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Sensitized thulium blue upconversion emission in $Nd^{3+}/Tm^{3+}/Yb^{3+}$ triply doped lead and cadmium germanate glass excited around 800 nm

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Bright blue upconversion emission by thulium ions in $PbGeO_3-PbF_2-CdF_2$ glass triply doped with $Nd^{3+}-Tm^{3+}-Yb^{3+}$ under diode laser excitation around 800 nm is reported. The results revealed that the $Nd^{3+}/Tm^{3+}/Yb^{3+}$-codoped sample generated ten times more 475 nm blue upconversion fluorescence than the Yb^{3+}-sensitized Tm^{3+}-doped one, under the same excitation power. The upconversion process also showed a strong dependence upon the Yb^{3+} concentration. The results also indicated that the neodymium ions played a major role in the upconversion process by transfering the 800 nm excitation to thulium ions. The population of the Tm^{3+} ions $^1G_4$ emitting level was accomplished through a multiion interaction involving ground-state absorption of pump photons around 800 nm by the $Nd^{3+}(^4I_{9/2}\rightarrow{}^2H_{9/2}, {}^4F_{5/2})$ and $Tm^{3+}(^3H_6\rightarrow{}^3F_4)$ ions followed by energy-transfer processes involving the $Nd^{3+}-Yb^{3+}(^4F_{3/2}, {}^2F_{7/2}\rightarrow{}^4I_{11/2}, {}^2F_{5/2})$ and $Yb^{3+}-Tm^{3+}(^2F_{5/2}, {}^3F_4\rightarrow{}^2F_{7/2}, {}^1G_4)$ pairs. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Infrared-to-visible frequency upconversion[1] in lanthanide doped materials has been extensively investigated owing to the potential applications in visible upconversion lasers, high density memories, and/or solid-state color displays. Thus, there exists a need for alternative solid-state materials capable of producing efficient frequency upconversion processes. To pursue that goal, the study of multiion interaction in different hosts has recently attracted much interest due to the fact that the interaction mechanism can be beneficial in the realization of photonic devices based upon rare-earth doped solid-state systems. The multiion interaction provides conditions for the so-called sensitization process where the species excited by a pump photon transfer its excitation to the other species present in the matrix. The ion–pair interaction referred to as energy transfer has been extensively investigated in Er^{3+}-, Pr^{3+}-, Tb^{3+}-, and Tm^{3+}-doped samples sensitized with trivalent ytterbium.[2–9] In ytterbium-sensitized hosts one takes advantage of the strong absorption cross section of Yb^{3+} ions in the region of 980 nm and the efficient energy-transfer mechanism[2] involving ytterbium and those rare-earth acceptors. For a number of applications, it is also interesting to access the visible wavelength emitting levels of such rare-ions employing an excitation source in the region of 800 nm, where high performance and low cost diode lasers is a well established technology. This is possible by exploiting the intense absorption cross section of Nd^{3+} ions in the 800 nm wavelength region in conjunction with a very efficient excitation transfer from excited neodymium ions to trivalent ytterbium. In this peculiar situation, the ytterbium ion plays a major role as an energy-transfer bridging ion between a donor (Nd^{3+}) and an acceptor ion such as Tm^{3+}, Tb^{3+}, or Ho^{3+}.[10–14] In this work we report on the generation of bright 475 nm blue upconversion fluorescence due to the excitation transfer between of Nd^{3+} to thulium ions bridged by ytterbium ions in Nd/Tm/Yb-codoped $PbGeO_3$-based glass under 800 nm semiconductor laser excitation.

II. EXPERIMENTAL SETUP

The glass samples were prepared with reagent grade PbF_2 and CdF_2 (P.A. Aldrich) and glassy $PbGeO_3$. Starting reagents were mixed in an agate mortar using *n*-heptane as homogenizing medium. After melting in an open Pt–Au crucible at 800 °C for 30 min in air, liquids were quenched at room temperature in graphite molds. Some 30 min annealing treatments at temperatures around the glass transition were performed. Rare-earth ions were introduced in the form of oxides (in several different concentrations). Starting $PbGeO_3$ glass was obtained using PbO (P.A. Aldrich) and GeO_2 (P.A. Aldrich) mixed and melted at 800 °C for 30 min and quenched to room temperature between two copper plaques. Metal contents in the samples were determined by atomic absorption spectrophotometry. Fluoride analyses was performed by use of a selective electrode.[15] Densities were measured with a helium picnometer (AccuPyc 1330 V2.02). Thermal analysis (differential scanning calorimetry-TA

