2.0 μm Ultra Broadband Emission from Tm$^{3+}$/Ho$^{3+}$ Co-Doped Gallium Tellurite Glasses for Broadband Light Sources and Tunable Fiber Lasers

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Abstract: A flat 2.0 μm ultra broadband emission with a full width at half maximum (FWHM) of 329 nm is achieved in 1 mol.% Tm$_2$O$_3$ and 0.05 mol.% Ho$_2$O$_3$ co-doped gallium tellurite glasses upon the excitation of an 808 nm laser diode. The influence of Tm$^{3+}$ and Ho$^{3+}$ contents on 2.0 μm spectroscopic properties of gallium tellurite glasses is minutely investigated by absorption spectra, emission spectra, and lifetime measurement. In addition, emission cross section and gain coefficient of Ho$^{3+}$ ions at 2.0 μm are calculated, and the maximum values reach 8.2 × 10$^{-21}$ cm$^2$ and 1.54 cm$^{-1}$, respectively. Moreover, forward and backward energy transfer probability between Tm$^{3+}$ and Ho$^{3+}$ ions are qualitatively evaluated by the extended spectral overlap method. Large ratio of the forward energy transfer from Tm$^{3+}$ to Ho$^{3+}$ to the backward one (19.7) and high forward energy transfer coefficient (6.22 × 10$^{39}$ cm$^6$/s) are responsible for effective 2.0 μm emission from Ho$^{3+}$ ions. These results manifest that Tm$^{3+}$/Ho$^{3+}$ co-doped gallium tellurite glass is suitable for potential applications of broadband light sources and tunable fiber lasers operating in eye-safe 2.0 μm spectral region.

Keywords: gallium tellurite glass; Tm$^{3+}$/Ho$^{3+}$ co-doped; 2.0 μm ultra broadband emission; energy transfer; tunable fiber laser

1. Introduction

In the past few decades, numerous studies have gone into achieving high-brightness broadband light sources and tunable fiber lasers operating at eye-safe 2.0 μm wavelength range because of broad applications in the fields of urology, gas sensing, remote atmospheric monitoring, and material processing, and their use as an efficient pumping source for obtaining mid-infrared supercontinuum [1–6]. It is well known that Tm$^{3+}$:3F$_4$ → 3H$_6$ and Ho$^{3+}$:5I$_7$ → 5I$_8$ radiative transitions are the most efficient and feasible ways to generate 2.0 μm emission when they are doped into an appropriate host glass. Moreover, both transitions work in the three-level quantum scheme and hence respective emission bands are relatively broad, which allows to obtain broadband emission from 1.7 to 2.1 μm [4,7]. Tm$^{3+}$ has an intense absorption band near 808 nm, which allows for the excitation of high-power and low-cost laser diode (LD). Another advantage of the pump scheme is the so-called “two-for-one” cross relaxation process (H$_4^+ + 3H_6 → 2F_4$) resulting in a quantum efficiency of near 200% [8]. Additionally, Tm$^{3+}$:3F$_4$ → 3H$_6$ transition is one of the broadest luminescent transitions among rare earth ions and thus enables a fair degree of wavelength tenability [8]. Compared with Tm$^{3+}$, the emission wavelength of Ho$^{3+}$:5I$_7$ → 5I$_8$ transition generates ~200 nm redshift, which overlaps with a crucial atmospheric transmission window and leads to lower absorption in some nonlinear crystals (e.g., ZnGeP$_2$) for the generation of mid-infrared light [7,9]. Moreover, the lifetime of Ho$^{3+}$:5I$_7$ energy level is
longer than that of Tm$^{3+}$-$^3$F$_4$ energy level, which is beneficial to reduce the laser threshold and achieve higher pulse energy in a Q-switched mode [9]. However, Ho$^{3+}$ cannot be promoted directly by commercially available 808 or 980 nm LD, owing to the inexistence of a suitable ground absorption band. Therefore, a Tm$^{3+}$/Ho$^{3+}$ co-doped system is developed to utilize direct commercial LD pumping [10–12]. In this case, Tm$^{3+}$ plays the role of a sensitizer that efficiently absorbs pumping energy and then transfers a part of this energy to Ho$^{3+}$, followed by the generation of 2.0 μm emission. This system can make the best use of an emission bandwidth of Tm$^{3+}$ and Ho$^{3+}$ near 2.0 μm so it is expected to achieve ultra broadband emission by adjusting Tm$^{3+}$ and Ho$^{3+}$ concentrations. In fact, a 303 nm tuning range from 1727 to 2030 nm has been obtained in Tm$^{3+}$/Ho$^{3+}$ co-doped silica fiber laser [13]. Compared with silica glass, tellurite glass is characterized by lower phonon energy (780 cm$^{-1}$), excellent infrared transmission range (up to 5 μm), higher rare earth ion solubility, and large refractive index (>1.95) [7,8,14]. It is worth mentioning that tellurite glass owns different structural units such as TeO$_4$, TeO$_3$:S, and TeO$_3$, which creates a range of electro-static fields around a rare earth ion and thus leads to the spectral broadening [15]. Richards et al. found that the full width at half maximum (FWHM) of Tm$^{3+}$-$^3$F$_4 \rightarrow ^5$H$_6$ emission band in the tellurite glass (200 nm) was larger than that in ZBLAN glass (125 nm) and silica glass (150 nm), indicating that tellurite glass host can extend the tuning range for 2.0 μm fiber lasers [8]. Recently, our group reported gallium tellurite glasses with excellent glass-forming ability, thermal stability, and 2.0 μm spectra properties [16,17]. Moreover, with the addition of 9 mol.% BaF$_2$, the emission intensity near 1.8 μm was 1.6 times as large as the original while the lifetime became 1.7 times as long as the original [18]. These outstanding optical properties hearten us to further explore whether Tm$^{3+}$/Ho$^{3+}$ co-doped gallium tellurite glasses is appropriate for broadband light sources and tunable fiber lasers.

