Enhancement of 2.0 μm fluorescence emission in new Ho^{3+}/Tm^{3+}/Yb^{3+} tri-doped tellurite glasses[*]

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For enhancing the 2.0 μm band fluorescence of Ho^{3+}, a certain amount of WO$_3$ oxide was introduced into Ho^{3+}/Tm^{3+}/Yb^{3+} tri-doped tellurite glass prepared using melt-quenching technique. The prepared tri-doped tellurite glass was characterized by the absorption spectra, fluorescence emission and Raman scattering spectra, together with the stimulated absorption, emission cross-sections and gain coefficient. The research results show that the introduction of WO$_3$ oxide can further improve the 2.0 μm band fluorescence emission through the enhanced phonon-assisted energy transfers between Ho^{3+}/Tm^{3+}/Yb^{3+} ions under the excitation of 980 nm laser diode (LD). Meanwhile, the maximum gain coefficient of Ho^{3+} at 2.0 μm band reaches about 2.36 cm^{-1}. An intense 2.0 μm fluorescence emission can be realized .

Solid state lasers around 2.0 μm band have important application prospect[1-3]. Owing to its unique energy level system for 2.0 μm emission of $^5I_7 \rightarrow {}^5I_8$ transitions, Ho^{3+}-doped glass materials are investigated[4,5]. Unfortunately, under the excitation of a commercial 800 nm or 980 nm laser diode (LD), Ho^{3+} ions have no corresponding absorption energy levels. Thus, Ho^{3+} ions are applied in the co-doping with other sensitizers, such as Tm^{3+} and Yb^{3+}, which can be efficiently pumped by a 800 nm or 980 nm LD[4,5]. Up to now, silica[6], silicate[7], bismuth[8,9] and chalcogenide[10] glasses have been investigated as hosts of Ho^{3+} to achieve intense infrared emission. Compared with these glasses above, Ho^{3+}-doped tellurite glass has obtained more attention due to its higher rare-earth ion solubility, easier preparation process, better physical stability and chemical durability, wider transparency window (0.35—5.00 μm) and higher refractive index (~2.0)[5,11,12].

Ho^{3+}/Tm^{3+}/Yb^{3+} tri-doping is an efficient scheme to realize intense 2.0 μm fluorescence of Ho^{3+} through the energy transfer (ET) processes between the doped rare-earth ions[5,13]. However, there are energy differences between the levels involved in the ET processes, such as ~1 900 cm^{-1} between Yb^{3+}:$^2F_{5/2}$ and Tm^{3+}:$^3H_5$, ~1 800 cm^{-1} between Yb^{3+}:$^2F_{5/2}$ and Ho^{3+}:$^5I_6$, and ~930 cm^{-1} between Tm^{3+}:$^3F_4$ and Ho^{3+}:$^5I_7$, which indicates that the phonons of glass host will be needed to compensate these differences in the ET processes. Obviously, the glass host with suitable phonon energy is more beneficial for these ET processes.

It is known that the structural units of WO$_3$ oxide have a relatively larger phonon energy (~930 cm^{-1}) compared with that of TeO$_2$ counterpart (~750 cm^{-1})[14,15], which is more suitable to bridge the energy differences between Ho^{3+}/Tm^{3+}/Yb^{3+} ions. Also, the introduction of a certain amount of WO$_3$ in the tellurite glass can improve the thermal stability of glass host and the luminescent properties of doped rare-earth ions to some extent. In this paper, WO$_3$ oxide was introduced into Ho^{3+}/Tm^{3+}/Yb^{3+} tri-doped tellurite glass with composition TeO$_2$-GeO$_2$-Li$_2$O-Nb$_2$O$_5$ to further enhance the 2.0 μm fluorescence of Ho^{3+}.

