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Mid-infrared luminescence and energy transfer of Tm^{3+} in silicate glasses by codoping with Yb^{3+} ions

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ABSTRACT

A kind of novel silicate glasses doped with Tm^{3+} sensitized by Yb^{3+} were prepared by conventional melt quenching method. The optical properties of the synthesized glasses were theoretically and experimentally investigated. Based on the absorption spectra and the Judd-Ofelt theory, the J-O intensity parameters (Ω_t), radiative transition probability (400.4 s^{-1}), fluorescence lifetime (4.99 ms) and absorption and emission cross sections ($\sigma_e = 2.51 \times 10^{-20}$ cm^2) were calculated. According to fluorescence spectra, the 1.8 μm emission of Tm^{3+} could be greatly enhanced by adding proper amount of Yb^{3+} under the excitation of 980 nm and the optimized concentration ratio of Tm^{3+} and Yb^{3+} was found to be 1:3 in the present silicate glass system. Besides, the energy transfer mechanism between Yb^{3+} and Tm^{3+} were thoroughly discussed. With the assistance of Yb^{3+}, the lifetime of Tm^{3+} from 0.54 ms increased to 1.42 ms. The energy transfer efficiency from Yb^{3+} to Tm^{3+} could reach 90.94%, and the energy transfer coefficient was 5.43×10^{-41} cm^6/s. The content of OH^- was measured. The above results showed that Tm^{3+}/Yb^{3+} codoping could be expected to a promising way to achieve high efficient 2 μm lasing pumped by a 980 nm LD.

1. Introduction

Solid state lasers in mid-infrared spectral region have numerous potential applications including eye-safe radar, high-resolution molecular spectroscopy, biomedical systems, remote sensing and so forth [1–3]. As we all know, rare earth ions Tm^{3+} and Ho^{3+} are the perfect candidates for 2 μm lasers owing to the energy level transition of $^3F_4 \rightarrow {}^3H_6$ (Tm^{3+}) and $^5I_7 \rightarrow {}^5I_8$ (Ho^{3+}). Compared with Ho^{3+}, the absorption peak of Tm^{3+} is around 800 nm, thus it can be pumped by a commercial 808 nm laser diode (LD) directly. Besides, the so called 'two-for-one' cross relaxation process may occur, which means two Tm^{3+} ions are pumped to the $^3F_4$ level by one pump photon with a 200% pumping quantum efficiency [4]. The emission bandwidth of Tm^{3+} is wider than that of Ho^{3+} in 2 μm spectral region therefore it is beneficial to produce shorter laser pulses [5]. Nevertheless, when excited by a commercially high power 808 nm LD the absorption peak of the Tm^{3+} ($^3H_6 \rightarrow {}^3H_4$ transition) is shorter and the absorption efficiency is lower, which is harmful to emit 2 μm lasers [4]. Yb^{3+} owns higher absorption cross section that can efficiently absorb the excitation emitting from commercial 980 nm LD and then transfer energy to Tm^{3+} ($^3H_5$ level) via a nonresonant energy transfer process [6]. The optimization of Yb^{3+} and Tm^{3+} doping concentration is also significant to further enhance 1.8 μm emission of Tm^{3+}.

Heavy metal oxide glasses exhibit a great deal of advantages such as lower maximum phonon energy, higher rare earth ions solubility and easy fabrication [4,7,8]. The Tm^{3+} doped and Er^{3+} doped tellurium germanate glass and its double-cladding fiber for 2 μm laser have been published [9,10]. Fluoride glass have developed rapidly depending on the low phonon energy, high doping level, low viscosity, and wide transparency from UV to IR [11]. But the cost and mechanical behavior limit the further development of the above matrix. However, silicate glasses have excellent thermal stability against crystallization and higher glass transition temperature and stable physical chemical properties [6,12]. Above all, it can be easily drawn into the fibers and the slope efficiency is much higher than that in other glass fibers [13]. Up to the present, watt-level 1.8 μm laser output in Tm^{3+} doped silicate glass fiber has been demonstrated [14]. In recent, large-mode-area single-mode-output silicate glass in all-solid photonic crystal fiber has been achieved [15]. In commercial, 2 μm single frequency and Q-switched fiber laser products have been produced by Advalue Photonics Company. As a traditional glass matrix, silicate still has a place in fiber laser field.

