

Spectroscopy of mid-infrared (2.9 μm) fluorescence and energy transfer in Dy^{3+} -doped tellurite glasses

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The decay processes relating to the potential ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ laser transition for 2.9 μm emission in single Dy^{3+} -doped tellurite (TZNF and TZN) glasses have been investigated in detail using time-resolved fluorescence spectroscopy. The selective laser excitation of the ${}^6\text{F}_{5/2}$ and ${}^6\text{H}_{9/2}$, ${}^6\text{F}_{11/2}$ energy levels at 805 and 1300 nm, respectively, have established that the decay processes of the lowest excited level (i.e., ${}^6\text{H}_{13/2}$) entirely favors multiphonon emission in a tellurite glass host. Detailed investigation of the ${}^6\text{H}_{13/2}$ luminescence decay characteristic revealed that two decay constants are involved in the TZNF glass composition; approximately 90% of the decay has a time constant (τ_1) of 19.6 μs . The remaining centers decay with a time constant $\tau_2 = 112 \mu\text{s}$ due to the Dy^{3+} fluorine bonds, which are possibly present in the TZNF glass matrix. Slight quenching of τ_1 for Dy^{3+} concentration increases to 2 mol. % may indicate energy transfer to OH^- molecules in the TZNF glass despite the low OH^- content, $[\alpha(\text{OH}^-) \sim 0.04 \text{ cm}^{-1}]$; further decrease of τ_1 (to 9.7 μs) was measured in TZN glass matrix, which is commensurate with the higher OH^- density ($\alpha = 0.15 \text{ cm}^{-1}$). © 2014 Optical Society of America

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1. INTRODUCTION

High-power mid-infrared light sources emitting in the 3 to 4 μm region are desirable for various applications, such as long-range free-space spectroscopy, sensing, and lidar that exploit the 3–5 μm atmospheric transmission window. The moderately spaced energy levels that exist above the ground state of the rare-earth ions Pr^{3+} , Nd^{3+} , and Dy^{3+} allow the possibility for a number of electronic transitions to fluoresce at mid-infrared wavelengths after excitation with moderate photon energies corresponding to wavelengths that are $<10,000 \text{ cm}^{-1}$. The majority of mid-infrared laser research has consequently centered on these ions when they are doped into low-phonon energy crystals, such as LaCl_3 [1] and KPb_2Cl_5 [2] and low-phonon energy glasses, e.g., the chalcogenides [3] and fluorides (e.g., ZBLAN [4]). Recently it has been reported that the fluorescence from the ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ transition of the Dy^{3+} ion is shown to be broader and red-shifted, when compared to ZBLAN glass, and exhibits a long decay constant of 5.9 s in tellurite (TeO_2) and germanate (GeO_2) glasses [5].

To further exploit the potential of this transition and to clarify the luminescence mechanism involved in the mid-infrared emission of the Dy^{3+} ion in tellurite glass, detailed spectroscopic studies are required that will reveal the important energy transfer (ET) and energy-level decay processes that relate to the ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ transition. To fulfill this objective, we have prepared a number of Dy^{3+} -doped tellurite (TZNF and TZN) glasses of varying Dy^{3+} concentration and measured the luminescence decay characteristics after

selective energy-level excitation of Dy^{3+} . The intrinsic luminescence decay constant of this level was determined and compared with the radiative lifetime calculated using the Judd–Ofelt theory.

2. EXPERIMENTAL PROCEDURE

The Dy^{3+} -doped tellurite (TZNF and TZN) glass samples used for the time-resolved luminescence spectroscopy measurements were prepared from high-purity raw materials: 99.99% purity TeO_2 , ZnF_2 , and Na_2O_3 . The glass compositions were:

1. TZNF: $(100-x)[75\text{TeO}_2-15\text{ZnO}-5\text{Na}_2\text{O}-5\text{ZnF}_2]-x[\text{Dy}_2\text{O}_3]$ with $x = 0.25, 0.5, 1$, and 2 mol. %.
2. TZN: $(100-x)[80\text{TeO}_2-10\text{ZnO}-10\text{Na}_2\text{O}]-x[\text{Dy}_2\text{O}_3]$ with $x = 3$ weight %.

The starting powder materials were melted in a Pt crucible in a dry glovebox environment at 900°C for 30 h to reduce OH^- content in the glass. The molten liquids were poured into polished-brass molds and annealed at 315°C for 4 h to remove any mechanical stress. The glass density was 5.33 g cm^{-3} , and the measured refractive index was 2.0 at 1800 nm. The samples were cut and polished into $4.3 \times 15 \times 20 \text{ mm}$ rectangular prisms. The Dy^{3+} density was calculated to be $1.14 \times 10^{20} \text{ ions cm}^{-3}$, $2.29 \times 10^{20} \text{ ions cm}^{-3}$, $4.58 \times 10^{20} \text{ ions cm}^{-3}$, and $9.16 \times 10^{20} \text{ ions cm}^{-3}$ for the tellurite (TZN) samples having $x = 0.25, 0.5, 1$, and 2 mol. %, respectively.

The absorption spectra in the range of 2000–10000 nm were measured using a FTIR spectrophotometer (Nicolet 6700).

The decay characteristics of the excited states of Dy^{3+} were measured using pulsed 12 mJ 4 ns laser excitation from a tunable optical parametric oscillator (OPO) pumped by the second harmonic of a Q-switched Nd-YAG laser (Brilliant B from Quantel). Tunable laser excitation from the OPO was used to excite the ${}^6\text{F}_{5/2}$, ${}^6\text{H}_{9/2}$, and ${}^6\text{F}_{11/2}$ energy levels at 805 and 1300 nm directly, respectively. The luminescence was detected using an InSb infrared detector (Judson model J-10 D cooled to 77 K) in conjunction with a fast preamplifier with a response time of $\sim 0.5 \mu\text{s}$ and analyzed using a digital 200 MHz oscilloscope (Tektronix TDS 410). All the fluorescence decay characteristics were measured at 300 K. To isolate the luminescence signals, bandpass filters—each with $\sim 80\%$ transmission at 1300, 1700, or 2850 nm with a half-width of 25 nm and an extinction coefficient of $\sim 10^{-5}$ outside this band—were used. Infrared emission spectrum was measured from 2400 to 4000 nm using a boxcar technique working in the static gate mode (gate = 1 μs) and a monochromator of 0.25 m with a spectral grating blazed at 2600 nm and the InSb (77 K) infrared detector and a germanium filter at the monochromator entrance.