In this investigation, we systematically study the effect of Tm$^{3+}$ and Ho$^{3+}$ concentrations on 2.0 μm spectroscopic properties of gallium tellurite glasses by absorption spectra, emission spectra, and lifetime measurement. A flat ultra broadband emission at 2.0 μm with FWHM of 329 nm is demonstrated by adjusting doping concentration. Furthermore, emission cross section and gain coefficient of Ho$^{3+}$-$^5$I$_7 \rightarrow ^5$I$_8$ transition are evaluated based on absorption spectra and emission spectra. Additionally, forward and backward energy transfer probabilities between Tm$^{3+}$ and Ho$^{3+}$ ions are qualitatively discussed by the extended spectral overlap method.

2. Materials and Methods

Gallium tellurite glasses with different nominal compositions of (81-x)TeO$_2$-10Ga$_2$O$_3$-9BaF$_2$+xTm$_2$O$_3$ (x = 0, 0.5, 1, 1.5, and 2), (80-y)TeO$_2$-10Ga$_2$O$_3$-9BaF$_2$-1Tm$_2$O$_3$-yHo$_2$O$_3$ (y = 0.05, 0.1, 0.15, 0.3, and 0.5), and 80.5TeO$_2$-10Ga$_2$O$_3$-9BaF$_2$-0.5Ho$_2$O$_3$ were prepared by standard melt-quenching method. A series of samples were labeled as TGBT-x (x = 0, 0.5, 1, 1.5, and 2), TGBTH-y (y = 0, 0.05, 0.1, 0.15, 0.3, and 0.5), and TGBH-0.5, respectively. Batches of 20 g mixtures by weighing and mixing high-purity reagents (99.99% minimum) were placed in the alumina crucible and melted in an electric furnace at ~950 °C for 30 min. The molten glasses were poured into a preheated cylindrical graphite mold, followed by annealing in the muffle furnace at 330 °C for 2 h, and then cooled down slowly to room temperature. The annealed samples were optically polished into Φ15 mm × 1.5 mm cylinders for subsequent measurements.