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Snitzer E. through a large number of experiments found that alkali metal-alkaline earth metal silicate glass was the most suitable candidate for laser glass [16]. Currently, the most widely used system is K_2O-BaO-SiO_2, R_2O-CaO-SiO_2 and Li_2O-MgO/CaO-Al_2O_3-SiO_2. The properties of Er^{3+}/Ho^{3+}, Er^{3+}/Tm^{3+}, Tm^{3+}/Ho^{3+} co-doped silicate glass are investigated based on these systems [17–20]. In this work, the advantages of alkali metal and alkaline-earth metal are combined. According to our earlier reports [21–23], it is proved that this matrix is suitable for 2 μm laser emission. In this work, Al^{3+} obtain non-bridging oxygen to form [AlO_4], which are able to enter silica-oxygen net thereby made the structure closely. CaO and BaO can be used to polarize non-bridging oxygen and weaken silicone bond, which can reduce viscosity of the host glass. La_2O_3 improve chemical stability and reduce the coefficient of thermal expansion. BaF_2 and CaF_2 are introduced into the glasses to reduce the content of hydroxyl group, which can weaken the emission. Furthermore, in the process of drawing fiber, fluoride can decrease the melt temperature and improve the solutions of rare earth ions availably [24]. According to our knowledge, in recent years, there have been many reports on Tm^{3+}/Yb^{3+} co-doped luminescent materials [25–29], but limited by the efficiency of energy transfer, the slope efficiency and output power are low and thermally damage cannot be avoided. There are few systematic studies focused on 1.8 μm emissions in Tm^{3+}/Yb^{3+} co-doped silicate glasses [30]. The theoretical study of the optical parameters of Tm^{3+} are compared with the experimental results and the effects of Yb^{3+} concentration on the spectroscopic properties of silicate glasses doped Tm^{3+} are discussed. The energy transfer process and the coefficients are analyzed by the extended spectral overlap method in detail.

2. Experimental details

Silicate glasses with the molar compositions of (98-x)(SiO_2-Al_2O_3-CaO-CaF_2-BaO -BaF_2-La_2O_3)-1Tm_2O_3-xYb_2O_3 (x = 0, 1, 2, 3, 4) had been denoted as STY-x. 20 g of the raw materials had been weighted and well mixed, then melted in a platinum crucible at the temperature about 1400 °C for 60 min. The melts had been poured onto a preheated (600 °C) stainless steel plate then further annealed at 600 °C for 4 h, after they had been cooled to room temperature (A large number of experimental results show that when melting temperature is 1350 °C, the glass is not melted completely, limited by equipment requirements the temperature cannot exceed 1450 °C. When annealed under 650 °C, there are crystalline in glass). The cooled samples had been cut and polished to the size of 20 × 20 × 1.5 mm^3 carefully, prepared for the optical property measurements.

The densities (3.58 g/cm^3) had been measured by Archimedes drainage method, refractive index (1.623) had been measured by using a Metricon Model 2010/M Prism Coupler. The absorption spectra had been recorded with a Perkin-Elmer Lambda 900UV/VIS/NIR spectrophotometer from 400 nm to 2100 nm. The emission spectra and the fluorescence decay curves had been obtained using an FLSP 920 instrument (Edinburgh instruments Ltd., UK) with a 980 nm LD as an excitation source. All the measurements had been performed at room temperature.

