Optical Materials 75 (2018) 274–279

Contents lists available at ScienceDirect

Optical Materials

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

Broadband ~3 μm mid-infrared emission in Dy^{3+}/Yb^{3+} co-doped germanate glasses

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ARTICLE INFO

Article history:
Received 24 September 2017
Received in revised form
17 October 2017
Accepted 21 October 2017

Keywords:
Optical materials
Mid-infrared emission
Germanate glass
Dy^{3+}/Yb^{3+} co-doped
Radiative properties
Energy transfer

ABSTRACT

The Dy^{3+}/Yb^{3+} co-doped germanate glasses with good thermal stability have been prepared by the conventional melt quenching method. The J-O intensity parameters and radiative properties such as spontaneous transition probilities (A_{rad}), fluorescence branching ratios (β) and radiative lifetimes (τ_{rad}) were investigated according to the absorption spectrum based on Judd-Ofelt theory. An intense emission around ~3 μm with the FWHM reaching to 322 nm was obtained in present glasses excited by 980 nm LD. The high spontaneous transition probability (63.94 s^{-1}), large emission cross section (6.0×10^{-21} cm^2) and superior gain performance corresponding to the Dy^{3+}: $^6H_{13/2} \rightarrow {}^6H_{15/2}$ transition were obtained. Moreover, the energy transfer mechanism was analyzed qualitatively, and it was found that the energy transfer from Yb^{3+}: $^2F_{5/2}$ to Dy^{3+}: $^6H_{5/2}$ level could be quite efficient. Hence, the results indicated that the prepared Dy^{3+}/Yb^{3+} co-doped germanate glass could be a potential candidate for ~3 μm mid-infrared solid state lasers.

1. Introduction

Solid state lasers operating in the ~3 μm mid-infrared wavelength region offer potential light sources for many applications, such as the applications in medical and sensing technologies owing to the strong absorption of radiation by water and hydroxy at near ~3 μm region, and other potential applications as eye-safe lasers, signal amplifiers and mid-IR optical parametric oscillators (OPO) [1–6]. Over the last several years, glasses doped with rare-earth ions are proved to be laser materials due to their high emission efficiencies. Rare-earth ions used as activators in various glass hosts could emit fluorescence corresponding to 4f-4f and 4f-5d electronic transitions, with the shielding of the outer 5s and 5p orbitals on the 4f electrons [7]. Among various rare earth ions, dysprosium has received particular attention because of its potential applications for ~3 μm laser owing to the $^6H_{13/2} \rightarrow {}^6H_{15/2}$ transition. The Dy^{3+} ion possesses a number of pump bands in the near infrared wavelength, such as 1.3 μm ($^6H_{15/2} \rightarrow {}^6H_{9/2} + {}^6F_{11/2}$) and 1.7 μm ($^6H_{15/2} \rightarrow {}^6H_{11/2}$), however, it is lack of commercially available high-power laser diodes (LD) corresponding to these pump bands of Dy^{3+} ion. Although there is a pump band at around 800 nm ($^6H_{15/2} \rightarrow {}^6F_{3/2} + {}^6F_{5/2}$), the pump efficiency of Dy^{3+} was rather small mainly because the absorption is weak at 808 nm wavelength band. Fortunately, Yb^{3+} ions can be used as a sensitizer to Dy^{3+} ions for mid-infrared lasers [8–11]. In the Dy^{3+}/Yb^{3+} co-doped system, the Yb^{3+} ion is excited to the excited state ($^2F_{5/2}$) under the excitation of a common 980 nm LD pump, then the accumulated excitation energy was transferred to Dy^{3+}: $^6H_{5/2}$, a series of nonradiatively decay occurred in the Dy^{3+} ions and the ~3 μm emission could be obtained ultimately.