Absorption spectra of samples were obtained by UV/VIS/NIR double beam spectrophotometer (Perkin-Elmer Lambda 900, Waltham, MA, USA) in the wavelength range from 350 to 2200 nm. The fluorescence spectra were recorded with a computer-controlled Omni 5015i spectrometer (Zolix, Beijing, China) under the excitation of an 808 nm LD. The fluorescence signal was collected by InAs detector equipped with a choppe and lock-in amplifier. In addition, the luminescence decay curves of Tm$^{3+}$ and Ho$^{3+}$ were recorded by a digital oscilloscope (TDS3012C, Tektronix, OR, USA) after the samples were pumped with 808 nm pulse laser controlled by a function generator (TFG3051C, Tektronix, OR,
USA). The pulse duration was 22.5 ms. All of the measurements were carried out at room temperature.

3. Results and Discussion

3.1. Absorption Spectra

Figure 1 shows the absorption spectra of Tm$^{3+}$ singly doped, Ho$^{3+}$ singly doped, and Tm$^{3+}$/Ho$^{3+}$ co-doped gallium tellurite glasses in the 350–2200 nm range. The typical absorption bands assigned to the transitions from the ground state to higher excited states of Tm$^{3+}$ and Ho$^{3+}$ are marked in the figure. For Tm$^{3+}$ singly doped glass, there are five absorption bands centered at 473, 687, 794, 1214, and 1700 nm, which are corresponding to respective transitions from the $3\text{H}_6$ ground state to the higher energy levels $3\text{F}_4$, $3\text{F}_2$, $3\text{H}_5$, and $3\text{F}_4$. For Ho$^{3+}$ singly doped glass, eight absorption peaks located at 418, 450, 486, 538, 644, 892, 1154, and 1952 nm appear, which are assigned to respective transitions from the $5\text{I}_8$ ground state to the higher energy levels $5\text{G}_5$, $5\text{G}_6$, $5\text{F}_4 + 5\text{S}_2$, $5\text{F}_5$, $5\text{I}_5$, $5\text{I}_6$, and $5\text{I}_7$. Energy levels above $1\text{G}_4$ energy level of Tm$^{3+}$ and $5\text{G}_5$ energy level of Ho$^{3+}$ are not clearly observed due to strong intrinsic bandgap absorption in the host glass.

In addition, the peak positions of each absorption band for the Tm$^{3+}$/Ho$^{3+}$ co-doped glass sample are very similar to those reported previously from other host glasses [7,19,20]. It is worth noting that there is a strong absorption band centered at 794 nm from Tm$^{3+}$: $3\text{H}_6 \rightarrow 3\text{H}_4$ transition, which indicates that the commercial high-power 808 nm LD can act as an effective pump source for Tm$^{3+}$ singly doped and Tm$^{3+}$/Ho$^{3+}$ co-doped samples. The inset of Figure 1 presents the integral absorption intensity at 538 nm as a function of Ho$_2$O$_3$ concentration. Good linear dependence on concentration reveals that Ho$^{3+}$ ions are homogeneously distributed in the present gallium tellurite glasses and the concentration is in accord with the nominal value [21].

![Figure 1](image_url)

**Figure 1.** Absorption spectra of TGBT-1, TGBH-0.5, and TGBTH-0.5 glasses. The inset shows integral absorption intensity at 538 nm as a function of Ho$_2$O$_3$ concentration.

3.2. Fluorescence Spectra and Energy Transfer Mechanism

To study the effect of Tm$^{3+}$ concentration on the 2.0 µm emission property and determine its optimum concentration, the fluorescence spectra of Tm$^{3+}$ singly doped samples with different content pumped by 800 nm LD were measured, as shown in Figure 2. There is no emission band in the host glass without containing Tm$^{3+}$. However,
the spectra are characterized by an intense emission peak at 1808 nm resulting from $^3F_4 \rightarrow ^3H_6$ transition along with a very weak emission band near 1488 nm corresponding to $^3H_4 \rightarrow ^3F_4$ transition when Tm$^{3+}$ ions are doped in the host glass. Moreover, with the increment of Tm$^{3+}$ concentration, 1.8 $\mu$m emission is stronger until the concentration of Tm$_2$O$_3$ reaches 1 mol.%, which can be accounted for by the enhancement of cross-relaxation process ($^3H_4 + ^3H_6 \rightarrow 2^3F_4$) due to shortening the distance among neighboring Tm$^{3+}$ ions. Then, the emission intensity decreases gradually with further increasing the concentration, which may ascribe to the concentration quenching phenomenon. The inset of Figure 2 shows that fluorescence intensity near 1488 nm is gradually reduced with increasing Tm$_2$O$_3$ concentration from 0.5 to 2 mol.%, which reveals that the cross-relaxation process becomes more significant and is in favor of the enhancement of 1.8 $\mu$m emission. Therefore, the optimum concentration of Tm$_2$O$_3$ is 1 mol.% in view of the 1.8 $\mu$m emission intensity.

