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Upconversion emissions in Yb^{3+}–Tm^{3+}-doped tellurite glasses excited at 976 nm

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Abstract Intense Tm^{3+} blue upconversion emission has been observed in Tm^{3+}–Yb^{3+} codoped oxyfluoride tellurite glass under excitation with a diode laser at 976 nm. Three emission bands centered at 475, 650 and 796 nm corresponding to the transitions $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3H_4$ and $^3F_4 \rightarrow {}^3H_6$, respectively, simultaneously occur. The dependence of upconversion intensities on Tm^{3+} ions concentration and excitation power are investigated. For fixed Yb_2O_3 concentrations of 5.0 mol%, the maximum upconversion intensity was obtained with Tm_2O_3 concentration of about 0.1 mol%. The blue upconversion luminescence lifetimes of the Tm^{3+} transitions $^1G_4 \rightarrow {}^3H_6$ are measured. The results are evaluated by the possible upconversion mechanisms.

Introduction

Some rare-earth ions can upconvert infrared light to visible light such as Er^{3+} and Tm^{3+} ions [1]. This phenomenon is of great interest because it can be utilized to build a new laser system. In recent years, particularly, high-power laser diodes have been employed as pumping sources with a view to develop compact upconversion visible laser system. The main interest in visible lasers arises from their wide range of applications in areas such as optical data storage solid-state color displays and medicine. In general, the blue upconversion laser can be achieved in Pr- or Tm-doped system. However, the output power in Pr-doped system is not high enough for many applications usually. The only high-power blue upconversion laser is Tm^{3+}-doped system [2, 3]. Because the blue upconversion emission intensity is low in single Tm^{3+} ions doped matrices, the introduction of Yb^{3+} ions as a sensitizing center can greatly enhance upconversion luminescence of Tm^{3+} ion activator [4, 5], while it may not cause obvious fluorescence quenching due to the peculiar energy level structure of Yb^{3+} ions. At present, several matrices about blue upconversion luminescence of Tm^{3+}–Yb^{3+}-doped have been studied containing ZBLAN [6], fluoroindate [7], fluorophosphates [8] and silica glasses [9]. Much interest is in fluoride glasses for upconversion matrices because of their large transparency window, the capability of incorporating large concentration of rare earth ions, especially their lower phonon energies which capable of high upconversion efficiency than other matrices. However, their poor chemical stability, considerable low laser damage threshold, weak mechanic strength and difficult to process make them unsuitable for practical application.

In this work, we investigate the upconversion sensitization luminescence of Tm^{3+} ions in a new oxyfluoride tellurite glass with a diode laser at 976 nm pumping wavelength. The purpose is to search the method and materials that have both high upconversion efficiency and advanced material property by

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exploring new matrices. The tellurite-based glass presents good optical quality, good glass stabilities and corrosion resistances, which are better than those in fluoride glasses, it is stable against atmospheric moisture, it exhibits low optical attenuation from 400 nm to 5.0 µm, and due to the > 2.0 refractive index, one expects to obtain significantly high radiative decay rates of rare-earth energy levels [10–12]. The material also exhibits high solubility allowing the incorporation of high lanthanide concentrations apart from being non-hygroscopic and to present high thermal stability against crystallization. Moreover, tellurite glass has the lowest phonon energy among oxide glasses, which is available to improve the blue upconversion efficiency of Tm^{3+} ions. In addition, inclusion of ZnF_2 in component is to improve the upconversion efficiency [13]. Our study shows that under the Yb^{3+} ions sensitization, the blue upconversion luminescence of Tm^{3+} is observed clearly by eyes and is enhanced to relatively high intensity with suitable Tm^{3+} concentration. For fixed Yb^{3+} concentrations, the maximum upconversion efficiency was obtained with Tm_2O_3 concentration of about 0.1 mol%. Therefore, it is suitable host to have both high upconversion efficiency and advanced material properties for various upconversion applications. To our knowledge, similar research has not been reported until now.

