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Energy transfer and upconversion luminescence in Tm^{3+}/Yb^{3+} co-doped lanthanum–zinc–lead–tellurite glasses ☆

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Abstract

A series of Tm^{3+}/Yb^{3+} co-doped lanthanum–zinc–lead–tellurite (TPZL) glasses pumped by a 980 nm laser diode (LD) were demonstrated to obtain a high efficiency of infrared-to-visible upconversion. Effects of PbO content on the thermal stability, structure and upconversion properties of Tm^{3+}/Yb^{3+} co-doped TPZL glasses had been investigated. The efficient visible upconversion fluorescences corresponding to the $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3F_4$ and $^3H_4 \rightarrow {}^3H_6$ transitions of Tm^{3+} were observed under 980 nm excitation. The upconversion intensities of blue, red and near infrared emissions in Tm^{3+}/Yb^{3+} co-doped TPZL glasses were obviously enhanced with increasing PbO content. The dependence of upconversion intensities on excitation power and the possible upconversion mechanisms had been evaluated by a proper rate equation model. Population density in different levels and coefficients of the energy transfer rate C_{Di} ($i = 2, 4, 6$) between Tm^{3+} and Yb^{3+} were estimated by fitting the simulated curves to the measured ones. The obtained three energy transfer coefficients C_{D2}, C_{D4}, and C_{D6} were determined to be 5.7×10^{-17}, 1.3×10^{-16} and 8.6×10^{-17} cm^3/s, respectively.

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Keywords: Tellurite glasses; Upconversion luminescence; Energy transfer; Rate equation

1. Introduction

In recent years, the study of blue lasers for use in color displays, high-density optical data storage and reading, biomedical diagnostics, optical communications and indicators have become a focus of research [1–4]. Tm^{3+} is one of the most studied rare-earth ions for blue laser operation based upon upconversion [5–7]. It has been found that the upconversion efficiency is strongly influenced by maximum phonon energy of host. As usual, the glass with lower phonon energy can lead to higher upconversion efficiency. For example, the maximum phonon energy of fluoride glass system is small enough to reduce the loss of nonradiative energy due to multiphonon relaxation [8]. However, it is difficult to fabricate fluoride glass fibers owing to their low chemical and mechanical stabilities. Although the phonon energy of tellurite glasses (~750 cm^{-1}) are slightly higher than fluoride glasses, the tellurite glasses also are interesting materials from the standpoint that they possess excellent properties for practical use such as high refractive index [9], high transmissivity of infrared radiation [10] and high chemical durability. To our knowledge, the upconversion fluorescence of Tm^{3+} ions in the rate equation model has seldom been reported in tellurite glasses. When Tm^{3+}/Yb^{3+} co-doped glasses are excited by 980 nm laser, owing to the strong absorption of Yb^{3+} ions in the region around 980 nm, Yb^{3+} ion as a sensitizer can greatly enhance upconversion efficiency through energy transfer.

In this letter, we investigate the effects of PbO doping on the thermal stability, structure, the maximum phonon

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energy and upconversion properties of Tm^{3+}/Yb^{3+} co-doped TPZL glasses. The efficient upconversion fluorescence bands around at 477, 653 and 796 nm are observed, and the possible upconversion mechanisms are discussed and estimated. And a proper rate equation model is proposed to interpret the theory.

2. Experimental

Glasses with the composition of (80–x) TeO_2–xPbO–17ZnO–3La_2O_3 (TPZLx, $x = 0$, 5, 10, 15, 20 mol%) were prepared. The starting materials are reagent grade TeO_2, PbO, ZnO, and La_2O_3, Tm_2O_3 and Yb_2O_3 with more than 99.99% purity, the Tm^{3+} and Yb^{3+} doping concentrations in the glasses were 0.05 and 4 wt%, respectively. About 25 g batches of starting materials were fully mixed and then melted in the Pt crucibles at 850 °C in an electronic furnace. After completely melting, the glass liquids were poured into a stainless mold and then annealed to room temperature. The obtained glasses were cut and polished carefully to $10 \times 10 \times 1.2$ mm in order to meet the requirements for optical measurements.

