Journal of Luminescence 157 (2015) 179–183

Contents lists available at ScienceDirect

Journal of Luminescence

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

Upconversion luminescence and mechanisms of $Nd^{3+}/Ho^{3+}/Yb^{3+}$ triply doped TeO_2–K_2O–Nb_2O_5 glasses

Yuebo Hu [a,*], Jianbei Qiu [b]

[a] Faculty of Mechanical and Electrical Engineering, Kunming University of Science and Technology, Kunming 650500, China
[b] Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China

ARTICLE INFO

Article history:
Received 22 March 2014
Received in revised form
23 August 2014
Accepted 27 August 2014
Available online 6 September 2014

Keywords:
$Nd^{3+}/Ho^{3+}/Yb^{3+}$ doped
TeO_2–K_2O–Nb_2O_5 glass
Upconversion luminescence
Mechanism
Energy transfer

ABSTRACT

$Nd^{3+}/Ho^{3+}/Yb^{3+}$ triply doped TeO_2–K_2O–Nb_2O_5 glasses were synthesized by the conventional melting-quenching technique. Single green upconversion (UC) luminescence centered at 532 nm, corresponding to the $(^5F_4, ^5S_2)\rightarrow{}^5I_8$ transitions of Ho^{3+}, was observed under 800 nm excitation. However, green and red emission bands centered at 547, 662 and 758 nm, corresponding to the $(^5F_4, ^5S_2)\rightarrow{}^5I_8$, $^5F_5\rightarrow{}^5I_8$ and $(^5F_4, ^5S_2)\rightarrow{}^5I_7$ transitions of Ho^{3+}, respectively, were simultaneously observed under 980 nm excitation. The dependence of UC luminescence intensity of Ho^{3+} under 800 and 980 nm excitations on Yb^{3+} concentration was studied. It was found, under 800 nm excitation, the 532 nm emission intensity of Ho^{3+} begin to reduce when the Yb^{3+} concentration is higher than 0.8 mol%. However, at the same concentration of Yb^{3+}, the emission quenching was not observed under 980 nm excitation. The UC mechanisms under two pumping sources were discussed in terms of the experiment results. It was found that the UC luminescence of Ho^{3+} mainly depends on ET under 800 nm excitation; however under 980 nm excitation, it mainly depends on ESA.

1. Introduction

In recent decades, there has been continuous interest in the upconversion (UC) process of infrared to visible light by rare earth (RE) ions doped glasses, due to the extensive applications in areas such as laser, optical data storage, color display, sensor, biomedicine and so on [1–4]. Among RE ions, Ho^{3+} is one of the most important RE active ions for UC luminescence due to the favorable energy level structure and abundant transitions at various wavelengths from the ultra-violet to infrared region [4,5]. However, Ho^{3+} cannot be pumped directly by commercial 808 or 980 nm laser diodes because of the lack of an appropriate ground absorption band. To solve this problem, Yb^{3+} is generally employed as a sensitizer ion to increase the emission intensity and efficiency of Ho^{3+} ion doped materials under ~980 nm excitation [6,7], and Nd^{3+} ion is considered as a good candidate for improving the pumping efficiency of 800 nm laser diode (LD), due to its intense absorption cross-section around 800 nm. Meanwhile, Nd^{3+} shows long lifetime of the $^4F_{3/2}$ level in glasses which is enough to enable efficient energy transfer (ET) to other RE ions [8,9].

Another, host materials play an important role in developing high-efficient RE ions UC luminescence. Tellurite glasses have shown to be a suitable host for RE luminescence, due to excellent properties on photonic devices applications such as low melting temperature (~800 °C), high refractive index (~2) adequate for nonlinear effects (harmonic generation), low phonon energy (~600–700 cm^{-1}) that increases the fluorescence efficiency by limiting nonradiative relaxations, large transmission window (350–6500 nm) and can be easily fiberized [7,10,11]. Thus, the $Nd^{3+}/Yb^{3+}/Ho^{3+}$ co-doped tellurite glass is expected to exhibit unique optical properties, and attracts much interest in investigation of UC process.

In this work, the UC spectroscopic properties of Ho^{3+} in $Nd^{3+}/Yb^{3+}/Ho^{3+}$ co-doped TeO_2–K_2O–Nb_2O_5 glass under 800 nm and 980 nm excitations were researched, and the UC luminescence mechanisms of Ho^{3+} under these two pumping sources were discussed. The dependence of UC luminescence intensity of Ho^{3+} under the two pumping sources on Yb^{3+} concentration was studied.