3. EXPERIMENTAL RESULTS

Figure 1 shows the visible to near-infrared [Fig. 1(a)] and mid-wave infrared [Fig. 1(b)] absorption spectra of Dy^{3+} (0.25, 0.5, 1, and 2 mol. %) doped tellurite (TZNF) and TZNF (3 wt. %) glass.

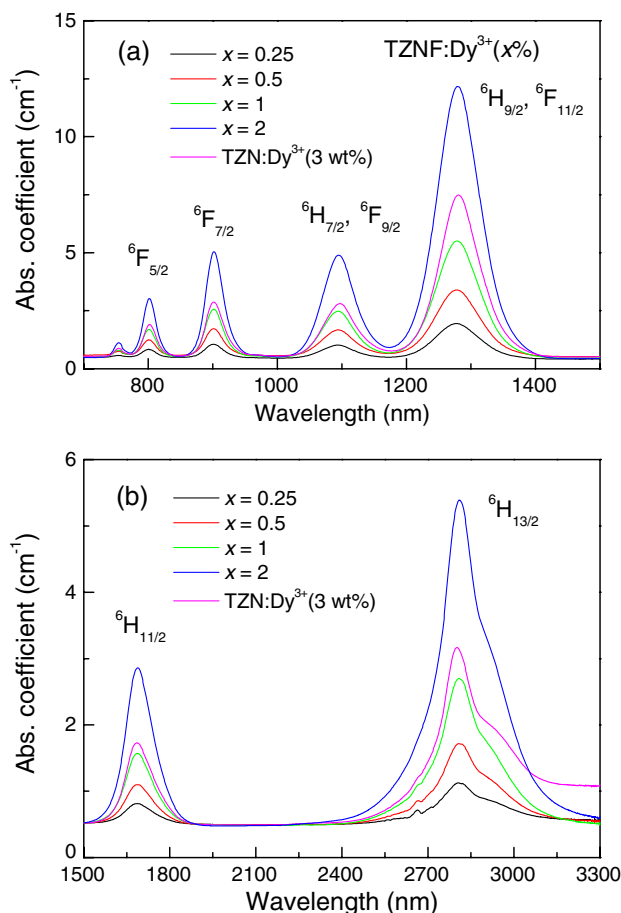


Fig. 1. Measured absorption spectrum of the Dy^{3+} ions measured in Dy^{3+} -doped TZNF (0.25, 0.5, 1, and 2 mol. %) and TZNF (3 wt. %) tellurite glasses from (a) 700–1500 nm and (b) 1500–3300 nm.

The spectrum shows a broad strong absorption band between 2400 and 3150 nm due to the ${}^6\text{H}_{15/2} \rightarrow {}^6\text{H}_{13/2}$ absorption transition, which increases linearly with the Dy^{3+} concentration. Using the absorption coefficient at 1280 nm as a function of the Dy^{3+} concentration (mol. %) in TZNF, it was estimated that the concentration of the 3 wt. % Dy^{3+} in TZNF glass was equivalent to 1.15 mol. %.

Figure 2 shows the mid-infrared spectrum of Dy^{3+} doped into TZNF (for $x = 0.25, 0.5, 1, 2$ mol. %) and TZNF (3 wt. %) samples. Figure 3(a) shows that the ${}^6\text{H}_{15/2} \rightarrow {}^6\text{H}_{13/2}$ absorption transition in Dy^{3+} -doped TZNF partially overlaps with a broad absorption band between 3000 and 4000 nm, which is attributed to free OH^- radicals [6]. For a comparison, Fig. 3(b) shows the OH^- absorption in ZBLAN and TZBiGe glasses where one can observe that the OH^- absorption peak located at 2920 nm in fluoride (ZBLAN) glass shifts to 3370 nm in tellurite (TZNF and TZBiGe) glass. The narrow absorption band with two peaks located at 3427 and 3508 nm is attributed to the presence of the CH^- radical. The peak positions are observed to be independent of the glass matrix.

The concentration of OH^- radicals is given by $N_{\text{OH}} = (N_A \alpha / \xi)$, where N_A is the Avogadro's constant (6.02×10^{23}), α is the absorption coefficient (in cm^{-1}), relevant to the OH^- vibration band at 3370 nm (or 2967 cm^{-1}), and ξ is the absorptivity of free OH^- groups in the glass. The absorption coefficient, α (cm^{-1}) was calculated using the relation $\alpha = \ln 10 \times OD \times d^{-1}$, where d is the sample thickness or the optical length (in centimeters) and OD is the optical density. Using $\xi = 49.1 \times 10^3 \text{ cm}^2 \text{ mol}^{-1}$ [7], we estimated the OH^- concentration in our samples to be $1.7 \times 10^{17} \text{ cm}^{-3}$ in TZNF glass and $1.8 \times 10^{18} \text{ cm}^{-3}$ in TZNF glass; values that are ~ 5 times smaller than the free OH^- density (of $9.2 \times 10^{18} \text{ cm}^{-3}$) found in Dy^{3+} -doped tellurite (TZNF) glass produced from drying the melt using oxygen gas bubbling [5]. By introducing 5 mol. % ZnF_2 , we have reduced the OH^- density to $1.7 \times 10^{17} \text{ cm}^{-3}$ in comparison with TZNF glass (where $N_{\text{OH}} \sim 1.8 \times 10^{18} \text{ cm}^{-3}$) using the same experimental procedure and care to avoid water contamination (see Table 1). This result is in agreement with previous investigations, which demonstrated that adding fluoride to the glass composition reduces the OH^- concentration [10].

