

# Optical properties of $\text{Er}^{3+}$ -doped telluride glasses with $\text{P}_2\text{O}_5$ addition for 1.5 $\mu\text{m}$ broadband amplifiers

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## Abstract

In this paper,  $\text{P}_2\text{O}_5$  has been introduced into  $\text{Er}^{3+}$ -doped telluride glasses. Emission and absorption spectra of the new glass are studied. It is observed that the nonradiative relaxation rate of  ${}^4\text{I}_{11/2}$ – ${}^4\text{I}_{13/2}$  transitions and the 1.5  $\mu\text{m}$  emission efficiency increases with the increase in  $\text{P}_2\text{O}_5$  content. The nonradiative relaxation rate of  ${}^4\text{I}_{11/2}$ – ${}^4\text{I}_{13/2}$  transition in a glass with 7 mol%  $\text{P}_2\text{O}_5$  is four times greater than that without  $\text{P}_2\text{O}_5$ . The  $\text{P}_2\text{O}_5$  additives can also increase the thermal stability of the telluride glass. The present results indicate that telluride glasses with  $\text{P}_2\text{O}_5$  addition may be a promising candidate medium for broadband erbium-doped fiber amplifiers.

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## 1. Introduction

In recent years,  $\text{Er}^{3+}$ -doped glasses with a broad 1.5  $\mu\text{m}$  emission band originating from  ${}^4\text{I}_{13/2}$ – ${}^4\text{I}_{15/2}$  transition of  $\text{Er}^{3+}$  have been extensively investigated for use in erbium-doped fiber amplifiers (EDFA) [1–3]. Among the reported materials,  $\text{Er}^{3+}$ -doped telluride glasses have exhibited a wide 1.5  $\mu\text{m}$  emission band, a large stimulated emission section, and a high 1.5  $\mu\text{m}$  emission efficiency. A telluride glass-based fiber with 76 nm flat gain bands has been reported in 1997 [4]. However, as a host for EDFA, telluride glass has some major drawbacks. One of them is the phonon energy of the glass is about  $770\text{ cm}^{-1}$ , which leads to the  ${}^4\text{I}_{11/2}$ – ${}^4\text{I}_{13/2}$  nonradiative relaxation rate too slow to allow efficient pumping at 980 nm.

To overcome the drawback, co-doping  $\text{Ce}^{3+}$  was reported [5,6] to enhance the 980 nm pumping efficiency through the non radiative energy transfer. Another method was carried out introducing  $\text{B}_2\text{O}_3$  [6], which has a large

phonon energy of B–O bond, resulting in the increase of the pumping efficiency at 980 nm through multi-phonon relaxation. In such a system, however, the multi-phonon relaxation rate of  ${}^4\text{I}_{13/2}$ – ${}^4\text{I}_{15/2}$  transition of  $\text{Er}^{3+}$  is also speeded up, leading to an obvious decrease of the 1.5  $\mu\text{m}$  emission efficiency, so it is not suitable for application.

In this paper, we report the effect of  $\text{P}_2\text{O}_5$  content on the optical and thermal properties of the  $\text{Er}^{3+}$ -doped tungsten–telluride glass.  ${}^4\text{I}_{11/2}$ – ${}^4\text{I}_{13/2}$  nonradiative transition as well as  ${}^4\text{I}_{11/2}$ – ${}^4\text{I}_{15/2}$  (0.98  $\mu\text{m}$ ) and  ${}^4\text{I}_{13/2}$ – ${}^4\text{I}_{15/2}$  (1.5  $\mu\text{m}$ ) radiative transitions are studied.

## 2. Experimental

$\text{Er}^{3+}$ -doped glasses,  $(40-0.4x)\text{TeO}_2-(30-0.3x)\text{WO}_3-(30-0.3x)\text{Li}_2\text{O}-x\text{P}_2\text{O}_5$  ( $x = 0, 1, 2, 3, 4, 5, 7$ ) (TWP for series, and  $\text{TW}_x\text{P}$ , where  $x = 0, 1, 2, 3, 4, 5, 7$ , for individual glass) and  $70\text{TeO}_2-20\text{ZnO}-10\text{Na}_2\text{O}$  (TZN glass) doped with  $\text{Er}^{3+}$  at a constant concentration of 1.0 mol% were prepared using the conventional melting and quenching method. Well-mixed powder in a crucible was allowed to melt at 750–850  $^\circ\text{C}$  for 1 h, and then was quenched into a

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preheated brass mold to form glass. The quenched sample was annealed around the glass transition temporarily for 2 h and then cooled inside the furnace down to room temperature. The obtained glass samples were cut and polished into  $10 \times 10 \times 2.0 \text{ mm}^3$  sized pieces.

