

Demonstration of enhanced population feeding of the 1.53 μ m emitting level of Er³⁺ in TeO₂–WO₃–Li₂O–P₂O₅ glasses using upconversion luminescence spectroscopy

Yongshi Luo, Jiahua Zhang, Xia Zhang, and Xiao-jun Wang

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Demonstration of enhanced population feeding of the 1.53 μm emitting level of Er^{3+} in $\text{TeO}_2\text{--WO}_3\text{--Li}_2\text{O--P}_2\text{O}_5$ glasses using upconversion luminescence spectroscopy

Yongshi Luo,^{1,2} Jiahua Zhang,^{1,a)} Xia Zhang,¹ and Xiao-jun Wang^{1,3}¹Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics (CIOMP), Chinese Academy of Sciences, 16 Eastern South Lake Road, Changchun 130033, People's Republic of China²Graduate School of Chinese Academy of Sciences, Beijing 100039, People's Republic of China³Department of Physics, Georgia Southern University, Statesboro, Georgia 30460, USA

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P_2O_5 is introduced into the Er^{3+} -doped tungsten tellurite glasses to speed up the $^4I_{11/2}\text{--}^4I_{13/2}$ relaxation. The properties of infrared to visible upconverted luminescence as a function of P_2O_5 contents are studied to demonstrate the enhanced feeding rate of the 1.53 μm emitting level of Er^{3+} , which is in good agreement with that obtained using infrared emission spectra. The contributions of excited state absorption and cooperation energy transfer to the red and green upconverted luminescences are quantitatively evaluated. The Er^{3+} -doped telluride glasses containing P_2O_5 could be a promising candidate as a host for broadband erbium-doped fiber amplifiers. © 2008 American Institute of Physics. [DOI: 10.1063/1.2891788]

I. INTRODUCTION

Er^{3+} -doped telluride glasses have been extensively investigated for its potential use in broadband erbium-doped fiber amplifiers (EDFAs) in the 1.53 μm window of optical communication.^{1–5} They have exhibited a wide 1.53 μm emission band, a large stimulated emission section, and a high emission efficiency.³ However, as a host for EDFA, telluride glass has a drawback that the phonon energy of the glass is as low as 770 cm^{-1} , which leads to a slow population feeding of the 1.53 μm emitting level, $^4I_{13/2}$, through the nonradiative $^4I_{11/2}\text{--}^4I_{13/2}$ relaxation upon pumping into the $^4I_{11/2}$ level of Er^{3+} at 980 nm. In this case, an intense green upconverted luminescence (UCL) originating from $^2H_{11/2} + ^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions and a red one from the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} are generated by depopulating the $^4I_{11/2}$ and $^4I_{13/2}$ levels, strongly suppressing the optical pumping efficiency for the 1.53 μm emission. To overcome this drawback, Shen *et al.*⁶ added WO_3 with phonon energy of 920 cm^{-1} to form tungsten tellurite (TW) glasses, in which the nonradiative relaxation rate was increased. Cho *et al.* selected B_2O_3 as an additive,⁷ remarkably speeding up the nonradiative relaxation. Unfortunately, the emission efficiency of the $^4I_{13/2}$ level also decreased quickly with increasing B_2O_3 contents because the B–O bond has a very large vibronic energy of about 1500 cm^{-1} . Therefore, an additive with appropriate phonon energy is required. In our previous work,⁸ we have selected P_2O_5 as an additive introduced into Er^{3+} -doped TW glasses. The study of near infrared emission spectra demonstrates that the nonradiative relaxation was further speeded up by a factor of 3.3 without reduction of the

quantum efficiency for the 1.53 μm emission because the P–O bond has a satisfied vibronic energy of about 1200 cm^{-1} .