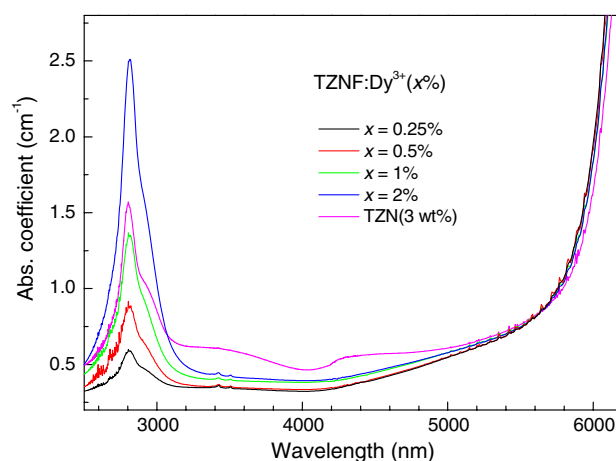


Fig. 2. Measured mid-infrared absorption coefficient of TZNF and TZNF tellurite glasses measured using a Nicolet 6700 FTIR spectrophotometer.

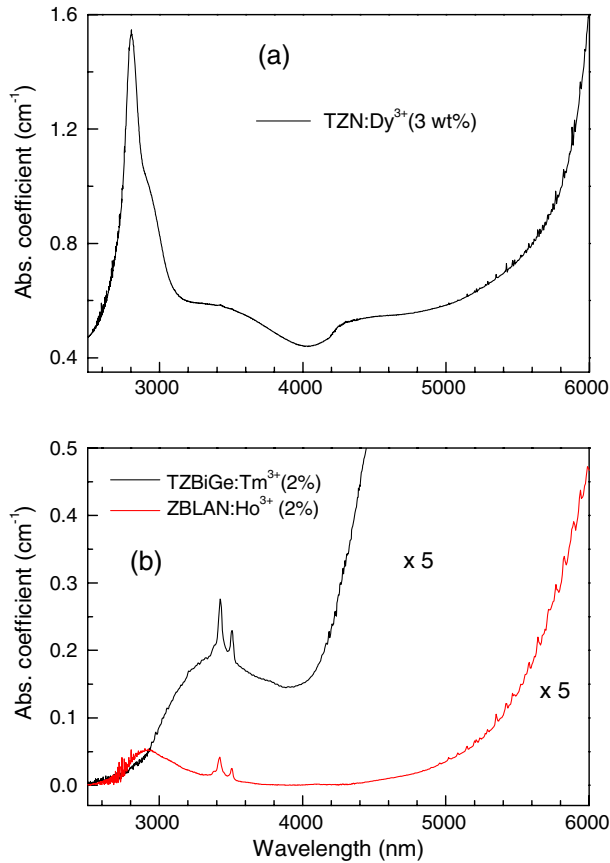


Fig. 3. Measured mid-infrared absorption spectrum of (a) Dy^{3+} -doped TZN (3 wt. %) and (b) TZBiGe:TM $^{3+}$ (2%) and ZBLAN:HO $^{3+}$ (2%) glass. The broad absorption band at 3370 nm is due to the free OH $^-$ radical impurities in TZN and TZNF and TZBiGe tellurites glasses. The OH $^-$ absorption is located at 2920 nm in ZBLAN glass (red curve), and the double narrow peaks at 3427 and 3508 nm are attributed to CH $^-$ molecules.

The measured luminescence spectrum of the ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ transition of Dy^{3+} in TZNF (1 mol. %) and TZN (3 wt. %) is shown in Fig. 4, which was generated using pulsed laser excitation from 4 ns (10 Hz) pulses at 1300 nm and sampling the luminescence signal using the boxcar technique. The measured emission band shows the maximum at 2890 nm for the TZNF and TZN samples. That peak position is shifted to lower energy when compared to the emission peak position measured for Dy^{3+} :ZBLAN, which is around 2875 nm. We did not see the emission peak shift to 3300 nm, either, which is the emission broadening reported by Richards *et al.* in [5] for Dy^{3+} :TZN glass. For instance, the mid-IR emission bandwidth is equal to 290 nm for TZNF and 280 nm for

TZN samples, which are larger than the bandwidth of 225 nm observed for ZBLAN.

The measured decay time of the luminescence intensity (normalized) of the ${}^6\text{H}_{9/2}$ and ${}^6\text{H}_{11/2}$ excited level of Dy^{3+} in TZNF (2 mol. %) sample at 1300 and 1700 nm, respectively, after pulsed laser excitation at 805 nm is shown in Fig. 5. The best fit to the luminescence transient using exponential functions is given by Eq. (1):

$$I(t) = A[\exp(-t/\tau) - \exp(-t/\tau_{\text{Rise}})], \quad (1)$$

where τ is the decay constant and τ_{Rise} is the luminescence rise time. The best fit using Eq. (1) provided τ equal to 1.04 μs (1300 nm) and 1.03 μs for 1700 nm emission and rise times of 0.253–0.246 μs , respectively.

The luminescence decay of the ${}^6\text{H}_{13/2}$ excited level of Dy^{3+} was measured (at 2850 nm) for TZNF (0.25, 0.5, 1, 2 mol. %) and TZN (3 wt. %) using pulsed laser excitation at 805 nm, with a 4 ns pulse duration, 10 Hz repetition frequency, and average energy of 12 mJ per pulse. A detailed investigation of the 2850 nm emission decay revealed that two decay components are needed to describe the luminescence decay, which was performed using an empirical relation given by Eq. (2):

$$I(t) = A[\exp(-t/\tau_1) + (1-f)\exp(-t/\tau_2) - \exp(-t/\tau_{\text{Rise}})], \quad (2)$$

where τ_1 and τ_2 are the decay constant, τ_{Rise} is the luminescence rise time, and $(1-f)$ is the contribution to the luminescence decay of the long decay component (τ_2). Figure 6 shows the experimental decay curves and the best fits of the 2850 nm emission decay (Dy^{3+}) measured for TZNF (1 mol. %) and TZN (3 wt. %) samples for comparison. The luminescence transient measured for TZNF (1 mol. %) sample shows clearly that it has two decay components, τ_1 and τ_2 . The best fit of the luminescence transient using Eq. (2) provided two decay constants, τ_1 , equal to 19.6 μs (contribution = 90%), and τ_2 , equal to 112 μs (contribution = 10%) for TZNF (1 mol. %) and a single exponential decay with $\tau_1 = 9.7 \mu\text{s}$ for the TZN (3 wt. %) sample. The rise times were 1.65 μs (TZNF) and 1.25 μs for TZN, respectively. The best-fit parameters of the ${}^6\text{H}_{13/2}$ excited level decay of Dy^{3+} ions in TZNF (x mol. %) and TZN (3 wt. %) are given in Table 2.