Experimental

Starting composition for sample preparation was in mol%: $50TeO_2–5B_2O_3–10GeO_2–5PbO–25ZnF_2–xTm_2O_3–5Yb_2O_3$, where $x = 0.01,0.1,0.2$ and 0.5. The well-mixed raw materials were melted at 750–800° in a corundum crucibles using an electronic furnace in non-oxidizing atmosphere for 20 min. The obtained glasses were annealed to room temperature gradually, and then were cut and polished carefully to $10 \times 20 \times 1\ mm^3$ in order to meet the requirements for optical measurements.

The optical absorption spectra were recorded by using Perkin–Elmer 900 spectrophotometer in the range of 400–2200 nm. Upconversion emission spectra were obtained by exciting the samples with a TRIAX550 spectrofluorimeter upon excitation of 980 nm LD. The sample and experiment condition is carefully controlled during the measurement to allow the quantitative comparison on their relative fluorescence intensities. The lifetime for the $^1G_4$ level of Tm^{3+} was measured using a modulated 980 nm LD and a Tektronix TDS3052 digital oscilloscope controlled by a computer. All the measurements were taken at room temperature.

Results and discussion

Absorption spectra and energy level diagram

Absorption spectra of all glasses were obtained at room temperature in the 400–2,000 nm spectral ranges. Figure 1 shows the absorption spectrum of the compound doped with 0.1 mol% Tm_2O_3. The shape and the position of each band are similar in different concentration of Tm^{3+} except the relative intensity of absorbance. The bands correspond to the transition from the ground state, $^3H_6$, to the different excited states of Tm^{3+} ions. The energy level diagram of Yb^{3+} and Tm^{3+} ions obtained in oxyfluoride tellurite glasses from the absorption spectra, identifying the level by comparison with the data for free ions is presented in Fig. 2.

Dependence of Tm^{3+} concentration and the analyses of energy transfer process

By exciting at 976 nm (Yb^{3+}:$^2F_{7/2} \rightarrow {}^2F_{5/2}$) oxyfluoride tellurite glasses doped 0.01, 0.1, 0.2, and 0.5 mol% Tm_2O_3 respectively, the upconversion spectra shown in Fig. 3 are obtained. The three upconversion emissions bands centered at 475, 650 and 796 nm are attributed to the transitions $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3H_4$ and $^3F_4 \rightarrow {}^3H_6$, respectively. Clearly, the blue emission at 475 nm is the strongest and the red emission at 650 nm is the weakest of the three bands when the concentration of Tm_2O_3 is 0.1 mol%. Figure 4 shows the trends of

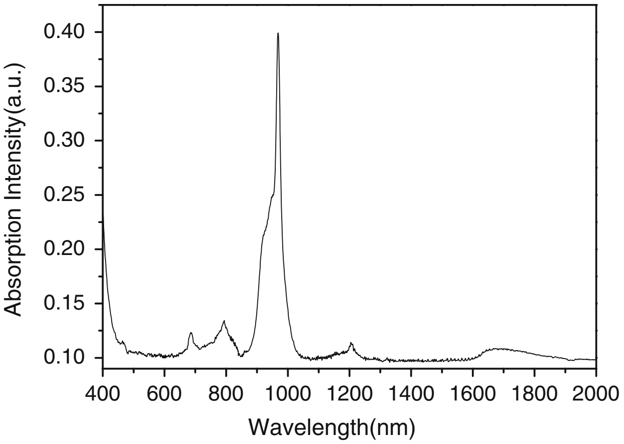

Fig. 1 Room temperature absorption spectrum of the glass doped with 0.1 mol% Tm_2O_3

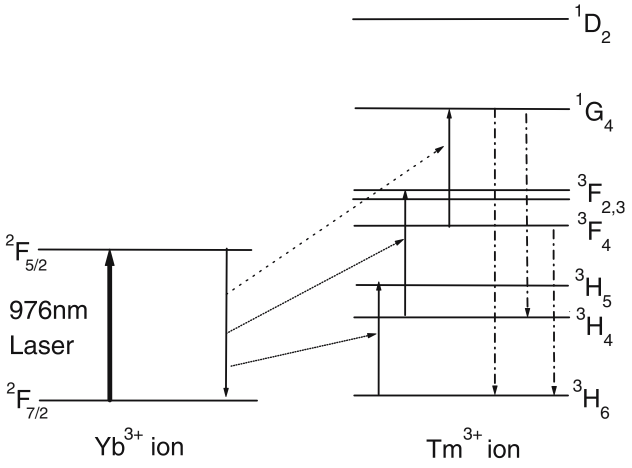

Fig. 2 Energy level diagram of Tm^{3+} and Yb^{3+} ions in oxyfluoride tellurite glasses. Upconversion excitation mechanism under excitation at 976 nm is indicated