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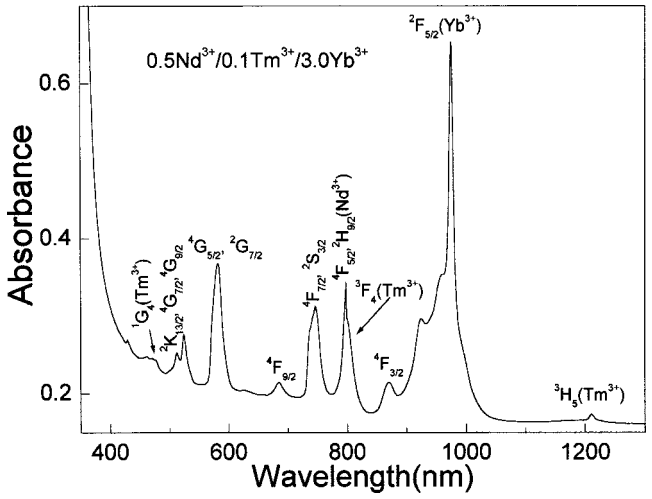

FIG. 1. Absorption spectrum for the Nd–Tm–Yb triply doped sample.

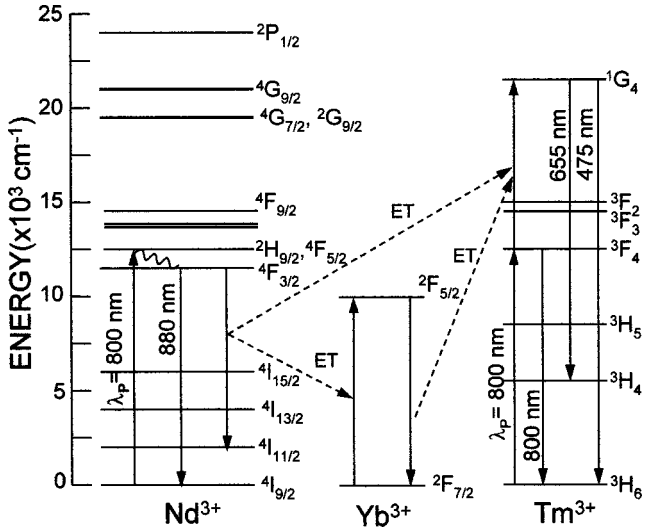

FIG. 2. Simplified energy-level diagram for the Nd–Tm–Yb system. Dashed arrows stand for energy-transfer processes.

Instruments-model 3100) were performed for powdered samples in aluminum pans with heating rates of 10 °C/min. X-ray powder diffractograms were obtained with a diffractometer (D-5000 Siemens) with the Cu $K\alpha$ filtered line at 0.02°/s scanning rate. TEM (transmission electronic microscopy, Phillips CM200) measurements have been performed. Electronic emission spectra were obtained with a spectrofluorimeter (SPEX F212I) equipped with a 450 W Xe lamp for excitation. A photomultiplier (Hamamatsu 900) and Ge detector (North Coast) were used for detection. Routine resolutions of 0.05 and 2 nm have been used in the visible and infrared absorption spectra, respectively. Figure 1 shows the absorption espectrum of our triply doped sample, indicating the major transitions for the three íons present in the host matrix.

In our upconversion measurements the fluorogermanate glass samples had a composition of $70\%PbGeO_3:15\%PbF_2:15\%CdF_2$ and triply doped with $Nd^{3+}/Tm^{3+}/Yb^{3+}$. The host material presents very good optical quality, is stable against atmospheric moisture, and it presents low optical attenuation in the 0.4–5.0 μm spectral region. The material also exhibits high solubility allowing the incorporation of high lanthanide concentrations apart from being nonhygroscopic and possess high thermal stability against crystallization. The samples thickness were ~1.0 mm and the excitation source was a cw diode laser operated around 800 nm delivering a maximum power of 70 mW. When tunability in the 800 nm region was required, an argon ion pumped Ti:sapphire laser was used. The pump beam was focused down onto the samples by a 5 cm focal length lens. The fluorescence signal was collected by a fiber bundle, and was dispersed by a 0.34 m scanning spectrograph with operating resolution of 0.5 nm and detected by an S-20 uncooled photomultiplier tube. Phase detection was used for data acquisition and storage. All measurements throughout our experiment were performed at room temperature.