Figure 7 shows the measured decay time of the ${}^6\text{H}_{13/2}$ excited level as a function of $[\text{Dy}^{3+}]$ or x (in mol. %). One can observe that the decay time is essentially unchanged and equal to the average value of 19.6 μs for $x = 0.25, 0.5$, and 1 mol. %. Consequently, the decay time value of 19.6 μs must be close to the intrinsic decay time of the ${}^6\text{H}_{13/2}$ excited state of Dy^{3+} in tellurite (TZNF and TZN) glasses. A decrease of the decay time to 13.8 μs and to 9.7 μs for Dy^{3+} :TZNF (2 mol. %)

Table 1. Experimental Values of the Absorption Coefficient, $\alpha(\text{OH}^-)^a$

Fluoride and Tellurite Glasses (Composition and Fabrication)	$\alpha(\text{OH}^-)$ (cm^{-1})	$\text{N}(\text{OH}^-)$ (cm^{-3})
ZBLAN:HO $^{3+}$ (2%) (53ZrF $_4$ -20BaF $_2$ -4LaF $_3$ -3AlF $_3$ -20NaF)	0.010	1.2×10^{17}
TZNF:Dy $^{3+}$ (0.25, 0.5, 1, 2%) (75TeO $_2$ -15ZnO-5Na $_2$ O-5ZnF $_2$) (using a dry glove box environment)	0.014	1.7×10^{17}
Fluorotellurite:HO $^{3+}$ from Ref. [8] (60TeO $_2$ -30ZnF $_2$ -10NaF) (using a physical and chemical dehydration)	0.027	3.3×10^{17}
TZBiGe:TM $^{3+}$ from Ref. [9] (using a dry glove box environment)	0.040	4.9×10^{17}
TZN:Dy $^{3+}$ (3 wt. %) (80TeO $_2$ -10ZnO-10Na $_2$ O) (using a dry glove box environment)	0.150	1.8×10^{18}
TZN:Dy $^{3+}$ (3 wt. %) from Ref. [5] (80TeO $_2$ -10ZnO-10Na $_2$ O) (105 min gas O $_2$ bubbling)	0.750	9.2×10^{18}

^aCalculated using the mid-IR absorption at 3.37 μm . Comparison with OH $^-$ absorption (at 2.92 μm) in ZBLAN is made.

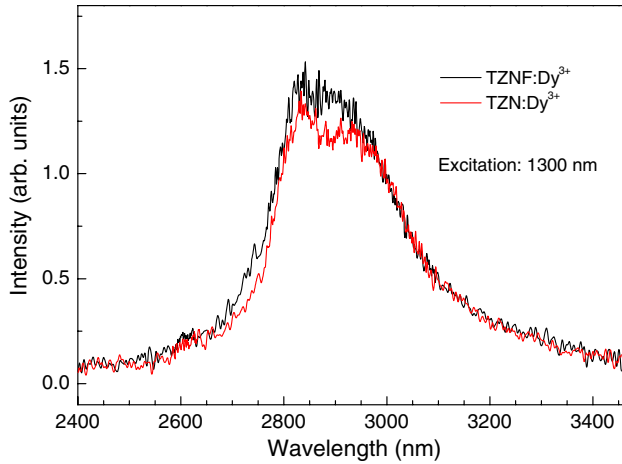


Fig. 4. Measured luminescence spectrum of the ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ transition of Dy^{3+} doped in TZNF (1 mol. %) and TZN (3 wt. %) glass using pulsed laser excitation at 1300 nm.

and $\text{Dy}^{3+}:\text{TZN}$ (3 wt. % or 1.15 mol. %) indicates that this shortening of the decay time is due to the higher OH^- concentration in the sample (of $\sim 1.8 \times 10^{18} \text{ cm}^{-3}$, see Table 1). This shortening of the decay time in tellurite glass indicates that a nonradiative (dipole–dipole) ET occurs from the $\text{Dy}^{3+} ({}^6\text{H}_{13/2})$ excited state to the vibration mode of free OH^- radicals; this ET is represented in Fig. 8.

A simplified energy-level diagram for Dy^{3+} -doped tellurite, which is used for the luminescence excitation showing how the ${}^6\text{H}_{13/2}$ state is populated by optical pumping at 805 and 1300 nm the 2.9 μm laser transition and the ET process to the free OH^- radical, is shown in Fig. 8.

