Visible upconversion luminescence mediated by energy transfer in fluorogermanate glass doped with Tm^{3+} and Ho^{3+}

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ABSTRACT

Multicolor blue (480 nm), green (540 nm) and red (655 nm) upconversion light generation in Tm^{3+}/Ho^{3+}-codoped fluorogermanate glass excited by high-order stimulated Raman scattering Stokes emissions, generated in an optical fiber pumped by a laser operating at 1.064 μm, is demonstrated. The excitation route for the 480 nm, 650, and 800 nm Tm^{3+} emissions is accomplished through stepwise multiphonon-assisted ground-state, and excited-state absorption of 1.06, 1.12, 1.18, and 1.24 μm pump photons. The 540 nm emission of Ho^{3+} ions is effectuated through an initial ground-state absorption ($^5I_8$-$^5I_6$) in conjunction with energy-transfer Tm^{3+} to Ho^{3+} connecting the $^5I_6$ - $^5F_2$, $^3K_8$ followed by rapid multiphonon relaxation to the $^5F_4$, $^5S_2$ green emitting levels. Energy-transfer Tm^{3+} ($^3H_5$-$^3H_6$) to Ho^{3+}($^5I_8$-$^5I_6$), and Tm^{3+}($^1G_4$) to Ho^{3+}($^5F_2$,$^3K_8$), also enhance the holmium ions upconversion excitation process. Pump power dependence of the emitted light, lifetime measurements, as well as the CIE-1931 color coordinates for fixed Tm^{3+} concentration and varying H^{3+} content, were also examined and discussed

1. Introduction

Generation of multicolor light in rare-earth doped solid-state materials pursuing application in color displays and LED-based illumination technology has been the subject of intense scientific and technological interest in the last few decades. Several hosts, combination of rare-earth ions, and excitation routes have been proposed in order to produce the three fundamental red-green-blue (RGB) colors exploiting the so-called frequency up-conversion (FUC) mechanism. Excitation of the up-converted visible emitting levels was accomplished in general via ytterbium sensitization, and with excitation using commercially available laser sources [1–6]. It has recently been demonstrated the generation of red, green, and blue fluorescence in Tm^{3+}/Er^{3+} codoped bulk glass owing to the efficient ion-pair Tm-Er interaction [6–8]. The excitation mechanism of Tm^{3+} and subsequently energy-transfer to Er^{3+} ions has proven very efficient when the 1200 nm absorption band of Tm^{3+} ions was used as the departure step of the frequency up-conversion excitation process [9,10]. Energy-transfer processes involving the ion-pair Tm^{3+}-Ho^{3+} in glass and crystals, have been the subject of scientific and technological interest for over the last three decades [11–15]. Several aspects of the Tm^{3+}-Ho^{3+} interaction have already been investigated for many purposes including the role of the dopant concentration for near-infrared solid-state laser performance [11], the

use of new host matrices [12], and detrimental effect in S^+-band amplifiers [12,13], amongst many. In addition, the effect of energy-transfer Tm-Ho in near-infrared excited frequency up-conversion mechanism in ytterbium-sensitized based Tm/Ho codoped phosphors has already been examined elsewhere [3,4,14,15]. However, little or no attention has been devoted to the investigation of the Tm-Ho energy-transfer and frequency up-conversion processes in Tm^{3+}/Ho^{3+} double-doped glasses excited by a near infrared source. In this report, along with the Tm^{3+} blue and red light emissions, the energy-transfer process enabled the generation of the green component of the primary colors with the substantial enhancement of the Ho^{3+} green emission.

2. Experimental

The preparation process of our samples followed the protocol already described elsewhere [16,17]. It suffices to mention here that they had a composition of 70%$PbGeO_3$:15%PbF_2:15%CdF_2 and were mono-doped, and double-doped with Tm^{3+} and Ho^{3+}, with concentrations of 0.1Tm^{3+} and 0.1Ho^{3+}, and 0.1Tm^{3+}/xHo^{3+} (x = 0.1; 0.2; 0.3; 0.4) in mol%. The host material presents very good optical quality, it is stable against atmospheric moisture, and it exhibits low optical attenuation in the 0.4–5.0 μm spectral region. The maximum phonon-energy for the 70%$PbGeO_3$:15%PbF_2:15%CdF_2 host material is ~ 800 cm^{-1} [16,17].