In order to get powerful mid-infrared emissions from rare-earth ions doped glass, the choice of host glass is as important as the choice of rare-earth ions. Regarding the ~3 μm emission by Dy^{3+} ions, the hosts are mainly focused on non-oxide glasses with low phonon energy, such as the fluoride and chalcogenide glasses. Y. Dwivedi et al. reported the spectroscopic of Dy^{3+}/Yb^{3+} ions co-doped in barium fluoroborate glass [11], Tian. Y et al. reported 2.9 μm emission from the Dy^{3+} doped fluoride glasses [12], Wang. Z. et al. reported ~3 μm emission from Dy^{3+} doped chalcogenide glasses [13,14]. Fluoride glass has low phonon energy and high rare earth ion solubility, but its poor chemical durability, mechanical strength and low damage threshold limit its further applications in high power or energy fiber laser systems [15]. For the chalcogenide glass, although it has lower phonon energy compared with the

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https://doi.org/10.1016/j.optmat.2017.10.034
0925-3467/

fluoride glass, it is difficult to draw into fiber due to its relatively low recrystallization temperature which is close to the fiber drawing temperature [16]. Up to now, there are few reported on 2.9 μm luminescence in Dy^{3+} doped heavy-metal oxide glasses. Among the heavy-metal oxide glasses, the germanate glass possesses some expected properties. It has better physicochemical properties than fluoride glass and higher rare-earth ions solubility than chalcogenide glass [17,18]. Moreover, it has high glass transition temperature (~600 °C) to resist thermal damage at high pumping power and large refractive index which could enhance emission cross section [19,20]. Thus, the germanate glass is quite suitable as host glass for mid-infrared laser. Particularly, the barium gallo-germanate glass has been investigated extensively as an exist window for high energy lasers operating in the infrared wavelength region [21]. To the best of our knowledge, the fluorescence corresponding to the $^6H_{13/2} \rightarrow {}^6H_{15/2}$ transition of the Dy^{3+} in germanate glasses has been under-reported.

In this paper, a series of germanate glasses have been prepared. The thermal properties were investigated via the differential scanning calorimeter (DSC). The radiative properties of the Dy^{3+} in the prepared glasses were evaluated according to the J-O theory and M-C theory. The effectively emission at ~3 μm was obtained upon the 980 nm LD excitation. Moreover, the energy transfer processes from Yb^{3+} to Dy^{3+} was studied. The results verify that the Dy^{3+}/Yb^{3+} co-doped germanate glasses could be potential materials for ~3 μm mid-infrared lasers.

2. Experimental

The glasses composed of GeO_2-Ga_2O_3-BaF_2-LiF-Y_2O_3 were prepared by traditional melt-quenching method with using high-purity reagent (≥99.99%). The glasses were doped with *x* mol% Dy_2O_3 and *y* mol% Yb_2O_3 (y = 0; x = 0.15, 0.5, and y = 1; x = 0.15, 0.5). The well-mixed 20 g batches of samples were placed in Al_2O_3 crucible and heated with a SiC-resistance electric furnace at 1350 °C for 30 min. The melts were then poured onto a preheated stainless mold, followed by annealing at 550 °C for 4 h to relinquish the inner stresses. After that, it was allowed to cool slowly to room temperature. The annealed samples were cut and polished into a shape of 20 × 20 × 1.20 mm^3 for optical measurements.

The density of samples were tested by Archimedes principle using distilled water as an immersion liquid with error limit of ±0.05%. Refractive indexes were measured by prism minimum deviation method at the wavelength of 1053 nm. The vitreous and/or crystalline nature of the glasses were identified by X-ray diffractometer (XRD) with Cu-Kα radiation (λ = 1.5406 Å) at 40 kV tube voltage and 40 mA tube current. The glass transition temperature (T_g), crystallization onset temperature (T_x) and crystallization peak temperature (T_p) were characterized by a NETZSCH DTA 404 PC differential scanning calorimeter at a heating rate of 10 K/min with error of ±5 °C. Absorption spectra were recorded with a Perkin-Elmer-Lambda 900 UV/VIS/NIR spectrophotometer in the range of 200–2000 nm. Photoluminescence spectra in the range of 2500–3500 nm were determined by a liquid-nitrogen-cooled PbS detector using an 808 nm and 980 nm laser diode (LD) as an excitation source. The same experimental conditions for different samples were maintained so as to get comparable results. All the measurements were performed at ambient temperature.