4. DISCUSSION

The reduction of the ${}^6\text{H}_{13/2}$ decay time with increased $[\text{Dy}^{3+}]$ may indicate ET from the ${}^6\text{H}_{13/2}$ level to the OH^- radical whose relevant absorption band partially overlaps the absorption sideband of the ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ transition. Because of this, the ET process $\text{Dy}^{3+} \rightarrow \text{OH}^-$ was investigated using

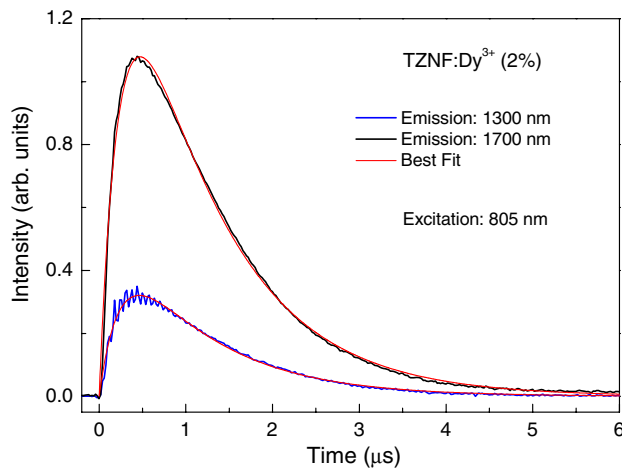


Fig. 5. Measured decay time of the luminescence intensity (normalized) of the ${}^6\text{H}_{9/2}$ and ${}^6\text{H}_{11/2}$ excited level of Dy^{3+} in TZNF (2 mol. %) sample at 1300 and 1700 nm, respectively, after pulsed laser excitation at 805 nm. The best fit to the luminescence transient using exponential functions provided the decay time constants τ equal to 1.04 μs for 1300 nm and 1.03 μs for 1700 nm emission and rise times of 0.253 and 0.246 μs , respectively.

$$\tau_1 = \left[\frac{1}{\tau_i} + W_t \right]^{-1}, \quad (3)$$

which assumes that the transfer mechanism is dominated by excitation migration on the ${}^6\text{H}_{13/2}$ levels, where τ_i is the intrinsic lifetime of the ${}^6\text{H}_{13/2}$ level, and W_t is the transfer rate constant. Using the measured decay time of $\tau_1 = 13.8 \mu\text{s}$ for TZNF (2 mol. %) and $\tau_1 = 9.7 \mu\text{s}$ for TZN (3 wt. %) and the intrinsic decay time $\tau_i = 19.6 \mu\text{s}$ of the ${}^6\text{H}_{13/2}$ excited level in Eq. (3), we calculated the transfer probability rate, W_t , of the ET process $\text{Dy}^{3+} ({}^6\text{H}_{13/2}) \rightarrow \text{OH}^-$ to be $W_t = 21286 \text{ s}^{-1}$ for TZN (2 mol. %) and $W_t = 52073 \text{ s}^{-1}$ for TZN (3 wt. %).

Using the Judd–Ofelt theory, we estimate the radiative lifetime of the ${}^6\text{H}_{9/2}$, ${}^6\text{F}_{11/2}$, ${}^6\text{H}_{11/2}$, and ${}^6\text{H}_{13/2}$ excited states of Dy^{3+} in tellurite (TZN) glass. In this calculation, the rate of spontaneous emission from the ${}^{2S+1}\text{L}_{J \rightarrow J'}$ state for an electric dipole transition is given by

$$A_{\text{ed}}(J \rightarrow J') = \frac{64\pi^4 e^2 \chi}{3(2J+1)\hbar \lambda^3} S_{\text{ed}}(J \rightarrow J'), \quad (4)$$

where $S_{\text{ed}} = \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle U^{(\lambda)} \rangle|^2$ and $\chi = ((n(n^2+2)^2)/9)$. The spectroscopic intensity parameters Ω_2 , Ω_4 , and Ω_6 are equal to $4.28 \times 10^{-20} \text{ cm}^2$, $1.32 \times 10^{-20} \text{ cm}^2$, and $2.53 \times 10^{-20} \text{ cm}^2$, respectively, for Dy^{3+} -doped tellurite ($65\text{TeO}_2\text{-}35\text{ZnO}$) [11]. Values of $|\langle U^{(\lambda)} \rangle|^2$ were obtained from the literature [12,13] for the radiative transitions of Dy^{3+} in LaF_3 (aquo ions). The refractive index is $n = 2.0$ at 1800 nm for TZN glass. For the ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ emission, electric plus magnetic dipole contributes, and the total radiative rate can be calculated using the integrated absorption coefficient according to the formula given by Eq. (5):

$$A_{\text{(ed+md)}}^{\text{meas}}(J \rightarrow J') = \frac{8\pi n^2 c}{N(\bar{\lambda}_{\text{emis}})^2 (\bar{\lambda}_{\text{abs}})^2} \frac{2J'+1}{2J+1} \int k(\lambda) d\lambda, \quad (5)$$

where $k(\lambda)$ is the absorption coefficient, c is the speed of light, and N is the active ions concentration, which is equal to $4.58 \times 10^{20} \text{ ions cm}^{-3}$ for 1 mol. % (Dy^{3+}). The calculated values of the radiative decays and branching ratios are given in Table 3. The radiative lifetime, τ_R of the ${}^6\text{H}_{13/2}$ excited state, is equal to 15.9 ms, where electric and magnetic dipole transitions are considered [from Eq. (5)]. τ_R is equal to 17.9 ms when considering only an electric dipole transition given by Eq. (4). We have determined that the luminescence efficiency of the ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2} \sim 3 \mu\text{m}$ transition of Dy^{3+} -doped TZNF tellurite glass at $T = 300 \text{ K}$ is 1.24×10^{-3} , which is primarily the result of large rates of multiphonon emission, which forces the nonradiative decay rate to be 50698 s^{-1} compared with the radiative decay rate of 63 s^{-1} . The multiphonon nonradiative decay rate (W_{nr}) was calculated using the relation, $W_{\text{nr}} = (1/\tau) - (1/\tau_R)$, and the results are presented in Table 3.

