

Effect of Ce₂O₃ on the 1.53 μm spectroscopic properties in Er³⁺-doped tellurite glasses*

ZHENG Shi-chao (郑世超)^{1**}, ZHOU Ya-xun (周亚训)², and XUE Rui (薛蕊)¹

1. Qingdao Huanghai University, Qingdao 266427, China

2. College of Information Science and Engineering, Ningbo University, Ningbo 315211, China

(Received 12 September 2014; Revised 8 October 2014)

©Tianjin University of Technology and Springer-Verlag Berlin Heidelberg 2015

Er³⁺/Ce³⁺ co-doped tellurite-based glasses with composition of TeO₂-ZnO-Na₂O are prepared by high-temperature melt-quenching technique. Effects of Ce₂O₃ content on the 1.53 μm band fluorescence spectra and fluorescence lifetime of Er³⁺ are measured and investigated. It is found that the tellurite glass containing Ce₂O₃ with molar concentration of 0.25% exhibits an increment of 13% in 1.53 μm fluorescence intensity and an increment of 15% in the ⁴I_{13/2} level lifetime. The results indicate that the prepared tellurite-based glass with a suitable Er³⁺/Ce³⁺ codoping concentration is an excellent gain medium applied for broadband Er³⁺-doped fiber amplifier (EDFA) pumped with a 980 nm laser diode.

Document code: A **Article ID:** 1673-1905(2015)02-0107-4

DOI 10.1007/s11801-015-4159-2

Tellurite glasses have technological and scientific importance due to their outstanding properties, such as high refractive index, high dielectric constant, good infrared transmittance, low glass transition and melting temperature, thermal and chemical stability and high crystallization resistance^[1-4]. Studies on erbium doped tellurite glasses have attracted much attention because of their exceptional qualities, such as high rare earth ion solubility, large absorption and emission cross-sections, compared with the commercial silica glasses used for the fabrication of erbium doped fiber amplifiers (EDFAs) in wavelength division multiplexing (WDM) network systems^[5,6].

The 980 nm pumping scheme is usually adopted for a commercial EDFA operating in 1.53 μm band in order to obtain a good noise figure. But due to the relatively low phonon energy of tellurite glass (~750 cm⁻¹), the strong up-conversion emission resulting from the ⁴I₁₁₂ excited state absorption (ESA) is observed in Er³⁺ single doped tellurite glasses, resulting in a weak 980 nm pump efficiency and 1.53 μm band fluorescence intensity. As the energy gap in Er³⁺:⁴I₁₁₂→⁴I_{13/2} transition is about 3 600 cm⁻¹, approximately 4–5 phonons need to be combined in order to bridge the energy gap. Thus, to accelerate the non-radiative relaxation process of Er³⁺ from ⁴I₁₁₂ to ⁴I_{13/2} levels is critical^[7,8]. Yang et al^[9] have demonstrated that codoping Er³⁺ and Ce³⁺ is an effective scheme to increase this non-radiative transition and then to improve the 1.53 μm fluorescence intensity through

the energy transfer (ET) process of Er³⁺:⁴I₁₁₂+Ce³⁺:²F_{5/2}→Er³⁺:⁴I_{13/2}+Ce³⁺:²F_{7/2}, which is shown in the inset of Fig.1. Since the absorption peak of Ce³⁺:²F_{5/2}→²F_{7/2} transition appears at about 2 200 cm⁻¹, there is only an energy difference of about 1 400 cm⁻¹ between two ET processes mentioned above. Thus, only 1–2 phonons need to be combined for bridging the energy mismatch. The less the phonons needed to bridge the energy difference, the higher the non-radiative relaxation rate.

In this paper, Ce₂O₃ component is introduced into the Er³⁺-doped TeO₂-ZnO-Na₂O glasses, and the effects of Ce₂O₃ on the 1.53 μm band fluorescence spectra and fluorescence lifetime are investigated and discussed.

The tellurite glasses with composition of (75-x)TeO₂-15ZnO-9.5Na₂O-0.5Er₂O₃-xCe₂O₃, where x is the molar concentration of 0%, 0.25% and 0.5%, were synthesized by a conventional melt-quenching method from powders of TeO₂, ZnO, Na₂CO₃, Er₂O₃ and Ce₂O₃. The prepared samples were denoted as TZNEC0–TZNEC2 for short, in which the component of Na₂O was introduced in Na₂CO₃ formation. All the starting materials were purer with purity more than 99.99%. Batches of 10 g samples were weighed and mixed finely, and then were melted in platinum crucibles at 1 000 °C for about 30 min in the air atmosphere. The obtained glass melts were annealed and cooled to room temperature gradually, and then were cut and well polished for optical measurements.

The Raman spectrum was measured by a Renishaw Micro-Raman instrument. The absorption spectra were

* This work has been supported by the National Natural Science Foundation of China (No.61178063), and the Scientific Research Foundation of Graduate School of Ningbo University (No.G13035).