Ho^{3+}/Tm^{3+}/Yb^{3+} tri-doped tellurite glasses with compositions of $(72-x)$TeO$_2$-15GeO$_2$-5Li$_2$O-5Nb$_2$O$_5$-0.5Ho$_2$O$_3$-0.5Tm$_2$O$_3$-2Yb$_2$O$_3$-xWO$_3$ (x=0, 15) in mole percent were prepared using conventional melt-quenching technique, which are labeled as TGW0 and TGW15 corresponding to WO$_3$ amount for clarity. Meanwhile, Ho^{3+} single-doped glass with composition of 74.5TeO$_2$-15GeO$_2$-5Li$_2$O-5Nb$_2$O$_5$-0.5Ho$_2$O$_3$ and Tm^{3+} single-doped glass with composition of 74.5TeO$_2$-15GeO$_2$-5Li$_2$O-5Nb$_2$O$_5$-0.5Tm$_2$O$_3$ were also prepared as reference and denoted as TGH and TGT, respectively. The starting materials of TeO$_2$, GeO$_2$, Li$_2$O, Nb$_2$O$_5$ and WO$_3$ were reagent-grade, and Ho$_2$O$_3$, Yb$_2$O$_3$ and Tm$_2$O$_3$ were high purity (99.99%). Batches of 10 g powders were weighed and mixed thoroughly, and then were melted at about

900 °C for 0.5 h in the dry gas atmosphere. The obtained glass melt was cast immediately into a preheated stainless steel mold, then was annealed at 10 °C below the glass transition temperature for 2 h, and finally was cooled down to the room temperature. All the glass samples were cut and polished into the same size of 10 mm×10 mm×1.5 mm to meet the requirements for further spectroscopic measurements.

The ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectrum of glass sample was recorded with a Perkin-Elmer-Lambda 950 spectra photometer. The fluorescence emission spectrum was measured with a Jobin Yvon Triax550 spectrophotometer under excitation of 980 nm LD with maximum power of 2 W. The Raman measurement was carried out using a confocal Raman spectroscopy Horbia Jobin Yvon (Model HR800 UV) with argon ions laser. The above measurements were performed at room temperature.

Fig.1 presents the measured UV-Vis-NIR absorption spectra ranging from 400 nm to 2 200 nm of Ho^{3+} single-doped TGH, Tm^{3+} single-doped TGT and Ho^{3+}/Tm^{3+}/Yb^{3+} tri-doped TGWx (x=0,15) glass samples. For TGH glass sample, there is no absorption match readily available 800 nm or 980 nm LDs except for some weak absorption bands of Ho^{3+} ions. Whereas for TGT and TGWx (x=0, 15) samples, strong absorption bands of Tm^{3+} ions at ~800 nm and especially Yb^{3+} ions at ~980 nm can be found, which are the bases for Tm^{3+} and Yb^{3+} sensitizing to Ho^{3+} ions. With the introduction of some WO_3 oxide, the absorption peak wavelength scarcely changes in TGW15 sample, which indicates that WO_3 oxide has little effect on the positions of the lowest Stark sub-levels of manifolds.
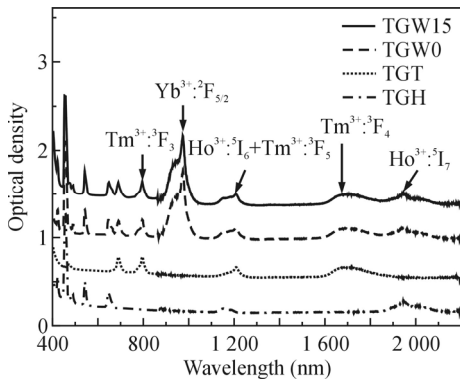

Fig.1 The measured absorption spectra of TGH, TGT and TGWx (x=0, 15) glass samples

Fig.2 shows the measured fluorescence emission spectra of TGH and TGWx (x=0, 15) glass samples ranging from 1 400 nm to 2 200 nm under the excitation of 980 nm LD. It is shown that no emission can be found in TGH sample because there is no absorption for Ho^{3+} ions around 980 nm, while TGWx (x=0, 15) samples emit a relatively weak 1.8 μm fluorescence and a very strong 2.0 μm fluorescence, which correspond to the transitions of Tm^{3+}:$^3F_4 \rightarrow {}^3H_6$ and Ho^{3+}:$^5I_7 \rightarrow {}^5I_8$, respectively. Pumped

