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Energy transfer induced 2.0 μm luminescent enhancement in $Ho^{3+}/Yb^{3+}/Ce^{3+}$ tri-doped tellurite glass

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ABSTRACT

Tellurite glasses doped with Ho^{3+}, Ho^{3+}/Yb^{3+} and $Ho^{3+}/Yb^{3+}/Ce^{3+}$ ions have been prepared using conventional melt-quenching method, and characterized respectively by the X-ray diffraction (XRD) pattern, differential scanning calorimeter (DSC) curve, UV–vis–IR absorption spectrum, upconversion spectrum, fluorescence spectrum and fluorescence decay curve to investigate the 2.0 μm band spectroscopic properties of Ho^{3+}, thermal stability and structural nature of glass hosts. Under the excitation of 980 nm laser diode (LD), an intense and broad 2.0 μm band infrared emission originated from the $^5I_7 \rightarrow {}^5I_8$ transition of Ho^{3+} was observed in the Ho^{3+}/Yb^{3+} co-doped tellurite glass and increased further with the addition of Ce^{3+}, which is attributed to the energy transfer (ET) from Yb^{3+} to Ho^{3+} as well as the cross-relaxation (CR) between Ho^{3+} and Ce^{3+}. The quantitative analyses of ET mechanism between the doped rare-earth ions, together with the investigation on the changes of upconversion emission intensity and 2.0 μm fluorescence lifetime with Ce^{3+} were presented to elucidate the observed 2.0 μm band luminescent enhancement. Meanwhile, important spectroscopic parameters, such as radiative transition probability, absorption and emission cross-sections, and gain coefficient for Ho^{3+}:$^5I_7 \rightarrow {}^5I_8$ transition, were calculated from the measured absorption spectrum to evaluate the potential radiative properties. Additionally, the measured DSC curve reveals the good thermal stability and the XRD pattern confirmed the amorphous structure of prepared glass host. The results indicate that $Ho^{3+}/Yb^{3+}/Ce^{3+}$ tri-doped tellurite glass is a potential active medium for developing 2.0 μm band infrared solid lasers.

1. Introduction

The infrared lasing sources around 2.0 μm have promising applications in many areas such as environment monitoring, remote sensing, eye-safe laser radar, medical surgery, frequency conversion and supercontinuum generation [1–6].

Until now, a large amount of reports about 2.0 μm lasing output come mainly from Ho^{3+}-doped glass systems owing to its radiative transition of $^5I_7 \rightarrow {}^5I_8$, which has a larger gain cross-section, longer radiative lifetime and laser wavelength than Tm^{3+} of $^3F_4 \rightarrow {}^3H_6$ transition (~ 1.85 μm) [7–9]. Unfortunately, special pump lasers are needed for Ho^{3+} other than the low-cost and readily commercial available 808/980 nm laser diodes (LDs) because there is no absorption energy level in Ho^{3+} matching with them [10,11]. Therefore, other rare-earth ions such as Er^{3+}, Tm^{3+} and Yb^{3+} are introduced as sensitizers in assisting the Ho^{3+} emission not only owing to their intense absorptions at around 808 and/or 980 nm bands, but also due to the effective energy transfers from them to Ho^{3+}. So far, a lot of investigations on 2.0 μm band emission using Ho^{3+}/Er^{3+}, Ho^{3+}/Tm^{3+} and Ho^{3+}/Yb^{3+} co-doped schemes have been carried out in many glass hosts such as silicate, bismuth and tellurite glasses [12–15]. However, strong visible upconversion luminescence originated from the excited state absorption (ESA) of Ho^{3+}:$^5I_6$ level is observed in these co-doped schemes, especially, when they are co-doped in a glass system with relatively low phonon energy [16–18], leading to a dramatic reduction of pumping efficiency for the 2.0 μm band emission. Therefore, developing an effective approach to suppress the upconversion luminescence would be beneficial in enhancing the 2.0 μm band emission of Ho^{3+}.

