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White light generation in Tm³⁺/Ho³⁺/Yb³⁺ doped PbO-GeO₂ glasses excited at 980 nm

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We report white light generation (WLG) in $Tm^{3+}/Ho^{3+}/Yb^{3+}$ doped PbO-GeO₂ glass under continuous-wave excitation at 980 nm. Intense blue (≈ 477 nm), green (≈ 545 nm), and red (≈ 658 nm) emissions were simultaneously observed at room temperature. The blue light is mainly due to the Tm^{3+} transition $^1G_4 \rightarrow {}^3H_6$. The green emission is due to the Ho^{3+} transitions $(^5S_2, {}^5F_4) \rightarrow {}^5I_8$ and the red luminescence is due to the Ho^{3+} transition $^5F_5 \rightarrow {}^5I_8$ and transition $^1G_4 \rightarrow {}^3F_4$ associated to the Tm^{3+} ions. Energy transfer processes from Yb^{3+} to Ho^{3+} and Yb^{3+} to Tm^{3+} ions were responsible for the WLG. Adjusting the relative concentration of the rare-earth (RE) ions, we could obtain emission in the white region of the CIE chromaticity diagram. The present results indicate that PbO-GeO₂ glass has large potential to be used for white displays. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4827863]

I. INTRODUCTION

In the last five decades, luminescence processes involving rare-earth (RE) doped materials have been studied by many authors motivated by its possible applications in color displays, solid state lasers, optical data storage, cellular biology, and improvements of solar cells.[1–5] Particularly, in the case of color displays, it is well known that to obtain light emission in different spectral regions it is necessary to have control of the relative intensities of the primary colors: red, green, and blue (RGB); the spectrum of the emitted light is characterized by coordinates in the CIE (Commission Internationale de l'Eclairage) chromaticity diagram. Of large interest is the study of white light generation (WLG) that corresponds to the chromatic coordinates x = 0.33 and y = 0.33.

One conventional way to obtain the primary colors is using ultraviolet excitation; photons with wavelength in the ultraviolet region are converted into visible light (down-conversion processes).[6–8] However, ultraviolet excitation may cause degradation of some host materials causing a decrease in the luminescence efficiency of the device.[9] An alternative to ultraviolet excitation when using materials doped with RE ions is the exploitation of the frequency upconversion (UC) process.

Reports on WLG using oxyfluoride glass-ceramics as host of Tm³⁺/Er³⁺/Yb³⁺ ions[10,11] and tellurite glass as host of Pr³⁺/Er³⁺/Yb³⁺ ions[12] were presented. The use of Tm³⁺/Ho³⁺/Yb³⁺ ions hosted in tellurite glasses,[13,14] aluminum-germanate glasses,[15] oxyfluoride nanoglass[16] and SrMoO₄ nanocrystals[17,18] was also investigated and presented good performance.

In this article, we report the observation of WLG from PbO-GeO₂ glass (labeled as PGO glass) doped with Ho³⁺, Yb³⁺, and Tm³⁺ for excitation at 980 nm. PGO glass is a good candidate for WLG because it has high refractive index (≈ 1.9), large transmission window from the blue region to the near-infrared, cutoff phonons of low energy (≈ 770 cm⁻¹) and it is resistant to moisture and chemically stable. Generally germanate glasses are good hosts for RE ions, however, to our knowledge, only a multicomponent aluminum-germanate glass with cutoff phonon of ≈ 880 cm⁻¹ was exploited for WLG.[15] The fabrication of the PGO glass is simpler than the one reported in Ref. 15 and the luminescence efficiency is larger due to the smaller cutoff phonon energy.

Besides, the appropriate choice of the relative Ho³⁺, Yb³⁺, and Tm³⁺ concentrations, it is shown that the excitation light intensity is an important parameter to obtain WLG in PGO glass because the intensities of the three primary colors generated in the UC process depend on the incident laser intensity in different ways. In the present paper, the UC process was characterized and the luminescence was evaluated according to the procedure of the CIE to associate the UC emitted spectrum with the chromaticity diagram.

