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Broadband 2 μm emission characteristics and energy transfer mechanism of Ho^{3+} doped silicate-germanate glass sensitized by Tm^{3+} ions

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HIGHLIGHTS

- 2.0 μm emission is obtained in Tm^{3+}/Ho^{3+} codoped silicate-germanate glass.
- Energy transfer is analyzed when pumped by conventional 808 nm LD.
- Present glass possesses good thermal stability and transition probability.
- Tm^{3+}/Ho^{3+} codoped silicate-germanate glass is a good candidate for broadband 2.0 μm laser.

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ABSTRACT

The Tm^{3+}/Ho^{3+} co-doped silicate-germanate glasses with good thermal properties were synthesized by high temperature melting method. 2.0 μm emissions with broad effective half-width (231.5 nm) were successfully obtained in present Tm^{3+}/Ho^{3+} co-doped glasses without obvious quenching upon excitation of a commercial 808 nm laser diode. To further understand 2 μm fluorescence behaviors of the prepared glasses, energy transfer mechanism, efficiency, rate and microparameters from different levels of Tm^{3+} to Ho^{3+} ions have been obtained and discussed. In short, the Tm^{3+}/Ho^{3+} co-doped silicate-germanate glass with excellent spectroscopic properties might be an attractive host material for 2 μm broadband solid laser.

1. Introduction

Over the past few decades, rare earth doped solid laser operating at 2.0 μm has drawn much attention owing to its extensive applications such as military system, eye-safe laser radar, atmosphere monitoring and so on [1–5].

In order to get a good rare earth doped 2.0 μm laser material, selecting appropriate rare earth ions is firstly necessary to take into consideration. Among rare earth ions, Tm^{3+}, which has a 1.8 μm emission via $^3F_4 \rightarrow {}^3H_6$ transition, can be pumped by commercially available 808 nm laser diodes. When the concentration of Tm^{3+} is high, it can accelerate cross relaxation process (CR) and improve quantum efficiency. Besides, another suitable rare earth ion, Ho^{3+}, whose emission cross section is far larger than that of Tm^{3+}, has 2.0 μm emission by $^5I_7 \rightarrow {}^5I_8$ transition [6]. However, Ho^{3+} doped glass faces a serious problem that it cannot be excited by commercially available laser diodes due to the lack of appropriate absorption bands [7]. The Tm^{3+}/Ho^{3+} co-doped system has been proved as a suitable and powerful system for 2 μm laser output. On the one hand, Tm^{3+}, regarded as a sensitizer, can effectively transfer energy from commercially available pump source to Ho^{3+} via the energy transfer between adjacent Tm^{3+}: $^3F_4$ and Ho^{3+}: $^5I_7$ energy levels. On the other hand, Tm^{3+} has a emission peak at the center wavelength 1.8 μm and Ho^{3+} has a strong emission peak at the center wavelength of 2.0 μm [8]. Thus, Tm^{3+}/Ho^{3+} co-doped glass is expected to obtain 2.0 μm broadband fluorescence.

To obtain a high-efficient mid-infrared emission, the choice of host material is as significant as the selection of rare earth ions. At present, there are many 2.0 μm laser output materials, such as crystals and glasses [9–11]. Compared with crystal materials, the glass materials exhibit more advantages, such as short producing period, easy preparation, and controllable physical properties [12–17]. Recent years, Tm^{3+}/Ho^{3+} co-doped in various glass systems have been investigated, including tellurite, fluoride, fluorophosphate, silicate and germanate glasses [18–23]. According to previous studies, fluoride glass has always been unable to overcome the shortcomings, such as poor chemical stability and mechanical strength, resulting in the difficulties of its further applications [21]. In addition, fluorophosphate glass is not

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conducive to their application due to its high phonon energy and narrow transmission range [22]. Although silicate glass has considerable advantages such as high mechanical strength and chemical stability which makes it the most universal matrix material, high phonon energy of silicate glass limits its luminescent efficiency [18]. It worth mentioning that germanate glass is considered as one of the promising materials ascribed to its optical properties and moderate phonon energy [23]. However, heavy metal glass including germanate and tellurite glasses are more expensive so that it is unsuitable for large-scale development. As we expected, silicate-germanate glass system, the combination of silicate glass and germanate glass, have been reported to possess high chemical stability and moderate phonon energy, which is more suitable as a mid-infrared fiber glass choice [24]. Up to now, few attempts have been made to investigate on the 2.0 μm emission in Tm^{3+}/Ho^{3+} co-doped silicate-germanate glass pumped by a conventional 808 nm LD and the corresponding energy transfer process.

In this work, we reported the Tm^{3+}/Ho^{3+} co-doped silicate-germanate glasses prepared by conventional melt-quenching technique to enhance optical properties. The density, differential scanning calorimetry (DSC), absorption spectra, and fluorescence spectra of prepared glasses have been investigated. The energy levels and energy transfer processes have been discussed in detail.

