

# Concentration-dependent luminescence properties in Er<sup>3+</sup>-doped TeO<sub>2</sub>-ZnO-La<sub>2</sub>O<sub>3</sub> glasses\*

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Erbium-doped tellurite-based glasses (Er<sup>3+</sup>:TeO<sub>2</sub>-ZnO-La<sub>2</sub>O<sub>3</sub>) are prepared by the conventional melt-quenching technique, and concentration-dependent luminescence properties of Er<sup>3+</sup> are investigated. A significant spectral broadening of the 1.53 μm fluorescence corresponding to <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition is observed, and the fluorescence decaying becomes a nearly exponential way with the increasing Er<sup>3+</sup> concentration. Radiation trapping is evoked to explain the broadening of <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> emission line of Er<sup>3+</sup> ions. The optimum doping content of Er<sub>2</sub>O<sub>3</sub> for 1.53 μm fluorescence emission is about 1.5 mol%.

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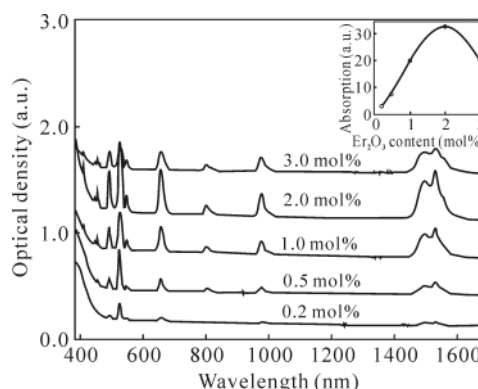
Tellurite-based glass is a promising material used for high-performance erbium-doped fiber amplifier (EDFA) owing to its excellent luminescence properties, for example, large emission cross-section and broad fluorescence width at 1.53 μm<sup>[1-3]</sup>. Meanwhile, with the integration development of wavelength division multiplexing (WDM) systems, the demand for compact and broad band optical amplifiers is urgent. In order to decrease the device volume, it is necessary that the Er<sup>3+</sup>-doped concentration in the glass fiber is sufficiently high to improve the signal gain per unit length. However, higher Er<sup>3+</sup>-doped concentration can induce some detrimental effects, such as concentration quenching and radiation trapping<sup>[4-10]</sup>, finally affecting fluorescence characteristics.

In this paper, the luminescence properties of Er<sup>3+</sup>-doped tellurite-based glasses with different doping levels are investigated, and the fluorescence decaying behavior and fluorescence concentration quenching for the <sup>4</sup>I<sub>13/2</sub> excited level of Er<sup>3+</sup> ions and the related mechanism are analyzed.

The tellurite-based glass samples with composition of (75-x) TeO<sub>2</sub>-20ZnO-5La<sub>2</sub>O<sub>3</sub>-xEr<sub>2</sub>O<sub>3</sub> (TZLx, x = 0.2, 0.5, 1.0, 2.0, and 3.0) were prepared using conventional melt-quenching method. All the starting materials were purer than 99.99%. Batches of 10 g samples were weighed and mixed finely, and then were melted in platinum crucibles at 900 °C for

about 30 min in the air atmosphere. A reducing OH group procedure was applied by bubbling dry oxygen gas for 10 min during melting. The obtained glass melts were annealed and cooled to room temperature gradually, and then were cut and well polished for optical measurements.

The measured absorption spectra of Er<sup>3+</sup>-doped tellurite-based glass samples in ultraviolet-visible and near infrared wavelength range at room temperature are shown in Fig. 1. The wavelengths of absorption peaks scarcely change with the Er<sub>2</sub>O<sub>3</sub> doping content. Due to the strong absorption of the



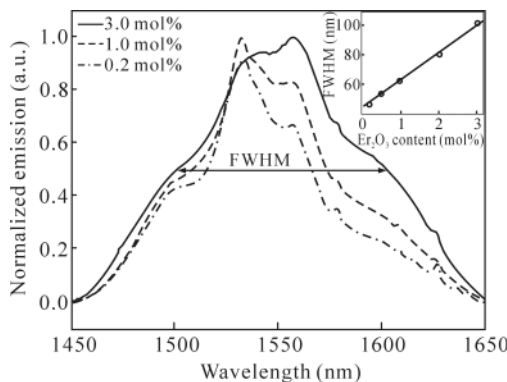
**Fig.1** Absorption spectra of tellurite-based glasses with different Er<sub>2</sub>O<sub>3</sub> doping contents

