Spectroscopic properties of $\text{Tm}^{3+}:\text{TeO}_2\text{-PbF}_2$ glasses in the near infrared

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ABSTRACT

Tm^{3+} -doped glasses have two emission bands that peak around 1470 nm and 1800 nm in the near infrared, making them potentially important in the development of fiber-optic amplifiers and fiber lasers. The relative strength and the quantum efficiency of these bands depend on the glass composition as well as the active ion concentration. In this study, we have investigated the variation of the luminescence strengths as a function of glass composition and Tm^{3+} ion concentration in a new type of Tm^{3+} -doped tellurite glass. In the experiments, two sets of samples with the host composition $(1-x)\text{TeO}_2\text{-(x)PbF}_2$ were prepared. In the first set, the active ion concentration was constant (1 mol. % Tm^{3+}) and $x=10, 15, 17, 20, 22$ and 25 mol. %. The second set had samples with $x=10$ mol. % and the active ion concentration varied from 0.2 to 1 mol. %. In the experiments, absorption measurements were first made to determine the spontaneous emission probabilities of the $4f\text{-}4f$ transitions of the Tm^{3+} ions. The calculations were made by using the Judd-Ofelt theory. The samples were then excited with a 785-nm diode to measure the relative emission strengths of the 1470-nm and 1800-nm bands. Our results show that as the Tm^{3+} ion concentration increases from 0.2 mol. % to 1 mol. %, the ratio of the 1470-nm intensity decreases from 0.98 to 0.18 relative to that of the 1800-nm band.

Keywords: Rare earth ion-doped glasses, tellurite glasses, fiber optic amplifiers, fiber lasers, near infrared spectroscopy.

1. INTRODUCTION

Recently, Tm^{3+} -doped gain media have attracted considerable attention because of their potential applications in the near infrared¹⁻⁵. Figure 1 shows the energy-level diagram of the Tm^{3+} ion. When excited around 800 nm, Tm^{3+} ions have two near-infrared emission bands centered at 1470 nm and 1800 nm due to the $^3\text{F}_4 \rightarrow ^3\text{H}_4$ and $^3\text{H}_4 \rightarrow ^3\text{H}_6$ transitions, respectively. These emission bands are important in the development of fiber-optic amplifiers and fiber lasers. An important advantage of the thulium-doped systems is that the $^3\text{H}_6 \rightarrow ^3\text{F}_4$ transition can be excited by using commercially available AlGaAs semiconductor diode lasers.

Many different hosts can be used for the synthesis of thulium-doped glasses including silicates, borates, phosphates, and tellurites. Until now, the optical amplifiers have been made by using rare-earth doped silica glasses despite the fact that the phonon cut-off frequency of these glass hosts is high. In addition, several researchers have pointed out that SiO_2 is not a suitable host for rare-earth ions because the ions tend to form clusters in the silica network. This clustering results in the concentration quenching of luminescence due to the non-radiative interaction of neighboring ions⁶. In our studies, tellurite-based glass hosts were preferred because of their favorable physical characteristics such as low melting temperature, high refractive index, good infrared transmission, and low phonon energy. In addition, tellurite glasses are resistant to atmospheric moisture and large concentrations of rare-earth ions can be incorporated into the glass matrix^{1,7}. Since TeO_2 cannot form a glass structure by itself, dopants such as PbF_2 are added to form TeO_2 -based bulk glasses.

In this study, we have investigated the variation of the luminescence strengths as a function of glass composition and Tm^{3+} ion concentration in a new type of Tm^{3+} -doped tellurite glass. In the experiments, two sets of samples with the host composition $(1-x)\text{TeO}_2\text{-(x)PbF}_2$ were prepared. In the first set, the active ion concentration was constant (1 mol. % Tm^{3+}) and $x=10, 15, 17, 20, 22$ and 25 mol. %. The second set had samples with $x=10$ mol. % and the active ion concentration varied from 0.2 to 1 mol. %. In the experiments, absorption spectra of the samples were first measured.

Fig 1. Energy levels of Tm^{3+} -doped glass.

The absorption spectra were analyzed by using the Judd-Ofelt theory to determine the intensity parameters, Ω_t ($t=2, 4, 6$), the spontaneous emission probabilities, and the radiative lifetimes of the 4f-4f transitions of the Tm^{3+} ion. The samples were then excited with a 785-nm diode to measure the relative emission strengths of the 1470-nm and 1800-nm bands. Our results show that as the Tm^{3+} ion concentration increases from 0.2 mol. % to 1 mol. %, the ratio of the 1470-nm intensity decreases from 0.98 to 0.18 relative to that of the 1800-nm band due to cross relaxation.