II. EXPERIMENTAL DETAILS

Glassy samples with composition 60PbO–40GeO₂ (in wt. %) and containing Yb₂O₃, Tm₂O₃, and Ho₂O₃ were prepared using the melting-quenching technique. The Yb³⁺ ions concentration was fixed using Yb₂O₃ (3.2 wt. %). Samples with different relative amounts of Tm₂O₃/Ho₂O₃: 0.4/1.6; 0.4/2.0; 0.4/1.0; 0.5/0.8; 0.5/0.9; 0.6/0.9 (in wt. %) were prepared and studied. The reagents were melted at 1200 °C in an alumina crucible, for 1 h, and stirred during the melting to obtain a homogeneous material, quenched in preheated brass mold, annealed at 420 °C for 1 h to avoid internal stress and cooled to room temperature. The fabricated

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glasses were cut and polished to obtain samples with 2.5 mm thickness and parallel faces. WLG was obtained for the following concentrations of the doped species: Yb_2O_3 (3.2 wt. %), Tm_2O_3 (0.6 wt. %), and Ho_2O_3 (0.9 wt. %) and only the results for these concentrations will be presented. The other concentrations correspond to different colors in the CIE diagram.

The optical absorption and luminescence measurements were performed at room temperature. The absorption spectra were measured using a commercial spectrophotometer and the luminescence experiments were made exciting the samples with a continuous-wave (CW) diode laser operating at 980 nm, in resonance with the Yb^{3+} transition ($^2F_{7/2} \rightarrow {}^2F_{5/2}$). The luminescence spectra were analyzed through a spectrometer attached to a photomultiplier and computer.

III. RESULTS AND DISCUSSION

The absorption spectrum of the sample with relative amount of Tm_2O_3/ Ho_2O_3 of 0.6/0.9 (in wt. %) is shown in Fig. 1. The 4f-4f absorption transitions from the ground to excited states associated to the Ho^{3+}, Tm^{3+}, and Yb^{3+} ions are indicated in the figure. The bands centered at $\approx$450, $\approx$680, and $\approx$800 nm are due to the Tm^{3+} transitions $^3H_6 \rightarrow {}^1G_4$, $^3H_6 \rightarrow {}^3F_{2,3}$, and $^3H_6 \rightarrow {}^3H_4$, respectively. The bands related to the Ho^{3+} ions, centered at $\approx$450, $\approx$480, $\approx$530, $\approx$640, and $\approx$930 nm, are due to transitions $^5I_8 \rightarrow ({}^5F_1; {}^5G_6)$, $^5I_8 \rightarrow ({}^5F_2; {}^5F_3)$, $^5I_8 \rightarrow ({}^5F_4; {}^5S_2)$, $^5I_8 \rightarrow {}^5F_5$, and $^5I_8 \rightarrow {}^5I_5$, respectively. The absorption band centered at $\approx$980 nm is associated to the Yb^{3+} ions (transition $^2F_{7/2} \rightarrow {}^2F_{5/2}$).

Figure 2 shows the luminescence spectra for excitation at 980 nm obtained with different laser intensities. The emission centered at $\approx$477 nm (blue light) corresponds to the Tm^{3+} ions (transition $^1G_4 \rightarrow {}^3H_6$). The luminescence centered at $\approx$650 nm (red light) may have contributions from Tm^{3+} ions (transition $^1G_4 \rightarrow {}^3F_4$) and Ho^{3+} ions (transition $^5F_5 \rightarrow {}^5I_8$). The emission at $\approx$550 nm (green light) is attributed to the Ho^{3+} (transition $({}^5S_2, {}^5F_4) \rightarrow {}^5I_8$). The Ho^{3+} transition $^5F_3 \rightarrow {}^5I_8$ is in the blue region, but we attribute most of

the blue light to Tm^{3+} ions (transition $^1G_4 \rightarrow {}^3H_6$) that is known to have very large oscillator strength.