by 980 nm LD, the relevant transitions including ET processes involved for the 2.0 μm emission in Ho^{3+}/Tm^{3+}/Yb^{3+} tri-doped tellurite glass are depicted on the energy level diagram shown in Fig.3. Firstly, Yb^{3+} ions populated at the ground state $^2F_{7/2}$ are excited to the $^2F_{5/2}$ level under the 980 nm excitation, then Yb^{3+} ions at the $^2F_{5/2}$ level transfer their energy to the neighboring Tm^{3+} and Ho^{3+} ions, and they are excited to $^3H_5$ and $^5I_6$ levels through the ET processes of Yb^{3+}:$^2F_{5/2}$+Tm^{3+}:$^3H_6$ →Yb^{3+}:$^2F_{7/2}$+Tm^{3+}:$^3H_5$ and Yb^{3+}:$^2F_{5/2}$+Ho^{3+}:$^5I_8$→Yb^{3+}: $^2F_{7/2}$+Ho^{3+}:$^5I_6$, respectively. After that, parts of Tm^{3+} ions at the $^3H_5$ level and Ho^{3+} ions at the $^5I_6$ level drop to their corresponding $^3F_4$ level and $^5I_7$ level respectively through the multi-phonon relaxation processes. Along with these processes, the existed ET processes from Ho^{3+}:$^5I_6$ level to Tm^{3+}:$^3H_5$ level and from Tm^{3+}:$^3F_4$ level to Ho^{3+}:$^5I_7$ level are beneficial for the population of Ho^{3+} ions at the $^5I_7$ level. Finally, the intense 2.0 μm fluorescence of Ho^{3+} is observed when Ho^{3+} ions at the $^5I_7$ level radiate to the ground states $^5I_8$.
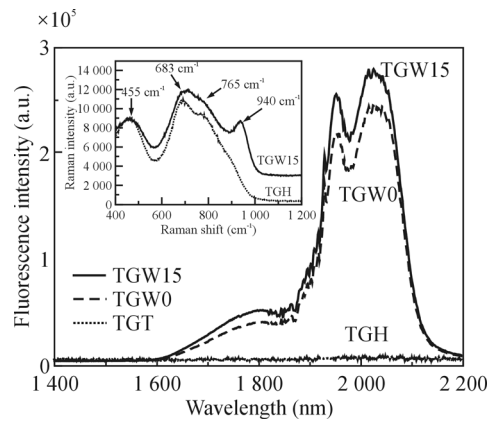

Fig.2 The measured fluorescence spectra of Ho³⁺ single-doped TGH and Ho³⁺/Tm³⁺/Yb³⁺ tri-doped TGWx (x=0, 15) glass samples (The inset is Raman spectra of TGW0 and TGW15 glass samples.)
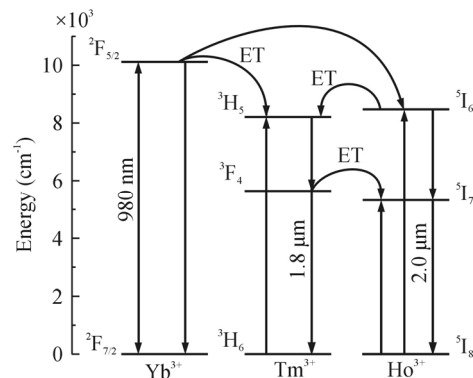

Fig.3 Energy level diagram of Ho³⁺, Tm³⁺ and Yb³⁺ ions and relevant transitions pumped at 980 nm

As mentioned above, the 2.0 μm fluorescence emission of Ho^{3+} ions is significantly larger than that of the 1.8 μm fluorescence of Tm^{3+} ions, and the reason is mainly attributed to the ET from Tm^{3+}:$^3F_4$ to Ho^{3+}:$^5I_7$

which leads to the accumulation of a large number of Ho^{3+} ions at $^5I_7$ level. Meanwhile, it is noticed that the introduction of WO_3 oxide results in the desired enhancement of 2.0 μm fluorescence, which is attributed to the enhanced ET between $Ho^{3+}/Tm^{3+}/Yb^{3+}$ ions. With the introduction of WO_3 oxide, the maximum phonon energy of glass host increases accordingly, which can be seen from the measured Raman spectra of TGWx (x=0, 15) samples shown in the inset of Fig.2. The Raman scattering band centered at around 455 cm^{-1} is related to the bending and stretching vibrations of Te-O-Te or O-Te-O linkages with O in an alternatively axial and equatorial position, the bands centered at around 683 cm^{-1} and 765 cm^{-1} are originated from the stretching vibrations of Te-O bonds in the $[TeO_4]$ trigonal bi-pyramid units and stretching vibrations between Te and non-bridging oxygen of $[TeO_{3+\delta}]$ trigonal pyramid units, respectively, while the new occurring band centered at around 940 cm^{-1} corresponds to the characteristic stretching vibrations of $W-O^-$ or W=O bonds associated with $[WO_4]$ and $[WO_6]$ units[14,15]. The large phonon energy of glass host is beneficial to compensate the energy differences between the relevant levels involved in the ET processes for $Ho^{3+}/Tm^{3+}/Yb^{3+}$ tri-doped glass sample, so a much strong fluorescence emission can be anticipated.

