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Ho^{3+}/Tm^{3+} codoped lead silicate glass for 2 μm laser materials

Ning Wang, Ruijie Cao, Muzhi Cai, Lingling Shen, Ying Tian, Feifei Huang, Shiqing Xu, Junjie Zhang *

College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, China

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ABSTRACT

The mid-infrared emission of low phonon (963 cm^{-1}) lead silicate glass system with Ho^{3+}/Tm^{3+} co-doped has been investigated. Luminescence at ~2.1 μm corresponding to $^5I_7 \rightarrow {}^5I_8$ transition in holmium was obtained by energy transfer between Tm^{3+} and Ho^{3+} ions. Energy transfer mechanism between them was analyzed. And the highest value of the luminescence intensity was obtained in glass co-doped with $1Tm_2O_3/0.3Ho_2O_3$. The full width at half maximum of the (Ho^{3+}/Tm^{3+}) emission reached to 350 nm in $1Tm_2O_3/0.1Ho_2O_3$ sample. Absorption and emission cross section have also been calculated and analyzed. The maximum emission cross section was 3.9×10^{-21} cm^2 around 2.0 μm. And when P > 0.4, a positive gain can be obtained at wavelengths >1941 nm. Results demonstrated that the prepared Ho^{3+}/Tm^{3+} co-doped lead silicate glasses have excellent spectroscopic properties in mid-infrared wavelengths and can obtain high gain in fiber lasers.

1. Introduction

Powerful and highly efficient fiber lasers at 2 μm region have shown promise as tools for a variety tasks in scientific and technical, such as precision medical laser surgery, eye-safe atmospheric sensing. Moreover, the laser operating in ultrafast pulse regime can also be devoted to time-resolved spectroscopy and as pumping source for the optical parametric oscillator (OPO) in the longer mid-IR regions [1–4].

The transitions of Tm^{3+}: $^3F_4 \rightarrow {}^3H_6$ and Ho^{3+}: $^5I_7 \rightarrow {}^5I_8$ have a corresponding peak emission wavelength around 2.0 μm, respectively, which indicate they are suitable for providing 2.0 μm emissions in fiber. Thulium (Tm)-doped fiber laser is an ideal candidate to generate a near 2.0 μm luminescent center which exhibits high-power and high efficiency characteristics. The thulium fiber laser can be excited with commercial diode laser pump sources emitting at 0.79 μm, and its output has a wide spectrum of laser gain tuning from at least 1.86 μm to around 2.09 μm [5]. Cross-relaxation ('two-for-one' excitation) between neighboring Tm^{3+} cations is especially resonant in silicate glass and can nearly double the slope efficiency [6]. To further extend the wavelength beyond 2 μm for a series of applications including medicine, remote sensing and the generation of longer wavelengths using nonlinear optics, a simple, efficient, and robust source of high-power radiation is required [7]. The transition from $^5I_7$ to $^5I_8$ of Ho^{3+} has a peak emission wavelength at 2.1 μm. Besides, compared to Tm^{3+}, Ho^{3+} ion has longer fluorescent lifetime and higher stimulated emission cross [8,9]. Thus, Ho^{3+} is clearly a good choice. However, since Ho^{3+} ion is lack of a corresponding ground absorption band around 808 or 980 nm, it cannot be pumped directly by a readily commercial diode lasers pump sources. Generally, Tm^{3+} or Yb^{3+} ion, which can exploit the commercial diode-pump able absorption, is co-doped as a sensitizer for Ho^{3+} ion, thus making it possible to produce emission at 2.1 μm, accompanying with the transition from $^5I_7$ to $^5I_8$ [10]. The energy transfers from Tm^{3+} and Yb^{3+} to Ho^{3+} ion are schemed in Fig. 1. Notably for the Tm^{3+}/Ho^{3+} co-doped system, theoretically, the maximal quantum efficiency could be expected to 2 due to the cross relaxation (CR) of Tm^{3+} ions: $^3H_4+{}^3H_6 \rightarrow {}^3F_4+{}^3F_4$ [11]. It is worth nothing that there have some extrinsic defects in observed luminescence behavior of doped samples. Pumping at 808 nm using Tm^{3+} as the sensitizer would results in a large quantum defect and heat deposition for a 2 μm laser. The combination of large quantum defect heating and low emission quantum efficiency seems to produce a large heat load.

Literature sources mention that a number of Ho^{3+}/Tm^{3+} co-doped glass systems have obtained radiation emissions in the region of 2 μm. These include silicate [12], phosphate [13], germanate [14], tellurite [15] glasses and so on. The silicate and phosphate possess robust mechanical resistance and good thermal stability which are required in constructing high-power fiber lasers. Nevertheless, these two systems are characterized by a high probability of non-radiative transfers caused by high phonon energy (1100–1200 cm^{-1}) [16]. Because of that, an alternative glass of low vibrational frequency of bond oscillation is necessary. Germanate and tellurite glasses have the suitably lower phonon

* Corresponding author.
E-mail address: jjzhang@cjlu.edu.cn (J. Zhang).