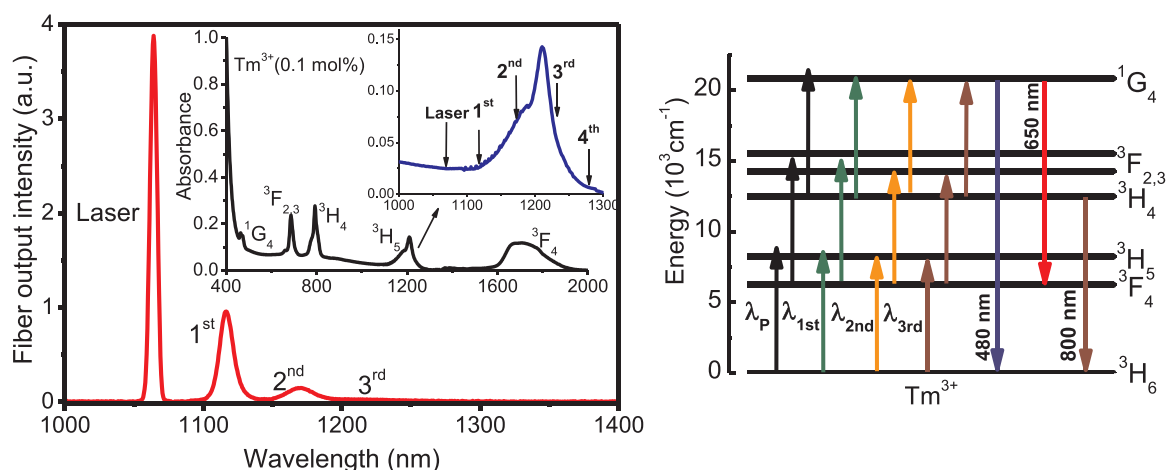**Fig. 1.** Left: Excitation light spectrum (red line), Tm absorption spectrum, and spectral detail of the excitation region around 1.2 μm, and 1-Right: energy-level diagram for the Tm^{3+} ion indicating the upconversion excitation mechanism, and excited-state emitting levels. Upwards arrows indicate multiple excitation(laser and SRS Stokes emissions) and downwards arrows stand for luminescence emissions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
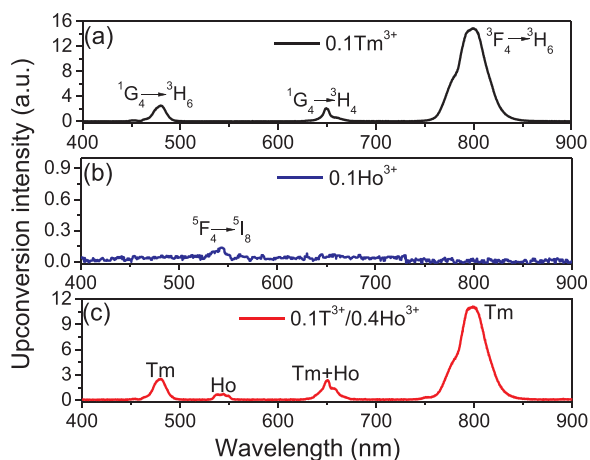

Fig. 2. Recorded emission spectrum of visible radiation emanating from the single-doped (Ho^{3+}, Tm^{3+}) and codoped(Ho^{3+}/Tm^{3+}) samples excited with 160 mW average power from the fiber output.