Emission spectra in the range of 900–1700 nm were measured using a TRIAX-550 spectrometer under excitation of 808 nm from a laser diode. Absorption spectra were measured using a UV-3101PC spectrometer. The lifetime of the  $^4\text{I}_{13/2}$  state for  $\text{Er}^{3+}$  was measured with a 500 MHz Tektronix digital oscilloscope under excitation of 808 nm light pulses from an optical parametric oscillator. The differential thermal analysis (DTA) data was collected using a Perkin–Elmer 7 Series Thermal Analysis System. All the measurements were taken at room temperature.

### 3. Results and discussion

#### 3.1. Infrared emission spectra of $\text{Er}^{3+}$

Fig. 1 shows the infrared emission spectra of  $\text{Er}^{3+}$  in the range 800–1700 nm in TWP samples. The value of full-width at half-maximum (FWHM) at 1.5  $\mu\text{m}$  emission is

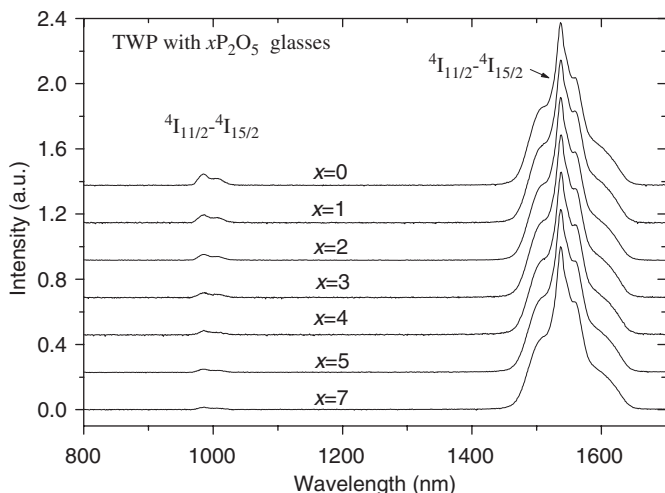


Fig. 1. Emission spectra from  $^4\text{I}_{11/2}$ – $^4\text{I}_{15/2}$  and  $^4\text{I}_{13/2}$ – $^4\text{I}_{15/2}$  transitions of  $\text{Er}^{3+}$  in  $(40-0.4x)\text{TeO}_2-(30-0.3x)\text{WO}_3-(30-0.3x)\text{Li}_2\text{O}-x\text{P}_2\text{O}_5$  ( $x = 0, 1, 2, 3, 4, 5, 7$ ) glasses. Emission intensities are normalized to the  $^4\text{I}_{13/2}$ – $^4\text{I}_{15/2}$  transition.

Table 1

Measured lifetime of  $\text{Er}^{3+}$ -adopted  $^4\text{I}_{13/2}$  level ( $\tau_1$ ), radiative transition rates ( $A_{10}$  and  $A_{20}$ ) calculated from the absorption spectra and measured intensity ratio  $\alpha$

Glass	$\tau_{1r}$ (ms) $^4\text{I}_{13/2}$	$\tau_1$ (ms) $^4\text{I}_{13/2}$	$\eta_1$ (%) $^4\text{I}_{13/2}$	$A_{10}$ ( $\text{s}^{-1}$ ) $^4\text{I}_{13/2}$ – $^4\text{I}_{15/2}$	$A_{20}$ ( $\text{s}^{-1}$ ) $^4\text{I}_{11/2}$ – $^4\text{I}_{15/2}$	$\alpha$
TW0P	4.11	3.3	80	243.18	333.56	28.7
TW1P	3.963.96	3.3	83	252.37	346.91346.91	37.7
TW2P	4.114.11	3.3	80	243.27	330.80330.8	55.4
TW3P	4.22	3.3	78	237.11	323.24	60.1
TW4P	4.124.12	3.4	82	242.85	334.83334.83	76.9
TW5P	4.23	3.7	87	236.54236.57	323.35	94.7
TW7P	4.27	4.2	98	233.97	321.54	135.5
TZN	4.5	3.67	81	220.20	304.51	21.1

about 65 nm, which is not affected with additional composition of  $\text{P}_2\text{O}_5$ . It can be seen that the ratio of the integrated intensity of the 1.5  $\mu\text{m}$  band to that of the 0.98  $\mu\text{m}$  (denoted as  $\alpha$  in Section 3.3 and listed in Table 1.) increases as  $\text{P}_2\text{O}_5$  content increases, as shown in Fig. 1. This ratio is mainly governed by  $^4\text{I}_{11/2}$ – $^4\text{I}_{13/2}$  nonradiative relaxation rate. It suggests that  $^4\text{I}_{11/2}$ – $^4\text{I}_{13/2}$  nonradiative relaxation rate increases with the increase of  $\text{P}_2\text{O}_5$ , which may modify the phonon energies of the glass.