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host glass in the ultraviolet range, the absorption bands at the wavelength shorter than 400 nm, i.e., the transitions to the multiplets above  ${}^2H_{9/2}$ , cannot be distinguished. A reasonably good linear increase with the  $Er_2O_3$  content varying from 0.2 mol% to 2.0 mol% and a sign of saturation at higher content are observed from the inset of Fig.1. Therefore, the solubility limit of  $Er_2O_3$  doping content in this tellurite-based glass is about 2.0 mol% ( $\sim 10^{21} \text{ cm}^{-3}$  of  $Er^{3+}$ ) for the current experimental condition.

Fig.2 shows the normalized emission spectra of  $Er^{3+}:{}^4I_{13/2} \rightarrow {}^4I_{15/2}$  transition which corresponds to 1.53  $\mu\text{m}$  fluorescence at three different  $Er_2O_3$  doping contents in the prepared glasses, in which a significant broadening of emission spectra with  $Er^{3+}$  doping is clearly observed. The fluorescence width at half-maximum (FWHM) increases rapidly from 52 nm to 103 nm with  $Er_2O_3$  content varying from 0.2 mol% to 3.0 mol% as presented in the inset of Fig.2. Meanwhile, the main peak at 1531 nm decreases gradually, while the side peak around 1556 nm increases accordingly. When the  $Er_2O_3$  doping content is over 3.0 mol%, the main peak completely disappears, while the side peak becomes the new main peak.



**Fig.2 Normalized fluorescence spectra of tellurite-based glasses with different  $Er_2O_3$  doping contents**

Because of the overlap of the absorption and emission spectra of  $Er^{3+}$  ions at 1.53  $\mu\text{m}$ , the broadening trend with increasing  $Er^{3+}$ -doped concentration should mainly be attributed to the radiation trapping<sup>[7,11]</sup>. The radiation trapping inevitably induces that the emission intensity at the bands located at lower energies with respect to the peak wavelength of 1531 nm increases accordingly, and then it leads to a broadening of the emission spectrum. The radiation trapping always occurs in a typical three-level system when the absorption and emission spectra overlap<sup>[8,11]</sup>.

The radiation trapping effect is in proportion to the  $Er^{3+}$ -doped concentration. The strength of radiation trapping can be scaled as  $f_{\text{trap}}$ , i.e., the fraction of emitted radiation which is re-absorbed within the sample, and it can be expressed as<sup>[11]</sup>

$$f_{\text{trap}} = \Omega [1 - \exp(-N_{Er} \sigma_a V^{1/3})], \quad (1)$$

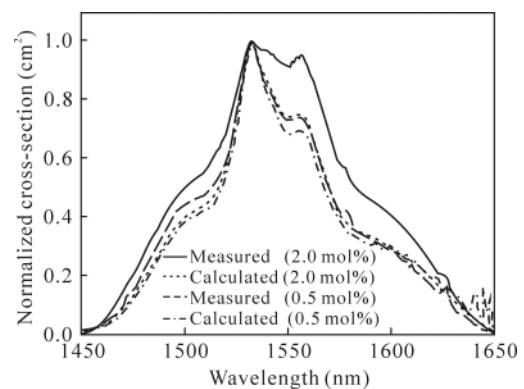
where  $\Omega$  is the fractional spectral overlap of the  ${}^4I_{13/2} \leftrightarrow {}^4I_{15/2}$  absorption and emission bands, and  $N_{Er}$ ,  $V$  and  $\sigma_a$  are the  $Er^{3+}$ -doped concentration, the sample volume and the absorption cross-section, respectively. The absorption cross-section can be determined from the measured absorption spectrum based on the formula of  $\sigma_a(\lambda) = 2.303 \cdot OD(\lambda) / (N_{Er} L)$ , where  $L$  is the bulk glass thickness, and  $OD(\lambda)$  is the optical density. The larger the value of  $f_{\text{trap}}$ , the stronger the radiation trapping in the sample. With the increasing of  $Er^{3+}$ -doped concentration, the fraction of trapped radiation increases, so the 1.53  $\mu\text{m}$  fluorescence spectrum of  $Er^{3+}$  ions broadens accordingly due to the enhanced radiation trapping effect.