III. RESULTS AND DISCUSSION

The simplified energy-level diagram, for the $Nd^{3+}/Tm^{3+}/Yb^{3+}$ system is illustrated in Fig. 2. The upconversion excitation process of the Tm^{3+} ion $^1G_4$ emitting level was achieved by an initial energy-transfer process from the 800 nm excited Nd^{3+} to Yb^{3+}. The excited Yb^{3+} then, transfer its energy to a neighbor Tm^{3+} ion at the $^3H_4$ level excited by a pump photon around 800 nm. The 800 nm pump photons promote both $Nd^{3+}(^4I_{9/2}\rightarrow{}^2H_{9/2}, {}^4F_{5/2})$ and $Tm^{3+}(^3H_6\rightarrow{}^3F_4)$ to excited-state levels by means of a ground-state absorption (GSA) process. The excited Nd^{3+} relaxes nonradiatively to the $^4F_{3/2}$ excited-state level and transfer its excitation to a nearby Yb^{3+} at the $^2F_{7/2}$ ground state and/or to an excited Tm^{3+} ion at the $^3F_4$ level. However, the energy-transfer mechanism involving the $Nd^{3+}-Yb^{3+}$ pair is the dominant mechanism, as will be seen in this article. The excited ytterbium at the $^2F_{5/2}$ state then transfers its energy to nearby Tm^{3+} ions at the $^3F_4$, promoting them to the upper $^1G_4$ excited-state emitting level. From the $^1G_4$ level, the Tm^{3+} ions radiatively relaxe to the $^3H_6$ ground state generating the intense upconversion fluorescence signal around 475 nm. The red emission band around 655 nm is assigned to the $^1G_4\rightarrow{}^3H_4$ transition. Some small contribution exists for the red emission originated from the $^3F_{2,3}\rightarrow{}^3H_6$ transition. In order to compare the effectiveness of the $Nd^{3+}-Yb^{3+}$ bridging mechanism, we have also investigated the upconversion process in Yb^{3+}-sensitized Tm^{3+}-doped samples under 800 nm excitation. Blue upconversion emission was readly observed and the signal could be seen by the naked eye. Blue upconversion emission in Tm^{3+}/Yb^{3+}-codoped fluoride crystals pumped around 800 nm has already been reported by Zhang *et al.*[16] and more recently.[17] The upconversion excitation process for blue emission in Tm^{3+}/Yb^{3+}-codoped samples pumped around 800 nm, has already been described elsewhere,[16,17] and it suffices to mention here that it is achieved through energy-transfer from Tm^{3+} to Yb^{3+} ions followed by the transfer from Yb^{3+} to Tm^{3+}. It is important to show that from the

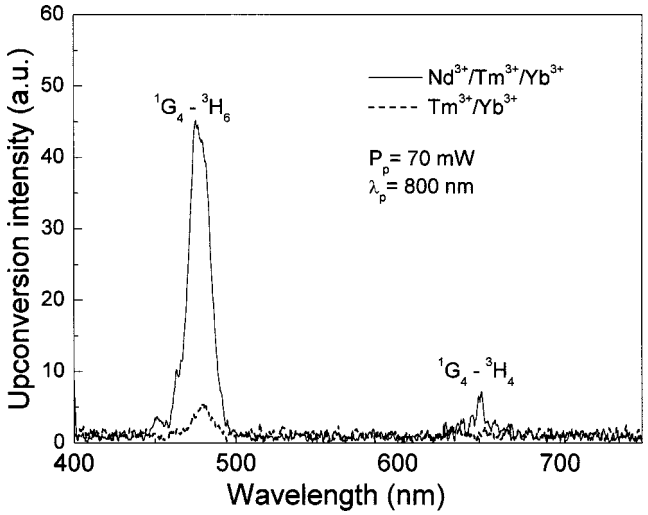

FIG. 3. Typical power spectra of the upconversion emission for the Nd–Tm–Yb triply doped sample (straight line) and Tm–Yb doubly doped (dashed line) one under the same power.

