assisted anti-Stokes excitation of the ytterbium-sensitizer followed by multiphonon-assisted sequential energy-transfer processes. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1413489]

There has recently been a great deal of interest in the conversion of infrared into visible light through energy upconversion in rare-earth doped (RED) glasses due to the potential application in photonics, which include optical data storage,[1] lasers,[2], sensors,[3] and optical displays.[4] In the reports of Ref. 4 by triply doping the glass with Tm^{3+}, Er^{3+}, and Pr^{3+}, blue, green, and red light was generated exploiting the frequency upconversion process excited by a pair of near-infrared (NIR) lasers with distinct wavelengths. A new approach has recently been proposed for the generation of either blue[5] or multicolored light[6] exploiting both cooperative upconversion from pairs of Yb^{3+} ions,[5] and/or energy-transfer upconversion in a Yb^{3+}/Eu^{3+}-codoped silica glass pumped at 973 nm,[6] respectively. Thulium-doped materials has also drawn much interest recently as a viable source of blue coherent radiation pumped by infrared lasers. A room temperature upconversion laser at 480 nm in a Tm^{3+}-doped fiber pumped at 1.12 μm was reported.[7] In a two wavelength pump configuration, laser operation at 455 nm has also been reported.[8] However, despite their higher upconversion efficiencies, monopumped systems are mostly desirable.[9] The advent of highly Yb^{3+}-doped materials allowed a noticeable improvement in the upconversion efficiency in RED glasses sensitized by ytterbium.[10,11] In the realization of RED-based photonic devices, the optical, mechanical, and thermal properties of the host material plays a major role and requires careful consideration. The glassy host is desired to possess a minimal absorption coefficient within the wavelength range of interest, ultrafast response times, suitability with waveguide fabrication processes, capability of incorporating high rare-earth concentrations, high optical damage threshold, and large nonlinearities. In this work we present efficient energy upconversion of infrared into blue, red, and NIR light and thermally enhanced upconversion efficiency in Tm^{3+}/Yb^{3+}-codoped TeO_2-based glasses.

The samples used had a composition of $60TeO_2$-$10GeO_2$-$10K_2O$-$10Li_2O$-$10Nb_2O_5$ doped with 1000 ppm/wt of Tm^{3+} ions and three different concentrations 30 000(I), 5000(II), and 1000 ppm/wt(III) of ytterbium. The material presents very good optical quality, is stable against atmospheric moisture, exhibits low optical attenuation from 400 nm to 5.0 μm, and due to the >2.0 refractive index, one expects to obtain significantly high radiative decay rates. The material also exhibits high solubility allowing the incorporation of high lanthanide concentrations apart from being nonhygroscopic and possesses high thermal stability against crystallization. The excitation source was a cw Nd:YAG laser operated at 1.064 μm.

The upconversion excitation process was accomplished by means of a multiphonon-assisted anti-Stokes excitation of the Yb^{3+} sensitizer followed by phonon-assisted sequential energy-transfer processes to the Tm^{3+} acceptor, as illustrated in the simplified energy-level diagram of Fig. 1. In the first step, an incident pump photon at 1.064 μm is absorbed by a Yb^{3+} ion through a multiphonon assisted anti-Stokes excitation process[12] promoting it to the $^2F_{5/2}$ excited state level. The excited Yb^{3+} relaxes and nonresonantly transfers its energy to a nearby Tm^{3+} ion, exciting it to the $^3H_5$ excited-state level. The thulium ion in the $^3H_5$ excited state relaxes nonradiatively to the $^3H_4$ metastable level. From that level, a second nonresonant energy-transfer process takes place from the same or another neighbor excited Yb^{3+} and promotes it

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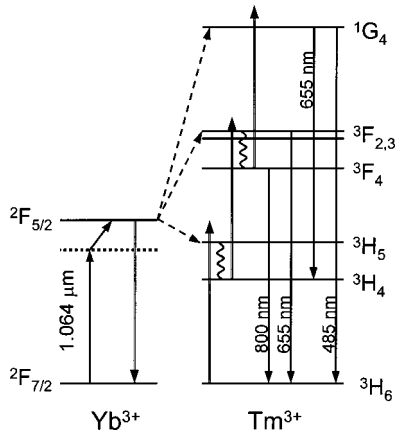

FIG. 1. Simplied energy-level diagram for the Tm^{3+}–Yb^{3+} pair pumped at 1.064 μm indicating the participation of phonons in the Yb^{3+} absorption and energy-transfer processes. The solid lines connected by a dashed line represent the energy-transfer process.