In this paper, we demonstrate the fast population feeding of the 1.53 μm emitting level of Er^{3+} in $\text{TeO}_2\text{--WO}_3\text{--Li}_2\text{O--P}_2\text{O}_5$ (TWP) glasses using UCL spectroscopy. The reduction of the UCL with increasing P_2O_5 contents indicates that the $^4I_{11/2}\text{--}^4I_{13/2}$ nonradiative relaxation rate is enhanced and its value is determined, which are in good agreement with those obtained using nearinfrared emission spectra. The dynamical processes in UCL under 980 nm and/or 808 nm excitation are systematically studied for different P_2O_5 content. The contributions of excited state absorption (ESA) and cooperation energy transfer (ET) to the red and green UCLs are quantitatively evaluated.

II. EXPERIMENTAL

Er^{3+} -doped glasses, $(40-0.4x)\text{TeO}_2-(30-0.3x)\text{WO}_3-(30-0.3x)\text{Li}_2\text{O}-x\text{P}_2\text{O}_5$ ($x=0,2,4,6$) (TWP_x), with Er^{3+} concentration of 1.0 mol % and a glass $\text{TWP}_0:0.1$ mol % Er^{3+} were prepared using the conventional melting and quenching method. Photoluminescence (PL) and UCL spectra were measured using a Hitachi F4500 spectrometer. An 808 nm emitting laser diode (LD) and a 980 nm emitting LD are used as pumping sources for UCL. Absorption spectra were collected using an UV-3101PC spectrometer. The lifetime of the $^4I_{13/2}$ level was recorded with a 500 MHz Tektronix digital oscilloscope under excitation of 532 nm pulses from an yttrium aluminum garnet laser.

^{a)}Author to whom correspondence should be addressed. Electronic mail: zhangjh@ciomp.ac.cn.

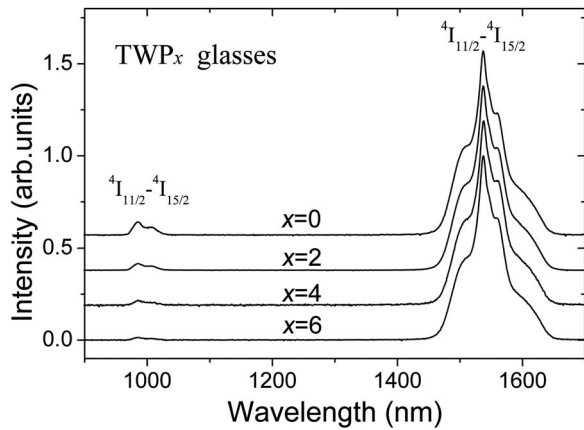


FIG. 1. The infrared emission spectra of Er^{3+} in TWP samples under 808 nm excitation; spectra are normalized to the intensity of $1.5 \mu\text{m}$ emission.

III. RESULTS AND DISCUSSION

A. Determination of the nonradiative $^4I_{11/2}$ - $^4I_{13/2}$ relaxation rates by using near infrared emission spectra in Er^{3+} -doped TWP glasses with various P_2O_5 contents

Figure 1 shows the near infrared emission spectra of Er^{3+} in TWP glasses under 808 nm excitation. The width of the $1.53 \mu\text{m}$ band is about 65 nm, which has been affected little with P_2O_5 addition. It can be seen that the integrated intensity ratio (α) of the $1.53 \mu\text{m}$ band to the $0.98 \mu\text{m}$ band increases as P_2O_5 content increases. As described in our previous work,⁸ this ratio has a relationship with the $^4I_{11/2}$ - $^4I_{13/2}$ nonradiative relaxation rate W_{21} , i.e., $W_{21} = \alpha A_{21}/A_{10}\tau_1$, where A_{21} and A_{10} are the radiative rates of $^4I_{11/2}$ - $^4I_{13/2}$ and $^4I_{13/2}$ - $^4I_{15/2}$ transitions, respectively; τ_1 is the lifetime of the $^4I_{13/2}$ level. We have calculated radiative transition rates by analyzing their absorption spectra (Fig. 2) using the Judd-Ofelt (JO) theory^{9,10} and found that these optical parameters are hardly influenced by the addition of P_2O_5 . Thus, the increase of α after P_2O_5 addition is the result of the enhanced $^4I_{11/2}$ - $^4I_{13/2}$ nonradiative relaxation rate due to phonon energy modification by P_2O_5 .