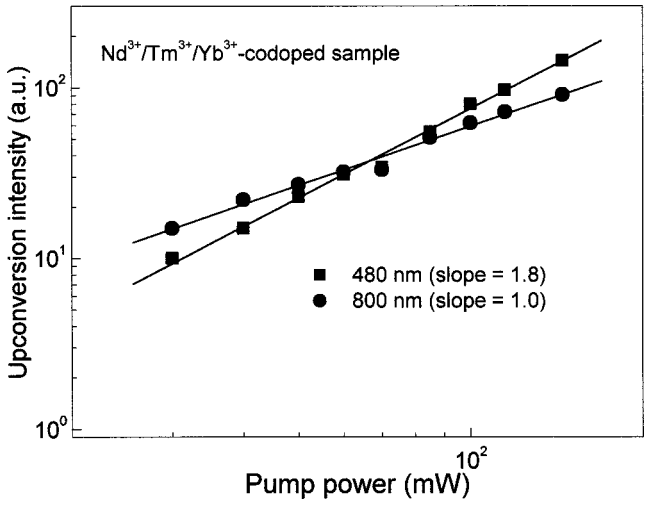

FIG. 4. Log–log plot of the upconversion emission intensity as a function of the excitation intensity around 800 nm.

results presented in this article, and reports of Ref. 13, no emissions were observed in either Tm^{3+}/Yb^{3+} doubly doped and/or Tm^{3+} singly doped samples under 800 nm excitation. Figure 3 shows typical upconversion fluorescence spectra associated with Tm^{3+} ions under 800 nm excitation, for a sample codoped with Yb^{3+} (dotted line) and a $Nd^{3+}/Tm^{3+}/Yb^{3+}$ triply doped sample (solid line). The spectra exhibit the three distinct bands centered around 475, 655, and 800 nm (not shown in the spectra of Fig. 3), corresponding to the $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3H_4$, and $^3F_4 \rightarrow {}^3H_6$ transitions of Tm^{3+} ions, respectively. It is observed that the presence of Nd^{3+} in the system, produces a tenfold enhancement in the blue emission associated to the $^1G_4 \rightarrow {}^3H_6$ transition of Tm^{3+} ions, as compared to samples doubly doped with Tm^{3+}/Yb^{3+}.

The dependence of the blue upconversion intensity upon the excitation power was examined and a quadratic power law behavior was obtained, as portrayed in the log–log plot of Fig. 4. The results indicate that two pump photons participate in the upconversion excitation mechanism and they excite both Nd^{3+} and Tm^{3+} through ground-state absorption. In order to emphasize the role played by Nd^{3+} ions as donors in the Tm^{3+} ions upconversion excitation process, the dependence of the blue emission intensity as a function of the pump wavelength around 800 nm, was also examined. The results demonstrated that the blue intensity dropped by a factor of two within a few nanometers of detuning from the peak wavelength of 803 nm, as presented in Fig. 5. The peak at 803 nm indicates that the maximum pump efficiency and consequently the maximum upconversion efficiency is obtained when the pump excitation is resonant with the neodymium $^4I_{9/2} \rightarrow {}^2H_{9/2}$, $^4F_{5/2}$ transition. Furthermore, the observation that the 880 nm fluorescence intensity steeply decreases with the Tm^{3+} concentration, indicates a very efficient energy-transfer mechanism from Nd^{3+} to Tm^{3+} via Yb^{3+}. This behavior is then clear evidence of the role played by the Nd^{3+} ion as a donor of 800 nm excitation to the thulium ion, via the Yb^{3+} bridging process. The investigation of the dependence of the 475 nm blue upconversion luminescence intensity upon the Yb^{3+} concentration was also carried out (see Fig. 6). As one observed the blue emission increased significantly with increasing ytterbium concentration, demonstrating the importance of the Yb^{3+} as an energy-transfer bridging ion in the process of Tm upconversion excitation. The deviation from the expected linear behavior for the curve, was also presented in Ref. 13, but still no plausible explanation is available for the results. It was also observed that the visible upconversion fluorescence in Tm^{3+}/Yb^{3+}-codoped samples excited around 980 nm,[17] exhibited much lower intensity when compared with triply doped samples under the same excitation conditions. The results clearly indicate that the upconversion excitation mechanism in Nd–Tm–Yb codoped samples excited around 800 nm is quite different from that of a Yb^{3+}-sensitized Tm^{3+}-doped samples excited around 980 nm.