** E-mail: 526522025@qq.com

measured with a Lamda 950 ultraviolet/visible/near infrared (UV/Vis/NIR) spectrophotometer in wavelength range of 400–1 700 nm. The fluorescence spectrum was measured with a Jobin Yvon Triax550 under excitation of a 975 nm laser diode (LD). The fluorescence lifetime of Er^{3+} ($^4\text{I}_{13/2}$ level) was measured with light pulse excitation of a 980 nm LD, and the fluorescence decaying curve was recorded with a digital oscilloscope (Tektonix TDS 1012, 100 MHz) after averaging 128 times.

Fig.1 shows the measured Raman spectrum of TZNEC0 glass sample. The Raman scattering band centered around 450 cm^{-1} is assigned to the stretching vibrations of Te-O-Te or O-Te-O linkages between two $[\text{TeO}_4]$ four-coordinate atoms, and the bands centered around 660 cm^{-1} and 750 cm^{-1} originate from the stretching vibration of Te-O bond in the continuous networks composed of $[\text{TeO}_4]$ trigonal bipyramid and $[\text{TeO}_{3+\delta}]$ trigonal pyramid structural units, respectively.

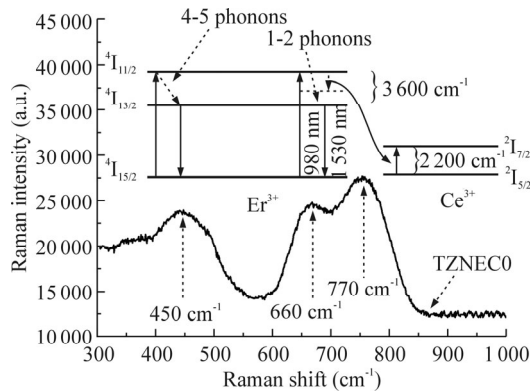


Fig.1 Raman spectrum of TZNEC0 glass sample (The inset shows the energy level diagrams of Er^{3+} and Ce^{3+} .)

Fig.2 reveals the measured absorption spectra of the prepared TZNEC0-TZNEC2 glass samples in the wavelength range of 400-1 700 nm. All the inhomogeneously broadened absorption bands are attributed to 4f-4f transition of Er^{3+} from the $^4\text{I}_{15/2}$ ground state to the different excited states denoted in Fig.2. With the addition of Ce^{3+} , the peak wavelength of each absorption band is almost unchanged but the ultraviolet band absorption cut-off wavelength shifts to a longer range because of the inter-configurational transition ($4f^1:2\text{F}_{5/2} \rightarrow 4f^0,5d^1$) of Ce^{3+} [10].

The Judd-Ofelt theory^[11,12] is a useful tool for analyzing the spectroscopic properties of rare-earth doped glass or crystal. According to the Judd-Ofelt theory and the least-square fitting approach provided in Ref.[13], the corresponding spectroscopic parameters of the electric dipole transition probability (A_{ed}), the magnetic dipole transition probability (A_{md}), the fluorescence branching ratio (β) and the radiative lifetime (τ_{rad}) of TZNEC0 glass sample are evaluated from the absorption spectrum and the refractive index of glass host. The obtained parameters are listed in Tab.1. It can be seen that the value of β for $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ radiative transition is a little more than

16%, which is smaller than the value for $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$ counterpart. It indicates that only portion less than one fifth of the total population in the $^4\text{I}_{11/2}$ level can radiatively feed back to the $^4\text{I}_{13/2}$ level if no additional non-radiative feeding route exists. Therefore, in order to improve the $1.53\text{ }\mu\text{m}$ band fluorescence emission, most of the excited Er^{3+} at $^4\text{I}_{11/2}$ level should be transitioned rapidly to the $^4\text{I}_{13/2}$ level via non-radiative relaxation process, and thus it is necessary to introduce Ce^{3+} into Er^{3+} single-doped tellurite glass.

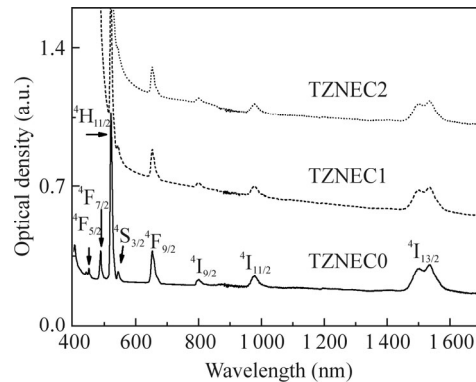


Fig.2 Absorption spectra of TZNEC0-TZNEC2 glass samples

Tab.1 Electric dipole transition probabilities (A_{ed}), magnetic dipole transition probabilities (A_{md}), fluorescence branching ratios (β) and radiative lifetime (τ_{rad}) in TZNEC0 glass