2. EXPERIMENTAL

2.1 Preparation of bulk glass samples

Tellurite glasses were prepared with the composition $(1-x)TeO_2 - (x)PbF_2$ where $x = 10, 15, 17, 20, 22$ and 25 in molar ratio. Two sets of samples were prepared. In the first set, the active ion concentration was constant (1 mol. % Tm^{3+}) and $x=10, 15, 17, 20, 22$ and 25 mol. %. The second set had samples with $x=10$ mol. % and the active ion concentration varied from 0.2 to 1 mol. %.

Fig. 2. The measured variation of the density as a function of (a) x (molar ratio of PbF_2) and (b) Tm^{3+} concentration.

All chemicals used were reagent grade of TeO_2 (99.999% purity, Aldrich Chemical Company), PbF_2 (99.99% purity, Aldrich Chemical Company), and Tm_2O_3 (99.9% purity, Sigma Chemical Company). Batches of 7g size were thoroughly

mixed and melted in a platinum crucible at 800 °C for 60 min by using an electrically heated furnace in air atmosphere. The glass melts were removed from the furnace at 800 °C and then air quenched by pressing between two rectangular graphite slabs at room temperature. The density of each glass was determined by using Archimedes' principle with distilled water as the immersion liquid. The density variation of the synthesized samples measured as a function of x and Tm^{3+} concentration is shown in Figs. 2(a) and (b).

2.2 Absorption and emission measurements

The absorption spectra of the polished glasses having thicknesses of 2 ± 1 mm were recorded with a spectrophotometer (Shimadzu UV-VIS-NIR 3101 PC) in the wavelength range of 400-2000 nm. The measured absorption data were used to calculate the absorption cross section using the Beer-Lambert law. The measurements were carried out at room temperature. Fluorescence intensity measurements were performed by using the experimental setup sketched in Fig. 3. The chopped output of a continuous-wave 785 nm diode laser was focused with a converging lens (L1, focal length = 5 cm) onto the samples to excite the Tm^{3+} ions from the ground state to the $^3\text{F}_4$ state.

Fig. 3. Schematic of the setup used for luminescence measurements.

Fig. 4. Absorption spectrum of 78TeO₂-22PbF₂ glass doped with 1mol. % Tm^{3+} ion in the visible and infrared region.

The total incident diode power was 25 mW. The emitted fluorescence was collected with a concave gold mirror (M1, radius of curvature = 7.5 cm) and imaged onto the entrance slit of a 0.5-m Czerny-Turner type monochromator (CVI, model DK 480). The fluorescence signal, was detected in two stages by using a preamplifier and a lock-in amplifier (Stanford Research, model SR830). The fluorescence signal was then digitized and acquired with a computer. In the measurements, the obtained spectra were not corrected for the spectral response of the PbS detector.

3. RESULTS

3.1 Radiative lifetime calculations

The absorption spectrum of 1.0 mol. % Tm_2O_3 doped 78 TeO_2 -22 PbF_2 glass is shown in Fig. 4. The spectrum shows six bands with peaks located at 452, 648, 685, 790, 1210, and 1666 nm corresponding to the ground state absorption of $^1\text{G}_4$, $^3\text{F}_2$, $^3\text{F}_3$, $^3\text{F}_4$, $^3\text{H}_5$ and $^3\text{H}_4$ levels, respectively. The positions of the absorption peaks for these glasses are very similar to thulium doped fluorozirconate-based glass, ZBLAN, and are therefore shifted slightly from thulium silicates⁸.

Fig. 5. Compositional dependence of the absorption bands of Tm^{3+} ion in the (a) visible and (b) near infrared wavelength region.

Figures 5 (a) and (b) show the effect of the glass composition on the spectral profiles of the absorption bands. The overall shape and the peak position of each transition remain unchanged. However, the integrated absorption cross-section of all the bands shows a dependence on glass composition except for that corresponding to the ${}^3\text{H}_6 \rightarrow {}^3\text{H}_5$ transition.