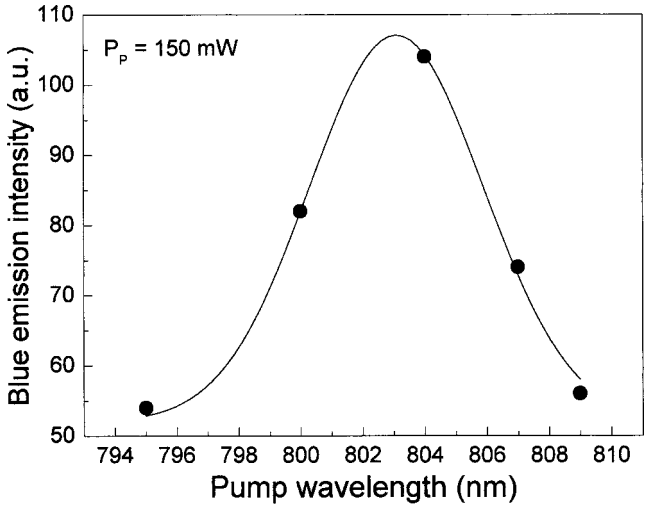

FIG. 5. Blue emission intensity as a function of the excitation wavelength for a fixed pump power.

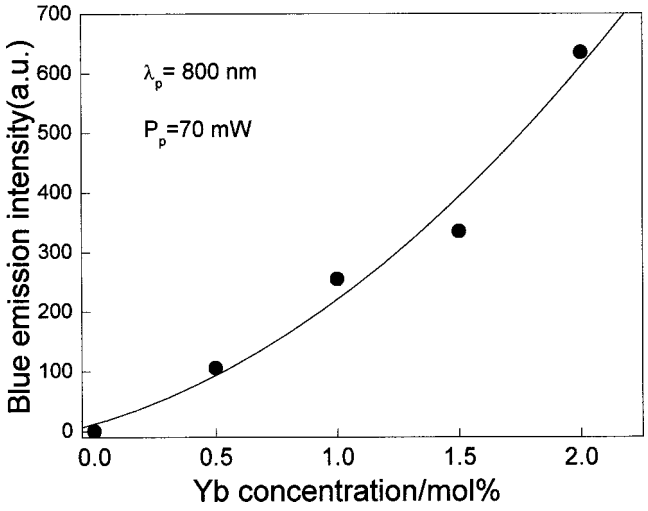

FIG. 6. Blue emission intensity as a function of the Yb concentration for a fixed excitation power and wavelength.

CONCLUSIONS

Bright blue upconversion emission through sensitization of thulium ions in lead and cadmium germanate glass triply doped with $Nd^{3+}-Tm^{3+}-Yb^{3+}$ under excitation around 800 nm was presented. It was demonstrated that for the same excitation power, the $Nd^{3+}/Tm^{3+}/Yb^{3+}$-codoped sample generated ten times more 475 nm blue upconversion fluorescence than the Yb^{3+}-sensitized Tm^{3+}-doped samples. The results also revealed that the upconversion process also presents a strong dependence upon the Yb^{3+} concentration. The population of the Tm^{3+} ions $^1G_4$ emitting level was obtained by means of a multiion interaction involving ground-state absorption of pump photons around 800 nm by the $Nd^{3+}(^4I_{9/2}\rightarrow{}^2H_{9/2}, {}^4F_{5/2})$ and $Tm^{3+}(^3H_6\rightarrow{}^3F_4)$ ions followed by energy-transfer processes involving the $Nd^{3+}-Yb^{3+}$ and $Yb^{3+}-Tm^{3+}$ pairs. Finally, one has shown the effectiveness of the neodymium–ytterbium interaction, providing the conditions for the thulium upconversion excitation by an 800 nm source.

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