emission intensities at the three bands with the change of Tm^{3+} ions concentration. The changes of the blue, red and IR emission are similar but the magnitude of the blue emission at 475 nm is much larger than those of red and IR emission which at 650 and 796 nm respectively. The emission intensity at 475 nm, corresponding to the $^1G_4 \rightarrow\ ^3H_6$ transition, increases first and a maximum is observed for a Tm_2O_3 concentration of 0.1 mol% and then decreases. This result can be explained as follows:

$$Tm^{3+}(^3H_6), Yb^{3+}(^2F_{5/2}) \rightarrow Tm^{3+}(^3H_4), Yb^{3+}(^2F_{7/2}) \quad (1)$$

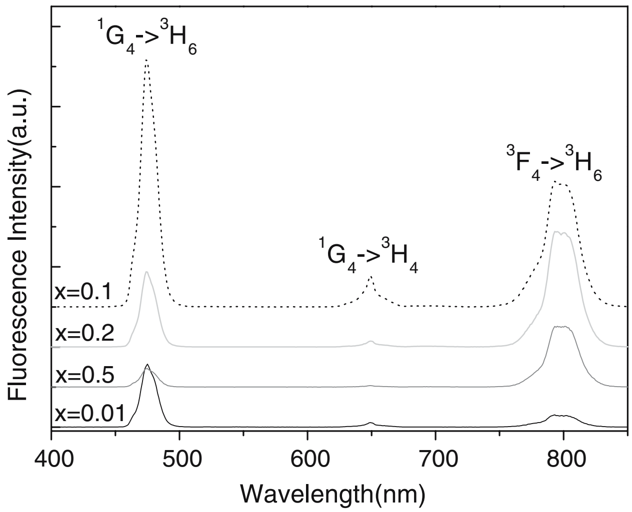

Fig. 3 Upconversion emission spectra obtained at room temperature under excitation at 976 nm in oxyfluoride tellurite glasses codoped with different Tm^{3+} ions and 5.0 mol% Yb_2O_3

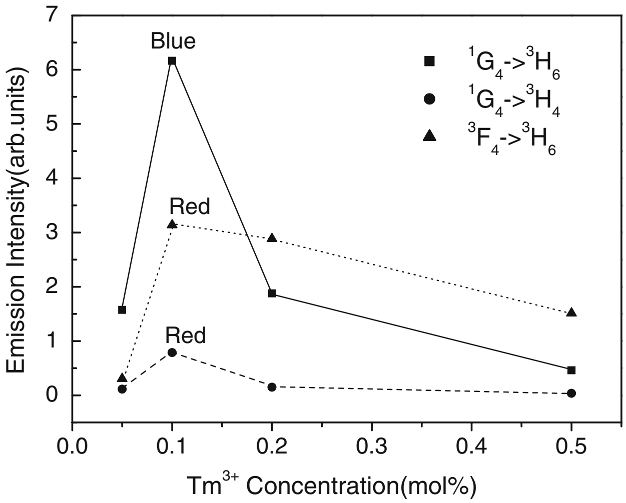

Fig. 4 Dependence of the blue, red and IR upconversion emission on different Tm_2O_3 concentration with 0.01, 0.1, 0.2 and 0.5 mol% in codoped with 5.0 mol% Yb_2O_3 ions obtained under excitation at 976 nm

