Journal of Non-Crystalline Solids 383 (2014) 157–160

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Intense red fluorescence from Ho/Yb codoped tellurite glasses

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ARTICLE INFO

Article history:
Received 26 November 2012
Received in revised form 5 March 2013
Available online 11 June 2013

OCIS:
(160.5690) Rare-earth-doped materials
(160.2540) Fluorescent and luminescent materials
(140.7300) Visible lasers
(300.2530) Fluorescence laser-induced

Keywords:
Tellurite glasses;
Upconversion;
Visible lasers;
Fiber materials

ABSTRACT

By optimizing the concentration ratio of Ho/Yb and using conventional melting and quenching methods, a group of Ho/Yb co-doped tellurite glasses with host composition of $78TeO_2$–$12ZnO$–$10Na_2O$ (mol.%, TZN) were made for red fiber laser development. Excited by 976 nm laser diode, intense green and red emissions were detected easily even by naked eyes. TZN glass codoped with 0.5 wt.% Ho_2O_3 and 3 wt.% Yb_2O_3 was found to present the strongest red emission with the intensity about three times higher than that of the green one, presenting a yellowish-orange color as observed. Besides direct energy transfer process from Yb to Ho as usual, it is believed that cooperative energy transfer upconversion from a pair of Yb donor ions to one Ho acceptor ion and excited state absorptions among different levels of Ho ion are commonly responsible for the observed intense red emission. © 2012 Elsevier B.V. All rights reserved.

1. Introduction

Recently, great attention has been directed to the fabrication of integrated and compact blue, green and red laser sources for a wide range of applications, such as color displays, high density optical data storage and reading, biomedical diagnostics, infrared lasers viewers and indicators [1–11]. Having three potential emission bands centered on 545 nm (green), 658 nm (red) and 755 nm (NIR), Ho^{3+} becomes one of the most widely-studied rare-earth ions and has been applied in the aspects of solid-state lasers, among which there exists an already reported green short-wavelength-emitting solid-state laser [4–9]. Compared with solid-state laser, fiber laser has some obvious advantages: relatively inexpensive, compact and easy to install, length-controllable, self-cooling at low-power level, small beam waist with radius of micrometer-level to increase the resolution of the displays, and delivering a high quality diffraction-limited beam compatible with current silica-based optical communication systems [2,3]. These merits make fiber lasers widely used in biological and disease researches, remote sensing and spectroscopy [11]. Serving as laser sources, fiber laser is compact and can generate and directly transmit diffraction-limited beam without further light shaping measures, which is more convenient than traditional gas laser and solid-state laser with fiber pigtails for laser guide and output [10]. Therefore, we are considering of using visible fiber lasers to replace solid-state lasers in these specific application areas.

Having developed Tb/Yb codoped tellurite glasses for green fiber laser development [2,3], we are striving hard to develop red fiber laser and therefore Ho/Yb codoped tellurite glass system entered into our insight to make full use of visible emission of Ho ions, sensitizing and anti-quenching effects of Yb ions, and further the lowest phonon-energy oxide glass network system of tellurite glasses.

Even with some reports on intense green emission [5–9,12,13], until now there have been very few reports on intense red emission from Ho/Yb codoped tellurite glasses. In this study, we fabricated a group of Ho/Yb codoped tellurite glasses aiming for red fiber development and probed deeply into the energy transfer mechanisms responsible for the observed visible emissions.

2. Experimental

$78TeO_2$–$12ZnO$–$10Na_2O$ (mol.%, TZN) is an optimized tellurite glass composition which can effectively block surface-crystallization during fiber drawing [14], and therefore TZN glass was chosen to be the host glass for doping rare earth ions. Based on our doping experience in Tb/Yb-TZN glass [2], we fixed the doping concentration of Yb to be 3 wt.% for this specific doping system, while the concentration of Ho increased from 0.1 to 0.9 wt.% with an interval of 0.2 wt.labeled

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http://dx.doi.org/10.1016/j.jnoncrysol.2013.04.051

as xH3Y-TZN ($x = 0.1, 0.3, 0.5, 0.7$ and 0.9). Reagent chemical powders with purity ≥99.9% were precisely weighted up, homogeneously mixed in a glass bottle, melted in a gold crucible at about 800 °C for 2 h inside a specially designed oxygen-atmosphere furnace in order to decrease the negative influence on photoluminescence intensity and lifetime by OH groups [14,15]. The molten liquids were poured onto a brass mold at 220 °C, annealed at 259 °C for 3 h to remove inner stress, and then slowly cooled down to room temperature. The glass samples were cut into specimens with the size of $10 \times 10 \times 1$ mm^3 and $10 \times 10 \times 3$ mm^3 and were polished to optical quality.

Characteristic temperatures, namely glass transition temperature (T_g) and onset crystallization peak (T_x), were determined by differential scanning calorimeter (DSC, NETZSCH STA, 404F3/PG) in Argon atmosphere with a scan rate of 10 °C/min. Linear refractive index, n, of these glasses was measured at 632.8 nm, 935 nm and 1549 nm using a prism coupler (Metricon, Model 2010/M). Optical absorption spectra were measured in the wavelength range from 400 nm to 1200 nm by spectrophotometer (Shimadzu, UV-3101PC). Fluorescence spectra were excited by a 976 nm continuous wave laser diode (LD), the average power of which is 1.3 W and the estimated pump intensity is 1 W/mm^2. A photomultiplier tube (Zolix, PMTH-S1-CR131) and an InGaAs detector (JUDSON, J22TE2-66C-R05M) were used for visible and near-IR sensitivity respectively. To probe the concentration dependence of the photoluminescence, the locations of the tested glass samples and the pumping source were kept unchanged and the excitation power was unvaried. All of the measurements were carried out at room temperature.