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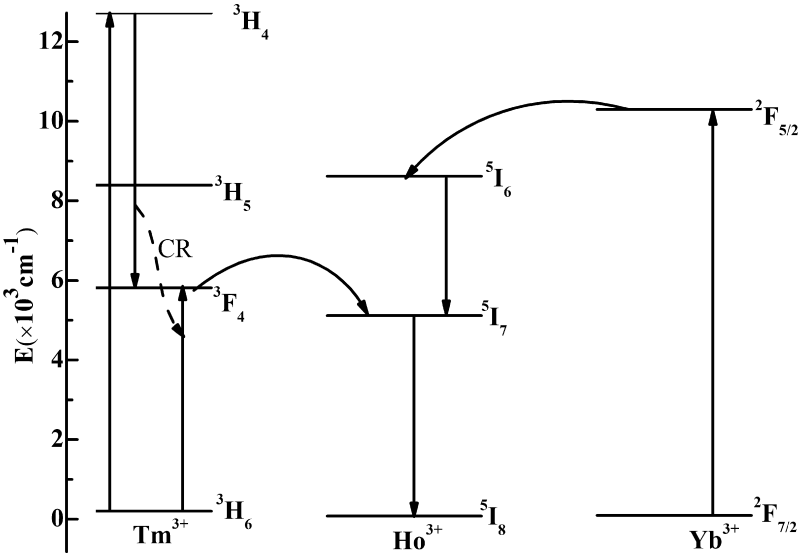

Fig. 1. Schematic of energy transfer from Tm^{3+} to Ho^{3+} ions and Yb^{3+} to Ho^{3+} ions.

energy that provides the necessarily high transmission of the fiber, and are capable of hosting relatively great quantities of activator ions [17]. However, in spite that germanate glasses also have good mechanical qualities, maximum phonon energies of 900 cm^{-1} [18,19], it tends to microscopic segregation, crystallization during fiber drawing. What's more, its raw materials are very high-cost. As for tellurite glasses, a consequence of weak structural bonds is a significantly lower mechanical strength which often makes it impossible to produce good quality optical fiber from them [15,20]. Silicate glasses remain to be the most successful fiber host materials. In order to further select a lower phonon energy as well as good thermal and mechanical parameters, we performed a composition of antimony-lead silicate glasses doped with Tm^{3+} and Ho^{3+} ions to obtain radiation emission of 1.7–2.2 μm.

2. Experiments

2.1. Glass syntheses

The glass system of (mol%) (100-x-y) (SiO_2 + PbO + Al_2O_3 + Na_2O + BaO + Sb_2O_3) doped with x mol% Tm_2O_3, y mol% Ho_2O_3 (where x = 0, 1; y = 0.1, 0.2, 0.3, 0.4) (where x = 0, 1; y = 0.1, 0.2, 0.3, 0.4) were melted in alumina crucible in Si-Mo resistance furnace in temperature of 1400 °C for 50 min. They were denoted as 0T-0.1H, 1T-0H, 1T-0.1H, 1T-0.2H, 1T-0.3H, 1T-0.4H, respectively. Analytical grades of SiO_2, Pb_3O_4, Al_2O_3, Na_2CO_3, $BaCO_3$, Sb_2O_5 and high purity (99.99%) Tm_2O_3 and Ho_2O_3 were used as the raw materials. Then the molten glasses were poured into the preheated stainless steel plate and exposed to the process of annealing in the temperature approximate to the transformation temperature (Tg) for 4 h. The annealed samples were finally cut and were polished with the dimensions of 10 × 10 × 1.2 mm^3 for determining spectral properties. The photograph of polished samples was showed in the insert of Fig. 3.

2.2. Measurements

The glass density was measured by using Archimedes' liquid-immersion method in distilled water. The refractive indexes were measured by the prism minimum deviation method at three wavelengths, 633, 1311 and 1539 nm (Mectricon Models 2010/M, Routine index resolution of ±0.0005). The Raman spectrum was performed on a Raman spectrometer (Renishaw inVia, space resolution <1 μm) with the excitation source of 532 nm. Characteristic temperatures were determined based on differential scanning calorimeter (DSC) measurements at the heating rate of 10 C/min performed using a NETZSCH DTA 404 PC differential scanning calorimeter. Absorption spectra measurements within the range from 300 to 2100 nm were taken using Perkin Elmer Lambda 900 UV/VIS/NIR double beam spectrophotometer (WalthamMA, resolution 0.1 nm). Fluorescence spectra of the samples were measured by a computer controlled FLS980 Spectrometer (Edinburgh Instruments, Highest Sensitivity >25,000:1 standard; >35,000:1 optional) with an 808 nm laser diode. TDS 3012C type Digital Phosphor Oscilloscope (100 MHz, 1.25GS/S) was used to measure and display the lifetime decay curves.

3. Results and discussion

3.1. Raman spectrum

The large nonradiative decay probability of excited rare earth ions by multi-phonon emission leads to low fluorescence quantum efficiency. For multi-phonon relaxation, one is predominantly interested in the highest frequency phonons in oxide glass. And the highest frequency phonons which are excited in the decay can be determined from Raman spectrum [21]. Fig. 2 shows the Raman spectrum of the matrix. It is clear that the largest phonon energy merely reaches to 963 cm^{-1}, much lower than that of silicate glass (~1080 cm^{-1}) [22]. The lower phonon energy leads to a smaller of the nonradiative decay probability and thus be helpful to increase the fluorescence quantum efficiency. The inset shows the Raman bands in the frequency region from 800 to 1200 cm^{-1}. It was seen that five peaks centered at 840, 882, 949, 1010, and 1048 cm^{-1} are observed by Gaussian fitting, which are attributed to the SiO_4 tetrahedra with four, three, two, one non-bridging oxygen ion and with four bridging oxygens, respectively [23,24]. The centre of the strong Raman band of the lead silicate glass at 963 cm^{-1} seems to be too high for isolated SiO_4 tetrahedra and some degree of polymerization of the tetrahedra is required [25]. Thus, lead oxide played the role of a modifier in our glass network and silicate network was depolymerized with the PbO doped, which are favor to improve the solubility of rare earth ions.