To obtain the intrinsic 1.53  $\mu\text{m}$  emission spectrum free from re-absorption, the emission spectra of  $Er^{3+}$  ions are calculated according to the reciprocity method of McCumber-Miniscalco<sup>[12,13]</sup>, which relates the absorption and emission cross-sections by

$$\sigma_e(\lambda) = \sigma_a(\lambda) \exp[(\epsilon - h\nu)/kT], \quad (2)$$

where  $\sigma_e$  is the stimulated emission cross-section,  $h$  is the Planck constant,  $\nu$  is the photon frequency,  $k$  is the Boltzmann constant, and  $\epsilon$  is the net free energy required to excite one  $Er^{3+}$  ion from the ground state  ${}^4I_{15/2}$  to excited state  ${}^4I_{13/2}$  at temperature of  $T$ .

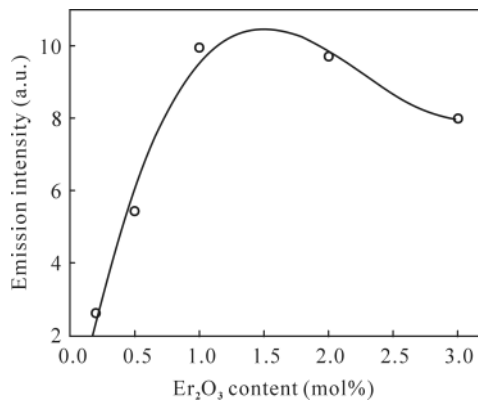
Fig.3 depicts the calculated stimulated emission cross-sections and the measured emission spectra of the 0.5 mol% and 2.0 mol%  $Er_2O_3$  doped glass samples, respectively. The shape of the calculated stimulated emission cross-section scarcely changes with the  $Er_2O_3$  doped content, and it is similar to that of the fluorescence emission of the glass with lower  $Er^{3+}$ -doped content. However, for the higher  $Er^{3+}$ -doped glass, the measured emission spectrum is largely deformed



**Fig.3 Calculated stimulated emission cross-sections and measured fluorescence spectra of  $Er_2O_3$  doped tellurite-based glasses**

relative to the intrinsic emission calculated by McCumber theory due to the radiation trapping.

Fig.4 shows the  $\text{Er}^{3+}$ -doped concentration dependence of  $1.53 \mu\text{m}$  fluorescence integral intensity for  ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$  emission in glass samples. The reduction of fluorescence intensity at the higher  $\text{Er}^{3+}$ -doped level is the result of concentration quenching, which is mainly ascribed to the energy migration among  $\text{Er}^{3+}$  ions, i.e., the excited  $\text{Er}^{3+}$  ion surrenders its energy to the next one through resonant energy transfer<sup>[14,15]</sup>. The migration alone does not result in a loss of excitation, but increases the likelihood that the excited  $\text{Er}^{3+}$  ion at  ${}^4\text{I}_{13/2}$  level can arrive at a quenching site (defect or OH group) and then return rapidly to the ground state via nonradiative relaxation process<sup>[11,16]</sup>. It results in the weakening of  $1.53 \mu\text{m}$  fluorescence emission. It is well known that the  $\text{Er}^{3+}$  ions populated at the  ${}^4\text{I}_{13/2}$  level increase with the increasing of  $\text{Er}_2\text{O}_3$  doped content, and hence the fluorescence intensity increases due to the improved spontaneous radiative transitions. On the other hand, however, the gradually enhanced concentration quenching effect induces the emission weakening to some extent. When the  $\text{Er}^{3+}$ -doped concentration increases to a high level, the latter becomes the main influence.