The densities were measured according to the Archimedes principle. Refractive indices were measured at 632.8 nm on SAIRON-SPA4000 prism coupler. The absorption spectra were recorded between 400 and 2000 nm with a Perkin-Elmer Lambda 950 UV-VIS-NIR spectrophotometer. The thermal stability was determined by differential thermal analysis (DTA) method at a heating rate of 10 °C/min. The visible upconversion fluorescence spectra were obtained with a TRIAX550 spectrofluorimeter upon excitation of 980 nm LD with a maximum power of 2 W. The integrated intensities for the blue and red emissions were also calculated to illustrate the variations of the fluorescence intensity. For IR measurements, the glasses were pulverized and mixed with KBr in order to obtain thin pellets with a thickness of about 0.3 mm. The IR spectra have been recorded in the range of 400–4000 cm^{-1} with a Nicolet FTIR-8900 spectrometer. The pump power P was measured on COHERENT-FIELDMATE PM10 laser power meter. For the fluorescence lifetime measurements, a 100 MHz oscillocope (Hitachi, V-1565) was to monitor the fluorescence decay as the time evolution of the output from the InGaAs-photodiode ($f = 160$ KHz). A 970 nm LD (SDL-6362-P1) was used and the pulse modulation was done to obtain a light pulse with 5 μs widths. The fluorescence lifetime of Yb^{3+}: $^2F_{5/2}$ level was measured with light pulses of 940 nm LD. The decay traces were recorded on a digital oscilloscope and fitted by single exponential functions to obtain the decay rates. In order to compare the luminescence intensity in different samples as accurate as possible, the position and the power of the pumping beam and the width (1 mm) of the slit to collect the luminescence signal were fixed under the same condition, and the samples were set at the same place in the experimental setup. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Thermal and physical properties of glasses

All the glasses of the system (80–x) TeO_2–xPbO–17-ZnO–3La_2O_3 with $x = 0$–20 are transparent. The value of glass transition temperatures (T_g), onset crystallization temperature (T_x), and the difference between T_x and T_g ($\Delta T = T_x - T_g$) in the samples, which are determined from DTA curves, are given in Table 1. With increasing PbO content, the values of T_x, T_g, and ΔT decrease. The difference between T_x and T_g, ΔT, has been frequently used as a rough estimate of the glass formation ability or glass stability. Since fiber drawing is a reheating process and any crystallization during the process will increase the scattering loss of the fiber and then degrade the optical properties, it is desirable for a glass host to have ΔT as large as possible [11]. The glasses have ΔT exceeding 100 °C, indicating these samples are stable against devitrification. As shown in Table 1, the smallest value of ΔT is 131 °C, which is bigger than that 129 °C of typical TZN tellurite glass. The result indicates that these glass samples have good thermal stability and are suitable for fiber drawing.

The value of density and refractive index for TPZLx ($x = 0$, 5, 10, 15, 20) series glasses are shown in Fig. 1. Both the density and refractive index increase monotonically with increasing PbO content. Such feature was explained as follows: due to the atomic mass of Pb^{2+} is bigger than that of Te^{4+}, with the gradual replacement of the Te^{4+} ions by Pb^{2+} ions, the average molecular weight of unit volume enhances, which results in densities increasing. Correspondingly, the refractive indices also increase.

3.2. Absorption spectra

Fig. 2 illustrates the absorption spectrum of Tm^{3+}/Yb^{3+} co-doped TPZL20 glass in the visible and near infrared region. The 1694, 1211, 793, 687 and 663 nm absorption bands correspond to the transitions of Tm^{3+} from the ground state $^3H_6$ to the excited states $^3F_4$, $^3H_5$, $^3H_4$, $^3F_3$ and $^3F_2$, respectively. And the intense absorption band centered at around 980 nm due to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of the Yb^{3+} ions. However, as we know that there is no absorption around 980 nm in Tm^{3+} doped glass. The results indicate that by using a 980 nm laser the Tm^{3+}/Yb^{3+} co-doped tellurite glass can be efficiently

Table 1
T_g, T_x, and ΔT of TPZL glasses

Glass code	Composition (mol%)	T_g (°C)	T_x (°C)	ΔT (°C)
TPZL0	80TeO_2–17ZnO–3La_2O_3	350	487	137
TPZL5	75TeO_2–5PbO–17ZnO–3La_2O_3	345	479	134
TPZL10	70TeO_2–10PbO–17ZnO–3La_2O_3	343	477	134
TPZL15	65TeO_2–15PbO–17ZnO–3La_2O_3	338	471	133
TPZL20	60TeO_2–20PbO–17ZnO–3La_2O_3	333	464	131
TZN [12]	70TeO_2–25ZnO–5Na_2O	355	484	129