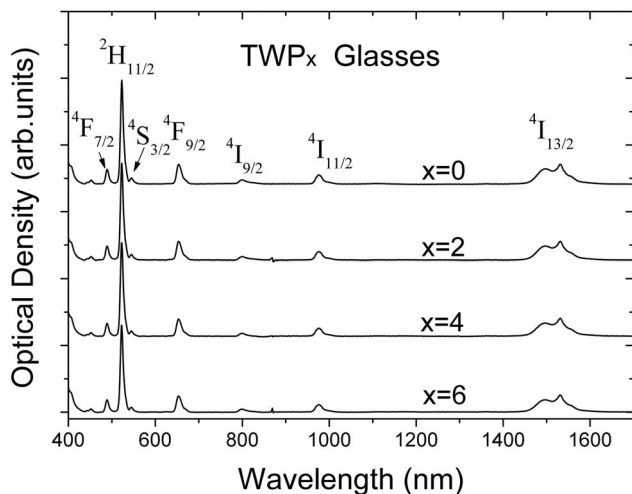


FIG. 2. Absorption spectra of TWP glasses doped with 1.0 mol % of Er^{3+} .

TABLE I. Parameters (W_{21} , τ_1 , τ_2 , τ_5) determined from different methods, normalized to the one of TWP₀ sample.

Parameters		Samples			
		TWP ₀	TWP ₂	TWP ₄	TWP ₆
W_{21}	α	1	1.67	2.63	3.37
	I_{G808}/I_{G980}	1	1.53	2.56	3.33
	I_{G980}/I_{G380}	1	1.5	2.5	3.24
τ_1	Time decay	1	1	1.03	1.06
	I_{G808}/I_{G380}	1	1.02	1.02	1.03
τ_5	I_{G380}	1	0.66	0.40	0.33
τ_2	$1/W_{21}(\alpha)$	1	0.60	0.38	0.30

The W_{21} rates calculated by α and the τ_1 determined by luminescence time decay measurement are listed in Table I. The value of W_{21} in TWP₆ glass is about 3.3 times higher than that in TWP₀ glass. It should be noted that the lifetime of the $^4I_{11/2}$ level (τ_2) is determined by $1/W_{21}$ because the radiative transition rate of the $^4I_{11/2}$ level is much smaller than W_{21} . All the data listed in Table I are normalized to the corresponding values from TWP₀ glass.

B. Determination of the nonradiative $^4I_{11/2}$ - $^4I_{13/2}$ relaxation rates using UCL in Er^{3+} -doped TWP glasses with various P_2O_5 contents

Figures 3(a) and 3(b) illustrate the UCL spectra of Er^{3+} in TWP glasses with different P_2O_5 contents under the 980 and 808 nm LD excitations, respectively. Three emission bands centered at 524, 546, and 655 nm are observed and assigned to the transitions to $^4I_{15/2}$ from $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$, respectively. Clearly, the red UCL at 655 nm is relatively weaker than the green, and all the UCL intensities decrease with increasing P_2O_5 contents. Importantly, the UCL under 980 nm excitation decreases faster than that under 808 nm excitation. One can observe that the intensity ratios of the red to the green emissions (I_R/I_G) do not change

