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Spectroscopic properties and energy transfer study of Nd^{3+}/Yb^{3+} co-doped in borosilicate glass for 1.0 μm emission

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ABSTRACT

The Nd^{3+}/Yb^{3+} co-doped borosilicate glasses are fabricated by using a conventional melt quenching technique in air atmosphere. The Spectroscopic properties of 1.0 μm emission in Nd^{3+}/Yb^{3+} co-doped borosilicate glasses are investigated under 808 nm excitation. The luminescence decay curves show a nonexponential character, the energy transfer microscopic parameters and transfer efficiencies are calculated. Results indicate that the energy transfer takes place via nonradiative electric dipole–dipole processes and is enhanced with the concentration of Nd^{3+} donor ions. The glass co-doped with 0.5 mol% Nd_2O_3 and 2 mol% Yb_2O_3 has a large microscopic parameters 100×10^{-40} $cm^6 s^{-1}$, high transfer efficiencies 73.58% and long fluorescence lifetime 0.3 ms at 1020 nm, which is of great potential as a candidate material in the development of multiple-pump-channel Yb^{3+} fiber lasers.

1. Introduction

Lasers and amplifiers built from fibers doped with rare earth ion have been carried out over the last 40 years. To date, the Nd^{3+} and Yb^{3+} ion are the most popular as the main dopant for a development of high power lasers, tunable lasers and luminescent solar concentrators in the near infrared range [1–3]. The Yb^{3+} has the advantage of avoiding upconversion, cross-relaxation, and excited-state absorption processes, which is due to its unique energy level structure, only the ground state $^2F_{7/2}$ and excited state $^2F_{5/2}$, and the energy interval is about 10,000 cm^{-1} [4,5]. On the contrary, the Nd^{3+} ion has a large number of excited states with high absorption probabilities [5]. When the Nd^{3+} ion is excited to any upper level, a fast nonradiative relaxation to the lower $^4F_{3/2}$ emitting level occured, and the overlap between the Nd^{3+} emission band of $^4F_{3/2} \rightarrow {}^4I_{11/2}$, $^4I_{9/2}$ and the Yb^{3+} absorption band of $^2F_{7/2} \rightarrow {}^2F_{5/2}$ may increase the population of the $^2F_{5/2}$ Yb^{3+} excited level via Nd^{3+}/Yb^{3+} energy transfer processes [6,7].

Among various glasses, borosilicate glass is an attractive host matrix for Yb^{3+}, because of its own benefits such as stable physical and chemical properties, low cost, high UV transparency, strong thermal resistance and small thermal expansion coefficient [8,9].

The energy transfer between Nd^{3+}/Yb^{3+} co-doped borosilicate glass system, the Nd^{3+} and Yb^{3+} ions play a role as sensitizer and activator, respectively. Because of the Nd^{3+} transition of $^4I_{9/2} \rightarrow {}^2H_{9/2}$, $^4F_{5/2}$ has higher energy than the $^2F_{5/2}$ of Yb^{3+} excited state, the excitation light source can use the AlGaAs laser diode instead of the typical InGaAs laser, making the Nd^{3+}/Yb^{3+} co-doped system more attractive.

In this work, the spectroscopy properties of 1.0 μm emission in Nd^{3+}/Yb^{3+} co-doped borosilicate glasses are investigated systematically under 808 nm excitation. The luminescence decay curves and energy transfer characterization of borosilicate glasses co-doped with different concentrations of Nd^{3+} and Yb^{3+} ions have been carried out to determine their capabilities of being used as a multiple pump channel laser. The excited state absorption and emission cross section of selective transition are obtained based on the Fuchbauer–Ladenburg formula and absorption spectra measurement. Besides, the energy transfer microscopic parameter and transfer efficiencies have been calculated by using the Dexter theories.

2. Experimental

The Nd^{3+}/Yb^{3+} co-doped borosilicate glasses are fabricated by using a conventional melt quenching technique in air atmosphere, with the following molar composition: $(60\text{-}a\text{-}b)SiO_2$–$20B_2O_3$–$1Al_2O_3$–$14Li_2O$–$5MgO$–$aNd_2O_3$–$bYb_2O_3$ (with $a=0$, 0.25, 0.5,1 and $b=0$, 2). Molar compositions and labels of the samples can be seen in Table 1.