3. Results and discussion

3.1. Physical and thermal properties

It is found that in the wavelength region of 620–1550 nm the refractive index changes greatly. For 0.5H3Y-TZN sample, the refractive index n at 1549 nm is 1.97322. As shown in Fig. 1, the working temperature range $\Delta T = T_g - T_x$ of 0.5H3Y-TZN78 glass is about 156 °C, which is significantly higher than that of TZN75 glass (105 °C) [14], bismuth tellurite glass (42 °C) [9] and Gallate-bismuth-lead-germanium glasses (129 °C) [16]. Larger ΔT indicates better thermal stability against surface crystallization during fiber drawing. Therefore, HY-TZN glasses are very suitable for fiber development.

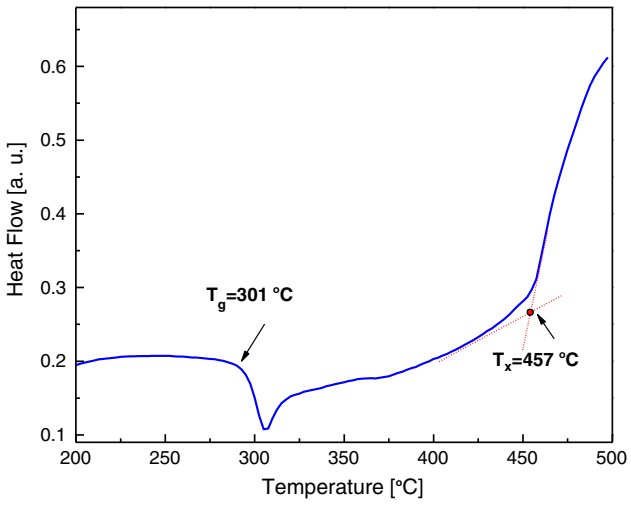

Fig. 1. DSC trace for 0.5H3Y-TZN glass sample.

3.2. Absorption spectroscopy

Assuming the same Fresnel reflection for samples with different thicknesses, the absorption coefficient α was calculated from the following equation, similar to the cut-back method used in fiber optics as indicated in Eq. (1) [15]:

$$\alpha = \ln(T_1/T_2)/(L_2 - L_1), \quad (1)$$

in which L is the thickness and T is the transmittance of the tested glass sample.

It is observed that the shapes and trends of absorptive spectra are similar for all the tested glasses, so we take 0.5H3Y-TZN glass as an example to explain transition mechanisms among different energy levels in detail. In the spectral region of 400–750 nm, Fig. 2 shows the absorption spectrum of 0.5H3Y-TZN glass sample, in which five main absorption transitions from Ho^{3+} ions are labeled as $^5I_8 \rightarrow {}^5G_5$ (417 nm), $^5I_8 \rightarrow {}^5G_6$ (452 nm), $^5I_8 \rightarrow {}^5F_3$ (485 nm), $^5I_8 \rightarrow ({}^5F_4, {}^5S_2)$ (537 nm), and $^5I_8 \rightarrow {}^5F_5$ (642 nm). As shown in the inset of Fig. 2 in the near-infrared range of 850–1250 nm, there are a sharp absorption peak at 976 nm and a broad absorption band centered at 950 nm assigned to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} ions, which is the result of the stark-splitting/shifting effects of Yb^{3+} ions when embedded in a certain structure and phonon-energy-dependent ligand field of this TZN host glass [2]. Considering the strongest absorption peak at 976 nm and these stark effects at 950 nm, we still believe that the best pumping wavelength should be 976 nm rather than 950 nm regardless of its large absorption area.

3.3. Fluorescence spectroscopy

HY-TZN glasses were pumped at 976 nm and the correspondent fluorescence spectra are reported in Fig. 3. Three strong fluorescence peaks from active Ho ions are found to be centered at 549 nm (green: $^5F_4$, $^5S_2 \rightarrow {}^5I_8$), 660 nm (red: $^5F_5 \rightarrow {}^5I_8$) and 1190 nm (NIR: $^5I_6 \rightarrow {}^5I_8$). However, the blue fluorescence within the range of 450–490 nm reported before [4] was not observed in all the HY-TZN glass samples, the reason for which is mainly due to different tellurite glass composition characterized by glass network units. Looking back upon the blue laser development, we found that blue upconversion emission of Ho ions has been observed in very few crystals only when dye lasers (600–650 nm) or higher power excitations were used [17]. That is to say, it is very difficult for Ho ions to emit blue light in glass materials.

In general, for Ho/Yb codoped glass systems such as fluoroindate [5], alkali bismuth gallate [6], and fluorozircoaluminate glasses [7], the green upconversion emission plays a dominant role in the luminescence color. In the case of TZN78 glasses, however, the intensity of the red emission is about three times higher than that of the green one, resulting in a yellowish-orange color to the human eyes with a photo inserted in Fig. 3. Intense red emission of Ho^{3+} presents a desirable warm-color background, while green emission is the most sensitive one to our naked eyes, all of which are indispensable components to produce multicolor [8]. The similar emission bands centered at about 1190 nm are also presented in Fig. 3, the results of which linearly fit the practical Ho_2O_3 concentration well.

As shown in Fig. 3, the fluorescence of green and red light changes with different Ho_2O_3 concentration. Increasing Ho_2O_3 concentration step by step, the visible fluorescence intensities at 549 nm and 660 nm reach the highest position with 0.5 wt.% Ho_2O_3 and then decline afterwards, while the near-infrared intensity at 1190 nm increases steadily until with 0.7 wt.% Ho_2O_3. For different application purpose, the optimum rare earth ion concentration should be clearly specified from case to case.