#### 3.2. The $^4\text{I}_{13/2}$ lifetime

Lifetimes of  $^4\text{I}_{13/2}$  level ( $\tau_1$ ) of  $\text{Er}^{3+}$  in TWP glass are measured and listed in Table 1. It can be seen that the lifetime of the  $^4\text{I}_{13/2}$  state increases from 3.3 to 4 ms with the increase of the  $\text{P}_2\text{O}_5$  content up to 7 mol%, while the radiative lifetime  $\tau_{1r}$  obtained from Judd–Ofelt analysis of the absorption spectra are almost unchanged, leading to the increase of 1.5  $\mu\text{m}$  emission efficiency  $\eta_1$ , as shown in Table 1.

#### 3.3. The $^4\text{I}_{11/2}$ – $^4\text{I}_{13/2}$ nonradiative relaxation rates

Fig. 2 depicts an energy level diagram of  $\text{Er}^{3+}$  at low energy levels. When pumped by 808 nm laser diode,  $\text{Er}^{3+}$  is excited from ground state to  $^4\text{I}_{9/2}$  level, which rapidly relaxes to  $^4\text{I}_{11/2}$  state through nonradiative decay. Subsequently, the  $^4\text{I}_{13/2}$  level is populated. The rate of  $^4\text{I}_{11/2}$ – $^4\text{I}_{13/2}$  relaxation is very important for creating population inversion of  $^4\text{I}_{13/2}$  level for optical amplification at 1.5  $\mu\text{m}$ . In the steady excitation, for  $^4\text{I}_{11/2}$  state, one has

$$A_{21}n_2 + W_{21}n_2 = n_1/\tau_1, \quad (1)$$

where  $A_{21}$  is  $^4\text{I}_{11/2}$ – $^4\text{I}_{13/2}$  radiative transition rate,  $W_{21}$  is  $^4\text{I}_{11/2}$ – $^4\text{I}_{13/2}$  nonradiative relaxation rate,  $n_2$  and  $n_1$  are the populations of the  $^4\text{I}_{11/2}$  and  $^4\text{I}_{13/2}$  levels respectively. Letting  $\alpha$  be the measured ratio of the 1.5  $\mu\text{m}$  emission intensity to that of the 0.98  $\mu\text{m}$ , we have

$$\alpha = CA_{10}n_1/A_{20}n_2, \quad (2)$$

where C is a calibration coefficient related to measurement device only. From Eqs. (1) and (2), we have

$$W_{21} = \alpha A_{20}/CA_{10}\tau_1 - A_{21}, \quad (3)$$

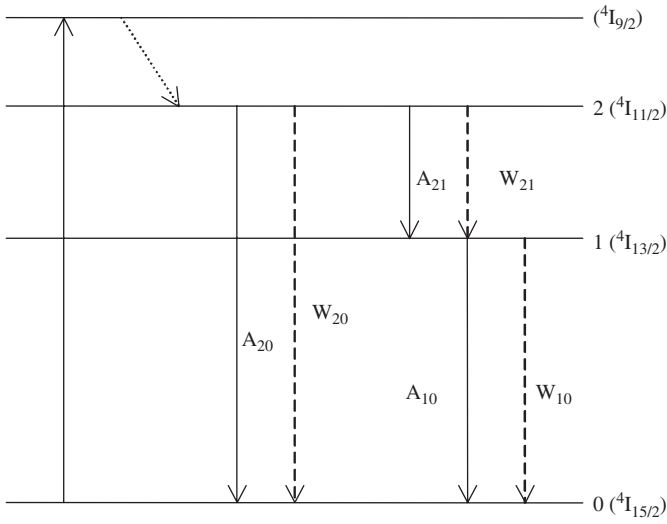


Fig. 2. An energy level diagram of Er<sup>3+</sup> ions. The transition from <sup>4</sup>I<sub>15/2</sub>–<sup>4</sup>I<sub>11/2</sub> indicates an optical transition under 980 nm excitation. Solid lines represent the radiative processes and dashed lines are the nonradiative processes.

P<sub>2</sub>O<sub>5</sub> is about four times higher than that in a glass without P<sub>2</sub>O<sub>5</sub>, and is about 6 times higher than that in TZN glass, which is also indicated in Fig. 3. Obviously, under 0.98 μm pumping, feeding of <sup>4</sup>I<sub>13/2</sub> of Er<sup>3+</sup> in TWP glass is more efficient than that in TZN glass.