Trivalent Ce^{3+} has been confirmed as an ideal candidate in suppressing the upconversion luminescence and enhancing the 1.53 μm band emission of Er^{3+} under the excitation of 980 nm LD, and this result is achieved by accelerating the decay rate from the pumping level $^4I_{112}$ to fluorescence emitting level $^4I_{13/2}$ of Er^{3+} through the CR process of Er^{3+}:$^4I_{11/2}$ + Ce^{3+}:$^2F_{5/2} \rightarrow Er^{3+}$:$^4I_{13/2}$ + Ce^{3+}:$^2F_{7/2}$ [19,20], which decreases the ESA of Er^{3+} at level $^4I_{11/2}$. It is known that the energy gap of Ho^{3+}:$^5I_6 \rightarrow {}^5I_7$ transition is similar to that of Er^{3+}:$^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition [21,22], therefore, it is expected that introducing Ce^{3+} into the Ho^{3+}-doped glass system can also suppress the

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upconversion luminescence and in turn enhance the 2.0 μm band emission through the similar CR process of Ho^{3+}:$^5I_6$ + Ce^{3+}:$^2F_{5/2}$ → Ho^{3+}:$^5I_7$ + Ce^{3+}:$^2F_{7/2}$. Indeed, the desired results have been reported when Ce^{3+} was introduced into Ho^{3+}/Yb^{3+} and Ho^{3+}/Er^{3+} co-doped glass systems [23,24]. However, the 2.0 μm band luminescent property especially the ET mechanism between the doped rare-earth ions which is responsible for the observed 2.0 μm band emission enhancement of Ho^{3+} are still needed to be further investigated.

In this paper, Ce^{3+} was introduced into Ho^{3+}/Yb^{3+} co-doped tellurite glass and the enhanced effect of Ce^{3+} on the 2.0 μm band emission of Ho^{3+} was investigated. The important spectroscopic parameters such as radiative transition probability, gain coefficient, absorption and emission cross-sections were calculated, and quantitative analyses of ET mechanism between doped rare-earth ions were presented to elucidate the observed 2.0 μm band luminescent phenomenon. In the present work, tellurite glass was selected as the glass host due to its excellent properties such as wide transparency in a broad wavelength range of 0.35–6 μm, large rare-earth ion solubility which is 10–50 times larger than in silica glass, low host phonon energy (~ 750 cm^{-1}) among oxide glasses, good mechanical stability and corrosion resistance compared with non-oxide glasses [25,26].

2. Experimental procedures

2.1. Glass preparation

Ho^{3+} single-doped, Ho^{3+}/Yb^{3+} co-doped and $Ho^{3+}/Yb^{3+}/Ce^{3+}$ tri-doped tellurite glasses were prepared for comparison with high-purity (99.9–99.99%) raw materials using conventional melt-quenching technique. The composition of tellurite glass in mole percent is $75TeO_2$–$20ZnO$-$5La_2O_3$, in which ZnO improves the glass forming ability while La_2O_3 increases the rare-earth solubility. Three rare-earth oxides Ho_2O_3, Yb_2O_3 and CeO_2 were added into it as dopants, in which the doped amounts of Ho_2O_3 and Yb_2O_3 were fixed to 0.5 mol% and 1.0 mol%, while that of CeO_2 was 0.2, 0.5 and 0.8 mol%, respectively. Accordingly, the as-prepared single-doped, co-doped and tri-doped glass samples are hereafter labeled as T-Ho, T-HoYb and T-HYC*x* (x = 0.2, 0.5 and 0.8 mol%). To prepare glass sample, batches of 10.0 g raw materials were weighed, mixed homogeneously and then melted in a platinum crucible at 900 °C for 30 min under the dry air environment kept by a homemade dehumidifier. After the melting, the glass melt was casted immediately into the preheated stainless steel mold and annealed at 340 °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 into the same size of 10 × 10 × 1.5 mm^3 for further physical and spectroscopic measurements.

2.2. Sample measurements

The UV–vis–NIR absorption spectrum of glass sample in the wavelength range of 350–2200 nm was recorded by a Perkin-Elmer-Lambda 950 spectrophotometer. The infrared transmission spectrum in the spectral range of 2500–5500 nm was obtained using Nicolet 380 Fourier Infrared (FTIR) spectrophotometer. Fluorescence spectrum in the visible and near-infrared band was measured by 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. The glass density was measured based on the Archimedes principle by precise weighing sample in air and pure water environment respectively. Refractive index was measured using a prism coupler of Sairon Tech-SPA4000 TM at wavelength 632.8 nm. After these, the glass sample was grinded into fine powder and powder X-ray diffraction (XRD) pattern in the diffraction angle (2θ) of 10–60° was recorded using a powder diffractometer with Cu Kradiation (40 kV25 mA) and a graphite monochromator, and thermal analysis in the temperature range of 200–550 °C was performed using a differential scanning calorimeter (DSC) of TA Instrument Q2000 at a heating rate of 10 K/min. The measured density, refractive index of glass sample and corresponding rare-earth doped concentration were listed in Table 1, displaying a slight increment of glass density and refractive index with the Ce^{3+} concentration.

