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Upconversion photon quantification of Ho^{3+} in highly transparent fluorotellurite glasses

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ABSTRACT

Multi-photon-excited green, red and oxblood UC emissions have been quantified in highly transparent Ho^{3+}/Yb^{3+} doped fluorotellurite (BALMT) glasses under the excitation of 977 nm laser. The net powers of green, red and oxblood emissions are determined to be 88.1, 103.8 and 66.1 μW in 0.196% Ho_2O_3 and 0.752% Yb_2O_3 co-doping case under the excitation power of 870 mW, and the net emission photon numbers are identified to be 242.7×10^{12}, 342.8×10^{12} and 250.8×10^{12} cps. The quantum yields (QYs) and luminous fluxes for visible UC emissions of Ho^{3+} are identified as a positive dependency with pumping powers, and when the excitation power density increase to 110.8 W/mm^2, the QY values for 550 nm green, 650 nm red and 753 nm oxblood UC emissions are up to 0.63×10^{-4}, 0.90×10^{-4} and 0.65×10^{-4}, respectively. The values of QY in Ho^{3+} doped BALMT glass are one order of magnitude larger than that in NMAG glasses. The macroscopic quantization for UC photon generation from Ho^{3+} in low-phonon fluorotellurite glasses provides a reliable reference for developing compact high-power-density illuminant for remote sensing, radar detection and medical diagnosis.

1. Introduction

Rare-earth (RE) ions doped infrared to visible frequency upconversion (UC) luminescence materials have attracted much attention due to their versatility in various optoelectronic devices, such as optical sensors, lasers, solar cells and compact light sources [1–10]. High-quality red and green irradiation light sources with high power density and compact structure are extremely desired for their potentials to replace conventional lighting sources in medical diagnosis, 3D projection and color display [11–16]. Among the RE ions, Ho^{3+} arouses much interest in recent years and it has been used in achieving powerful visible UC emissions due to its special energy level structure. The 550 nm green UC luminescence of Ho^{3+} shows a great potential in eye surgery and 3D projection display and Yb^{3+} ion is generally employed as a sensitizer to increase UC emission efficiency for Ho^{3+} ions doped materials under ~980 nm commercial diode lasers [17–25].

The requirements for UC emission are strongly influenced on the phonon energy of the glass matrixes, halide glasses have the lowest phonon energies among the multitudinous glass systems, while their physicochemical stability needs to be further improved [26–32]. Oxide glass systems have stable physical and chemical properties, but most of them have too large phonon energy to achieve the efficient UC emission. Fortunately, tellurite glass is a great glass matrix with the lower phonon energy and the higher visible transmittance in oxide glass family. As shown in Fig. 1, the fluorotellurite glass has a good permeability in the violet-blue region, and it could be used as the lighting sources for 3D display [32–42]. Meanwhile, the addition of fluoride ion also changes the glass ligand field structure, reducing the presence of hydroxyl in the glass matrix and those changes are more conducive to the UC conversion of the launching [43–52]. Hence, it is of significance to give considerable interest to RE^{3+}-ion-doped fluorotellurite glass. Moreover, quantitative characterization of Ho^{3+}-doped glasses will be beneficial to securing an efficient green luminescence for color display.

In this work, Ho^{3+}/Yb^{3+} co-doped fluorotellurite glasses have been prepared and characterized. Efficient two-photon-excited green and red UC fluorescence was observed and recorded under the excitation of 977 nm laser at room temperature. When the excitation power density is 110.8 W/mm^2, the total luminous flux of this sample in visible range reached to 0.065 lm, and the quantum yields (QYs) of 550 nm green, 660 nm red and 753 nm oxblood UC emissions are as high as 0.63×10^{-4}, 0.90×10^{-4} and 0.65×10^{-4}, respectively. High quantum yield and large total emission flux in Ho^{3+} ion-doped fluorotellurite glass manifest itself as an

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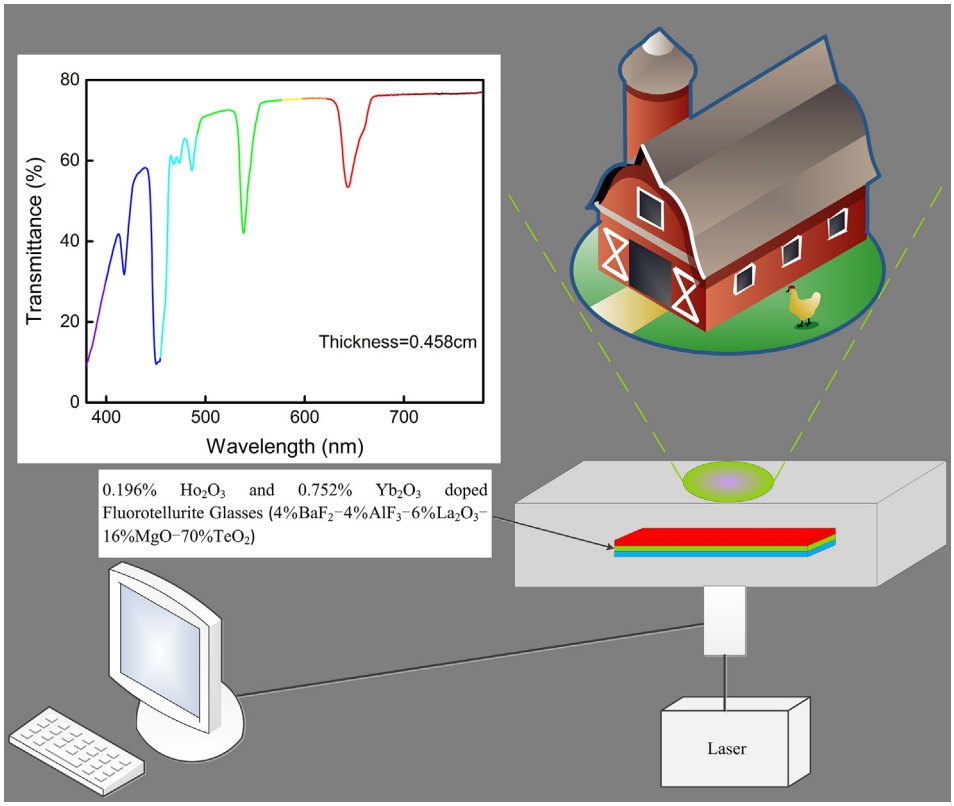