There is a significant difference between the decay times measured for the ${}^6\text{H}_{13/2}$ level of Dy^{3+} in TZNF and TZN glasses compared to the characteristic decay time reported in [5] of 5.9 s. In this latter work, we speculate that a number of trapped electrons may have been created from Dy^{3+} after two-photon absorption of the 808 nm diode laser light. These weakly bound electrons are released and captured back into higher excited states of the Dy^{3+} ion emitting near 3 μm , exhibiting a long decay constant of 5.9 s relative to the

Table 2. Experimental Values of the Intrinsic (τ_1 , τ_2) Lifetimes, Luminescence Rise Time (τ_{Rise}), and f Parameter^a

Dy ³⁺ :TZNF (mol. %)	Decay 1 (τ_1) (f)	Decay 2 (τ_2) (1-f)	Rise Time (τ_{Rise})
0.25	(19.61 ± 0.15) μ s ($f = 0.96$)	(112 ± 4) μ s (0.04)	(1.14 ± 0.27) μ s
0.5	(19.80 ± 0.18) μ s ($f = 0.94$)	(112 ± 4) μ s (0.06)	(1.25 ± 0.31) μ s
1	(19.57 ± 0.14) μ s ($f = 0.90$)	(111.9 ± 4.2) μ s (0.10)	(1.66 ± 0.30) μ s
2	(13.8 ± 0.20) μ s ($f = 0.98$)	(112 ± 4) μ s (0.02)	(1.79 ± 0.34) μ s
Dy ³⁺ :TZN (3 wt. %)	(9.73 ± 0.51) μ s (100%)	—	(1.26 ± 0.25) μ s

^aObtained from best fitting of the luminescence decay of the $^6\text{H}_{13/2}$ excited state of Dy³⁺ at 2850 nm using Eq. (2) in tellurite TZNF and TZN glasses. Luminescence measurements were made at $T = 300$ K.

repopulation time of the $^3\text{H}_{13/2}$ state. This is characteristic of a phosphorescent process. The observed broader emission may be due to the presence of a lattice defect interaction with a nearby Dy³⁺ ion.

To gauge the potential performance of Dy³⁺ when doped into tellurite glass, a rate-equation analysis was used to

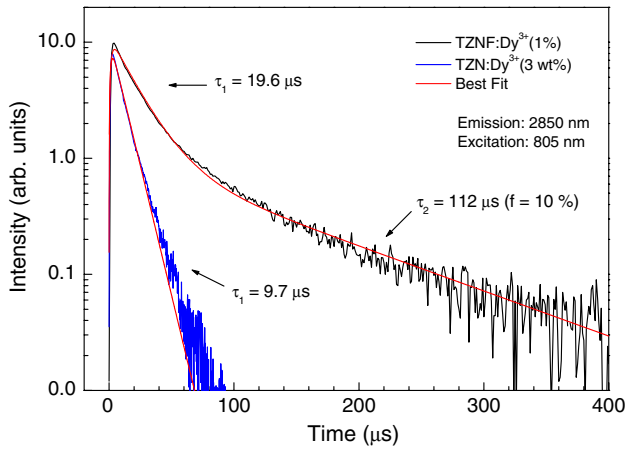


Fig. 6. Measured decay time of the $^6\text{H}_{13/2}$ excited level of Dy³⁺ doped in TZNF (1 mol. %) and TZN (3 wt. %) glasses measured at 2850 nm after pulsed laser excitation at 805 nm. The best fit to the decay time using Eq. (2) provided two decay constants $\tau_1 = 19.6$ μ s (90%) and $\tau_2 = 112$ μ s (10%) for TZNF (1 mol. %), and a single exponential decay with $\tau_1 = 9.7$ μ s for the TZN (3 wt. %) sample. The luminescence risetimes were equal to 1.65 μ s for TZNF and 1.25 μ s for TZN, respectively.

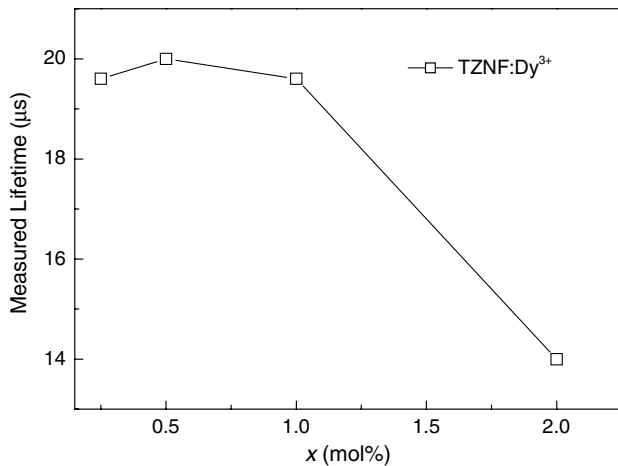


Fig. 7. Experimental decay time of the $^6\text{H}_{13/2}$ level as a function of $[\text{Dy}^{3+}]$ or x (mol. %) in the TZNF glass samples.

describe the cw operation of Dy³⁺-doped TZNF fiber lasers. Figure 8 shows the simplified energy-level scheme used to describe the Dy³⁺-doped tellurite laser system for cw laser pumping of the n_4 level ($^6\text{F}_{11/2}$). n_1 , n_2 , n_3 , n_4 , n_5 , n_6 , n_7 , and n_8 are the populations of the $^6\text{H}_{15/2}$, $^6\text{H}_{13/2}$, $^6\text{H}_{11/2}$, $^6\text{F}_{11/2}$, $^6\text{F}_{9/2}$, $^6\text{F}_{7/2}$, $^6\text{F}_{5/2}$, and $^6\text{F}_{3/2}$ energy levels of Dy³⁺, respectively, and $n_1 + n_2 + n_3 + n_4 + n_5 + n_6 + n_7 + n_8 = 1$ and $n_{\text{OH}} = 1$. The n_5 , n_6 , n_7 , and n_8 populations, however, are considered negligible in tellurite glass because no fluorescence was observed from the $^6\text{F}_{9/2}$, $^6\text{F}_{7/2}$, $^6\text{F}_{5/2}$, and $^6\text{F}_{3/2}$ energy levels, and the decay time is short as a result of the strong nonradiative decay produced by multiphonon relaxation. The rate equations for the simplified system for 1300 nm pumping are

$$\frac{dn_1}{dt} = -R_p n_1 + \frac{n_2}{\tau_{R_2}} + W_{nR}(21)n_2 + \frac{B_{31}}{\tau_{R_3}} n_3 + \frac{B_{41}}{\tau_{R_4}} n_4 + W_l n_2, \quad (6)$$

