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Infrared fluorescence, energy transfer process and quantitative analysis of thulium-doped niobium silicate-germanate glass

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HIGHLIGHTS

- Tm^{3+}-doped novel niobium silicate-germanate glasses were prepared.
- Studied glass system has a good thermal stability.
- Judd-Ofelt analysis and spectroscopic properties were carried out.
- The value of emission cross-section can reach 12.2×10^{-21} cm^2.

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ABSTRACT

Infrared fluorescence, energy transfer process, thermal stability and quantitative analysis of Tm^{3+} doped novel niobium silicate-germanate glasses have been investigated. The thermal stability changes indicate that the introduction of La_2O_3 to substitute for Nb_2O_5 can improve the anti-crystallization of present glass system. Intense 1.8 μm fluorescence has been achieved and the value of emission cross section can reach as high as 12.2×10^{-21} cm^2. Besides, the microparameters of energy transfer were analyzed by the extended overlap integral method. Hence, the results indicate that the excellent spectroscopic characteristics of this kind of silicate-germanate glass together with the good thermal properties may become a promising matrix applied for 1.8 μm band near-infrared laser.

1. Introduction

Over the past several years, fiber lasers operating in the 2 μm wavelength region have been attracting more and more attentions, due to their wide potential applications in eye-safe laser surgery, remote chemical sensing, coherent laser radar, and laser imaging, et al. [1–4]. Therefore, considerable efforts have been devoted to the development of 2 μm laser activated by Ho^{3+} or Tm^{3+}, because the laser around 2 μm can be obtained from the $Tm^{3+}{:}^3F_4 \rightarrow {}^3H_6$ transition and $Ho^{3+}{:}^5I_7 \rightarrow {}^5I_8$ transition, respectively. Compared with Ho^{3+}, Tm^{3+} is a favorable ion to achieve 2 μm emission for its high quantum efficiency, which is resulted from the cross relaxation energy transfer [5], strong absorption band around 800 nm, corresponding to commercial laser diode (LD), and broad gain bandwidth for tunable lasers [6]. In fact, diode-pumped Tm^{3+} lasers near 1.8 μm have been successfully obtained in many crystal and glass host matrices [7,8]. Generally speaking, except sensitizer, the powerful infrared emissions generated from Tm^{3+} are also closely related to the host glasses. The host materials should have high solubility of the Tm^{3+} ions because of the energy cross-relaxation process among Tm^{3+} ions. So far, silica glasses [9], silicate glasses [10,11], germanate glasses [5,12], and tellurite glasses [13] doped with Tm^{3+} ions have been investigated by research. However, the maximum phonon energy of silica-based glass is high due to its defined structure [11]. The phonon energy of fluoride-based glass is low, but it requires a more complex fabrication route and has low mechanical strength which limits its applications. Also, practical applications in mid-infrared tellurite-based glass are restricted due to its strong upconversion, and low laser damage threshold [8,14,15]. Tm^{3+}-doped germanate glasses have been intensively studied as one of the promising candidates in mid-infrared optical applications. However, the germanate glasses have expensive raw materials. As is well known, silicate glass has easy fabrication procedure, good thermal stability and wide glass forming region. But the phonon energy of silicate glass

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(~1100 cm^{-1}) is large. In order to compensate for deficiencies of silicate glass and germanate glass, we try to synthesize mixed glasses, silicate-germanate (SG) glasses. Introducing appropriate amount of GeO_2 into silicate glass can decrease phonon energy, which is able to avoid nonradiative decay for Tm^{3+} ions and enhance radiative transition rates. On the other hand, adding GeO_2 is beneficial for energy conservation due to its lower melting temperature than that of silicate glass. Additionally, the GeO_2 and Nb_2O_5 are chosen as key component added in present glass system, because high refractive index (~1.99 and ~2.95, respectively) can increase the stimulated absorption and emission cross sections [16].

Hence, we selected niobium silicate-germanate glass with appropriate phonon energy as the studied host glass in this paper. Particular effort was devoted to thermal properties improvement of present glass by introducing La_2O_3 to substitute for Nb_2O_5. To our knowledge, La^{3+} doped host is less reported for ~2 μm radiations but investigations on enhancement of upconversion luminescence [17]. The effect of La_2O_3 introduction on thermal stability and 1.8 μm emission properties in Tm^{3+} doped niobium silicate-germanate glasses excited by a conventional 808 nm laser diode (LD) has been systematically investigated. Additionally, attention was paid to the OH^- content in this niobium silicate-germanate glass system. We investigated the absorption spectra, and then calculated the J-O intensity parameter Ω_t (t = 2, 4, 6), radiative parameters (such as spontaneous radiation transition probability A_{rad}, radiation lifetime τ_{rad}) of Tm^{3+} in present glass. The absorption (σ_{abs}) and emission cross section (σ_{em}) of Tm^{3+} at 1.8 μm have been evaluated. Moreover, the energy transfer mechanisms and micro-parameters of the energy transfer processes were investigated. All these results show that niobium silicate-germanate glasses have high thermal stability and excellent spectroscopic properties, which is a promising host material applied for near-infrared laser.