![Figure 2](image_url) **Figure 2.** Fluorescence spectra of TGBT-x glasses under excitation at 800 nm laser diode (LD). The inset presents emission spectra in the range from 1400 nm to 1560 nm.

Figure 3 presents the fluorescence decay traces of Tm$^{3+}:^3F_4$ energy level monitored at 1808 nm in TGBT-x glass samples. It is found that the fluorescence lifetime of $^3F_4$ energy level decreases monotonically from 1.42 to 0.24 ms with the increment of Tm$_2$O$_3$ concentration from 0.5 to 2 mol.%, which may be due to the enhancement of energy transfer probability toward unidentified impurities in samples such as OH$^-$ groups. In addition, the fluorescence decay curves are well fitted by single-exponential and $R^2$ is above 0.999, indicating that the radiative decay process is prominent compared with the nonradiative decay process, benefitted from low maximum photon energy and the presence of BaF$_2$. A similar single-exponential phenomenon has been observed in Tm$^{3+}$-doped heavy metal gallate glasses and tellurite glasses [22,23].

In the case where the concentration of Tm$_2$O$_3$ was 1 mol.%, the influence of Ho$^{3+}$ concentration on 2.0 $\mu$m emission property of Tm$^{3+}$/Ho$^{3+}$ co-doped glass samples was further investigated. Figure 4 exhibits the fluorescence spectra of Tm$^{3+}$/Ho$^{3+}$ co-doped TGBTH-y samples in the range from 1400 to 2200 nm under the excitation of 808 nm LD. It is noted that two emission bands from Tm$^{3+}$ centered at 1488 and 1808 nm appear in TGBTH-y samples, while a new double peak at 2.0 $\mu$m arises, originating from Ho$^{3+}:^5I_7 \rightarrow ^5I_8$ transition, with the incorporation of Ho$^{3+}$ ions. With gradually enhancing Ho$_2$O$_3$ from 0 to 0.5 mol.%, 1.8 $\mu$m emission intensity reduces and 2.0 $\mu$m emission intensity increases while...
1488 nm peak intensity is almost constant, which is ascribed to the presence of an effective energy transfer process from Tm$^{3+}$:3$F_4$ to Ho$^{3+}$:5$I_7$ energy level and thus makes their intensity values approximately equal. The inset of Figure 4 shows Ho$_2$O$_3$ concentration dependence of the largest emission bandwidth, defined as full width at half maximum (FWHM), in TGBTH-$y$ samples. It is found that FWHM increases from 193 to 329 nm with the addition of 0.05 mol.% Ho$_2$O$_3$ and then decreases gradually to 152 nm with further boosting Ho$_2$O$_3$ concentration to 0.5 mol.%. It is worth mentioning that a flat ultra broadband 2.0 $\mu$m emission with FWHM of 329 nm is achieved in 1 mol.% Tm$_2$O$_3$ and 0.05 mol.% Ho$_2$O$_3$ co-doped gallium tellurite glasses, which is due to energy transfer process from Tm$^{3+}$:3$F_4$ to Ho$^{3+}$:5$I_7$ energy level and partial overlap of Tm$^{3+}$:3$F_4 \rightarrow 3$H$_6$ and Ho$^{3+}$:5$I_7 \rightarrow 5$I$_7$ transitions. The value is larger than that of Tm$^{3+}$/Ho$^{3+}$ co-doped silicate-germanate glass (231.5 nm) [20] and silicate glass (189 nm) [24] and is slightly lower than that of Yb$^{3+}$/Tm$^{3+}$/Ho$^{3+}$ triply doped gallo-germanate glass (343 nm) [25]. Larger FWHM will provide a better opportunity to achieve broad amplified spontaneous emission (ASE) sources and tunable fiber lasers [4,7]. In addition, the dependence of Ho$^{3+}$:5$I_7$ lifetime on Ho$_2$O$_3$ concentration is presented in Figure 5. It is noted that the fluorescence lifetime of Ho$^{3+}$:5$I_7$ energy level is gradually prolonged from 1.46 to 2.08 ms with increasing Ho$_2$O$_3$ concentration from 0.05 to 0.3 mol.% because of improved energy transfer from Tm$^{3+}$:3$F_4$ to Ho$^{3+}$:5$I_7$ energy level. However, with further increasing the concentration, the lifetime begins to decrease due to the effect of concentration quenching. The relationship between the lifetime and doping concentration is very similar to that reported previously in Tm$^{3+}$/Ho$^{3+}$ co-doped silicate and tellurite glasses [24,26].