When the concentration of Tm_2O_3 is 0.05 mol% lowly, $Tm^{3+}(^3H_6)$ is excitated to $Tm^{3+}(^3H_4)$ by $Yb^{3+}(^2F_{5/2})$ as given by (1) and the energy back-transfer can be assumed to be very low and negligible. As the concentration of Tm^{3+} increase, the emission intensity of $^1G_4 \rightarrow\ ^3H_6(Tm^{3+})$ transition increases remarkably while the back-transfer increases correspondingly and the equilibrium between transfer and back-transfer process occurs and the blue emission intensity is up to maximum at $Tm_2O_3 = 0.1$ mol%. After then, the energy back-transfer from Tm^{3+} to Yb^{3+} is higher than energy transfers from Yb^{3+} to Tm^{3+}, so the Tm^{3+} concentration of level $^1G_4$ decreases and the blue emission intensity decreases. The reasons of both $^1G_4 \rightarrow\ ^3H_4$ and $^3F_4 \rightarrow\ ^3H_6$ transitions are same. But when $Tm_2O_3 > 0.1$ mol%, the Tm^{3+} concentration of the level $^1G_4$ are higher than that of level $^3F_4$. Therefore, the emission intensity of IR at 976 nm is higher than that of blue at 475 nm.

Figure 5 illustrates the dependence of $^1G_4$ level lifetime on the concentrations of Tm^{3+} in oxyfluoride tellurite glasses. When the concentration of Tm_2O_3 is low, the lifetime of $^1G_4$ level is high that means the energy transfer from Yb^{3+} to Tm^{3+} is very efficient and the back-transfer is low [14]. When the concentrations of Tm^{3+} increase, the fluorescence lifetimes of $^1G_4$ level decrease rapidly. Thus, it is concluded that the energy back-transfer occurs from Tm^{3+} to Yb^{3+} and blue upconversion luminescence is quenched in high Tm^{3+} concentration regions. The mechanism governing energy back-transfer is a non-resonant energy transfer, depending largely on the Tm^{3+} concentration of $^3F_4$

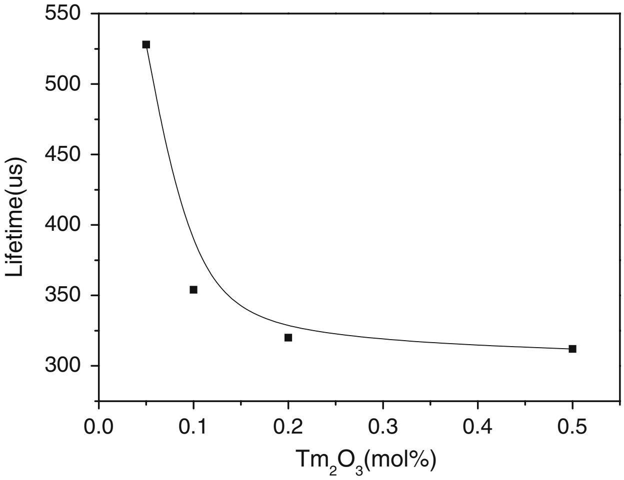

Fig. 5 Lifetime of $^1G_4$ level of Tm^{3+} versus concentration of Tm^{3+} in 5 mol% Yb_2O_3 doped oxyfluoride tellurite glasses

and $^3H_4$ level, which can be excited to $^1G_4$ level by $Yb^{3+}(^2F_{5/2})$ gradually.

Upconversion mechanism

In order to analyze the upconversion mechanism which populates the $^1G_4$ level, the pump power dependences of the emission corresponding to $^1G_4 \rightarrow {}^3H_6$ transition at 475 nm, $^1G_4 \rightarrow {}^3H_4$ transition at 650 nm and $^3F_4 \rightarrow {}^3H_6$ transition at 796 nm was investigated on the excitation intensity at 976 nm and the results were depicted in log-log plots of Fig. 6. The experimental data have been fit to straight lines with slopes of 2.8, 2.2 and 1.7, respectively. Taking into account these results, it would be concluded that the processes for the blue, red and IR emissions under excitation at 976 nm are based in successive three, two and two transfers, respectively, from Yb^{3+} ions (see Fig. 2). According to the energy matching conditions, the cubic and quadratic dependence on excitation power, the possible upconversion mechanisms for the emission bands are discussed based on the simplified energy levels of Tm^{3+} presented in Fig. 2 [15, 16]. The upconversion sensitization passage of Tm^{3+}, Yb^{3+} codoped oxyfluoride tellurite glasses is shown as follows:

$$^2F_{5/2}(Yb) + {}^3H_6(Tm) \rightarrow {}^2F_{7/2}(Yb) + {}^3H_5(Tm) \sim {}^2F_{7/2}(Yb) + {}^3H_4(Tm) \qquad (2)$$

$$^2F_{5/2}(Yb) + {}^3H_4(Tm) \rightarrow {}^2F_{7/2}(Yb) + {}^3F_2(Tm) \sim {}^2F_{7/2}(Yb) + {}^3F_4(Tm) \qquad (3)$$

$$^2F_{5/2}(Yb) + {}^3F_4(Tm) \rightarrow {}^2F_{7/2}(Yb) + {}^1G_4(Tm). \qquad (4)$$

For the blue emission, the mechanism of the three-photon process is similar to that observed in other Yb^{3+}:Tm^{3+}-doped system [17, 18]. Absorption of pump photons populates the long-lived $^2F_{5/2}$ level in Yb^{3+}. Non-resonant energy transfer from the Yb^{3+} ion to the Tm^{3+} ion then takes place causing excitation to the $^3H_5$ level in Tm^{3+} along with the emission of photons. This transition transferred to the $^3H_5$ level of Tm^{3+}. This population relaxes rapidly to the $^3H_4$ level by non-radiative multiphonon decay as Eq. (2). Then from the $^3H_4$ level second transition to the $^3F_2$ level is caused. This transfer releases 1,090 cm^{-1} to the matrix phonons. The $^3F_2$ state again relaxes by multiphonon relaxation to the $^3F_4$ state as Eq. (3) and a third non-resonant transfer excites it by a third Yb^{3+} ion to the $^1G_4$ state with 1,490 cm^{-1} of energy released as Eq. (4). The $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3H_4$ and $^3F_4 \rightarrow {}^3H_6$ transition can emit fluorescence at 475, 650 and 796 nm, respectively.

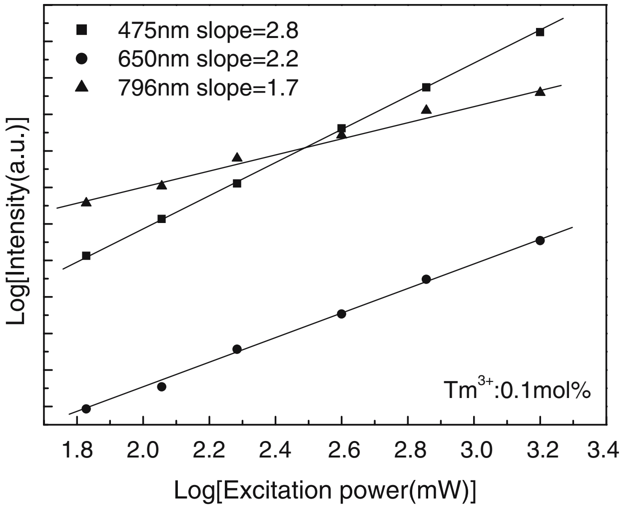

Fig. 6 Log-log plot of upconversion luminescence as a function of pump power at 976 nm

Conclusion

We have demonstrated intense Tm^{3+} blue upconversion emission in Tm^{3+}–Yb^{3+} codoped oxyfluoride tellurite glass under excitation with a diode laser at 976 nm. Three intense emission bands centered at 475, 650, 796 nm are observed under 976 nm excitation, which are assigned to the transition $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3H_4$ and $^3F_4 \rightarrow {}^3H_6$, respectively and are based on three, two and two photon absorption processes accordingly. The dependence of upconversion fluorescence on Tm^{3+}

doping concentration and pump power is investigated. The result shows that the blue emission intensity doped with 0.1 mol% Tm^{3+} is stronger than that of other Tm^{3+} concentration. The energy transfers from $Yb^{3+} \rightarrow Tm^{3+}$ and back-transfer from $Tm^{3+} \rightarrow Yb^{3+}$ processes are analyzed. The discussion of upconversion mechanisms reveals that the 475 nm blue signal is attributed to Tm^{3+} ions excited by a stepwise phonon-assisted energy transfer process, and 650 nm red and 796 nm IR upconversion luminescence are identified as also from Tm^{3+} ions populated via efficient cross-relaxation and energy transfer.

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