The absorption cross-section σ_{abs} for a ground-state absorption can be calculated from

$$\sigma_{abs}(\text{cm}^{-2}) = \frac{2.303 \log_{10}(I_0/I)}{cl}, \quad (1)$$

where $\log(I_0/I)$ is the absorbance, l is the thickness of the sample in cm, and c is the Tm^{3+} ion concentration in the glass. The Tm^{3+} ion concentration of each sample was calculated by using the batch composition and the measured density. The absorption cross-section for the ground state absorption bands of each level was integrated by using the following equation:

$$\Sigma_{abs} = \int \sigma_{abs}(\lambda) d\lambda. \quad (2)$$

In Eq. (2), Σ_{abs} is the integrated absorption-cross section and λ is the wavelength. Integrated absorption-cross section of all the levels except ${}^3\text{H}_5$ level varies considerably with the PbF_2 content. The spectral intensity, also known as the integrated absorbance, for the observed absorption bands was determined experimentally using the following formula:

$$f_{\text{exp}} = \int_{\text{band}} \mu(\lambda) d\lambda. \quad (3)$$

Here, $\mu(\lambda)$ is the absorption coefficient and is given by

$$\mu(\lambda) = \frac{2.303 \log_{10}(I/I_0)}{l}. \quad (4)$$

Table 1. Compositional dependence of the Judd-Ofelt intensity parameters.

Glass composition (mol %)			Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	Ω_6 (10^{-20} cm^2)
TeO_2	PbF_2	Tm_2O_3			
90	10	1.0	3.33	0.84	0.48
85	15	1.0	3.37	1.05	1.10
83	17	1.0	6.39	1.07	1.40
80	20	1.0	9.82	1.10	1.68
78	22	1.0	6.78	1.06	1.59
75	25	1.0	4.14	1.09	1.30

The Judd-Ofelt theory relates the theoretically determined oscillator strength $f_{cal}(J, J')$ of a transition (from the ground state to an excited state) to the integrated absorbance of the transition. For an electric dipole transition, the calculated oscillator strength for the transition from the ground state (SLJ) to the excited state ($S'L'J'$) is given by

$$f_{cal}(J, J') = \frac{8\pi^3 e^2}{3ch} \frac{(n^2 + 2)^2}{9n} \frac{\bar{\lambda}}{(2J + 1)} \times \sum_{t=2,4,6} \Omega_t \left| \langle SLJ \| U^{(t)} \| S'L'J' \rangle \right|^2, \quad (5)$$

where $\bar{\lambda}$ is the mean wavelength for the absorption bands (or bands in the case of overlapping Stark manifolds), n is the refractive index, and J is the total angular momentum quantum number of the ground state⁹. Since the reduced matrix elements $U^{(t)}$ are not strongly host dependent, we have used the values calculated by Kaminskii in LaF_3 ⁹. The three Judd-Ofelt intensity parameters Ω_2 , Ω_4 , and Ω_6 were obtained by doing a least squares fitting of $f_{cal}(J, J')$ with the experimentally determined oscillator strengths¹⁰. The results are given in Table 1. Figure 6 further shows the variation of the Judd-Ofelt intensity parameters as a function of composition.

Fig. 6. Variation of the Judd-Ofelt intensity parameters, Ω_i with fractional PbF_2 content x .

The Judd-Ofelt theory can be used to calculate the radiative lifetimes of the thulium ion as a function of the host composition. The spontaneous emission probability for an $SLJ \rightarrow S'L'J'$ electric-dipole transition can be calculated from

$$A(J, J') = \frac{64\pi^4 e^2}{3h(2J+1)} \frac{n(n^2+2)^2 \bar{\nu}^3}{9} \times \sum_{t=2,4,6} \Omega_t \left| \langle SLJ \| U^{(t)} \| S'L'J' \rangle \right|^2$$

$$= \frac{64\pi^4 e^2}{3h(2J+1)} \frac{n(n^2+2)^2 \bar{\nu}^3}{9} S^{ed}(J, J')$$
(6)

Above, $\bar{\nu}$ is the mean wave number of the transition. The total spontaneous fluorescence probability, W_R , for the i^{th} excited state is given as the sum of the $A(J, J')$ terms calculated over all terminal states. W_R is related to the radiative lifetime τ_R and the branching ratios, β , of the level through

$$\frac{1}{\tau_R(i)} = \sum_j A(i, j) = W_R$$
(7)

and

$$\beta = \frac{A(J, J')}{W_R}.$$
(8)