![Fluorescence decay curves](image-url)  
**Figure 3.** Fluorescence decay curves of Tm$^{3+}$:3$F_4$ energy level monitored at 1808 nm in TGBT-$x$ glass samples.
creasing Ho$_2$O$_3$ concentration from 0.05 to 0.3 mol.% because of improved energy transfer from Tm$^{3+}$:3F$_4$ to Ho$^{3+}$:5I$_7$ energy level. However, with further increasing the concentration, the lifetime begins to decrease due to the effect of concentration quenching. The relationship between the lifetime and doping concentration is very similar to that reported previously in Tm$^{3+}$/Ho$^{3+}$ co-doped silicate and tellurite glasses [24,26].

**Figure 4.** Fluorescence spectra of TGBTH-y glasses pumped by 800 nm LD. The inset shows Ho$_2$O$_3$ concentration dependence of full width at half maximum (FWHM).

**Figure 5.** Fluorescence decay curves of Ho$^{3+}$:5I$_7$ energy level monitored at 2050 nm in TGBTH-y glass samples.

According to above-mentioned results, the concerned energy transfer mechanisms in Tm$^{3+}$/Ho$^{3+}$ co-doped gallium tellurite glasses are shown in Figure 6 with the help of the simplified energy level diagram of Tm$^{3+}$ and Ho$^{3+}$. When samples are excited by 808 nm LD, Tm$^{3+}$ ions are initially motivated from the $^3$H$_6$ ground state to the $^3$H$_4$ excited state. Then, a small part of Tm$^{3+}$ ions on the $^3$H$_4$ excited state decay radiatively to the $^3$F$_4$ energy
level, emitting fluorescence at 1488 nm, while the majority of ions return nonradiatively to the $^3F_4$ energy level by multiphonon relaxation process and effective cross-relaxation process (CR) between two nearby Tm$^{3+}$ ions ($^3H_4 + ^3H_6 \rightarrow ^3F_4$). Tm$^{3+}$ ions on the $^3F_4$ state return radiatively to the ground state, producing 1.8 $\mu$m photon. On the other hand, they excite Ho$^{3+}:^5I_8$ energy level to the $^3I_2$ energy level via energy transfer process between two adjacent Tm$^{3+}$ and Ho$^{3+}$ ions (Tm$^{3+}:^3F_4$Ho$^{3+}:^5I_8 \rightarrow$ Tm$^{3+}:^3H_6$Ho$^{3+}:^3I_7$). Finally, strong 2.0 $\mu$m emission from Ho$^{3+}$ is observed by Ho$^{3+}:^5I_7 \rightarrow ^5I_8$ transition. It is worth noting that based on absorption spectra, the energy gap between $^3H_4 \rightarrow ^3F_4$ and $^3H_6 \rightarrow ^3F_4$ transitions is about 830 cm$^{-1}$, indicating that the cross-relaxation process has nonresonant character and only one or two phonons are demanded to bridge the energy gap because the maximum phonon energy of this gallium tellurite glass is nearly 787 cm$^{-1}$ [18].