The multi-wavelength excitation source utilized in this investigation exploited the so-called cascade stimulated Raman scattering (SRS) process in optical fibers [18]. The fundamental source of radiation was a Q-switched laser operating at 1.064 μm, producing peak powers of 5.0 − 10.0 kW. The pump beam was injected into a 5.0 m long single-mode standard SiO$_2$-GeO$_2$ optical fiber with ∼ 10 μm core-diameter, using a ×10 microscope objective. A typical coupling efficiency of ∼ 35% was obtained in our measurements. The output light from the fiber consisted of the 1.064 μm fundamental laser radiation and the cascade SRS Stokes emissions around 1.12, 1.18, 1.24, and 1.30 μm, corresponding to the 1st, 2nd, 3rd, and 4th Stokes SRS bands, respectively [18]. The spectral content of the fiber output light was employed as the multi-wavelength excitation source for the active ions in the present study. The number of Stokes emissions generated, and the amount of power in each wavelength component depend upon the laser power coupled into the fiber for a fixed fiber length [18]. The optimized power for the fundamental laser injected into the fiber was 500 mW, producing around 160 mW average power at the fiber exit. The power was distributed in 56% (1.064 μm), 27% (1st Stokes), 8% (2nd Stokes) and 9% (3rd Stokes), corresponding to 84, 41, 12, and 13.5 mW, respectively. Fig. 1 shows the spectral content of the fiber output light in addition to the Tm^{3+} absorption spectrum in the glass sample. It is also shown in Fig. 1 (top-right inset) the position of the Raman Stokes emissions immersed in the $^3H_5$ thulium absorption band around 1.2 μm

used as the departure of the up-conversion excitation route. The fourth peak appearing in the top-right inset (around 1.30 μm) is generated along with the 1–3 peaks. However, it lays out of the absorption band centered around 1.2 μm, and as such has no appreciable effect for the pump scheme. It is important to point out that all pump wavelengths (fundamental and cascade SRS emissions) participate in the thulium upconversion excitation. However, the SRS Stokes emission wavelengths laying inside $^3H_5$ band provides higher efficiency, despite the fact that they possess lower power. The 150 mW average power exiting beam from the fiber was focused down onto the ∼ 1.0–2.0 mm thick samples, using a 5 cm focal length lens. The beam waist at the samples location was ∼ 40 μm. The luminescence signal was collected at 90° and directed to a fiber integrated spectrograph with operation in the ultra-violet(UV), visible(VIS) and near infrared (NIR) spectral region, and spectral resolution of ≤ 1.0 nm. The lifetimes were measured using the expression $\tau_{eff} = [I_{em}(t)dt]/I_{em}(0)$ [19], where τ_{eff} is the calculated effective lifetime, $I_{em}(t)$ stands for the time dependence of emission intensity and $I_{em}(0)$ is the initial intensity. The effective lifetime, obtained by integrating the normalized decay curve, gives a better description of radiative decays that are not described by a single exponential function [20,21].

3. Results and discussion

Fig. 2 shows typical upconversion luminescence spectra from the single-doped Tm^{3+} (a), Ho^{3+} (b), and Tm^{3+}/Ho^{3+}-codoped (c) samples under 160 mW total average excitation power. The spectrum for the single and co-doped samples exhibit the well-known emission bands centered around 480, 540, 650, and 800 nm associated with thulium and holmium. The emissions at 480 nm, 650 nm, and 800 nm are assigned to the $^1G_4$-$^3H_6$, $^1G_4$-$^3F_4$, $^3H_4$-$^3H_6$ transitions of Tm^{3+} ions. The emission at 540 nm is identified as due to the $^5F_4$, $^5S_2$ transition to the $^5I_8$ ground-state, of holmium ions. The proposed upconversion excitation route follows the simplified energy-level diagram for the Tm and Ho active ions, portrayed in Fig. 3. The excitation pathway for the 480 nm, 650 nm, and 800 nm Tm^{3+} emissions is accomplished through stepwise multiphonon-assisted ground-, and excited-state absorption, which have already been thoroughly studied elsewhere [8–10]. The 540 nm emission of Ho^{3+} ions is effectuated through an initial ground-state absorption ($^5I_8$-$^5I_6$) followed by Tm to Ho energy-transfer connecting the $^5I_6$-$^5F_2$, $^3K_8$ followed by rapid multiphonon relaxation to the $^5F_4$, $^5S_2$ green emitting level. In addition, Tm^{3+} ($^3H_5$-$^3H_6$) to Ho^{3+} ($^5I_8$-$^5I_6$), and Tm^{3+} ($^1G_4$) to Ho^{3+} ($^5F_2,^3K_8$), energy-transfer processes also enhance the upconversion excitation of holmium ions. This implies that the overall energy-transfer mechanism from Tm^{3+} to Ho^{3+} is the