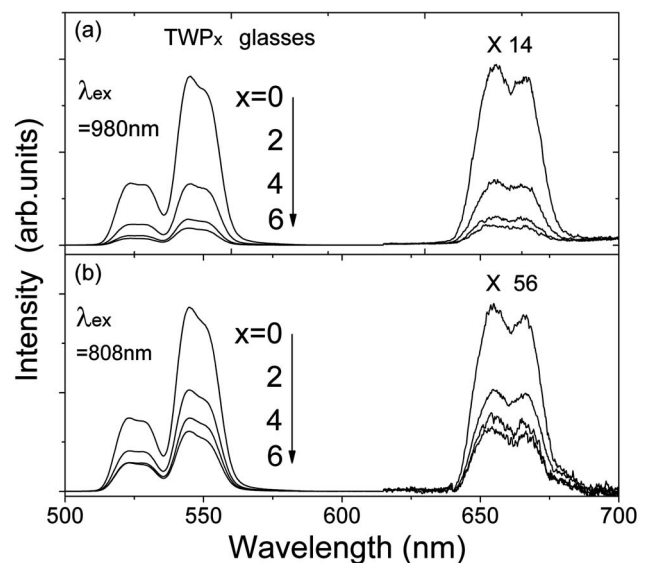


FIG. 3. UCL spectra of Er^{3+} in TWP glasses under the excitations of 980 and 808 nm.

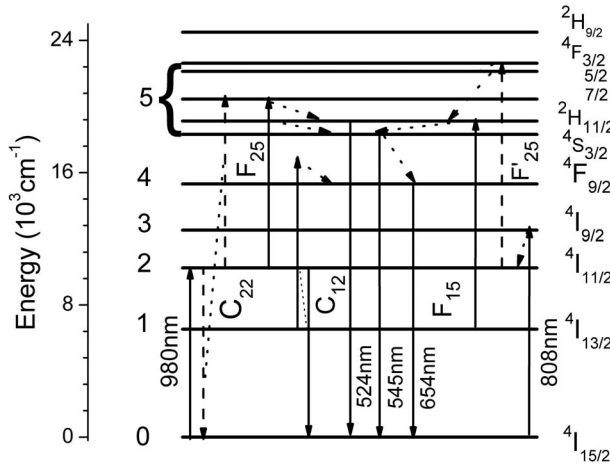


FIG. 4. Energy level diagram of Er^{3+} ions under excitations of 980 nm/808 nm.

with increasing P_2O_5 contents. Moreover, the value of the ratio upon 980 nm excitation is about four times as high as that upon 808 nm excitation.

The upconversion processes of Er^{3+} include the ESA and cooperation ET.^{11–17} The possible upconversion mechanisms upon excitation of 980 nm and/or 808 nm are illustrated in the energy level diagram of Er^{3+} , as shown in Fig. 4. Under steady excitation by 980 nm, we have the following rate equations:

$$dn_1/dt = (A_{21} + W_{21})n_2 - n_1/\tau_1 = 0, \quad (1)$$

$$dn_2/dt = F_{02}n_0 - n_2/\tau_2 = 0, \quad (2)$$

$$dn_4/dt = W_{54}n_5 + C_{12}n_1n_2 - n_4/\tau_4 = 0, \quad (3)$$

$$dn_5/dt = C_{22}n_2^2 + F_{25}n_2 - n_5/\tau_5 = 0, \quad (4)$$

and for 808 nm excitation, we have

$$dn_1/dt = (A_{21} + W_{21})n_2 - n_1/\tau_1 = 0, \quad (5)$$

$$dn_2/dt = (W_{32} + A_{31})n_3 - n_2/\tau_2 = 0, \quad (6)$$

$$dn_3/dt = F_{03}n_0 - n_3/\tau_3 = 0, \quad (7)$$

$$dn_4/dt = W_{54}n_5 + C_{12}n_1n_2 - n_4/\tau_4 = 0, \quad (8)$$

$$dn_5/dt = C_{22} + n_2^2 + F'_{25}n_2 + F_{15}n_1 - n_5/\tau_5 = 0, \quad (9)$$

where n_i and τ_i are the population and lifetime of the i th level, respectively. W_{ij} is the nonradiative transition rate from the i th level to the j th level, F_{ij} is the pumping rate from the i th level to the j th level, C_{ij} is the coefficient for ET between an ion in the i th level and another one in the j th level, and A_{ij} is the radiative transition rate of the i th level to the j th level. In the present glass, W_{ij} (except W_{10}) is much larger than the total radiative transition rate of the i th level; the lifetime of the i th energy level is determined by $1/W_{ij}$.