![Figure 6. Simplified energy level diagram and energy transfer mechanisms for Tm$^{3+}$/Ho$^{3+}$ co-doped system.](image)

### 3.3. Gain Properties and Energy Transfer Coefficients between Tm$^{3+}$ and Ho$^{3+}$ Ions

To evaluate the gain properties of Tm$^{3+}$/Ho$^{3+}$ co-doped gallium tellurite glasses, absorption and emission cross sections of Tm$^{3+}$ and Ho$^{3+}$ ions, corresponding to Tm$^{3+}:^3H_6+^3F_4$ and Ho$^{3+}:^5I_8+^5I_7$ transitions, were determined by McCumber theory [27], as shown in Figure 7a. It is noted that the peak absorption cross section ($\sigma_a$) of Ho$^{3+}$ is $5.6 \times 10^{-21}$ cm$^2$ at 1952 nm, which is higher than that of germanate glass ($4.6 \times 10^{-21}$ cm$^2$) [28], lead silicate glass ($3.9 \times 10^{-21}$ cm$^2$) [29], and silicate-germanate glass ($2.8 \times 10^{-21}$ cm$^2$) [30]. Furthermore, the corresponding peak emission cross section ($\sigma_e$) reaches $8.2 \times 10^{-21}$ cm$^2$ at 2042 nm, which is higher than that of germanate glass ($5.2 \times 10^{-21}$ cm$^2$) [28], lead silicate glass ($4.2 \times 10^{-21}$ cm$^2$) [29], silicate-germanate glass ($4.8 \times 10^{-21}$ cm$^2$) [30], and tellurite glass ($6.7 \times 10^{-21}$ cm$^2$) [19], indicating that high laser gain can be achieved in the fiber prepared by the present glass. After absorption and emission cross sections of Ho$^{3+}$ ions were obtained and it was assumed that Ho$^{3+}$ ions are only in either the $^5I_7$ or $^5I_8$ energy level, the gain coefficient $G(\lambda)$ near 2.0 $\mu$m was computed by the expression to estimate the gain property qualitatively [31].

$$G(\lambda) = N[\rho \sigma_e - (1 - p)\sigma_a]$$ (1)
where \( N \) stands for the total population of Ho\(^{3+} \) ions and \( p \) represents the population inversion defined as the ratio between the population at the \(^{5}\!I_7 \) energy level and the total population. Figure 7b describes the effect of \(^{5}\!I_7 \rightarrow ^{5}\!I_8 \) transition wavelength on the gain coefficient in gallium tellurite glasses when \( p \) increases from 0 to 1 in steps of 0.2. It is found that the position of maximum gain moves toward shorter wavelength when \( p \) increases, which is a typical feature of the quasi-three-level system. Furthermore, positive gain coefficient occurs when \( p \) equals 0.2, revealing a low pumping threshold. In addition, the maximum gain coefficient reaches 1.54 cm\(^{-1} \) at 2048 nm, which is larger than that of lead silicate glass (0.89 cm\(^{-1} \)) [32], germanate-tellurite glass (0.27 cm\(^{-1} \)) [33], and tellurite glass (0.37 cm\(^{-1} \)) [19]. It is worth noting that overlay area between Tm\(^{3+} \) emission and Ho\(^{3+} \) absorption sidebands is much larger than that between Ho\(^{3+} \) emission and Tm\(^{3+} \) absorption cross sections, meaning that the forward energy transfer probability from Tm\(^{3+} \):\(^{3}\!F_4 \) to Ho\(^{3+} \):\(^{5}\!I_7 \) energy level is more efficient than the backward one. In order to evaluate forward and backward energy transfer probabilities between Tm\(^{3+} \) and Ho\(^{3+} \) ions qualitatively, a method proposed by Miyakawa and Dexter was adopted [34]. The probability rate of energy transfer from Tm\(^{3+} \) to Ho\(^{3+} \) can be computed by the following formula [34]:

\[
W_{D \rightarrow A} = (\frac{2\pi}{\hbar}) |H_{DA}|^2 S_N^D
\]  