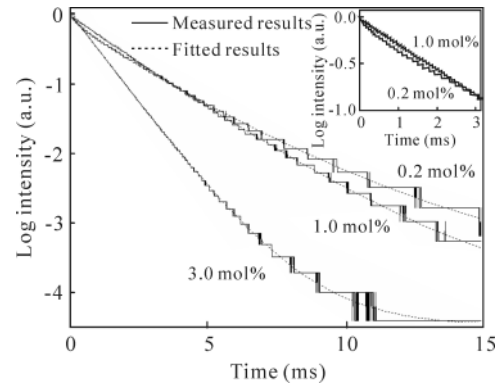


**Fig.4 Fluorescence integrated intensity of  ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$  transition as a function of  $\text{Er}_2\text{O}_3$  doped content**

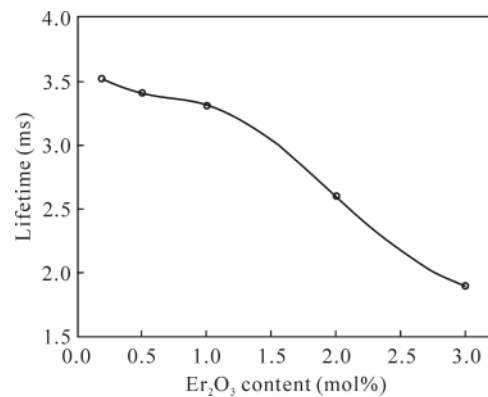
The decaying curves of the excited state  ${}^4\text{I}_{13/2}$  level with different  $\text{Er}_2\text{O}_3$  doped contents are shown in Fig.5. With the increasing of  $\text{Er}_2\text{O}_3$  doped content, the fluorescence decaying behavior varies from a non-exponential one to a nearly single-exponential one. An evident non-exponential decaying behavior of  $\text{Er}^{3+}$  ions can be observed at the beginning in the glass prepared with the lower  $\text{Er}^{3+}$ -doped concentration as shown in the inset of Fig.5. Therefore, a simple exponential fit is not appropriate for the lifetime determination in this case. Instead, a mean-duration time  $\tau_{\text{mean}}$  is introduced, defined by Inokuti and Hirayama<sup>[17]</sup> as

$$\tau_{\text{mean}} = \frac{\int t\varphi(t) dt}{\int \varphi(t) dt}, \quad (3)$$

where  $\varphi(t)$  is the measured decaying curve, and  $t$  is the time. Fig.6 gives the dependence of  $\text{Er}^{3+}$  ion lifetime at  ${}^4\text{I}_{13/2}$  level on the  $\text{Er}_2\text{O}_3$  doped content, and an evident reduction of  $\text{Er}^{3+}$  ion lifetime is clearly observed, which indicates the increasing of the energy migration rate among  $\text{Er}^{3+}$  ions.



**Fig.5 Fluorescence decaying curves and fitting results with different  $\text{Er}_2\text{O}_3$  doped contents**



**Fig.6 Fluorescence lifetime of  $\text{Er}^{3+} : {}^4\text{I}_{13/2}$  level as a function of  $\text{Er}_2\text{O}_3$  doped content**

The observed evidently non-exponential decaying behavior of  ${}^4\text{I}_{13/2}$  level  $\text{Er}^{3+}$  ions at the beginning stage indicates that besides the intrinsic fluorescence decay, there exists other channel from which the excited  $\text{Er}^{3+}$  ions at  ${}^4\text{I}_{13/2}$  level relax to the ground state of  ${}^4\text{I}_{15/2}$  level rapidly. As the energy gap between the  ${}^4\text{I}_{13/2}$  level and the next lower lying  ${}^4\text{I}_{15/2}$  level is larger ( $\sim 6500 \text{ cm}^{-1}$ ), the maximum phonon energy of tellurite-based glass is around  $750 \text{ cm}^{-1}$ , and about nine phonons need to be involved in the phonon assisted transition of  ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ , so it can be anticipated that the probability of multi-phonon relaxation is very small. Therefore, a large portion of the nonradiative transition phenomenon from  ${}^4\text{I}_{13/2}$  level

Er<sup>3+</sup> ions is related to the energy transfer to OH groups in this case. Since the energy gap between the <sup>4</sup>I<sub>13/2</sub> and <sup>4</sup>I<sub>15/2</sub> levels of Er<sup>3+</sup> ion approximately corresponds to the energy of the second harmonic of the free OH group stretching vibration, the <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> nonradiative transition can be bridged by only two OH phonons, which makes the process much more probable than the multiphonon relaxation decay alone. Although a reducing OH group procedure is applied by bubbling dry oxygen gas for 10 min during glass melting, a clear absorption band at about 3400 cm<sup>-1</sup> is still present, which indicates the presence of a certain amount of free OH groups. Thus, the residual OH groups may have a strong quenching effect on the fluorescence decay.