Initial level →final level	A_{ed} (s^{-1})	A_{md} (s^{-1})	β (%)	τ_{rad} (ms)
$^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$	186.92	92.05	100	3.58
$^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$	29.01	24.92	16.78	
$^4\text{I}_{15/2}$	267.41		83.22	3.11
$^4\text{I}_{9/2} \rightarrow ^4\text{I}_{11/2}$	1.54	5.34	2.19	
$^4\text{I}_{13/2}$	72.79		23.15	
$^4\text{I}_{15/2}$	234.74		74.66	3.18
$^4\text{F}_{9/2} \rightarrow ^4\text{I}_{9/2}$	5.45		0.19	
$^4\text{I}_{11/2}$	121.13		4.20	
$^4\text{I}_{13/2}$	139.26		4.83	
$^4\text{I}_{15/2}$	2 617.67		90.78	0.35
$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{9/2}$	107.33		3.79	
$^4\text{I}_{11/2}$	64.48		2.28	
$^4\text{I}_{13/2}$	795.02		28.08	
$^4\text{I}_{15/2}$	1 864.90		65.86	0.35

Fig.3 displays the measured $1.53\text{ }\mu\text{m}$ band fluorescence spectra corresponding to $\text{Er}^{3+}: ^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition of TZNEC0-TZNEC2 glass samples in the wavelength range of 1 400–1 700 nm. The fluorescence intensity of TZNEC1 glass sample is increased by about 13% compared with that of the TZNEC0 glass sample. As discussed above, with the introduction of Ce_2O_3 component, the energy mismatch reduces from $3\text{ }600\text{ cm}^{-1}$ to $1\text{ }400\text{ cm}^{-1}$. The

smaller the energy mismatch, the less the phonons needed to bridge. Therefore, the Ce₂O₃ addition into tellurite glasses makes the non-radiative relaxation process increased significantly. As a result, the population accumulation of ⁴I_{13/2} level should get more dense, and a much stronger ⁴I_{13/2}→⁴I_{15/2} fluorescence emission can be anticipated. However, when the amount of Ce₂O₃ component reaches about 0.5% (TZNEC2), the fluorescence intensity does not continue to increase as expected, and on the contrary, it decreases by about -12% compared with that of TZNEC0 sample. The decrease of fluorescence intensity may be attributed to the higher Ce³⁺ concentration, which results in the backward energy transfer from Ce³⁺ to Er³⁺. Therefore, there is an appropriate doped concentration for Er³⁺/Ce³⁺ codoping scheme.

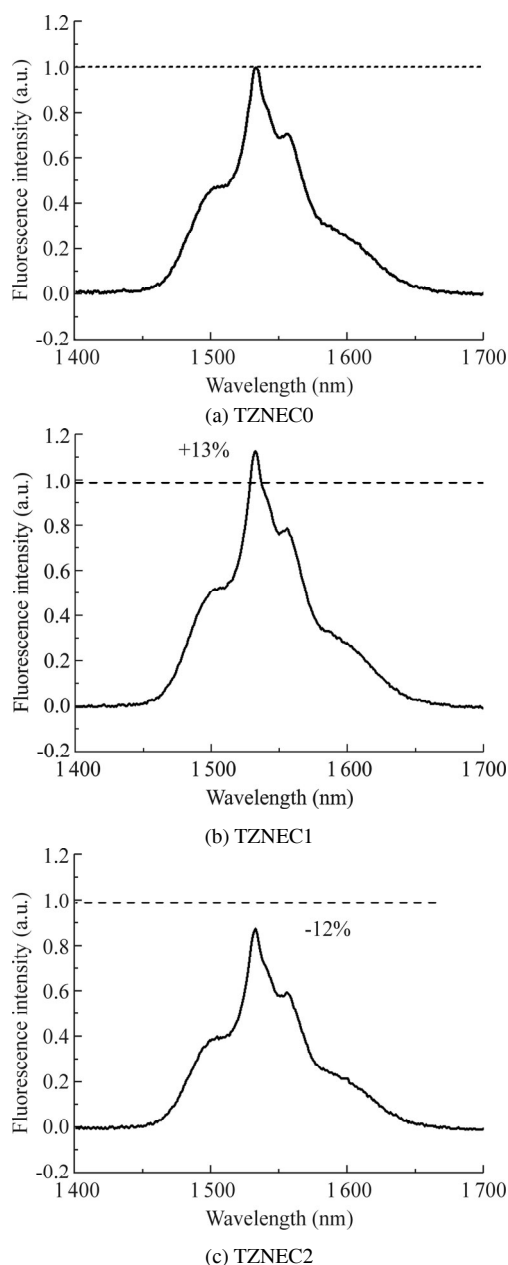


Fig.3 Fluorescence spectra of TZNEC0–TZNEC2 glass samples under 980 nm excitation

Another experimental parameter required to characterize the emission properties of rare-earth ions in a glass host is the fluorescence lifetime. In particular, for optical amplifiers or lasers at the 1.53 μm band, the important parameter is the ⁴I_{13/2} lifetime. The longer the lifetime, the higher the population inversion between ⁴I_{13/2} level and the ground state^[14].