Fig. 1. Schematic diagram of 3D projection system adopting glass phosphor as the lighting source. Inserted photo: transmittance in the visible region of fluorite glasses.

ideal candidate for making high-quality light sources without signal interfering.

2. Experimental methods

2.1. Materials and methods

Ho^{3+}/Yb^{3+} doped fluorotellurite (BALMT) glasses were prepared from high-purity barium fluoride (BaF_2), aluminum fluoride (AlF_3), lanthanum oxide (La_2O_3), magnesium oxide (MgO), tellurium oxide (TeO_2), holmium oxide (Ho_2O_3) and ytterbium oxide (Yb_2O_3) powders. The molar host composition of BALMT glasses is 4% BaF_2–4% AlF_3–6% La_2O_3–16% MgO–70% TeO_2. Additional XHo_2O_3–YYb_2O_3 were added, where $X = 0.196\%$, $Y = 0.376\%$ and $X = 0.196\%$, $Y = 0.752\%$ in molar ratios, respectively. The well-mixed raw materials were first melted in a platinum crucible at 850 °C for 15 min using an electric furnace, subsequently followed by quenching on an aluminum plate. All the samples were annealed at 340 °C for two hours and cooled down to room temperature inside the furnace to relax the inner stress, and then sliced and polished with two parallel sides for optical measurements.

2.2. Measurements and characterization

The density of 0.196% Ho_2O_3 and 0.376% Yb_2O_3 co-doped glass was measured to be 5.42 $g{\cdot}cm^{-3}$, thus the number density of Ho^{3+} ions is 8.512×10^{19} cm^{-3}, and the refractive indices were measured to be 2.0062 at 635.96 nm and 1.9596 at 1546.9 nm. The refractive indices at all other wavelengths can be given by Cauchy's equation $n = A + B/\lambda^2$ with $A = 1.9501$ and $B = 22{,}681$ nm^2. The absorption spectrum was recorded with a Perkin Elmer UV–VIS-NIR Lambda 750 spectrophotometer. The visible fluorescence spectra were captured by a Hitachi F-7000 fluorescence spectrophotometer adopting a 975 nm laser as the pumping source.

The spectral power distribution of glass samples was determined in an integrating sphere with a 3.3-inch diameter connected to a QE65000 CCD detector (Ocean Optics) and a USB4000 CCD detector (Ocean Optics) with a 600 μm core optical fiber, and a fiber-pigtailed 977 nm multimode diode laser was adopted as the excitation source. A standard halogen lamp (Labsphere, SCL-050) was used to calibrate this measurement system, and spectral power distribution of the lamp was acquired through fitting the factory data based on the blackbody radiation law.

3. Results and discussion

3.1. Radiative transition properties of Ho^{3+} and Yb^{3+} co-doped BALMT glasses

In order to objectively demonstrate the multi-photon excitation mechanism of the UC emission fluorescence, sensitive fluorescence spectrophotometer adopting a 975 nm pumping laser was used to record the surface luminescence of Ho^{3+}/Yb^{3+} co-doped BALMT glasses, and the fluorescence spectra are shown in Fig. 2. The three emission bands centering around 545, 658 and 754 nm wavelengths are assigned to the $^5F_4 + {}^5S_2 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $^5F_4 + {}^5S_2 \rightarrow {}^5I_7$ transitions, respectively. For those three luminescence peaks, the dependence of integrated up-conversion emission intensities on excitation powers was derived and presented in Fig. 3. The fitted slopes of the log-log plots for the 545, 658 and 754 nm emissions are 1.99, 2.01 and 1.81, respectively, confirming that the $^5F_4 + {}^5S_2 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $^5F_4 + {}^5S_2 \rightarrow {}^5I_7$ transitions are populated predominantly by two-photon absorption processes.

The absorption spectrum in Fig. 4 shows there is no resonant energy level in Ho^{3+} coinciding with the wavelength of commercial