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Enhanced 1.80 μm fluorescence in $Er^{3+}/Yb^{3+}/Tm^{3+}$ tri-doped tellurite glass for fiber lasers

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ABSTRACT

Improving the lasing emission property of rare-earth doped vitreous material is a research topic. In this paper, $Er^{3+}/Yb^{3+}/Tm^{3+}$ tri-doped tellurite glasses with and without WO_3 component were synthesized using melt-quenching technique and the effect of WO_3 addition on the 1.80 μm band fluorescence of Tm^{3+} was investigated. The obtained samples were characterized by X-ray diffraction (XRD) pattern, differential scanning calorimeter (DSC) curve, Raman spectrum, UV/Vis/NIR absorption spectrum, near-infrared emission spectrum and fluorescence decay curve. The XRD pattern confirmed amorphous structural nature of synthesized tellurite glass, the DSC curve revealed good thermal stability with $\Delta T > 100$ °C and the Raman spectrum displayed a stretching vibration band around 920 cm^{-1} for glass host with WO_3. Under the excitation of 980 nm laser diode (LD), the intense 1.80 μm band fluorescence of Tm^{3+} originated from the $^3F_4 \rightarrow {}^3H_6$ transition was observed in the $Er^{3+}/Yb^{3+}/Tm^{3+}$ tri-doped tellurite glass and the intensity increases further with the addition of a certain amount of WO_3, which is attributed to the enhanced energy transfers from Yb^{3+} (Er^{3+}) to Tm^{3+} ions due to the increased phonon energy of glass host. The energy transfer mechanism between them was elucidated by analyzing fluorescence decay behavior of Tm^{3+} and quantitatively calculating energy transfer coefficient as well as phonon contribution ratio. Meanwhile, based on the absorption spectrum, some important spectroscopic parameters such as Judd-Ofelt parameter, spontaneous radiative transition probability, fluorescence branching ratio, absorption and emission cross-sections, and gain coefficient spectrum were calculated to reveal spectroscopic properties of doped Tm^{3+} ions. The obtained results indicate that $Er^{3+}/Yb^{3+}/Tm^{3+}$ tri-doped tellurite glass with an appropriate amount of WO_3 is a promising gain medium applied for the 1.80 μm band solid-state lasers.

1. Introduction

In recent years, extensive studies have been conducted on fiber lasers operating in ~2.0 μm band because of their wide applications in environment monitoring, remote sensing, medical laser surgery, optical sensor, laser-guided military weapon and so on [1–6]. Among trivalent rare-earth ions, Tm^{3+} exhibits good prospects as it can generate lasing emissions covering several important bands up to the mid-infrared range under proper excitations besides its excellent nature of large degree of stark splitting of $^3H_6$ ground state [7,8]. For example, the $^3H_4 \rightarrow {}^3F_4$ lasing emission of Tm^{3+} at around 1.47 μm corresponding to the S-band region is important to achieve the gain band extension towards the short wavelength side of conventional erbium-doped fiber amplifier (EDFA) operating at current C-band (1530–1570 nm) communication window [9,10], while the $^3F_4 \rightarrow {}^3H_6$ radiative transition of Tm^{3+} at around 1800 nm is considered to play a key role in extending lasing capability into the 1600–1900 nm atmospheric window [11,12]. What's more, a couple of Er^{3+} and Tm^{3+} co-dopants are recognized as an efficient scheme to obtain intense fluorescence emissions in both the near-infrared and mid-infrared spectrum range [13]. In addition, as another type of active ions, Yb^{3+} is known as a useful co-dopant both for Er^{3+} and Tm^{3+} ions due to its large absorption cross-section and relatively long lifetime at around 980 nm pump wavelength [1,14].

For most of luminescent studies involving doped Tm^{3+} ions, the host materials are focused on silicate [3,7,15–17], fluoride [18,19], phosphate [20,21], fluoro-phosphate [22,23], tellurite [24,25],

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germanate [26,27] and chalcogenide [28,29] glasses. Among these glass materials, tellurite glass has attracted considerable interests for its excellent advantages. More specifically, tellurite glass not only exhibits proper physical and chemical durability, but also possesses high linear and nonlinear refractive indices, high rare-earth solubility and large gain coefficient, which make it a promising material for photonic applications such as optical fiber amplifiers and nonlinear optical devices [30–32]. Although tremendous progress has been made, unfortunately, some limitations of conventional tellurite glass, such as relatively low phonon energy (~750 cm^{-1}) which causes strong up-conversion luminescence [32] and unsatisfactory thermal stability, have hindered its extensive applications. Indeed, finding effective method to improve the luminescent properties of doped rare-earth ions in vitreous materials has always been a research topic. It is known that as glass former, the presence of WO_3 component in the tellurite glass matrix produces a more complex network structure with a great variety of sites for rare-earth ions, which can induce the inhomogeneous broadening of fluorescence emissions [33,34]. What's more, it can improve the chemical stability and meanwhile increase the linear and nonlinear refractive indices [35–37]. The high index of doped glass can increase the local field correction at rare-earth site, which leads to large radiative transition probability [33,38]. All these are beneficial to the enhancement of fluorescence intensity and broadband emission of doped rare-earth ions.

In the present work, a certain amount of WO_3 oxide was introduced into the $Er^{3+}/Yb^{3+}/Tm^{3+}$ tri-doped tellurite glass with conventional compositions TeO_2-ZnO-Na_2O to improve the 1.80 μm band fluorescence of Tm^{3+}. In order to demonstrate the effect of WO_3 oxide on the luminescent property and thermal stability, the measurements of absorption spectrum, fluorescence spectrum including decay curve, Raman spectrum, XRD pattern and DSC curve were performed on the prepared glass samples, together with the theoretical calculations of some important spectroscopic parameters such as Judd-Ofelt intensity parameter, spontaneous radiative transition probability, fluorescence branching ratio, absorption/emission cross-sections and gain coefficient spectrum. Furthermore, the energy transfer mechanism between Er^{3+}, Yb^{3+} and Tm^{3+} ions was investigated to understand the role of host phonon in the energy transfer process.