### 3.4. Thermal stability of TWP glass

Differential thermal analysis trace of the TW5P sample at a heat rate of 600 °C/h has been done. The difference between the glass transition temperature (*T<sub>g</sub>*) and the onset crystallization temperature (*T<sub>x</sub>*), Δ*T* = *T<sub>x</sub>*–*T<sub>g</sub>*, has been frequently used as a rough estimate of glass formation ability or glass thermal stability. To avoid crystallization during fiber drawing, it is desirable for a glass host to have as large a Δ*T* as possible. In our experiment, *T<sub>g</sub>* is about 386 °C and *T<sub>x</sub>* is about 567 °C, and the temperature difference Δ*T* of the glasses is above 180 °C, which is greater than 125 °C, the temperature difference for a tungsten–telluride glass without P<sub>2</sub>O<sub>5</sub> composition [9], indicating that the TW5P glass has better thermal stability.

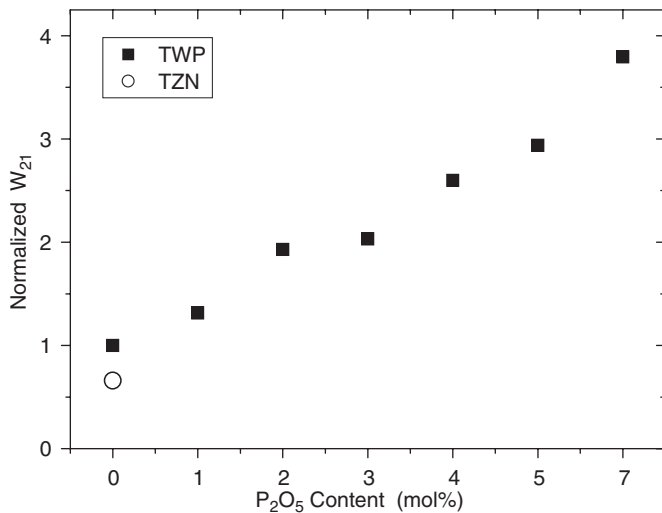


Fig. 3. The <sup>4</sup>I<sub>11/2</sub>–<sup>4</sup>I<sub>13/2</sub> nonradiative relaxation rates for various P<sub>2</sub>O<sub>5</sub> contents in TWP glasses. The rates (*W*<sub>21</sub>) for TWP glass (squares) and TZN glass (circle) are normalized, respectively, to the rate of TW0P glass.

where *A*<sub>21</sub> can be neglected because *W*<sub>21</sub> ≫ *A*<sub>21</sub>. Hence, we obtain

$$W_{21}/W_{21}(0) = \alpha A_{20} A_{10}(0) \tau_1(0) / \alpha(0) A_{20}(0) A_{10} \tau_1, \quad (4)$$

where *W*<sub>21</sub>(0), *A*<sub>10</sub>(0), *A*<sub>20</sub>(0) and α(0) are the parameters corresponding to the TW0P glass. According to the Judd–Ofelt theory [7,8], *A*<sub>20</sub> and *A*<sub>10</sub> are calculated from the measured absorption spectra and listed in the Table 1. Using Eq. (4), *W*<sub>21</sub> values with the unit of *W*<sub>21</sub>(0) are then calculated and plotted in Fig. 3.

As indicated in Fig. 3, *W*<sub>21</sub> increases with the increase of P<sub>2</sub>O<sub>5</sub> content, which has large phonon energy of P–O bond, resulting in the increased multi-phonon relaxation between <sup>4</sup>I<sub>11/2</sub> and I<sub>13/2</sub> levels of Er<sup>3+</sup>. The nonradiative relaxation rate of the <sup>4</sup>I<sub>11/2</sub>–<sup>4</sup>I<sub>13/2</sub> transition in a glass with 7 mol%

## 4. Conclusions

Adding P<sub>2</sub>O<sub>5</sub> into Er<sup>3+</sup>-doped telluride glasses can increase both the nonradiative relaxation rate of the <sup>4</sup>I<sub>11/2</sub>–<sup>4</sup>I<sub>13/2</sub> transition and the 1.5 μm emission efficiency. The nonradiative relaxation rate of <sup>4</sup>I<sub>11/2</sub>–<sup>4</sup>I<sub>13/2</sub> transition of the TWP glass with 7 mol% P<sub>2</sub>O<sub>5</sub> is about four times higher than that in a glass without P<sub>2</sub>O<sub>5</sub>, indicating an obvious improvement of population feeding efficiency of <sup>4</sup>I<sub>13/2</sub> from <sup>4</sup>I<sub>11/2</sub> level pumped at 980 nm. The P<sub>2</sub>O<sub>5</sub> additives can also increase the thermal stability of the telluride glass. The present results indicate that telluride glasses with P<sub>2</sub>O<sub>5</sub> addition may be a promising candidate medium for broadband erbium-doped fiber amplifiers.

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