3. Results and discussion

3.1. Absorption spectra and Judd-Ofelt theory analysis

The absorption spectra of Tm^{3+} doped and Tm^{3+}/Yb^{3+} co-doped silicate glass samples over the wavelength region of 400–2000 nm are presented in Fig. 1. The five absorption bands of Tm^{3+} centered around 460, 681, 790, 1210, and 1700 nm corresponds with the ground state ($^3H_6$) to excited states ($^1G_4$, $^3F_{2,3}$, $^3H_4$, $^3H_5$, and $^3F_4$) respectively. In the view of the strong intrinsic absorption band gap in the host glass, energy levels before $^1G_4$ level are not identified totally.

For rare earth ions doped glasses, crystals and ceramics, the Judd-Ofelt (J-O) theory [31,32] plays vital role in analyzing the spectroscopic properties (intensity parameters Ω_t, spontaneous emission probabilities, radiative lifetimes, fluorescence branching ratios and so on). As a part of the J-O theory, the intensity parameters Ω_t (t = 2, 4, 6) are calculated making use of the absorption value according to the procedure measured above [33].

Table 1 lists the parameters acquired from STY-3 sample and the comparison with other glass hosts. It is shown that Ω_2 in the STY-3 glass is the largest, indicating that in this matrix there are stronger covalent bond between Tm^{3+} and O^{2-} ions and lower symmetry of the coordination structure surrounding the Tm^{3+} ions [34,35]. The value of Ω_4/Ω_6 determines the spectroscopy quality of the host materials [36].

According to the intensity parameters obtained from J-O theory, the radiative properties can be worked out by the expressions illustrated in the literature and the results are shown in Table 2 [6,33]. It is seen that the spontaneous emission probability of the Tm^{3+}:$^3F_4 \rightarrow {}^3H_6$ transition is 400.4 s^{-1}, which is much larger than that in sodium aluminophosphate glass (106.2 s^{-1}) [37], Oxyfluoride glass (127.23 s^{-1}) [35]. Since A is related to the refractive index, higher A can provide more opportunities to obtain 2 μm laser [38].

3.2. Fluorescence spectra and energy transfer mechanism between Yb^{3+} and Tm^{3+}

The fluorescence spectra of STY-x glasses pumped by 980 nm LD are illustrated in Fig. 2(a). We can found that there is no fluorescence in Tm^{3+} singly doped glass, while a group of emission band near 1.8 μm emitted from the Tm^{3+} comes out with the assistance of Yb_2O_3. This confirms the lack of absorption band near 976 nm for Tm^{3+} and the existence of energy transfer from Yb^{3+} to Tm^{3+}. Besides, with the adding of the Yb_2O_3 concentration, the fluorescence intensity of Tm^{3+} increases at the same time, which can be accounted for shortening the distance between Yb^{3+} and Tm^{3+} to raise the energy transfer probability from Yb^{3+} to Tm^{3+}. Once the concentration of Yb_2O_3 reaches the maximum value of 3 mol%, when increase the Yb_2O_3 concentration further, the fluorescence intensity will be weaken by concentration quenching or other dif-

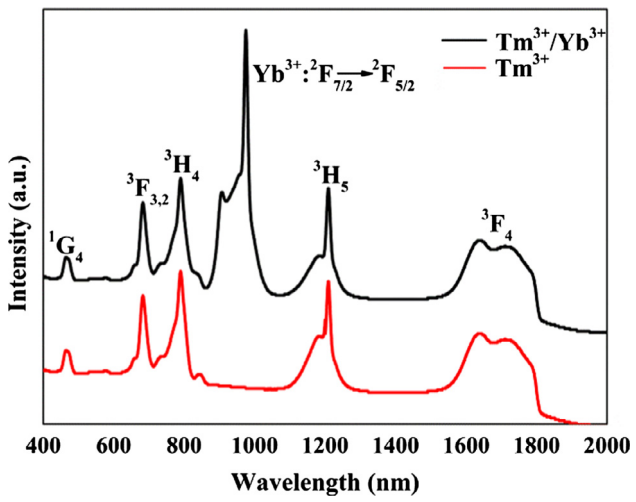

Fig. 1. The absorption spectra of Tm^{3+} doped and Tm^{3+}/Yb^{3+} co-doped silicate glasses.