Using Eqs. (1)–(9), the green UCL intensities under 980 and 808 nm excitations can be, respectively, written as

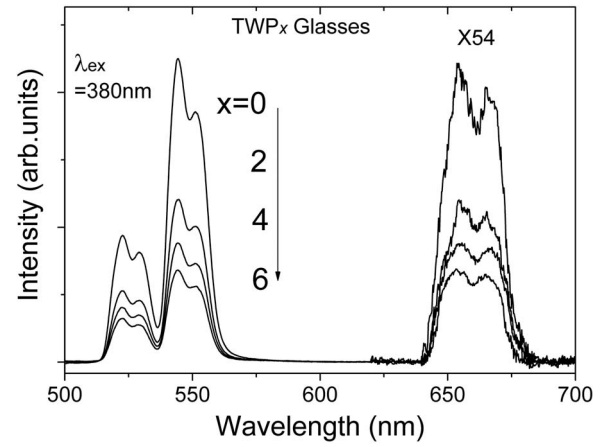


FIG. 5. Emission spectra of Er^{3+} in TWP glasses under the excitation of 380 nm.

$$I_{G980} = A_{50}n_5 = A_{50}\tau_5(F_{25}F_{02}n_0\tau_2 + C_{22}F_{02}^2n_0^2\tau_2^2) \quad (10)$$

and

$$I_{G808} = A_{50}n_5 = A_{50}\tau_5(F_{15}F_{03}n_0\tau_1 + F'_{25}F_{03}n_0\tau_2 + C_{22}F_{03}^2n_0^2\tau_2^2). \quad (11)$$

If we consider the radiative transition rates to be independent of P_2O_5 contents based on the analysis by the JO theory and keep the excitation intensity constant, only the variations of τ_i ($i=1, 2, 5$) with P_2O_5 contents are of interest. The values of τ_5 are obtained by measuring the intensities of the green emission upon 380 nm excitation into level 5. Under steady excitation at 380 nm, one has $n_5/\tau_5 = F_{05}n_0$, so the intensity of the green band (I_{G380}) is the measure of τ_5 . Figure 5 shows the PL spectra of Er^{3+} in TWP glass with different P_2O_5 contents under 380 nm excitation, exhibiting the reduction of the green band with increasing P_2O_5 contents. The values of τ_5 are determined from the PL spectra in Fig. 5 and listed in Table I. If we denote the τ_1 that was determined from time decay measurements by $\tau_1(\text{TD})$ and the τ_2 from intensity ratio measurements by $\tau_2(\alpha)$, ideal linear relationships are observed between I_{G980} and $\tau_2(\alpha)\tau_5$, and between I_{G808} and $\tau_1(\text{TD})\tau_5$, as shown in Figs. 6(a) and 6(b), respectively. As the result, only the first term on the right

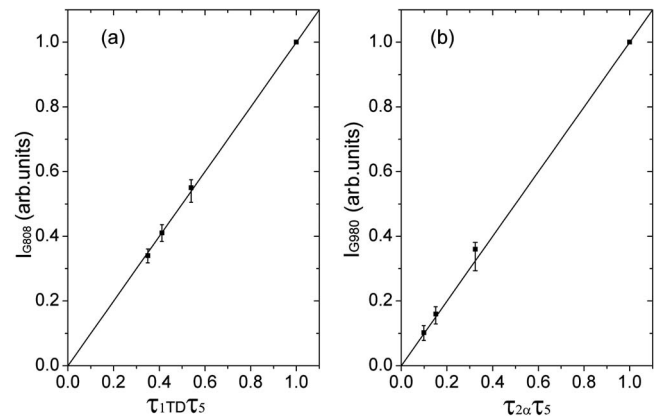


FIG. 6. A plot of I_{G980} vs $\tau_2(\alpha)\tau_5$, and I_{G808} vs $\tau_1(\text{TD})\tau_5$, analyzed using linear curve fit.