The UC process that originates the multicolor emission is illustrated in Fig. 3. It is known that the Yb^{3+} transition $^2F_{7/2} \rightarrow {}^2F_{5/2}$ has larger cross-section than the Tm^{3+} and Ho^{3+} transitions originating from the ground state. Hence, we consider that when the sample is excited by the 980 nm laser, Yb^{3+} ions absorb efficiently the infrared radiation. Due to the large Yb^{3+} concentration, energy transfer (ET) from the excited Yb^{3+} ions to the Ho^{3+} and Tm^{3+} ions is the dominant process contributing for the UC luminescence. The energy mismatch in the ET events is compensated by emission of phonons. In the case of Ho^{3+} ions, the green emission is due to two consecutive ET events from excited itterbium ions: Yb^{3+} ($^2F_{5/2}$) $\xrightarrow{ET}$ Ho^{3+} ($^5I_6$) $\xrightarrow{ET\,from\,Yb^{3+}}$ Ho^{3+} ($^5F_4$) $\xrightarrow{light\,emission}$ Ho^{3+} ($^5I_8$). The Ho^{3+} ions may contribute for the emission centered at $\approx$658 nm according to following steps

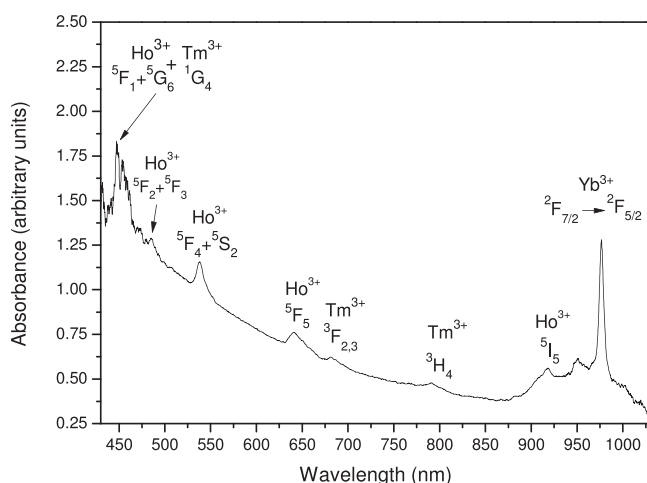FIG. 2. Luminescence spectrum of the $Tm^{3+}/Ho^{3+}/Yb^{3+}$ doped PbO-GeO$_2$ glass for excitation at 980 nm with different laser intensities.

FIG. 1. Absorbance spectra of the $Tm^{3+}/Ho^{3+}/Yb^{3+}$ doped PbO-GeO$_2$ glasses. The labels indicate the excited state reached from the ground state of each rare-earth ion.