(2)

where \( |H_{DA}| \) represents the matrix element of the perturbation Hamilton between initial and final states in the energy transfer process, \( S_N^D \) stands for the overlap integral between the m-phonon emission sideband of donor ions (D referring to Tm\(^{3+} \) here) and the k-phonon absorption sideband of acceptor ions (A referring to Ho\(^{3+} \) here), and \( N (N = m + k) \) denotes the total phonons in the energy transfer process. Subsequently, Tarelho et al. propose a method to determine the spectral sideband based on calculated emission and absorption cross sections for rare earth (RE) ions, as described by the following equations [35]:

\[
\sigma_e^D (m\text{-phonons}) = \sigma_e^D (\lambda_m^+) \approx \frac{S_0^m e^{-S_0}}{m!} (\pi + 1)^m \sigma_e^{D (\exp t)} (E - m\hbar\omega_0)
\]  

(3)

\[
\sigma_a^A (k\text{-phonons}) = \sigma_a^A (\lambda_k^-) \approx \frac{S_0^k e^{-S_0}}{k!} (\pi)^k \sigma_a^{A (\exp t)} (E + k\hbar\omega_0)
\]  

(4)

where \( S_0 \) represents the Huang-Rhys factor with the value of 0.31 for RE\(^{3+} \) ions, \( \hbar\omega_0 \) stands for the phonon energy of the host, and \( \pi = 1/(e^{\hbar\omega_0/kT} - 1) \) is the average occupancy of phonon mode at temperature \( T \). In addition, \( \lambda_m^+ = 1/(1/\lambda - m\hbar\omega_0) \) and \( \lambda_k^- = 1/(1/\lambda + k\hbar\omega_0) \) signify the wavelengths of Tm\(^{3+} \) with m-phonon emission and Ho\(^{3+} \) with k-phonon absorption, respectively. If we neglect the k-phonon annihilation process and just consider the m-phonon creation process, forward (D \( \rightarrow \) A) and backward (A \( \rightarrow \) D) energy transfer coefficients can be estimated by the following equations [35]:

\[
C_{D \rightarrow A} = \frac{6e^{g_{low}^D}}{(2\pi)^3 n^2 g_{up}^D} \sum_{N=0}^{\infty} \sum_{k=0}^{N} P_+^{(N-k)} P_+^k \int \sigma_e^D (\lambda_k^-) \sigma_a^A (\lambda) d\lambda
\]  

(5)

\[
C_{A \rightarrow D} = \frac{6e^{g_{low}^A}}{(2\pi)^3 n^2 g_{up}^A} \sum_{N=0}^{\infty} \sum_{k=0}^{N} P_-^{(N-k)} P_+^k \int \sigma_e^A (\lambda^-) \sigma_a^D (\lambda) d\lambda
\]  

(6)

\[
P_+^{(N-k)} \equiv \exp[-(2\pi + 1)S_0] \frac{S_0^{(N-k)}}{(N-k)!} (\pi + 1)^{(N-k)}
\]  

(7)

\[
P_-^k \equiv \exp[-2\pi S_0] \frac{S_0^k}{k!} (\pi)^k
\]  

(8)