2. Experimental

The glass samples were prepared with the high purity raw materials and according to the following composition in mol%

* Corresponding author. Tel.: +86 87165170917; fax: +86 87165194243.
E-mail address: huyb@kmust.edu.cn (Y. Hu).

http://dx.doi.org/10.1016/j.jlumin.2014.08.055
0022-2313/

of $65TeO_2 \cdot 15K_2O \cdot 15Nb_2O_3 \cdot (4.8-x)\ Gd_2O_3 \cdot xYb_2O_3 \cdot 0.1Nd_2O_3 \cdot 0.1Ho_2O_3$ ($x=0$, 0.2, 0.5, 0.8, 1.0 and 1.5) and $65TeO_2 \cdot 15K_2O \cdot 15Nb_2O_3 \cdot (3.9-y)Gd_2O_3 \cdot 1.0Yb_2O_3 \cdot 0.1Nd_2O_3 \cdot yHo_2O_3$ ($y=0.1$, 0.3, 0.5, 0.8 and 1.0) by the conventional melt-quenching technique. About 5 g batches of starting materials were thoroughly mixed and then melted at 900 °C for 30 min in platinum crucible in a SiC Globar furnace in the normal atmosphere. The melts were cast quickly into stainless steel plates which were kept around 200 °C. The obtained glasses were annealed at 340 °C for 4 h, and cooled naturally to room temperature inside the furnace to avoid internal stress. Subsequently, glass samples were cut and polished.

The characteristic temperatures (T_g glass transition temperature, T_c crystallization temperature and T_m glass melting point temperature) were measured using a differential thermal analysis (DTA) unit (SDT Q600 V8.2 build 100) with a rate of 10 °C/min in an Ar atmosphere. The UC luminescence spectra were measured by exciting the samples with the 800 nm and 980 nm LDs, and recorded by using a HITACHI F-7000 Fluorescence spectrophotometer. The UV/VIS/NIR absorption spectra were recorded in the wavelength range from 400 to 1100 nm using with a Model U-4100 Spectrophotometer. Specimens with the size of $4.0 \times 4.0 \times 1.0\ mm^3$ with optically flat surfaces were used in the measurements. All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the DTA curve of $Nd^{3+}/Ho^{3+}/Yb^{3+}$ triple doped TeO_2–K_2O–Nb_2O_5 glass. The characteristic temperatures T_g, T_c and T_m are determined. The values of T_g, T_c and T_m derived from DTA curve are 380, 463 and 586 °C, respectively. The melting point temperature of this glass is only 586 °C which indicates that the glass samples containing above-mentioned component may be prepared at lower temperature. It is well known that large temperature difference between T_g and T_c can effectively prevent the growing up of crystal nucleus quickly. ΔT (T_c – T_g) is 83 °C below 100 °C which indicates that the performance against nucleation and crystallization of this glass is weaker than that of the other oxide glasses. To get stable and transparent glass, the annealing temperature was selected to be 340 °C.

Fig. 2 shows the absorption spectrum of the sample containing 1.0 mol% of Yb^{3+} between 400 and 1100 nm wavelength range.

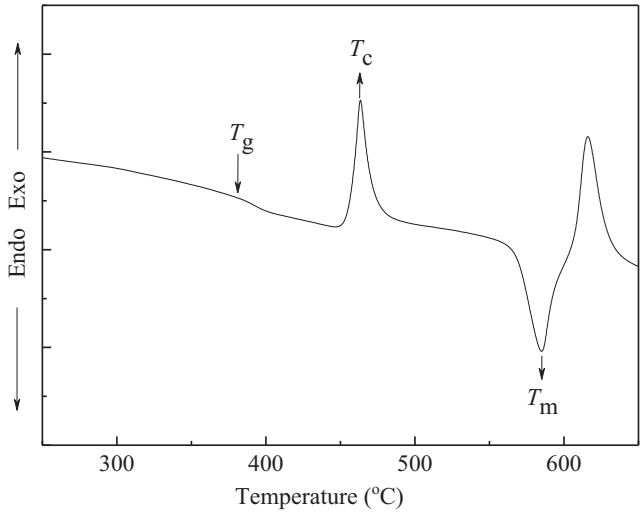

Fig. 1. DTA curve of $Nd^{3+}/Ho^{3+}/Yb^{3+}$ triply doped TeO_2–K_2O–Nb_2O_5 glass containing 1.0 mol% of Yb^{3+}.