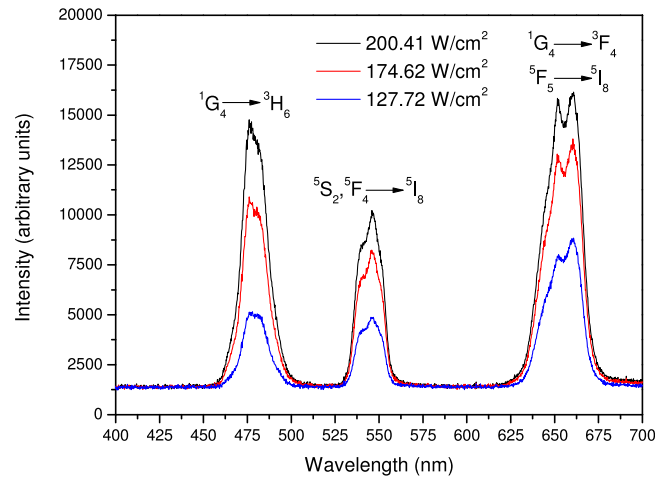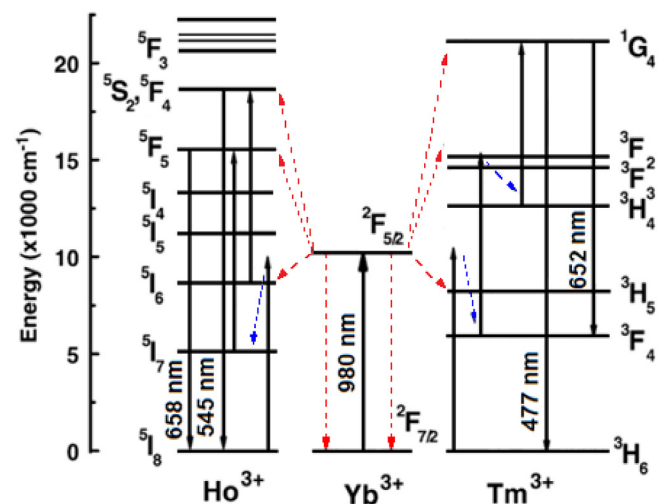FIG. 3. Simplified energy level diagram of Ho^{3+}, Yb^{3+}, and Tm^{3+} ions. The radiative transitions and energy transfer from Yb^{3+} to Ho^{3+} and Yb^{3+} to Tm^{3+} are indicated by black solid lines and red dashed lines, respectively. Phonon emissions are represented by dashed blue lines.
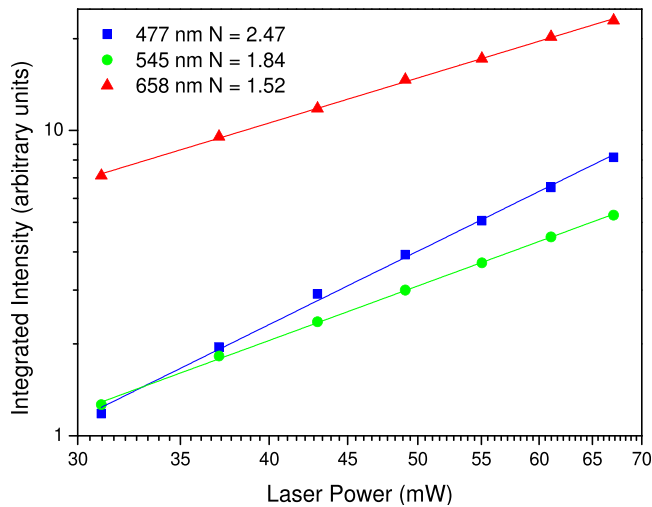
FIG. 4. Dependence of the upconversion intensity with the laser power. The slopes of the straight lines are indicated by $N = 1.52$, 1.84, and 2.47 corresponding to emissions centered at 658, 545, and 477 nm, respectively.

FIG. 6. Photography of the sample under 980 nm CW laser excitation (Laser intensity: 200.41 W/cm^2).

that include non-radiative decay (NRD) between neighbor levels: Ho^{3+} ($^5I_6$) $\xrightarrow{NRD}$ Ho^{3+} ($^5I_7$) $\xrightarrow{ET\,from\,Yb^{3+}}$ Ho^{3+} ($^5F_5$) $\xrightarrow{light\,emission}$ Ho^{3+} ($^5I_8$). In the case of Tm^{3+} ions, the luminescence at ≈ 477 nm and ≈ 652 nm are associated to the transitions $^1G_4 \rightarrow ^3H_6$ and $^1G_4 \rightarrow ^3F_4$, respectively. The $^1G_4$ state is populated through the following pathway: Yb^{3+} ($^2F_{5/2}$) $\xrightarrow{ET}$ Tm^{3+} ($^3H_5$) $\xrightarrow{NRD}$ Tm^{3+} ($^3F_4$) $\xrightarrow{ET\,from\,Yb^{3+}}$ Tm^{3+} ($^3F_2$) $\xrightarrow{NRD}$ Tm^{3+} ($^3H_4$) $\xrightarrow{ET\,from\,Yb^{3+}}$ Tm^{3+} ($^1G_4$). The emission at ≈ 658 nm is attributed to the Ho^{3+} ions (transition $^5F_5 \rightarrow ^5I_6$).

The UC luminescence intensity, I_{UC}, as a function of the laser power, P, was measured to identify the number of laser photons that participate in the UC process and to corroborate the proposed UC pathways. The linear behavior shown in the log-log plot of Fig. 4 indicates absence of saturation and the
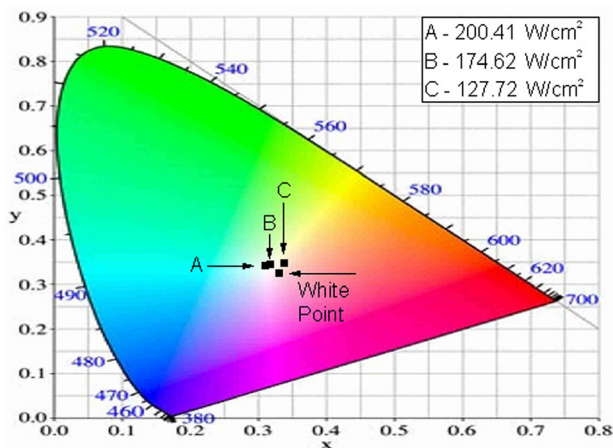