Table 1
Density (ρ), refractive index (n) and the concentration of doped ions in T-Ho, T-HoYb and T-HYC*x* (x = 0.2, 0.5 and 0.8) tellurite glasses.

Sample	T-Ho	T-HoYb	T-HYC0.2	T-HYC0.5	T-HYC0.8
ρ(g/cm^3)	5.437	5.506	5.507	5.509	5.512
n	2.047	2.058	2.059	2.061	2.064
N_{Ho} (× 10^{20}/cm^3)	2.123	2.096	2.093	2.087	2.076
N_{Yb} (× 10^{20}/cm^3)	/	4.192	4.186	4.174	4.152
N_{Ce} (× 10^{20}/cm^3)	/	/	0.837	2.087	3.322

3. Results and discussion

3.1. Structure behavior and thermal property

The measured XRD patterns of Ho^{3+} single-doped (T-Ho), Ho^{3+}/Yb^{3+} co-doped (T-HoYb) and $Ho^{3+}/Yb^{3+}/Ce^{3+}$ tri-doped (T-HYC*x*, x = 0.2, 0.5 and 0.8) tellurite glasses are presented in Fig. 1, which display the similar nature with an broad hump but no any sharp crystalline peaks in the diffraction angle (2θ) of 10–60°, indicating the absence of long-range atomic arrangement or three dimensional network periodicity, i.e. the structural nature of synthesized tellurite glasses exhibits an amorphous state [27,28]. Meanwhile, the result also indicates that the introduction of rare-earth ions like Ho^{3+}, Yb^{3+}, Ce^{3+} or their co-doping does not induce any crystallinity to the host glass.

Thermal stability of glass host is generally characterized by the glass transition temperature (T_g), crystallization onset temperature (T_x) and the difference ($\Delta T = T_x - T_g$) [29,30]. Among them, ΔT is frequently used as a rough indicator of glass stability against crystallization because the nucleation is difficult to grow into large crystal quickly when this difference is large [31], while a large T_g indicates a good resistance to thermal damage caused by the high power laser. Therefore, it is desirable for glass host to have both T_g and ΔT as large as possible. As a representative, the measured DSC curves of T-HoYb and T-HYC0.5 glass samples in the temperature range of 200–550 °C are displayed in Fig. 2, together with the values of T_x and T_g determined by taking the point of intersections. It is seen that the values of T_g and ΔT in T-HYC0.5 glass

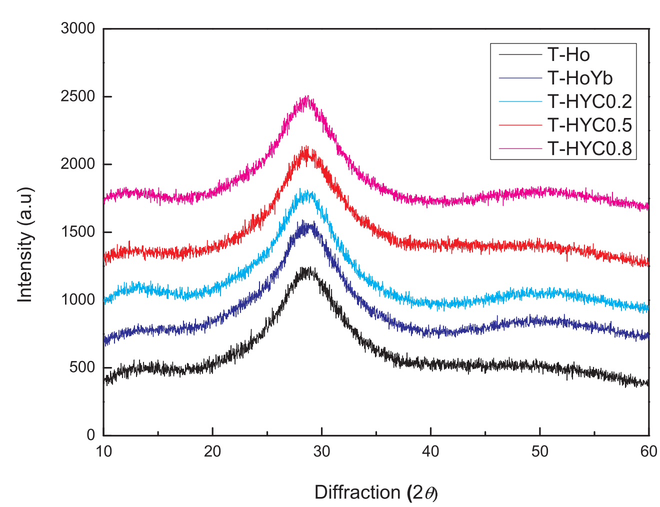

Fig. 1. The XRD patterns of T-Ho, T-HoYb and T-HYC*x* (x = 0.2, 0.5 and 0.8) tellurite glasses.