The measured decay curve of ⁴I_{13/2} level for TZNEC0 sample is shown in Fig.4, and the lifetime values for all samples are obtained from single exponential fitting and listed in Tab.2. The trend of ⁴I_{13/2} level lifetime values is similar to the observed 1.53 μm fluorescence intensity. The longest lifetime of 3.16±0.01 ms is found for the sample TZNEC2.

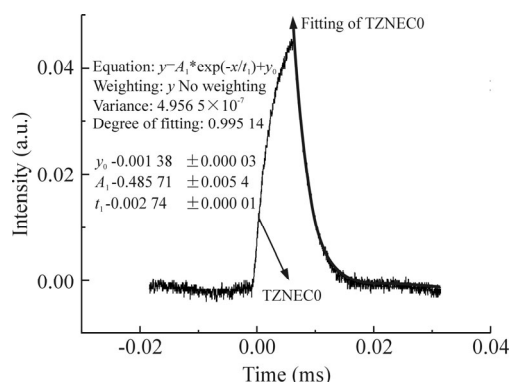


Fig.4 Decay curve of ⁴I_{13/2} level of Er³⁺ in TZNEC0 sample under 980 nm excitation

Tab.2 The measured fluorescence lifetime values (τ_m) of TZNEC0–TZNEC2 samples

Glass sample	Lifetime (ms) (± 0.01 ms)
TZNEC0	2.74
TZNEC1	3.16
TZNEC2	2.97

In this paper, Er³⁺/Ce³⁺ co-doped tellurite glasses were prepared by high-temperature melt-quenching technique. The tellurite glass containing 0.25% amount of Ce₂O₃ (TZNEC1) exhibits an increment of 13% in fluorescence intensity, and the ⁴I_{13/2} level lifetime maintains a large value (3.16 ms). The results indicate that the prepared TeO₂-ZnO-Na₂O tellurite glass with suitable Er³⁺/Ce³⁺ codoping concentration is an excellent gain medium applied for broadband EDFA under 980 nm excitation.

References

[1] Z. Q. Wu, Y. Cheng, W. W. Zhou, T. Y. Wu and H. J. Yang, Journal of Optoelectronics-Laser **25**, 897 (2013). (in Chinese)
 [2] Y. X. Zhou, X. C. Xu, F. Chen, J. H. Lin and G. B. Yang, Optoelectronics Letters **8**, 273 (2012).

- [3] H. F. Zhang, Y. Wu and F. Cheng, *Journal of Optoelectronics-Laser* **24**, 1733 (2013). (in Chinese)
- [4] S. C. Zheng, Y. W. Qi, S. X. Peng, D. D. Yin, Y. X. Zhou and S. X. Dai, *Optoelectronics Letters* **9**, 0461 (2013).
- [5] I. Jlassi, H. Elhouichet, M. Fefid and C. Barthou, *Journal of Luminescence* **130**, 2394 (2010).
- [6] S. B. Lin, P. F. Wang, J. B. She, H. T. Guo, S. N. Xu, P. F. Zhao, C. L. Yu, C. X. Liu and B. Peng, *Journal of Luminescence* **153**, 29 (2014).
- [7] M. S. Figueiredo, F. A. Santos, K. Yukimitu, J. C. S. Moraes, L. A. O. Nunes, L. H. C. Andrade and S. M. Lima, *Journal of Luminescence* **157**, 365 (2015).
- [8] S. C. Zheng, Y. X. Zhou, D. D. Yin, X. C. Xu and X. S. Wang, *Optical Materials* **35**, 1526 (2013).
- [9] J. Yang, L. Zhang, L. Wen, S. Dai, L. Hu and Z. Jiang, *Chemical Physics Letters* **384**, 295 (2004).
- [10] J. Qiu, Y. Shimizugawa, Y. Iwabuchi and K. Hirao, *Applied Physics Letters* **71**, 43 (1997).
- [11] B. R. Judd, *Physical Review* **127**, 750 (1962).
- [12] G. S. Ofelt, *Journal of Chemical Physics* **37**, 511 (1962).
- [13] S. Tanabe, *Journal of Non-Crystalline Solids* **259**, 1 (1999).
- [14] N. G. Boetti, J. Lousteau, A. Chiasera, M. Ferrari, E. Mura, G. C. Scarpignato, S. Abrate and D. Milanese, *Journal of Luminescence* **132**, 1265 (2012).