FIG. 5. CIE chromaticity diagram. Points A, B, and C with coordinates (0.31; 0.35), (0.32; 0.35) and (0.34; 0.35) correspond to the light emitted by the sample studied in this work, excited with different laser intensities. The standard white light corresponds to (0.33; 0.33).
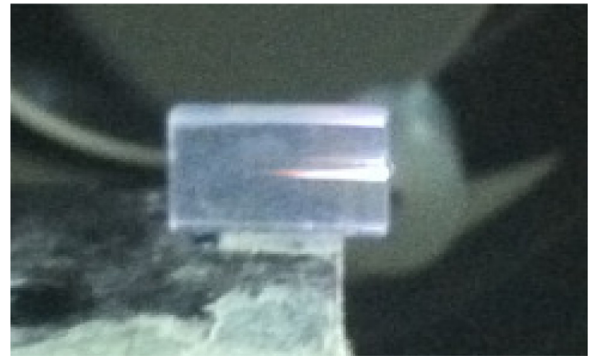
slopes of the straight lines give the number of laser photons, N, contributing for emission of each UC photon. The slopes determined are 2.47 (blue emission), 1.52 (red emission), and 1.84 (green emission) indicating the participation of three laser photons for the blue generation and two laser photons for the red and green emissions. These results are in agreement with the pathways illustrated by Fig. 3 and indicate that the red emission is essentially due to the Ho^{3+} ions.

In order to evaluate the appropriateness of the samples to WLG the UC emission spectrum was converted to the CIE chromaticity diagram and plotted in Fig. 5. The calculated CIE coordinates (0.31; 0.35), (0.32; 0.35), and (0.35; 0.35) for the sample with Tm_2O_3 (0.6 wt. %) and Ho_2O_3 (0.9 wt. %) excited with different intensities are very close to the ideal white light. The other samples with different relative concentrations of Tm_2O_3 and Ho_2O_3 produced a set of CIE coordinates that correspond to different colors in the visible range.

Figure 6 shows a photo of the sample emitting strong white light for excitation with 200.41 W/cm^2 using a CW diode laser (980 nm). The use of a proper glass is very important for obtaining large UC emissions since the quantum efficiency of the RE ions depend strongly on the glass matrix.[1] The PGO glass presents cutoff phonon energy smaller than borate, silicate, and phosphate glasses and thus is a better upconverter. Of course the choice of the RE ions (their concentration, RGB oscillator strengths, and excitation wavelength) is another relevant point to achieve efficient WLG. We recall that in our recent paper based on the same glass but doped with $Er^{3+}/Yb^{3+}/Tm^{3+}$ (Ref. 19), we could not find the good relative concentration of the RE ions to reach the white region of the CIE chromaticity diagram and catch the standard white point. The exchange of Er^{3+} ions by Ho^{3+} ions was crucial in order to obtain larger green and red emissions and then we obtained the appropriate balance between the three primary colors. Incidentally, we notice that this behavior was observed for other glasses[13–15] showing that the choice of $Tm^{3+}/Ho^{3+}/Yb^{3+}$ is better than $Er^{3+}/Yb^{3+}/Tm^{3+}$.

IV. SUMMARY

We demonstrated the simultaneous generation of the blue, green, and red light by frequency upconversion

luminescence in rare-earth doped PbO-GeO_2 glass under CW excitation at 980 nm. Intense upconversion luminescence bands at $\approx$477 nm, $\approx$550 nm, and $\approx$660 nm were observed. White light generation was obtained adjusting the concentration of Ho^{3+}, Tm^{3+}, and Yb^{3+} ions and the laser intensity. The results indicate that PbO-GeO_2 glass (doped with $Tm^{3+}/Ho^{3+}/Yb^{3+}$) excited with commercially available diode lasers is a potential candidate for applications in white displays.

ACKNOWLEDGMENTS

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