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Spectroscopic properties and energy transfer mechanism in Dy^{3+}/Tm^{3+} codoped fluoroaluminate glasses modified by TeO_2

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Abstract

This paper investigates 2.9 μm emission properties and energy transfer processes in the Dy^{3+}/Tm^{3+} codoped fluorotellurite glass. The measured absorption spectra demonstrate that the codoped sample can be efficiently pumped by an 800 nm excitation. Judd–Ofelt and radiative parameters are calculated and discussed. Higher spontaneous emission probability (39.6 S^{-1}) provides a better probability to obtain laser action. Obvious 2.9 μm emission of Dy^{3+}: $^6H_{13/2}\rightarrow{}^6H_{15/2}$ transition is observed after codoping with Tm^{3+} and the optimum ratio in this system is 1:1. Energy transfer processes between the two ions are discussed and the related microscopic interaction parameters are calculated. Hence, these results indicate that the Dy^{3+}/Tm^{3+} codoped fluorotellurite glass is a suitable material for developing solid state laser at approximately 3.0 μm.

Keywords: Mid-infared; Fluorotellurite glass; Judd–Ofelt; Energy transfer

1. Introduction

Rare earth (RE) doped fiber lasers developed for emissions in the infrared wavelength region longer than 2 μm are gaining popularity for several applications, such as remote sensing, atmospheric pollution monitoring, and medical surgery [1–6]. In particular, 3 μm glass lasers have major applications in medical and sensing technologies because of the strong absorption peak of water at this wavelength. To date, RE ions for 3 μm emissions mainly involve Er^{3+}, Ho^{3+}, Dy^{3+} ions [7–9]. Compared with erbium and holmium, Dy^{3+} doped fiber lasers can achieve longer laser wavelength because of the smaller energy gap of Dy^{3+}: $^6H_{13/2}\rightarrow{}^6H_{15/2}$ than those of Er^{3+}: $^4I_{11/2}\rightarrow{}^4I_{13/2}$ and Ho^{3+}: $^5I_6\rightarrow{}^5I_7$ transitions. In fact, these materials are very important for medical applications because Dy^{3+} doped fiber laser overlaps excellently with the fundamental vibration (3400 cm^{-1}) of OH bonds, thereby presenting more precise ablation of shallow tissue. However, only Er^{3+} doped materials have been extensively investigated because of its 2.7 μm emission from $^4I_{11/2}\rightarrow{}^4I_{13/2}$ transition and efficient 800 or 980 nm absorption bands. Er-doped and Er–Pr-codoepd fluoride fiber lasers (ZrF_4–BaF_2–LaF_3–AlF_3–NaF) have been developed to obtain higher power output in the past decades [10]. At present, Fortin has reported a 2938 nm erbium-doped fluoride glass fiber laser delivering a record output power of 30 W [11]. Dy^{3+}-doped Middle-infrared (MIR) materials have been developed more slowly. A small number of investigations on Dy^{3+} doped MIR materials have focused mainly on fluoride and chalcogenide glasses [12]. The intrinsic difficulty to efficiently obtain laser action of Dy^{3+} is mainly due to the lack of absorption bands for the common pump source. Tm^{3+} has been used as an efficient sensitized ion for Dy^{3+} doped materials because of its 800 nm absorption band and energy transfer (ET) process from Tm^{3+}: $^3H_4$ level to Dy^{3+}: $^6F_{5/2}$ level. Enhanced 2.9 μm emission has been reported in Dy^{3+}/Tm^{3+} codoped chalcogenide, fluoride and

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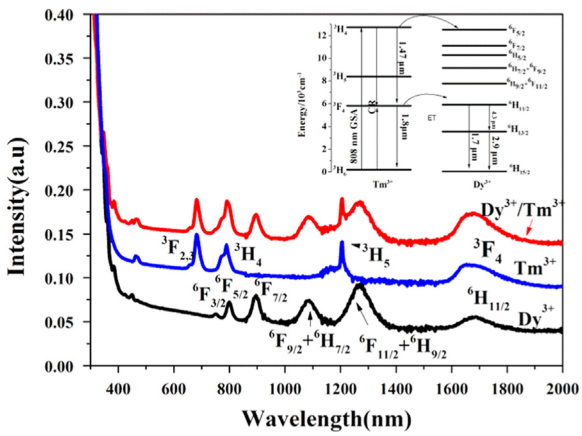

Fig. 1. Room-temperature absorption spectra of Dy^{3+}, Tm^{3+} singly doped and codoped FT glasses in the spectral range from 300 nm to 2200 nm. The inset is the related energy level diagram of the two ions.

fluorosphoaphate glasses [13]. However, few reports have been detailed the intensity parameters discussion and ET quantitative calculation on Dy^{3+}/Tm^{3+} codoped materials.