2. Experimental procedures

2.1. Glass preparation

$Er^{3+}/Yb^{3+}/Tm^{3+}$ tri-doped tellurite glasses with compositions $(77\text{-}x)TeO_2\text{-}10ZnO\text{-}10Na_2O\text{-}xWO_3\text{-}0.3Er_2O_3\text{-}2.5Yb_2O_3\text{-}0.2Tm_2O_3$ ($x = 0, 9$) in mole percent were prepared using conventional melt-quenching technique and are labeled as T-ErYbTm0 and T-ErYbTm9 corresponding to the WO_3 amount for clarity. Meanwhile, Er^{3+}/Yb^{3+} and Tm^{3+}/Yb^{3+} co-doped tellurite glasses with compositions ($77.2TeO_2\text{-}10ZnO\text{-}10Na_2O\text{-}0.3Er_2O_3\text{-}2.5Yb_2O_3$) and ($77.3TeO_2\text{-}10ZnO\text{-}10Na_2O\text{-}0.2Tm_2O_3\text{-}2.5Yb_2O_3$) were also prepared in order to better identify the absorption bands of Er^{3+} and Tm^{3+}, and they are denoted as T-ErYb and T-TmYb respectively. During the glass preparation, the component Na_2O was introduced in Na_2CO_3 compound and the chemicals used (together with their purity) are the following: TeO_2 (99.99%), ZnO (99.99%), Na_2CO_3 (99.995%), Er_2O_3 (99.99%), Yb_2O_3 (99.99%) and Tm_2O_3 (99.99%). Batches of 10.0 g compounds were weighed and thoroughly mixed and then melted in a high-purity platinum crucible at 950 °C for 30 min in an atmosphere of dry air. After the melting, the high temperature melt was casted immediately into the preheated stainless steel mold and annealed at 350 °C for 2 h to reduce the thermal stress, then cooled slowly down to the room temperature at a rate of 10 °C/h. Finally, all the obtained glass samples were cut and polished for further physical and spectroscopic measurements.

2.2. Sample measurements

The density was measured based on the Archimede's principle by precise mass measurements of glass sample in air and pure water environment. Refractive index was measured using a prism coupler of Sairon Tech-SPA4000 TM at wavelength 632.8 nm. Powder X-ray diffraction (XRD) pattern was recorded using a power diffractometer with Cu K radiation (40 kV25 mA) and a graphite monochromator. Thermal analysis was performed on prepared glass using a differential scanning calorimeter (DSC) of TA Instrument Q2000 at a heating rate of 10 K/min. Raman spectrum was measured by a Renishaw Micro-Raman instrument. UV/Vis/NIR absorption spectrum was recorded with a Perkin-Elmer-Lambda 950 spectrophotometer. Fluorescence spectrum was measured using an Edinburgh Instruments FLS980 fluorescence spectrometer under the excitation of 980 nm LD. Fluorescence decay curve was recorded with a digital oscilloscope (Tektronix TDS 1012, 100 MHz) after averaging 128 times under pulse excitation of 980 nm LD.

3. Results and discussion

3.1. Structure behavior and thermal property

In order to explore the local structural nature of prepared glass samples, the XRD analyses of $Er^{3+}/Yb^{3+}/Tm^{3+}$ tri-doped tellurite glasses (T-ErYbTm9 and T-ErYbTm0) with and without WO_3 component were carried out and the obtained XRD results are displayed in Fig. 1. It can be seen that both tellurite samples exhibit the similar XRD patterns with an obvious broad hump between $2\theta = 20^\circ$ and 40° but have not any sharp diffraction peaks. This proves the absence of network periodicity for long range atomic periodic arrangement or in other words, it demonstrates the structural disorder i.e. the amorphous state structure for the prepared glasses [38].

In consideration of practical applications in photonic devices such as fiber lasers and amplifiers, it is better that the prepared tellurite glass possesses good thermal stability so that it can resist the detrimental effects aroused by temperature rise. The thermal stability of glass host is characterized by three temperature parameters, i.e. the glass transition temperature (T_g), crystallization onset temperature (T_x) and their difference $\Delta T(= T_x - T_g)$ [39–41],

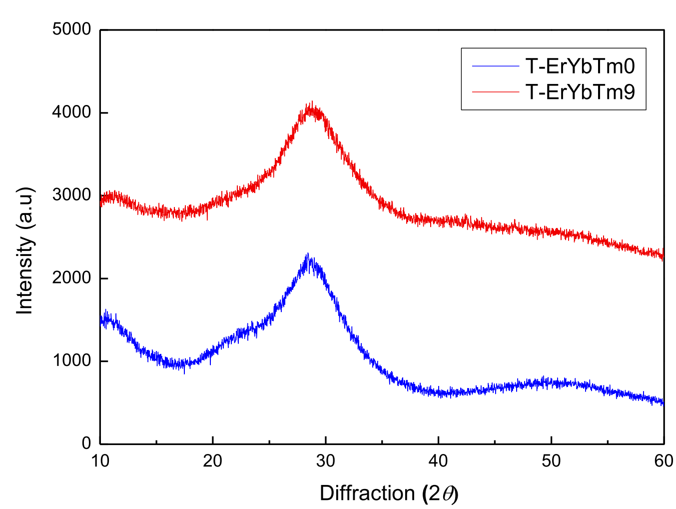

Fig. 1. The XRD patterns of T-ErYbTm0 and T-ErYbTm9 glass samples.