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JOURNAL OF RARE EARTHS, Vol. 34, No. 4, Apr. 2016, P. 368
JOURNAL OF RARE EARTHS
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Spectroscopic properties and energy transfer of Nd^{3+}/Ho^{3+}-doped Ga_2O_3-GeO_2 glass by codoping Yb^{3+} ion

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Received 8 June 2015; revised 4 February 2016

Abstract: This study presented the luminescence properties of $Nd^{3+}/Yb^{3+}/Ho^{3+}$ dopant ions inside a host based on Ga_2O_3-GeO_2-Li_2O (GGL) glass. The measured differential scanning calorimetry result showed that GGL glass exhibited excellent stability against devitrification with ΔT=135 ºC. Obvious 543 and 657 nm emissions were observed in Nd^{3+}/Ho^{3+}-codoped sample. The incorporation of Yb^{3+} into Nd^{3+}/Ho^{3+}-codoped glass system had resulted in enhanced upconversion emission intensity under the excitation of 808 nm and/or 980 nm laser diode (LD). The possible mechanisms and related discussions on this phenomenon were presented. It was noted that the presence of Yb^{3+} yielded an enhancement about 7 and 11 times in the 543 and 657 nm emission intensities respectively under 808 nm excitation due to the energy transfer from Nd^{3+} to Ho^{3+} via Yb^{3+} ion. Here Yb^{3+} played a major role as a bridging ion. While enhanced 543 and 657 nm emission intensities under the excitation of 980 nm LD originated from the sensitization effect of Yb^{3+}. Our results showed that $Nd^{3+}/Ho^{3+}/Yb^{3+}$ triply doped GGL glass might be a promising candidate for the development of visible-laser materials.

Keywords: upconversion luminescence; $Nd^{3+}/Yb^{3+}/Ho^{3+}$; Ga_2O_3-GeO_2 glass; energy transfer; rare earths

In recent years, high-power laser diode (LD) has attracted a great deal of interest because of their technological importance in developing compact up-conversion (UC) visible-laser systems as pumping sources[1,2]. Although several approaches have been pursued, the frequency UC laser by developing rare-earth (RE)-doped glass materials has important advantages over the others[3–8]. Using trivalent RE ions, such as Er^{3+}, Tm^{3+} and Ho^{3+} luminescence centers have been the focus of the research on UC luminescence materials[1,7–12]. In particular, the Ho^{3+} ion is an extensively studied RE ion due to its numerous radiative emissions in the visible and IR, which provides broad potential applications toward NIR/Vis solid-state lasers[9,13]. However, Ho^{3+} cannot be excited directly by the commercial 980 and/or 808 nm LD[14,15]. Codoping with other RE ions with strong absorption bands at a wavelength of ~800 nm, such as Nd^{3+}, could efficiently pump the Ho^{3+} via the $^4I_{9/2}\rightarrow{}^4F_{5/2}$, $^2H_{9/2}$ transition of Nd^{3+} ions[1,14,15]. On the other hand, UC luminescence could be obtained from the levels of RE^{3+} ions which can not be excited and/or enhanced without incorporation of Yb^{3+} ions due to intense absorption band of Yb^{3+} located at 1 μm corresponding to the emission band of a commercially available high-power InGaAs LD[3].

Over the past years glass materials have aroused wide interest based on their obvious advantages such as relatively easy synthesis compared with crystals, which urges us to study it in a wide range of composition and to obtain large samples[9]. Holmium has been widely studied in various fluoride glasses[13,16]. However, by considering the poor chemical durability of fluoride glasses, it is considered to be more important to search for novel glass systems to be used as host materials. The glasses based on Ga_2O_3-GeO_2 system as a promising group of heavy metal oxide glasses have been paid great attention for optoelectronics applications because of their excellent optical properties, such as the good transparency in the mid-infrared, and the possibility to incorporate a large amount of RE ions, etc.[17–20]

Herein, the main objective of this work is to carry out a detailed study on photoluminescence properties of the $Nd^{3+}/Yb^{3+}/Ho^{3+}$-doped Ga_2O_3-GeO_2-Li_2O (GGL) glass upon excitation of 808 nm and/or 980 nm to examine their suitability as potential UC emission laser. Effects of Yb^{3+} concentration on UC luminescence characteristics and mechanisms have also been investigated and discussed under the excitation of 808 and 980 nm. Simultaneously the fluorescence spectra in the range of 1000–2050 nm have been investigated under the 808 nm excitation.

Foundation item: Project supported by the National Natural Science Foundation of China (51002070), Foundation of He'nan Educational Committee (14A430034, 16A430040), Funding Scheme for Young Teachers of Higher School in Henan Province (2012GGJS-192), and the Science and Technology Program of Luoyang City (1401051A)

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DOI: 10.1016/S1002-0721(16)60035-2

1 Experimental

GGL glasses with the molar composition of (99-x)($15Ga_2O_3$-$75GeO_2$-$10Li_2O$)-$0.5Nd_2O_3$-$0.5Ho_2O_3$-x Yb_2O_3 (x=0, 0.1, 0.3, 0.5, 0.7, named as GGL1, GGL2, GGL3, GGL4 and GGL5) were prepared using a conventional melting-quenching method from powders with analytical-reagent chemicals of Li_2CO_3, Ga_2O_3 (99.99%) , GeO_2 (99.999%) and R_2O_3 (R=Nd, Yb, Ho) (99.99%) in platinum crucible for 20 min at around 1480 ºC, followed by a quenching in air on a stainless-steel plate. After annealing, all the samples were polished and cut into the size of 20 mm×20 mm×2.0 mm. Meanwhile the GGL glasses based on $15Ga_2O_3$-$75GeO_2$-$10Li_2O$ and 99($15Ga_2O_3$-$75GeO_2$-$10Li_2O$)-$0.5Nd_2O_3$-$0.5Yb_2O_3$ were prepared.