The host should be considered in developing more efficient optical devices based on RE ions in addition to active ions [3,14]. The host must have low phonon energy to avoid luminescence quenching so as to develop more efficient optical devices [15]. At present, Dy^{3+} doped MIR materials have been limited in fluoride (ZBLAN) and chalcogenides glasses, which, compared to oxide glasses, have low phonon energy and better optical properties [16]. However, they have poor chemical and durable properties as well as low temperature of glass transition, suggesting that they are inadequate for used in lasers [17]. New host materials that can support lasing in the 3 μm MIR region are therefore desired. Fluorotellurite glasses combine the favorable properties of fluoride and oxide glasses, such as relative lower phonon energy among all oxide glasses, more stable chemical and physical properties compared to those of fluoride glasses, and easy fibering [18,19]. Today, Er^{3+} doped fluorotellurite glasses are popular for its 1.5 and 2.7 μm emissions [20,21]. However, few investigations have been conducted on Dy^{3+}/Tm^{3+} codoped fluorotellurite glasses for its 2.9 μm emission, and no study has explored the quantitative energy transfer calculation on Dy^{3+}/Tm^{3+} codoped fluorotellurite glass.

The enhanced 2.9 μm emission properties and corresponding ET mechanism of Dy^{3+}/Tm^{3+}codoped fluorotellurite glass are investigated in this work. A combination of experimental absorption data and Judd–Ofelt analysis is discussed. In addition, the macroscopic ET mechanism and microscopic parameters are analyzed and calculated. Finally, the appropriate operational regime of the Dy^{3+}/Tm^{3+} doped fluoride fiber laser around 2.9 μm is established.

2. Experimental

The investigated glass has the following molar compositions: $90(AlF_3–YF_3–CaF_2–BaF_2–SrF_2–MgF_2)–10TeO_2–DyF_3–XTmF_3$ (X=0, 0.5, 1, 1.5, designed as DTX, respectively). All of the samples were prepared using high-purity YF_3, AlF_3, CaF_2, BaF_2, SrF_2, MgF_2, TeO_2 DyF_3 and TmF_3 powders. Well-mixed 25 g batches of the samples were placed in platinum crucibles and melted at 950 °C for 30 min. The melts were then poured onto a preheated copper mold and annealed in a furnace around the glass transition temperature. The annealed samples were fabricated and polished to the size of 20 mm × 15 mm × 1 mm for the optical property measurements.

The characteristic temperatures (temperature of glass transition T_g and temperature of onset crystallization peak T_x) of the samples were determined using a NetzschSTA449/C differential scanning calorimetry at a heating rate of 10 K/min. The density and refractive index of the samples were measured by Archimedes method using distilled water as immersion liquid and prism minimum deviation method, respectively. Furthermore, the absorption spectra were recorded with a Perkin-Elmer Lambda 900 UV/Vis/NIR spectrophotometer in the range of 300 nm to 2000 nm, and the emission spectra were measured under 800 nm laser diode (LD) pump with a Triax 320 type spectrometer (Jobin-Yvon Co., France). All measurements were carried out at room temperature.

3. Results and discussion

3.1. Absorption spectra and Judd–Ofelt (J–O) analysis

The room-temperature absorption spectra of Dy^{3+}, Tm^{3+} singly doped and codoped FT glasses in the spectral range from 300 nm to 2200 nm are shown in Fig. 1.The related energy level diagram of the two ions is shown in the inset of Fig. 1. Absorption bans corresponding to the transitions starting from the $^6H_{15/2}$ of Dy^{3+} ground state to the higher levels $^6H_{11/2}$, $^6H_{9/2}+^6F_{11/2}$, $^6H_{7/2}+^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$ are labaled accordingly. The absorption bands centered at 682, 793, 1208, and 1662 nm are attributed to the absorptions from the ground state $^3H_6$ of Tm^{3+} to the excited states of $^3F_{2,3}$, $^3H_4$, $^3H_5$, and $^3F_4$, respectively. The Dy^{3+} singly doped sample has weak absorption band around 800 nm and the introduction of Tm^{3+} ions greatly enlarges the absorption coefficient around 800 nm. The samples prepared in this paper can be pumped by a commercial 800 nm LD.

Judd–Ofelt (J–O) theory [22–25] determines the important spectroscopic and laser parameters of RE doped glasses. From the absorption spectrum, the experimental oscillator strength (f_{exp}) of the transitions is calculated as

$$f_{\exp} = \frac{2.303mc^2}{\pi e^2 N d\lambda^2} \int \mathrm{OD}(\lambda)\mathrm{d}\lambda \quad (1)$$

where m and e are the mass and charge of electron, c is the speed of light in vacuum, N is the concentration of RE ions, $\int \mathrm{OD}(\lambda)\mathrm{d}\lambda$ is the integrated absorption coefficient, and d is the sample thickness.

According to J–O theory, the theoretical oscillator strength (f_{cal}) of an electron-doped absorption transition from the initial state $<(S, L,) J>$ to the final state $<(S', L',) J'>$ can be