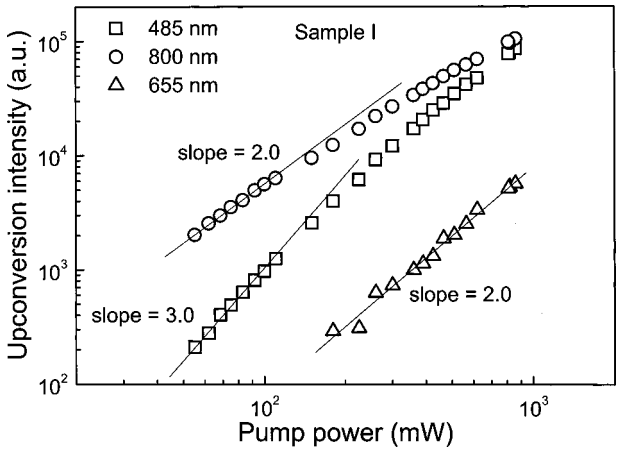

FIG. 3. Log–log plot of the visible and NIR upconversion emission intensity as a function of the excitation power at 1.064 μm for sample (I) at room temperature.

to the $^3F_{2,3}$ level. The $^3F_{2,3}$ state also relaxes by a multiphonon-assisted process to the $^3F_4$ state. The signature of this step of the upconversion process is the 800 nm emission owing to the $^3F_4 \rightarrow {}^3H_6$ transition. Finally, a third nonresonant anti-Stokes energy-transfer process is effectuated exciting the Tm^{3+} ion in the $^3F_4$ to the $^1G_4$ upper excited state. From the $^1G_4$ level the Tm^{3+} ions radiatively relax to the $^3H_6$ ground state generating the intense upconversion fluorescence signal around 485 nm. The emission band around 655 nm is assigned to both the $^1G_4 \rightarrow {}^3H_4$ and $^3F_{2,3} \rightarrow {}^3H_6$ transitions. A typical room-temperature upconversion luminescence spectrum of radiation emanating from sample (I) for a pump power of 800 mW is portrayed in Fig. 2. As one sees, the upconversion emission presents three distinct bands centered around 485, 655, and 800 nm, corresponding to the $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3H_4$ as well as the small contribution due to the $^3F_{2,3} \rightarrow {}^3H_6$, and $^3F_4 \rightarrow {}^3H_6$ transitions of Tm^{3+} ions, respectively. It is important to point out that the blue emission around 485 nm was intense enough to be seen with the naked eye with daylight illumination in the laboratory. The dependence of the upconversion emission intensities upon the excitation power was investigated and the results are presented in Fig. 3. At low power levels ($\leqslant$90 mW) the results revealed a cubic power law behavior with pump intensity for the visible emission signals and a quadratic power law behavior was observed for the 800 nm signal. However, for higher excitation power levels, saturation of the energy upconversion process is observed with the slope for the blue emission dropping down to less than 2.5 and further down to 2.0, while the 800 nm emission intensity saturates first reaching approximately 1.0 in the same power interval. For the highest excitation power of 800 mW launched onto the sample $\sim$0.1 μW blue absolute fluorescence power was measured. The observed excitation power dependence and the measured upconversion fluorescence emission wavelengths corroborate the upconversion excitation process for our system which was assumed by many in different host materials.[11,13–16] The saturation behavior observed in our measurements is attributed to the depletion of the ground state of the thulium ions owing to the efficient Yb^{3+} to Tm^{3+} energy-transfer process.[14] Figure 4 shows the dependence of the energy upconversion process upon the temperature and the results revealed a sevenfold enhance-

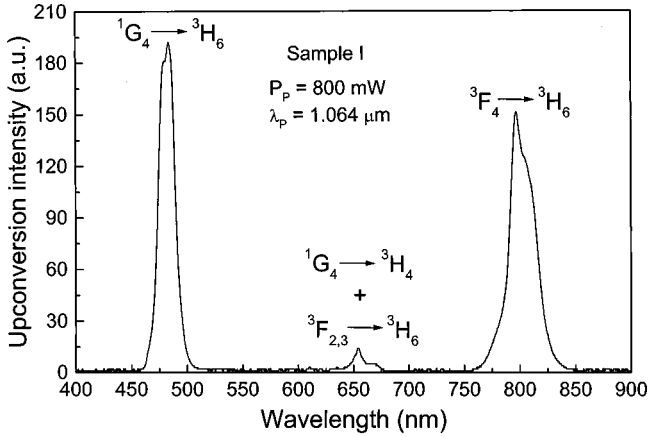

FIG. 2. Room-temperature energy upconversion emission spectrum for the Tm^{3+}/Yb^{3+}-codoped sample (I) for an excitation power of 800 mW at 1.064 μm launched onto it.