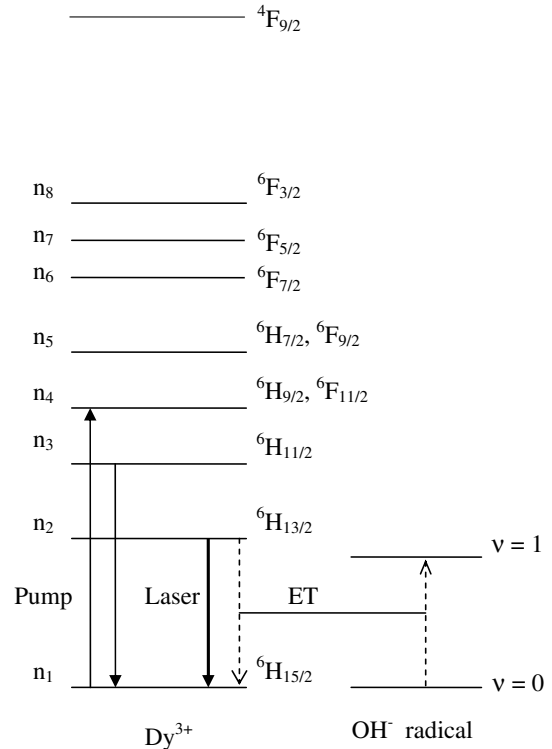


Fig. 8. Simplified energy-level diagram for Dy³⁺-doped tellurite (TZNF) glass used for the rate equation analysis showing how the $^6\text{H}_{9/2}$ and $^6\text{F}_{11/2}$ states are populated by optical excitation at 1300 nm, and the 2.9 μ m laser transition and ET process to the OH⁻ radical.

Table 3. Experimental Values of the Intrinsic (τ_i) and Radiative Lifetimes (τ_R), Luminescence Branching Ratios ($\beta_{i,j}$), Multiphonon Decay Rates (W_{nr}), and W_t as a Function of $[\text{Dy}^{3+}]$ in TZNF^a

${}^6\text{H}_J \rightarrow {}^6\text{H}_{15/2}$ (emission) ^c	Radiative Lifetime ^b	Intrinsic Total Decay Time ^b	Branching Ratio ^b	$W_{nr}(i \rightarrow f)$ (s^{-1}) ^b
${}^6\text{H}_{9/2} \rightarrow {}^6\text{F}_{11/2} i = 4$ (1345 nm)	$\tau_{R4} = 0.76$ ms	$\tau_{4i} = 1.03$ μs (expt.)	$\beta_{43} = 0.01$ $\beta_{42} = 0.03$ $\beta_{41} = 0.96$	9.9×10^5
${}^6\text{H}_{11/2}$ ($i = 3$) (1700 nm)	$\tau_{R3} = 4.86$ ms	$\tau_{3i} = 1.04$ μs (expt.)	$\beta_{32} = 0.06$ $\beta_{31} = 0.94$	1×10^6
${}^6\text{H}_{13/2}$ ($i = 2$) (2905 nm) [Dy^{3+}] (mol. %)	$\tau_{R2} = 15.9$ ms τ (μs) ^{b6} ${}^6\text{H}_{13/2}$ (expt.)	$\tau_{2i} = 19.6$ μs (expt.) Wt (s^{-1}) ^b	$\beta_{21} = 1$	5×10^4 (expt.)
0.25	19.6	~ 0		
0.5	19.8	~ 0		
1	19.6	~ 0		
2	13.6	21286		
3 wt. %	9.7	52073		

^aLuminescence measurements were made at $T = 300$ K.^bExperimental and calculated values obtained in this work.^cWavelength of emission band (centroide).

$$\frac{dn_2}{dt} = -\frac{n_2}{\tau_{R2}} - W_{nr}(21)n_2 + \frac{\beta_{32}}{\tau_{R3}}n_3 + \frac{\beta_{42}}{\tau_{R4}}n_4 + W_{nr}(32)n_3 - W_t n_2, \quad (7)$$

$$\frac{dn_3}{dt} = W_{nr}(43)n_4 - \frac{n_3}{\tau_{R3}}, \quad (8)$$

$$\frac{dn_4}{dt} = R_p n_1 - \frac{n_4}{\tau_{R4}}, \quad (9)$$

where $R_p = \sigma_{14}(I_p/h\nu_p)$ is the pump rate (s^{-1}), I_p is the intensity of the pump light (W cm^{-2}), and $h\nu_p$ is the photon energy of the pump radiation, where $\sigma_{14} = 4.46 \times 10^{-20} \text{ cm}^2$ (at 1280 nm). β_{ij} represents the luminescence branching ratio, and τ_{Ri} is the radiative lifetime of the ${}^6\text{H}_{13/2}$, ${}^6\text{H}_{11/2}$, and (${}^6\text{F}_{11/2}$, ${}^6\text{H}_{9/2}$) excited states where $i = 2, 3$, and 4, respectively. Experimental values of the intrinsic total decay times (τ_{2i} , τ_{3i} , τ_{4i}), radiative lifetimes (τ_{R2} , τ_{R3} , τ_{R4}), the luminescence branching ratios (β_{41} , β_{42} , β_{43} , β_{31} , β_{32}), and the multiphonon decay rates [$W_{nr}(21)$, $W_{nr}(32)$, $W_{nr}(43)$] and W_t as a function of $[\text{Dy}^{3+}]$ concentration in tellurite are listed in Table 3.

Figure 9(a) shows the decomposition of the mid-infrared emission spectrum using a three Gaussian fit that shows three emission bands with peaks at 2590, 2870, and 3042 nm. Assuming that this emission starts from the bottom of the ${}^6\text{H}_{13/2}$ excited level, one can obtain the three main Stark level splitting of the ${}^6\text{H}_{15/2}$ ground state of Dy^{3+} in tellurite glass. The three Stark levels are located at 0, 197, and 576 cm^{-1} and have the Boltzmann distribution filling factor $f_B = 0.70$, 0.367, and 0.043, respectively (calculated for $T = 300$ K).