2. Experimental

The glass samples with the composition of $44SiO_2$ - $10GeO_2$ - 20CaO - $(5 - x)Nb_2O_5$ - xLa_2O_3 - $15K_2CO_3$ -$5Na_2CO_3$ -$1Tm_2O_3$ (x = 0, 2, 4 mol%) were prepared by the conventional high temperature melt-quenching method, which are denoted as SGL0, SGL2, SGL4, respectively. The samples were prepared from high purity (⩽99.99%) raw materials of SiO_2, GeO_2, CaO, Nb_2O_5, K_2CO_3, Na_2CO_3, La_2O_3 and Tm_2O_3. Each batch of 25 g was weighted and separately mixed well. The well mixed batches were melted in platinum crucibles at 1400 °C for 1 h. Then the melts were cast into a preheated steel plate and annealed at around 520 °C for 2 h to remove internal stresses before they were cooled slowly with the furnace to room temperature. All the annealed glass samples were cut and polished to the same size of 15 mm × 15 mm × 1.5 mm for the optical property measurements, whereas others were cut and polished for refractive index measurements.

The refractive index n_d at 632.8 nm of the samples were measured by the prism minimum deviation method. The density was measured by the Archimedes method. The n_d values for SGL0, SGL2 and SGL4 are 1.60, 1.61 and 1.67, respectively. The characteristic temperatures of prepared samples were characterized using a Netzsch STA 449/C differential scanning calorimetry (DSC) at a heating rate of 10 K/min. The absorption spectra of the rare earth ions doped samples were recorded with a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrophotometer in the range of 300–2000 nm at room temperature. IR transmittance spectrum was measured using a Vector-33 FTIR spectrophotometer (Bruker, Switzerland) with a 1 cm^{-1} resolution. The fluorescence spectra in the range of 1600–2000 nm were measured by a combined fluorescence lifetime and steady state spectrometer (FLSP920, Edingburg Co. England), which was detected with a liquid-nitrogen cooled PbS detector. The pump resource is 808 nm LD. For the fluorescence lifetime measurements, the instrument applied was an HP 546800B 100-MHZ oscilloscope with light pulse of the 808 nm LD. All experiments were carried out at room temperature.

3. Results and discussion

3.1. Anti-crystallization ability

The temperature of glass transition T_g and temperature of onset crystallization peak T_x were determined by DSC using Netzsch STA 449/C. The ΔT ($\Delta T = T_x - T_g$) defined as the temperature gap between T_g and T_x. ΔT has been frequently quoted as a rough criterion to measure thermal stability and forming ability of glass, the larger ΔT means the better inhibition of crystallization and nucleation process [18,19]. It is desirable for a glass to have ΔT as large as possible. Since fiber drawing is a reheating process, and any crystallization during reheating process will enhance the scatting loss of the fiber. Usually, ΔT should be more than 120 °C to minimize probability of crystallization during the drawing process [20]. Additional, Hruby developed the glass formation factor of the materials, which is given by $k_{gl} = (T_x - T_g)/(T_m - T_g)$, T_m is the melting temperature of glass. The parameter K_{gl} is more suitable for estimating the thermal stability of glass than ΔT. The large the K_{gl} is, the strong the glass forming stability possesses.

The characteristic temperature parameters of the analyzed glasses, as well as thermal stability parameters (ΔT, K_{gl}) in various glass systems are listed in Table 1. As shown in Table 1, it can find that no outset crystallization peak of SGL4 is apparent, indicating its good thermal stability [21]. In addition, the glass transition temperature (T_g) increases from 523 °C to 697 °C, which indicates that the introduction of La_2O_3 to substitute for Nb_2O_5 can improve the thermal stability of this niobium silicate-germanate glass system. As a result of comparing with Nb^{5+}, La^{3+} has larger molecular ratio and coordination number. The T_g is an important factor for laser materials, high T_g (697 °C) makes glass good thermal stability to resist thermal damage at high pumping intensity. The ΔT and K_{gl} of SGL0 and SGL2 glass samples are 122 °C, 134 °C, and 0.145, 0.181, respectively, which is much larger than that of the fluoride glass (76 °C, 0.133) [22] and germanate (113 °C, 0.142) [23]. Compared with the characteristic temperatures in Table 1, a conclusion can be drawn that the prepared silicate-glasses in this study prove a better thermal stability, which are good for crystal-free fiber drawing and fabrication.

3.2. Transmittance property

Fig. 1 presents the transmittance spectra of SGL0 and SGL2 glass samples in the wavelength range from 2500 nm to 5500 nm. The samples have good transparency in the range of 2.5–4.5 μm. As we all know, the typical absorption band near 3 μm is assigned to the stretching vibration of free OH^- groups, which strongly affects the lifetime of rare earth ions. And, it has been demonstrated OH^- play an important role of quenching centers in Tm^{3+} doped glass [24]. From Fig. 1, it can be seen that the maximum transmittance reaches as high as 90%, and the rest 10% loss is the Fresnel reflections dispersion and absorption of the glass sample. The IR cutoff wavelength, which is the transmission of light in a 1 mm thick sample is up to 10% [25]. The IR absorption cut-off edge of SGL2 glass sample extends to 4.8 μm, higher than that of fluorophosphate glass (4.5 μm) [26], which indicates that the investigated glass is a good kind of mid-IR material. Additionally, the absorption band around 4250 nm is owing to the CO_2 absorption.