Considering the electric multiple energy transfer from Er<sup>3+</sup> ions to free OH groups, the fluorescence decay of Er<sup>3+</sup> ions can be expressed by the well-known Inokuti-Hirayama equation<sup>[17]</sup>

$$I(t) = I(0)\exp\left(-\frac{t}{\tau} - \gamma t^{1/2}\right), \quad (4)$$

where  $\gamma$  is a parameter describing the direct donor-acceptor energy transfer, and  $\tau$  is the lifetime of the Er<sup>3+</sup> at <sup>4</sup>I<sub>13/2</sub> level in the imaginary OH group free glass. Based on Eq.(4), the obtained fitting curves are presented in Fig.5, and it shows a good agreement between the measured and the fitted results. The obtained lifetime  $\tau$  and the fitted parameter  $\gamma$  are listed in Tab.1.

**Tab.1 Fitted lifetime  $\tau$  and energy transfer parameter  $\gamma$**

	TZL0.2	TZL0.5	TZL1.0	TZL2.0	TZL3.0
Er <sub>2</sub> O <sub>3</sub> (mol %)	0.2	0.5	1.0	2.0	3.0
$\tau$ (ms)	4.61	4.14	3.76	2.65	1.92
$\gamma$ (s <sup>-1/2</sup> )	6.47	3.14	1.97	0.68	0

Analyses of the decaying behavior of Er<sup>3+</sup>:<sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition indicate that when the Er<sup>3+</sup>-doped concentration in the glass is low, there will be a limited energy migration among Er<sup>3+</sup> ions. In this case, a direct Er<sup>3+</sup> ion to OH group energy transfer is dominant, and the resulted decaying curve shows a non-exponential behavior as expressed in Eq.(4). On the other hand, when the Er<sup>3+</sup>-doped concentration increases, the distance between Er<sup>3+</sup> ions decreases, and the interaction among Er<sup>3+</sup> ions strengthens accordingly. Therefore, the energy migration among Er<sup>3+</sup> ions begins to be dominant, and fluorescence decay reveals an exponential behavior. When the Er<sub>2</sub>O<sub>3</sub> doped content in the glass exceeds 1.0 mol%, the value of  $\gamma$  approaches to zero, which indicates that the direct energy transfer from Er<sup>3+</sup> ions to OH groups can be negligible compared with the energy migration among Er<sup>3+</sup> ions in the nonradiative relaxation process of excited

Er<sup>3+</sup> ions at <sup>4</sup>I<sub>13/2</sub> level.

It is found that the solubility limit of Er<sub>2</sub>O<sub>3</sub> doped content is about 2.0 mol% in the tellurite-based glasses with the composition of TeO<sub>2</sub>-ZnO-La<sub>2</sub>O<sub>3</sub>. With the Er<sub>2</sub>O<sub>3</sub> doped content increases from 0.2 mol% to 3.0 mol%, the FWHM corresponding to 1.53  $\mu$ m emission increases rapidly from 52 nm to 103 nm, which is ascribed to the radiation trapping. Meanwhile, the results show that the fluorescence decay of Er<sup>3+</sup> at <sup>4</sup>I<sub>13/2</sub> level deviates from the single-exponential behavior due to the energy transfer from Er<sup>3+</sup> ions to OH groups for the lower Er<sup>3+</sup>-doped glasses. When the Er<sub>2</sub>O<sub>3</sub> doped content exceeds 1.0 mol%, the migration-induced energy transfer among Er<sup>3+</sup> ions dominates the energy transfer, and the fluorescence decay reveals a nearly single-exponential behavior. Accordingly, the 1.53  $\mu$ m fluorescence intensity of Er<sup>3+</sup> begins to saturate, and then decreases due to the concentration quenching effect.

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