3. Results and discussions

3.1. Thermal stability

The characteristic temperatures (the temperature of glass transition T_g, temperature of onset crystallization T_x and temperature of peak crystallization T_p) of the prepared glass were determined through the differential scanning calorimeter (Netzsch) curves as shown in Fig. 1. T_g is an important factor for laser glass, and a higher one (570 °C) which is higher than that of tellurite (354 °C) [22], bismuth (365 °C) [23], fluorophosphate glass (430 °C) [24] and comparable to other germanate glass (540 °C) [25] indicates that the prepared glass has a strong resistance to the thermal damage at high pumping power. ΔT (T_X - T_g) is another crucial factor used to evaluate the glass thermal properties. A large ΔT means the glass possesses an excellent thermal ability against the nucleation and crystallization. The ΔT (150 °C) of the prepared glass is larger than that of ZBLAN (67 °C) [26], fluoride (80 °C) [27] and is comparable to other germanate glass (129 °C) [28]. Therefore, the prepared glass possessing good resistance to devitrification has potential application in fiber laser.

3.2. Absorption spectra and J-O analysis

The absorption spectra of the Dy^{3+} singly doped, Dy^{3+}/Yb^{3+}-codoped samples at room temperature in the wavelength region of 200–2000 nm are shown in Fig. 2. It could be discerned ten absorption bands centered at around 321, 349, 386, 451, 749, 800, 900, 1084, 1269 and 1690 nm, which correspond to the transitions from the $^6H_{15/2}$ ground state to excited levels $^4P_{3/2}$, $^4K_{17/2}$, $^4I_{15/2}$, $^4F_{9/2}$, $^6F_{3/2}$, $^6F_{5/2}$, ($^6F_{7/2}$ + $^6H_{5/2}$), ($^6F_{9/2}$ + $^6H_{7/2}$), ($^6F_{11/2}$ + $^6H_{9/2}$) and $^6H_{11/2}$, respectively, according to the absorption spectrum of Dy^{3+} single doped germanate glass. The shapes and the peak positions of each transition in Dy^{3+} single doped germanate glasses nearly do not change when compared with the Dy^{3+}/Yb^{3+} co-doped germanate glasses and are very similar to those in other Dy^{3+}-doped glasses [29,30]. Those phenomenons could be explained by the reason that the Dy^{3+} ions are homogeneously incorporated into the glass network without clustering and any changes in the local ligand field [31]. The absorption band centered at 800 nm originating from the Dy^{3+}: $^6H_{15/2} \rightarrow {}^6F_{5/2}$ transition is very weak which indicates the samples cannot be efficiently excited by 808 nm LD. However, according to the absorption spectrum of Dy^{3+}/Yb^{3+} co-doped germanate glass, the Yb^{3+} ions could be pumped effectively by 980 nm LD corresponding to the Yb^{3+}: $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition, as shown in Fig. 2, which indicates the co-doped samples are suitable for commercialized 980 nm LD pumping. In this work, Yb^{3+} ions were added to sensitize Dy^{3+} ions through the energy transfer from Yb^{3+}: $^2F_{5/2}$ level to Dy^{3+}: $^6H_{5/2}$ level, then nonradiatively decay to

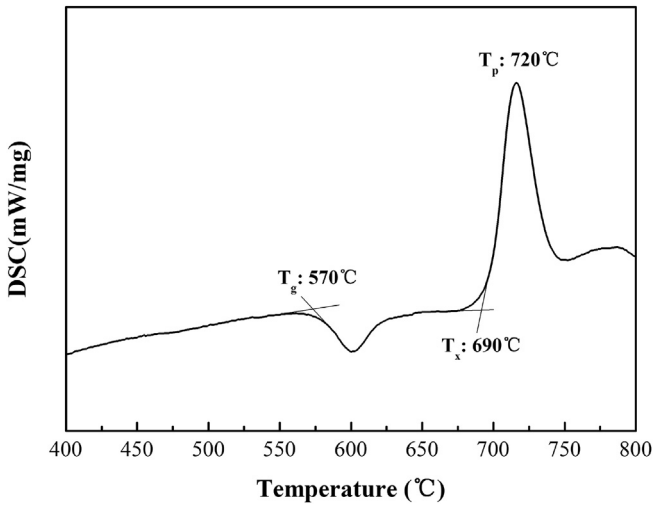

Fig. 1. DSC curves of prepared glass.