Figure 9(b) shows the calculated population inversion (in mol. %) as a function of the pump intensity for $[\text{Dy}^{3+}] = 1 \text{ mol\%}$ obtained by numerical simulation of the rate equations for pumping at 1325 nm for each laser emission decomposed in Fig. 9(a). The population inversion shown in the ordinate of Fig. 9(b) was obtained using the relation $\Delta n = n_2 - f_B n_1$, where n_1 and n_2 are the population of the ${}^6\text{H}_{15/2}$ and ${}^6\text{H}_{13/2}$ levels taken after the equilibrium or the steady-state regime has been achieved, and f_B is the fractional population factor of the ground state for each laser emission. One can see that

a population inversion is obtained first for the 3042 nm laser transition, having a threshold intensity equal to 15 kW cm^{-2} . The intensity thresholds for the laser transitions at 2870 and 2590 nm are 136 and 260 kW cm^{-2} , respectively.

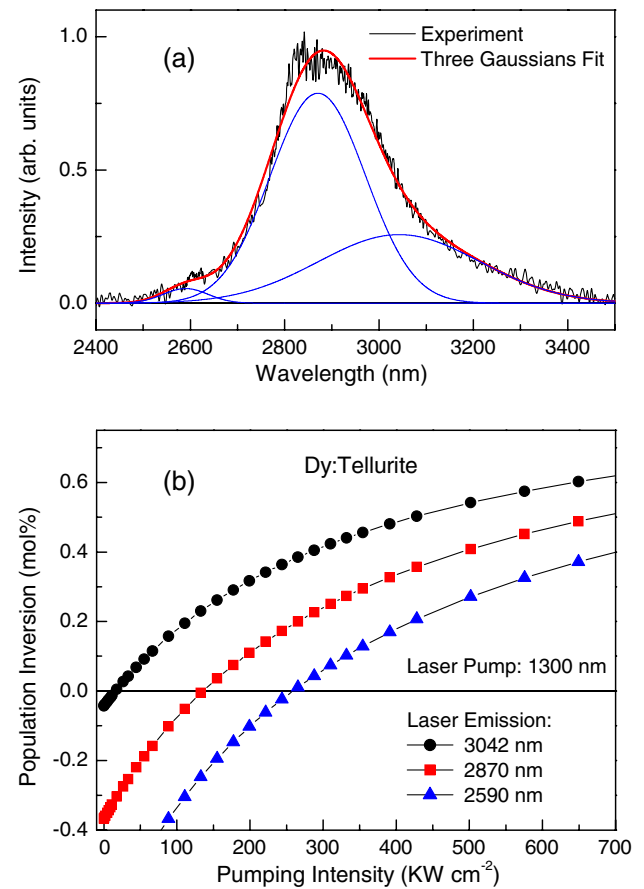


Fig. 9. (a) Decomposition of the mid-infrared fluorescence using a three Gaussian fit that suggests emission bands with peaks located at 2590, 2870, and at 3042 nm. (b) The calculated population inversion (in mol. %) as a function of the pump intensity for $[\text{Dy}^{3+}] = 1 \text{ mol\%}$ for pumping at 1300 nm for each laser emission exhibited in (a). The absorption cross section is equal to $2.06 \times 10^{-20} \text{ cm}^2$ at 1300 nm, and the relation between pumping rate, R_p (s^{-1}), and the pumping intensity, I_p (W cm^{-2}), is given by I_p (W cm^{-2}) = $7.38 \times R_p$ (s^{-1}).

5. SUMMARY AND CONCLUSIONS

We have observed that the ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ emission band of Dy^{3+} in tellurite glass (TZN and TZNF) has a peak at $\sim 2.9 \mu\text{m}$, and the bandwidth (290 nm) is significantly larger than the bandwidth (225 nm) measured in ZBLAN glass. It was observed that the decay time of the ${}^6\text{H}_{13/2}$ level is essentially concentration independent up to concentrations of 1 mol. %, and the intrinsic lifetime is $19.6 \mu\text{s}$ in tellurite glass. A decrease in the level decay time was observed in two higher concentrations, which is due to the ET process, $\text{Dy}^{3+} ({}^6\text{H}_{13/2}) \rightarrow \text{OH}^-$. Two decay components in the emission decay characteristics were measured for the ${}^6\text{H}_{13/2}$ excited level in TZNF. The shorter decay component of $19.6 \mu\text{s}$ had the largest contribution to the decay characteristic, and the longest decay component of $112 \mu\text{s}$ contributed to 10% of total luminescence decay for $[\text{Dy}^{3+}] = 1 \text{ mol. \%}$; this longer decay component may be due to the presence of ZnF_2 (at 5 mol. %) in the tellurite (TeO_2) base glass that decreases the ion-host field strengths for a small part (i.e., $\sim 10\%$) of the Dy^{3+} ions. This may create a local phonon of some intermediate energy between the fluoride ($\sim 405 \text{ cm}^{-1}$) and tellurite ($\sim 570 \text{ cm}^{-1}$) glass that sets the decay-time characteristic of Dy^{3+} -doped TZNF between $20 \mu\text{s}$ (TZN) and $650 \mu\text{s}$ measured for Dy^{3+} -doped ZBLAN. This idea is supported by the fact that the luminescence decay of the ${}^6\text{H}_{13/2}$ level exhibits two distinct components (with decay time values of 20 and $112 \mu\text{s}$) in Dy^{3+} (1 mol. %)-doped TZNF in contrast with the single exponential decay (with a decay time of $9.7 \mu\text{s}$) measured for Dy^{3+} (3 mol. %)-doped TZN, as shown in the results presented in Fig. 6. (Increasing the ZnF_2 component to 20 mol. % in the TZNF glass host may lead to a larger contribution by the longer time component to the overall decay.) Our numerical simulation suggested that Dy^{3+} (1 mol. %)-doped TZN may exhibit a population inversion for laser emission at 3042 nm when the pump threshold, for 1300 nm light, of 15 kW cm^{-2} is exceeded.

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