where \( g_{low}^D (g_{low}^A) \) and \( g_{up}^D (g_{up}^A) \) stand for the degeneracies of the respective lower and upper states of the donor (acceptor), respectively. In addition, \( P_+^{(N-k)} \) and \( P_-^k \) represent the probability of \( (N-k) \)-phonon emission by the donor and \( k \)-phonon absorption by the
acceptor, respectively. Based on above equations, forward and backward energy transfer coefficients between Tm$^{3+}$ and Ho$^{3+}$ ions were obtained and are listed in Table 1. It is noted that the energy transfer coefficient of Tm$^{3+}$ → Tm$^{3+}$ migration is the largest due to the largest overlapping area, as shown in Figure 7a. Additionally, the ratio of forward to back energy transfer coefficient ($C_{Tm-Ho}/C_{Ho-Tm}$) reaches 19.7, indicating that the forward energy transfer from Tm$^{3+}$ to Ho$^{3+}$ is more effective than the backward one and thus ensures to achieve a strong 2.0 µm emission from Ho$^{3+}$. Comparing the percentage of each phonon participation, one can observe that both energy transfer processes between Tm$^{3+}$ and Ho$^{3+}$ are almost resonant energy transfer with non-phonon creation or annihilation. It is worth mentioning that the forward energy transfer coefficient from Tm$^{3+}$:3F$_4$ to Ho$^{3+}$:5I$_7$ energy level (6.22 × 10$^{39}$ cm$^6$/s) in the present glass is larger than that of germinate-tellurite glass (1.42 × 10$^{39}$ cm$^6$/s) [33] and silicate-germanate glass (3.39 × 10$^{39}$ cm$^6$/s) [20]. Therefore, Tm$^{3+}$/Ho$^{3+}$ co-doped gallium tellurite glass with FWHM of 329 nm, larger emission cross section, and high $C_{Tm-Ho}$ is a promising candidate for mid-infrared tunable fiber lasers.

![Figure 7. (a) Absorption and emission cross sections of Tm$^{3+}$ and Ho$^{3+}$ ions, corresponding to Tm$^{3+}$:H$_6$↔3F$_4$ and Ho$^{3+}$:I$_8$↔5I$_7$ transitions; (b) the effect of 5I$_7$→5I$_8$ transition wavelength on the gain coefficient in gallium tellurite glasses.](image)

| Energy Transfer                  | Number of Phonons | Energy Transfer Coefficient (cm$^6$/s) |
|----------------------------------|-------------------|----------------------------------------|
| Tm$^{3+}$ → Tm$^{3+}$(migration) | 0                 | 8.98 × 10$^{-39}$                      |
| (3F$_4$ + 3H$_6$ ↔ 3H$_6$ + 3F$_4$) | 99.86             | 1.62 × 10$^{-39}$                      |
| Tm$^{3+}$ → Ho$^{3+}$(direct transfer) | 0                 | 6.22 × 10$^{-39}$                      |
| (3F$_4$ ↔ 5I$_7$)                | 94.95             | 5.05                                   |
| Ho$^{3+}$ → Tm$^{3+}$(back transfer) | 0                 | 3.16 × 10$^{-40}$                      |
| (5I$_7$ → 3F$_4$)                | 99.32             | 0.68                                   |

4. Conclusions

In brief, dependence of Tm$^{3+}$ and Ho$^{3+}$ concentrations on 2.0 µm spectroscopic properties of Tm$^{3+}$/Ho$^{3+}$ co-doped gallium tellurite glasses under an 808 nm excitation is studied in detail. A flat ultra broadband emission at 2.0 µm with FWHM of 329 nm is achieved in gallium tellurite glasses co-doped with 1 mol.% Tm$_2$O$_3$ and 0.05 mol.% Ho$_2$O$_3$, benefitting from efficient energy transfer process from Tm$^{3+}$:3F$_4$ to Ho$^{3+}$:5I$_7$ energy level and partial
overlap of Tm$^{3+}$:F$_4$ $\rightarrow$ 3H$_6$ and Ho$^{3+}$:5I$_7$ $\rightarrow$ 5I$_8$ transitions. Furthermore, the present glass shows a long lifetime of Ho$^{3+}$:5I$_7$ energy level (2.08 ms), high emission cross section (8.2 x 10^{-21} \text{ cm}^2), and gain coefficient (1.54 cm$^{-1}$) near 2.0 µm. Additionally, forward and backward energy transfer probabilities between Tm$^{3+}$ and Ho$^{3+}$ ions are qualitatively calculated by the extended spectral overlap method. Larger C$_{\text{Tm-Ho}}$/C$_{\text{Ho-Tm}}$ (19.7) and high forward energy transfer coefficient (6.22 x 10^{39} \text{ cm}^6/\text{s}) ensure effective 2.0 µm emission. Consequently, these results indicate that this gallium tellurite glass is a very prospective candidate in constructing broadband light sources and tunable fiber lasers operating in eye-safe 2.0 µm spectral range.

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