2. Experimental

In this study, the host glass samples are composed (in mol%) of $30SiO_2$-$30GeO_2$-$8CaCO_3$-$12Li_2CO_3$-$5Nb_2O_5$-15BaO. Meanwhile, 1 mol% Ho_2O_3 and X mol% Tm_2O_3 (where X = 0.25, 0.5, 0.75, 1.5) were added to the prepared samples, which is denoted as SGHT1, SGHT2, SGHT3 and SGHT4, respectively. Besides, 1.5 mol% Tm_2O_3 and no rare earth ion doped glass samples are marked as SGT and SG. Analytical reagent SiO_2, GeO_2, $CaCO_3$, Li_2CO_3, Nb_2O_5, BaO and 4 N purity grade Tm_2O_3, Ho_2O_3 have been used to prepare the batches. After weighing and grinding, batches of raw materials in alumina crucible with ceramic lid have been melted by conventional melting quenching method at 1450 °C for 30 min and then poured the molten liquid onto a preheated 500 °C steel plate. The resultant glasses have been annealed in a preheated annealing furnace for 3 h and cooled down slowly to the room temperature to remove their inner stress. All annealed samples were fabricated and polished to the size of 10 mm × 10 mm × 1.5 mm for spectroscopic measurements.

The density of the samples was measured using Archimedes' water-immersion method on an analytical balance. The characteristic temperatures (temperature of glass transition T_g and onset crystallization peak T_x) of samples were measured with NETZSCH DTA 404 PC differential scanning calorimeter. The absorption spectra of glass samples were determined by Lambda 900UV–VIS-NIR spectrophotometer in the range of 400–2200 nm. Fluorescence spectra were recorded using a computer controlled Triax 320 type spectrometer within the wavelength range of 1600–2200 nm. All the measurements were carried out at room temperature.

3. Result and discussion

3.1. Thermal stability

As is known to us all, the characteristic temperatures containing temperatures of glass transition T_g, onset crystallization T_x and their difference (ΔT) mainly play a vital role in the thermal stability of glasses. Fig. 1 showed the characteristic temperatures of the prepared glass. It could be seen from Table 1 that the present silicate-germanate glasses possessed a larger T_g, T_x and ΔT than those in other glass systems, which indicated this system was beneficial to the drawing of optical fibers [25] and had a better thermal stability to resist thermal damage [26].

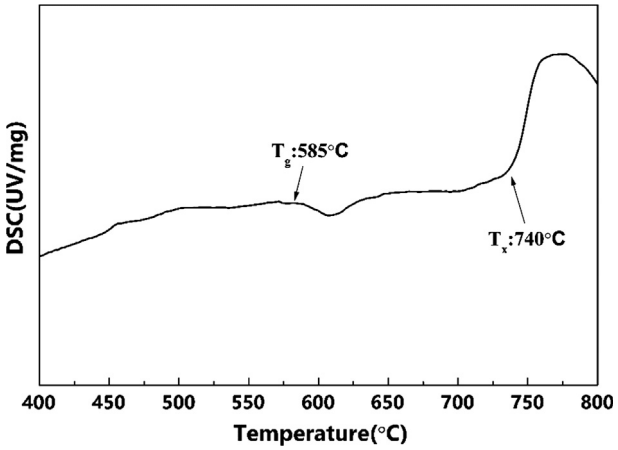

Fig. 1. DSC curve of silicate-germanate glass.

Table 1
Characteristic temperatures of different glasses.

Sample	T_g (°C)	T_x (°C)	ΔT (°C)	References
Silicate-germanate glass	585	740	155	This work
Fluorophosphate glass	418	530	112	[27]
Germanate glass	563	686	123	[6]
Fluoride glass	332	408	76	[28]
Tellurite glass	333	440	107	[29]

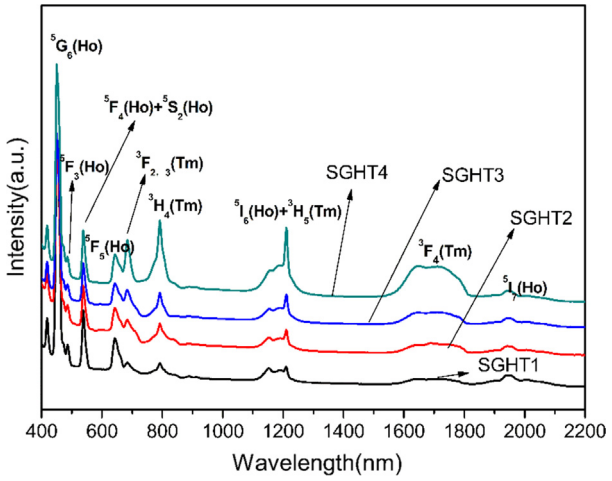

Fig. 2. Absorption spectra of Tm^{3+}/Ho^{3+} co-doped silicate-germanate glasses with various concentration of Tm^{3+} ion.

3.2. Absorption spectra

Fig. 2 showed the optical absorption spectra of Tm^{3+}/Ho^{3+} co-doped silicate-germanate glass samples in the wavelength range from 400 nm to 2200 nm, whose results were same to previous Tm^{3+}/Ho^{3+} co-doped other hosts [30,31]. The absorption bands corresponding to the transitions started from the $^3H_6$ ground state to the higher states $^3F_4$, $^3H_5$, $^3H_4$, ($^3F_2$, $^3F_3$), the absorption peaks of these energy levels were centered at the wavelengths of 1700, 1208, 791 and 684 nm, respectively. The absorption peaks appearing at 1946, 1152, 640, 538, 482 and 450 nm corresponded to the energy transitions of Ho^{3+} from the $^5I_8$ ground state to higher states of $^5I_7$, $^5I_6$, $^5F_5$, ($^5F_4$, $^5S_2$), $^5F_3$ and $^5G_6$. It can be observed that the absorption peak at 800 nm corresponded to the transition of Tm^{3+} ion from $^3H_6$ ground state to $^3H_4$ state, which indicated it could be pumped by commercially available 808 nm laser diodes. Few apparent changes of absorption peak position