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Table 1
Glass composition and labels.

Glass composition (mol%)	Label
$59SiO_2$–$20B_2O_3$–$1Al_2O_3$–$14Li_2O$–$5MgO$–$0.25Nd_2O_3$	Nd0.25
$59SiO_2$–$20B_2O_3$–$1Al_2O_3$–$14Li_2O$–$5MgO$–$0.5Nd_2O_3$	Nd0.5
$59SiO_2$–$20B_2O_3$–$1Al_2O_3$–$14Li_2O$–$5MgO$–$1Nd_2O$	Nd1
$58SiO_2$–$20B_2O_3$–$1Al_2O_3$–$14Li_2O$–$5MgO$–$2Yb_2O_3$	Yb2
$57SiO_2$–$20B_2O_3$–$1Al_2O_3$–$14Li_2O$–$5MgO$–$0.25Nd_2O_3$–$2Yb_2O_3$	Nd0.25Yb2
$57SiO_2$–$20B_2O_3$–$1Al_2O_3$–$14Li_2O$–$5MgO$–$0.5Nd_2O_3$–$2Yb_2O_3$	Nd0.5Yb2
$57SiO_2$–$20B_2O_3$–$1Al_2O_3$–$14Li_2O$–$5MgO$–$1Nd_2O_3$–$2Yb_2O_3$	Nd1Yb2

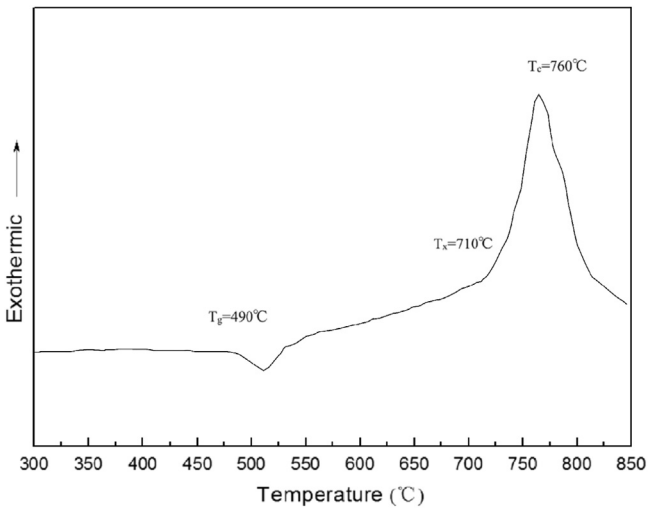

Fig. 1. DTA curve of the borosilicate host glass glass ($\Delta T/\Delta t = 10$ °C/min).

Reagent grade commercial oxides (> 99.5% pure) are used as the raw materials, and the rare earth oxides Nd_2O_3, Yb_2O_3 (> 99.9% pure) are introduced to the batch as the dopant. Mixed batch is well homogenization by grinding in an agate mortar with a pestle, then put into a platinum crucible, and melted in an electric furnace at around 1350 ± 10 °C for 2 h. The glass samples are formed by casting molding and finally annealed at 480 °C for 10 h to remove thermal strains. The samples are cut and polished to achieve a very smooth surface for optical and spectroscopic properties test. The density of the samples are determined by the Archimedes' method with water as the immersion liquid. The refractive index is measured on an Abbe refractometer at a sodium wavelength (589.3 nm). Differential thermal analysis (DTA) is performed using a SETARAM TAG24 analyser. The absorption spectrum is recorded using a spectrophotometer (Perkin-Elmer Lambda9). The near-infrared emission spectra and luminescence lifetime are measured by exciting the samples at 808 nm laser diode ($P_{pump} = 1$ W). All the spectroscopic measurements are performed at room temperature.