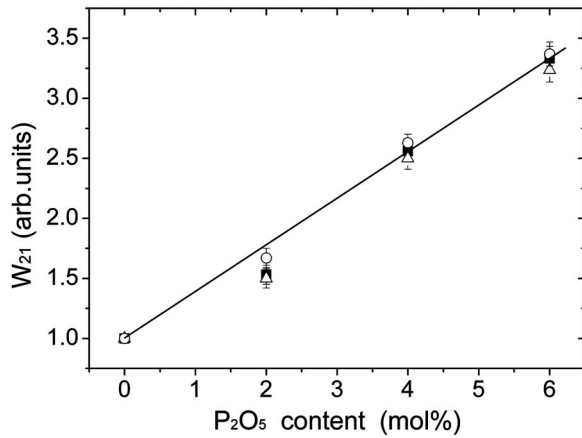


FIG. 7. A comparison of W_{21} determined by ratios α , τ_5/I_{G980} , and I_{G808}/I_{G980} as a function of P_2O_5 contents.

side of Eqs. (10) and (11) play the dominant role on the green UCL. This reveals that the ET process involving interaction between two ions has a negligible contribution to the green UCL for both 980 and 808 nm excitations at the present doping concentration of Er^{3+} in this work, and the green UCL is dominantly governed by the ESA process of the $^4I_{11/2}$ level (F_{25}) for 980 nm excitation and the $^4I_{13/2}$ level (F_{15}) for 808 nm excitation.

In this case, from Eqs. (10) and (11), we rewrite

$$I_{G980} = A_{50}F_{25}F_{02}n_0\tau_2\tau_5, \quad (10')$$

$$I_{G808} = A_{50}F_{15}F_{03}n_0\tau_1\tau_5. \quad (11')$$

From Eqs. (10') and (11'), the $W_{21}(=1/\tau_2)$ can be obtained by τ_5/I_{G980} or also by I_{G808}/I_{G980} due to almost unchanged τ_1 . Figure 7 gives a comparison of W_{21} determined by ratios α , τ_5/I_{G980} , and I_{G808}/I_{G980} as a function of P_2O_5 contents. Obviously, these W_{21} determined by different measurements are in good agreement with each other and have a linear relationship with P_2O_5 contents. The value of W_{21} in TWP_6 glass is about 3.3 times higher than that in TWP_0 glass. τ_1 can be also obtained by I_{G980}/τ_5 using Eq. (11'). These W_{21} and τ_1 determined by different measurements are listed in Table I. Now we focus on the relative intensities of the red UCL to the green (I_R/I_G) upon 980 and 808 nm excitations. Using Eqs. (1)–(9), (10'), and (11'), we have the simplified expressions of the ratio I_R/I_G for the different wavelength excitations,

$$\frac{I_R}{I_G}(980) = \frac{\tau_4 A_{40}}{\tau_5 A_{50}} \left(W_{54}\tau_5 + \frac{C_{12}F_{02}\tau_1 n_0}{F_{25}} \right), \quad (12)$$

$$\frac{I_R}{I_G}(808) = \frac{\tau_4 A_{40}}{\tau_5 A_{50}} \left(W_{54}\tau_5 + \frac{C_{12}F_{03}\tau_2 n_0}{F_{15}} \right). \quad (13)$$

The first terms on the right side of Eqs. (12) and (13) are the contributions by the multiphonon relaxation from the green emitting levels, $^4S_{3/2}$ (level 5), to the red emitting level, $^4F_{9/2}$ (level 4), and the second terms are the cooperation ETs, which are Er^{3+} concentration dependent. Figure 8 shows the comparison of the red UCL spectra in TWP_0 glasses doped with 1 and 0.1 mol % Er^{3+} upon 980 and