Fig.4 shows the stimulated absorption cross-section (σ_{abs}) and emission cross-section (σ_{em}) of $Ho^{3+}:^5I_7\leftrightarrow^5I_8$ transitions in TGW15 sample, which are calculated from the measured absorption spectrum based on the Beer-Lambert law and McCumber theory[16,17]. The emission cross-section peak of 1.05×10^{-20} cm^2 locates at 2 038 nm, which is much larger than that in fluorophosphate[18] and germinate[19] glasses. The large emission cross-section is mainly due to the high refractive index of glass host, which is favorable for achieving intense 2.0 μm fluorescence emission. To evaluate the amplifying ability of prepared TGW15 sample, the gain coefficient $G(\lambda)$ of Ho^{3+} is calculated on the basis of σ_{abs} and σ_{em} according to[9,20]

$$G(\lambda) = N\left[P\sigma_{em}(\lambda) - (1-P)\sigma_{abs}(\lambda)\right], \qquad (1)$$

where P represents the population inversion, and N stands for the total concentration of doped Ho^{3+} ions, which can be calculated from the measured sample density and initial composition. The inset of Fig. 4 shows the calculated gain coefficient spectra of $Ho^{3+}:^5I_7\rightarrow^5I_8$ transition in TGW15 sample with various P values ranging from 0 to 1. The maximum gain coefficient of Ho^{3+} ions is 2.36 cm^{-1} at 2 042 nm in TGW15 glass sample, which is larger than that of 1.62 cm^{-1} in silicate glass[20]. Therefore, owing to the higher gain coefficient of Ho^{3+} ions in this paper, it is expected that $Ho^{3+}/Tm^{3+}/Yb^{3+}$ tri-doped tellurite glass with a certain amount of WO_3 oxide has an advantage in application for 2.0 μm band infrared lasing devices.
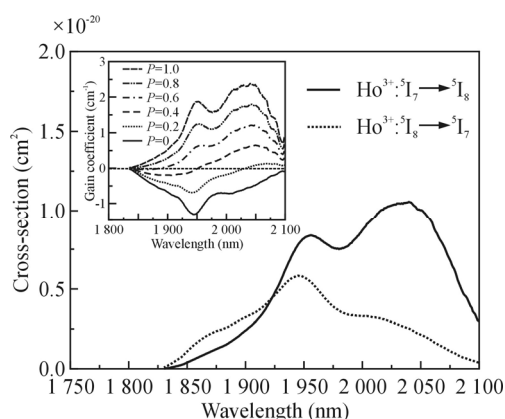

Fig.4 The calculated stimulated absorption and emission cross-sections of Ho^{3+} for 2.0 μm transition (The inset shows gain coefficient spectra of Ho^{3+} in the TGW15 glass sample with different P.)

$Ho^{3+}/Tm^{3+}/Yb^{3+}$ tri-doped tellurite glasses with a certain amount of WO_3 oxide were prepared using conventional melt-quenching technique, and the 2.0 μm fluorescence properties of Ho^{3+} ions was investigated. Compared with the sample without WO_3 oxide, the $Ho^{3+}/Tm^{3+}/Yb^{3+}$ tri-doped tellurite glass with WO_3 oxide exhibits a much stronger 2.0 μm fluorescence under the excitation of 980 nm LD which is attributed to the enhanced ET. This result indicates that $Ho^{3+}/Tm^{3+}/Yb^{3+}$ tri-doped tellurite glass with a certain amount of WO_3 oxide is a promising gain medium for 2.0 μm laser.

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