3. Results and discussion

3.1. Thermal properties

The thermal behavior of the borosilicate host glass is measured using DTA. About 15 mg powders are placed in a alundum crucible and a heating rate of 10 °C/min is fixed from room temperature up to 800 °C under nitrogen atmosphere. Fig. 1 shows the DTA curve of the studied glass. The first endothermic peak is observed which corresponds to the glass transition, and the first exothermic peak is due to the crystallization process (temperature of glass

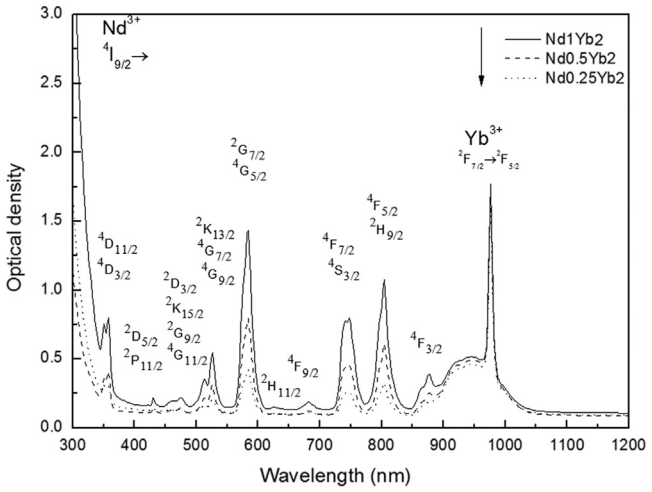

Fig. 2. Room temperature absorption spectrum in the range from 300 to 1200 nm of the Nd^{3+}/Yb^{3+} co-doped borosilicate glasses.

transition T_g, temperature of onset crystallization T_x and temperature of peak crystallization T_c). For this glass, the difference between these two temperatures ($\Delta T = T_x - Tg$) is 220 °C, which is related to the thermal stability of the glass. Generally, the ΔT of the glass sample should be higher than 100 °C to obtain a wide operating temperature range and to avoid crystallization during fiber drawing [10,11].

3.2. Absorption and Judd–Ofelt analysis

The room temperature absorption spectrum of the borosilicate glasses co-doped with 0.25 mol% Nd^{3+} 2 mol% Yb^{3+}, 0.5 mol% Nd^{3+} 2 mol% Yb^{3+},1 mol% Nd^{3+} 2 mol% Yb^{3+} in the wavelength region of 300–2000 nm are given in Fig. 2. The corresponding absorption bands of Nd^{3+} and Yb^{3+} are labeled in the figure, respectively. It can be seen that the absorption bands of Nd^{3+} are associated with transitions starting from the $^4I_{9/2}$ ground state to the excited multiplets, except for the unique Yb^{3+} absorption band corresponding to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition centered at 975 nm. Obviously, the co-doped sample does not change the level positions and the shapes of the absorption bands when compared with the singly doped one. It is similar to the spectra of the other samples, with the areas of the transition bands as a function of the Nd^{3+} and Yb^{3+} concentrations. On the basis of these data it can be concluded that Nd^{3+} and Yb^{3+} ions are introduced into the borosilicate glass network not gathered at the local ligand field. Furthermore, for the glass sample co-doped with 1 mol% Nd^{3+} 2 mol% Yb^{3+}, a strong absorption band of 800 nm ($^2I_{9/2} \rightarrow {}^4F_{5/2}$, $^2H_{9/2}$) can be observed and thereby the Nd^{3+}/Yb^{3+} doped sample glass can be excited by 808 nm LD.

On the basis of the ground state absorption of three samples singly doped with Nd^{3+} (0.25, 0.5, and 1 mol%), the Judd–Ofelt intensity parameters and oscillator strengths of the Nd^{3+} doped glasses can be evaluated via the Judd–Ofelt formalism. These parameters are obtained by solving a system of equations from the five main absorption bands, as shown in Table 2, in which the experimental and calculated oscillator strengths of these bands are compared.

According to previous studies, the value of Ω_2 reflects the symmetry of the glass while the values of Ω_4 and Ω_6 give an indication for the overall intensity of the spectral transition [8,12]. The obtained values of the Judd–Ofelt intensity parameters Ω_t ($t = 2$, 4, and 6) are listed in Table 3, with average values of $\Omega_2 = 4.88 \times 10^{-20}$, $\Omega_4 = 5.16 \times 10^{-20}$, and $\Omega_6 = 9.5 \times 10^{-20}$ cm^2. These values are higher than in most fluorophosphate, chalcogenide and tellurite