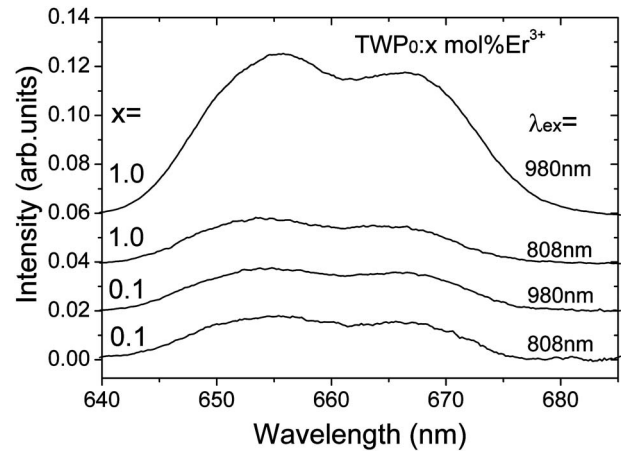


FIG. 8. Red UCL spectra of TWP_0 samples with 0.1 and 1 mol % Er^{3+} under the excitations of 980 and 808 nm; each one is normalized to the intensity of green emission.

808 nm excitations, where the spectral intensity is normalized to the green UCL. It is observed that the relative intensities of the red UCL for 980 nm excitation is stronger than that for 808 nm excitation in TWP_0 glass doped with 1 mol % Er^{3+} . This phenomenon can be explained well using Eqs. (12) and (13). It is known that τ_1 is two orders of magnitude larger than τ_2 ,⁴ and F_{ij} are in the same order of magnitude; the second term on the right side of Eq. (12) is thereby larger than that of Eq. (13), i.e., $C_{12}F_{02}\tau_1 n_0/F_{25} \gg C_{12}F_{03}\tau_2 n_0/F_{15}$. When decreasing Er^{3+} concentration (n_0) from 1 to 0.1 mol %, the relative intensities of the red UCL for 808 nm excitation is unchanged, as shown in Fig. 8, implying that the first term on the right side of Eq. (13) is larger than the second term for Er^{3+} concentration by at least less than 1 mol %. Moreover in Fig. 8, the red UCL for 980 nm excitation is about four times stronger than that for 808 nm excitation for Er^{3+} concentration of 1 mol % and decreases close to that for 808 nm excitation as Er^{3+} concentration is reduced to 0.1 mol %. This indicates that the second term on the right side of Eq. (12) is indeed concentration dependent and about three times larger than the first term for Er^{3+} concentration of 1 mol %.

IV. CONCLUSIONS

The introduction of P_2O_5 into the Er^{3+} -doped tungsten tellurite glasses speeds up population feeding of the $1.53 \mu m$ emitting level, $^4I_{13/2}$, through nonradiative $^4I_{11/2} \rightarrow ^4I_{13/2}$ relaxation and simultaneously suppresses UCL without affecting the emission efficiency of the $^4I_{13/2}$ level. The enhanced rate by a factor of 3.3 for P_2O_5 content of 6% is obtained using UCL spectroscopy, which is in good agreement with that determined using infrared emission spectra. The green UCL is dominantly governed by the ESA process at the present doping concentration of Er^{3+} . The contribution of cooperative ET process to the red UCL is much bigger for 980 nm excitation than that for 808 nm excitation. In UCL of TWP glasses with Er^{3+} concentration of 1 mol %, the red emitting level is dominantly populated by multiphonon relaxation from the green emitting levels for 808 nm excitation and by cooperative ET as well as a small contribution from the mul-

tiphonon relaxation for 980 nm excitation. The red/green UCL ratio in Er^{3+} -doped TWP glasses is controllable by adjusting excitation wavelength and doping concentrations. The telluride glass with P_2O_5 addition is a promising candidate as a host for broadband EDFAs with good performance pumping at 980 nm.

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