Thermal analyses of samples were carried out using a Netzsch STA 449/C differential scanning calorimetry (DSC) at a heating rate of 10 ºC/min from room temperature to 850 ºC. Densities were measured according to the Archimedes' principle using distilled water as the medium. Refractive index was obtained by prism coupler. Measured density and refractive index of host glass are 3.995 g/cm^3 and 1.6699 respectively. The absorption spectra of GGL1-GGL5 samples and transmission spectrum of host glass were measured with a PERKIN-ELMER Lambda 900 UV-Visible-NIR spectrophotometer with the resolution of 1 nm respectively. The fluorescence spectra in the range of 1000–2050 nm were obtained through a computer-controlled Triax 320 spectrofluorimeter with the resolution of 1 nm under excitation of an 808 nm LD, and the signal was detected with a PbSe detector (1000–5000 nm). The UC luminescence measurements were obtained with a computer-controlled Triax 320 spectrofluorimeter (Jobin-Yvon Corp.) upon continuous wave excitation of 808 nm and 980 nm LD (Coherent Corp). Emitted light was focused onto the monochromator and monitored at the exit slit by R928 photomultiplier tube (500–750 nm). All the optical measurements were performed at room temperature.

2 Results and discussion

2.1 Thermal property

Fig. 1 illustrates the DSC curve of GGL host glass. The measured glass transition temperature (T_g), the onset crystallization temperature (T_x), and the difference (ΔT) between T_x and T_g are 652, 517, and 135 ºC, respectively, as shown in Fig. 1. The difference ΔT between the T_g and T_x could be a rough indicator of glass stability against devitrification. Fiber drawing contains a reheating process and should avoid any crystallization which could lead to the scattering loss and decrease the optical properties of fiber[21]. Herein it is necessary to obtain a large ΔT value as much as possible. The ΔT value achieved to 135 ºC for GGL host glass, indicating excellent glass stability against devitrification for fiber drawing in comparison with that of the fluorozirconate glass[21]. Transparent GGL host glass has been prepared as exhibited in the inset of Fig. 1.

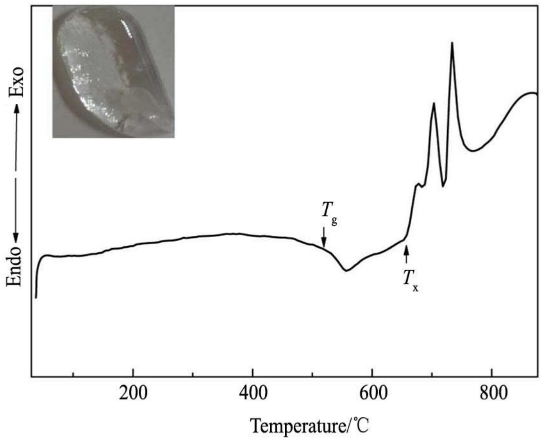

Fig. 1 DSC curve of GGL host glass (Inset shows the picture of transparent host glass)

2.2 Absorption spectra

Fig. 2 shows the absorption spectra in the range of 250–2000 nm for $Nd^{3+}/Ho^{3+}/Yb^{3+}$-doped samples when Yb^{3+} concentration changes from 0 to 0.7 mol.%. Each assignment corresponds to the excited level of RE^{3+} ions. Thirteen absorption bands of RE^{3+} are observed in Fig. 2, centered at the respective wavelengths of 1948, 1151, 970, 871, 802, 740, 680, 643, 580, 530, 452, 415 and 355 nm. The peak positions of RE^{3+}-doped samples do not change with the incorporation of Yb^{3+}. The samples illustrate the short cutoff band less than 350 nm. Fig. 2 inset shows the transmission spectrum of host glass.

2.3 Analysis of UC and fluorescence spectra under the excitation of 808 nm

Fig. 3 shows typical room-temperature visible emission for the $Nd^{3+}/Ho^{3+}/Yb^{3+}$-doped samples pumped at 808 nm LD. The insets (a) and (b) of Fig. 3 depict the

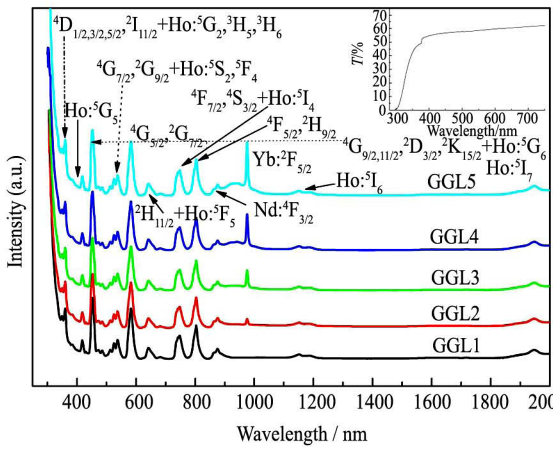

Fig. 2 Absorption spectra of $Nd^{3+}/Yb^{3+}/Ho^{3+}$-doped GGL glasses (Inset shows the transmission spectrum of host glass)