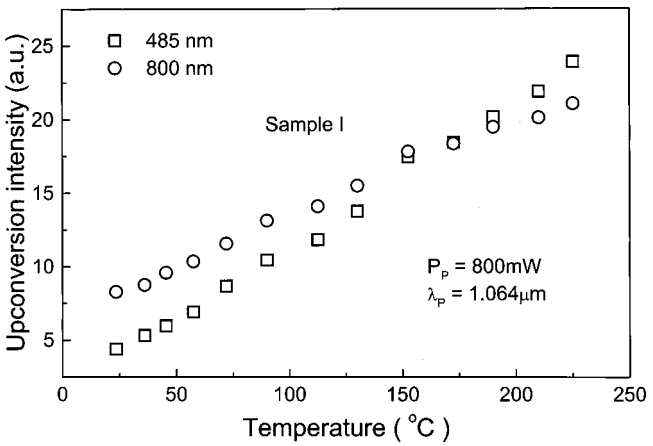

FIG. 4. Temperature dependence of the blue and NIR upconversion emission intensity for sample (I) at a fixed excitation power of 800 mW.

ment in the blue emission when the sample was heated at a fixed pump power in the temperature range of 20–235 °C. Accordingly, the sevenfold enhancement gave rise to a recorded 0.7 μW overall blue fluorescence power. One can also observe a threefold maximum enhancement in the 800 nm emission intensity followed by saturation and the onset of a decreasing process. The energy upconversion efficiency temperature enhancement has already been described in detail elsewhere for Er^{3+}- and Pr^{3+}-doped glasses sensitized by Yb^{3+} and pumped at 1.064 μm[17–19] and it suffices to mention here that the upconversion excitation of the rare-earth ion-activated emitting levels is accomplished by means of multiphonon-assisted anti-Stokes excitation of the sensitizer ions,[12] followed by successive energy-transfer processes to the active emitter. Therefore the effective pumping of the Tm^{3+} ions luminescent excited states depends upon the phonon population in the host material. This mechanism is explained by introducing a temperature dependent effective absorption cross section for the Yb^{3+}-sensitizer $\sigma_Y(T)$, such that $\sigma_Y(T)=\sigma_Y^0 F(T)$, where σ_Y^0 is the Yb^{3+}-sensitizer absorption cross section at resonance peaked at 975 nm and $F(T)=[\exp(h\nu_{\text{phonon}}/k_B T)-1]^{-p}$ accounts for the phonon population in the host material. The exponent p is associated with the number of optical phonons involved in the sensitizer excitation, $h\nu_{\text{phonon}}$ is the phonon energy, k_B is the Boltzmann constant, and T the absolute temperature. For the TeO_2-based glasses, we may assume that $p=1$ since the energy mismatch between the pump photon and the ytterbium transition corresponds approximately to the value of the phonon for tellurium-oxide glasses ($\sim$800 cm^{-1}). As a result, the Yb^{3+}-sensitizier absorption cross section is an increasing function of the temperature. The dependence of the blue emission intensity upon the ytterbium concentration was also investigated and the results showed a linear behavior instead of the expected cubic dependence, owing to the high pump power which saturated the upconversion process and also a contribution due to back-transfer from Tm to Yb ions.[14,20]

In conclusion, we have presented the generation of intense 0.7 μW power blue emission around 485 nm through efficient energy upconversion in Tm^{3+}-doped Yb^{3+}-sensitized TeO_2-based glasses excited at 1.064 μm. High brightness 800 nm radiation was also obtained in addition to a less intense signal around 655 nm. The energy upconversion excitation mechanism for the Tm^{3+}-ion-activated excited-state emitting levels was ascribed to a multiphonon-assisted anti-Stokes excitation of the Yb^{3+} sensitizer followed by phonon-assisted sequential energy-transfer processes to the Tm^{3+} acceptor.

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