Spontaneous fluorescence probabilities (W_R) and radiative lifetimes, τ_R , for the metastable levels of Tm^{3+} ion in the glasses were determined by using Eq. (6). By using the matrix elements given in Ref. 9 for the Tm^{3+} ion, the expressions for S^{cd} appearing in Eq. (6) can be written as

$$S^{cd}[{}^3H_4\rightarrow{}^3H_6]=0.527\Omega_2+0.718\Omega_4+0.228\Omega_6$$

and

$$S^{cd}[{}^3F_4\rightarrow{}^3H_4]=0.129\Omega_2+0.133\Omega_4+0.213\Omega_6$$

for the emission bands at 1800 and 1470 nm, respectively. Best-fit values of the intensity parameters given in Table 1 above were then used for the calculation of the radiative lifetimes. The results for the ${}^3H_4\rightarrow{}^3H_6$ and ${}^3F_4\rightarrow{}^3H_4$ transitions are shown in Table 2. Note that the radiative lifetimes reach a minimum around $x=20$ mol.%.

Table 2. Calculated radiative lifetimes of the ${}^3H_4\rightarrow{}^3H_6$ and ${}^3F_4\rightarrow{}^3H_4$ transitions for different host compositions.

Glass composition (mol %)			$\tau_R = (1/W_R)$ (ms)	
TeO ₂	PbF ₂	Tm ₂ O ₃	3F_4	3H_4
90	10	1.0	0.521	2.880
85	15	1.0	0.395	2.771
83	17	1.0	0.253	1.771
80	20	1.0	0.180	1.191
78	22	1.0	0.224	1.690
75	25	1.0	0.326	2.316

3. 2 Investigation of cross-relaxation effects

With increasing concentration, thulium-doped samples begin to exhibit effects due to cross relaxation. The mechanism of cross relaxation is schematically shown in Fig. 7. After excitation to the 3F_4 level, a Tm^{3+} ion may decay non-radiatively to the 3H_4 level and promote a nearby Tm^{3+} ion initially in the ground state to the 3H_4 level.

Fig. 7. Schematic representation of cross-relaxation effects in thulium-doped glass.

This results in the emission of two photons at 1800 nm with one pump photon and enhances the relative strength of the 1800-nm band with respect to that of the 1470-nm band. In order to investigate the effect of cross relaxation, we

measured the emission spectra of the $^3\text{H}_4 \rightarrow ^3\text{H}_6$ and $^3\text{F}_4 \rightarrow ^3\text{H}_4$ transitions as a function of the host composition and ion concentration. Fig. 8(a) shows the variation of the measured emission intensity as a function of wavelength for the $^3\text{H}_4 \rightarrow ^3\text{H}_6$ and $^3\text{F}_4 \rightarrow ^3\text{H}_4$ transitions for samples with 0.2 (a), 0.5 (b), and 1.0 (c) mol. % Tm^{3+} . Note that as the concentration is increased, one can clearly see the onset of cross relaxation and the intensity of the 1470-nm emission decreases relative to that of the 1800-nm band. As can be seen from Fig. 8(b), as the Tm^{3+} ion concentration increases from 0.2 mol. % to 1 mol. %, the ratio of the 1470-nm intensity decreases from 0.98 to 0.18 relative to that of the 1800-nm band.

Fig. 8. (a) Measured variation of the emission intensity as a function of the wavelength for the $^3\text{H}_4 \rightarrow ^3\text{H}_6$ and $^3\text{F}_4 \rightarrow ^3\text{H}_4$ transitions for samples with 0.2 (a), 0.5 (b) and 1.0 (c) mol. % Tm^{3+} . (b) Ratio of the 1470-nm intensity to the 1800-nm intensity as a function of Tm^{3+} ion concentration.

4. CONCLUSIONS

In conclusion, we have described the synthesis and spectroscopic characterization of a new class of thulium-doped glasses: $(1-x)\text{TeO}_2-(x)\text{PbF}_2$. In the experiments, the absorption and emission spectra of the samples were measured. From the analysis of the absorption spectra, the spontaneous emission probabilities and radiative lifetimes of the 4f-4f transitions were determined as a function of host composition. Our results indicate that the shortest radiative lifetimes are obtained for the samples with the composition $80\text{TeO}_2-20\text{PbF}_2$. The samples were then excited with a 785-nm diode to measure the relative emission strengths of the 1470-nm and 1800-nm bands. The results show that as the Tm^{3+} ion

concentration increases from 0.2 mol. % to 1 mol. %, the ratio of the 1470-nm intensity decreases from 0.98 to 0.18 relative to that of the 1800-nm band due to cross relaxation. This suggests that samples with concentration less than 0.2 mol. % Tm may be more suitable for the design of 1470-nm fiber-optic amplifiers.

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