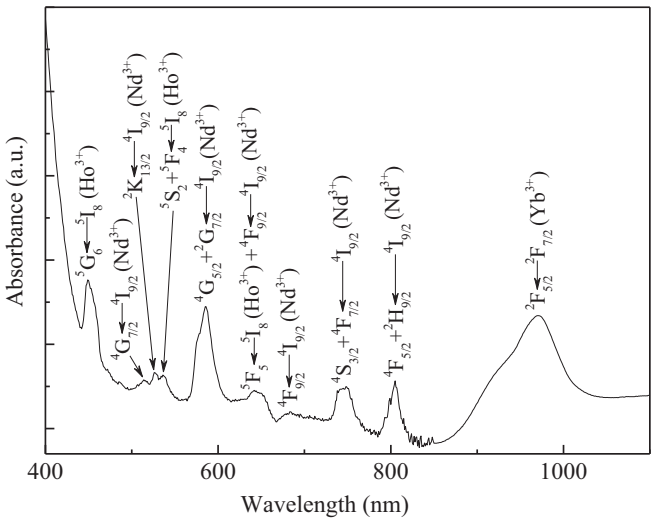

Fig. 2. Absorption spectrum of $0.1Nd^{3+}/0.1Ho^{3+}/1.0Yb^{3+}$ triply doped TeO_2–K_2O–Nb_2O_5 glass.

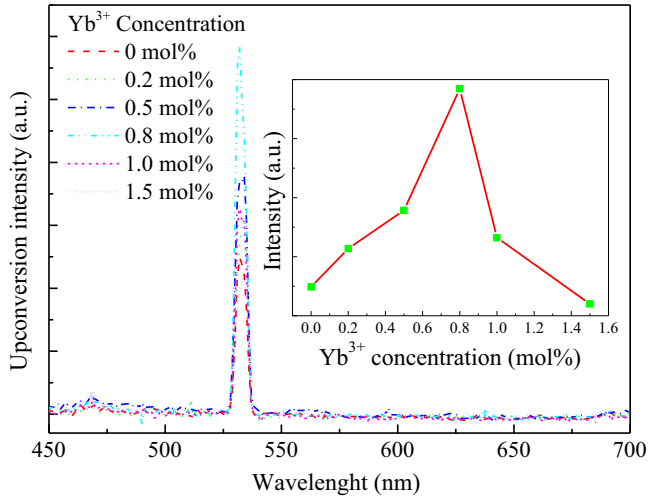

Fig. 3. Dependence of UC luminescence intensity in $Nd^{3+}/Ho^{3+}/Yb^{3+}$ triply doped TeO_2–K_2O–Nb_2O_5 glass under 800 nm excitation on Yb^{3+} concentration (mol%, $x=0$, 0.2, 0.5, 0.8, 1.0 and 1.5).

The bands correspond to transitions from the ground to excited states of Nd^{3+}, Ho^{3+} and Yb^{3+} have been marked on the presented spectrum, and the involved states of the ions can be recognized in respective energy level diagrams in Fig. 5. Yb^{3+} has intense absorption at the wavelength region at 980 nm, which arises from the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. In addition, due to the influence of the glass matrix's band gap energy, the absorption bands below 400 nm cannot be observed. The glass presents a good transparence in visible region, indicating that it is suitable for practical UC applications in the visible region.

Fig. 3 shows the UC emission spectra of $Nd^{3+}/Ho^{3+}/Yb^{3+}$ triply doped TeO_2–K_2O–Nb_2O_5 glass samples under the excitation of 800 nm. A distinct UC emission band centered at 532 nm and a very faint UC emission band centered at 469 nm are observed from these spectra, which could be ascribed to the $(^5F_4, {}^5S_2) \rightarrow {}^5I_8$ and $^5F_2 \rightarrow {}^5I_8$ transitions of Ho^{3+} ions, respectively. There is no emission band originating from Nd^{3+} in this spectral region. To explore the effect of Yb^{3+} concentration on emission intensity of Ho^{3+} under 800 nm excitation, the inset shows the dependence of UC luminescence intensity of 532 nm on Yb^{3+} concentration under 800 nm excitation. The intensity of 469 nm emission band is not presented because it is too weak to distinguish in all of samples. As