

Influence of OH groups on 1.5- μm emission of $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped tungsten-tellurite glasses

Jiacheng Li (李家成), Hefang Hu (胡和方), and Fuxi Gan (干福熹)

Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800

Received August 14, 2003

The $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped $\text{TeO}_2\text{-WO}_3\text{-ZnO}$ glasses bubbling with different times were prepared. The infrared (IR) transmission spectra, emission spectra and fluorescence lifetime of Er^{3+} at 1.5 μm were measured. The quench effects of OH groups on emission intensity of Er^{3+} at 1.5 μm as well as the relationships between fluorescence decay rate and OH group content were investigated. The constant $k_{\text{OH-Er}}$, which represents the strength of the interactions between Er^{3+} ions and OH groups, is approximately $17.0 \times 10^{-20} \text{ cm}^4/\text{s}$, and is comparable to that for Er^{3+} in $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped phosphate glasses.

OCIS codes: 160.2750, 160.5690, 300.2140, 300.6250, 160.4670.

Broadening and flattening erbium-doped fiber amplifier (EDFA) is a key device in the wavelength-division-multiplexing (WDM) transmission system. It increases the transmission capacity greatly. Er^{3+} -doped tellurite fiber pumped at 1480 nm with 50-dB gain and 76-nm gain-width has been reported^[1]. But the poor glass thermal stability and strong upconversion emission made tellurite glass not an ideal host for broadband EDFA. 980 nm pumping is more favorable than 1480-nm pumping for its low noise characteristics. Tungsten-tellurite glass has higher phonon energy of 930 cm^{-1} compared with that of tellurite glass ($\sim 750 \text{ cm}^{-1}$), which makes it possible to pump at 980 nm. Tungsten-tellurite glass also has good thermal stability and Er^{3+} has a large emission cross-section and emission bandwidth at 1.5 μm in tungsten-tellurite glass^[2]. On the other hand, hydroxyl groups in glass are serious quenchers for the 1.5- μm emission of Er^{3+} . The quenching effects of OH on the $^4I_{13/2}$ levels of Er^{3+} in silicate, borosilicate, phosphate, germanate, and germanotellurite glasses have been reported^[3-6]. However, by now there is still no relevant report on the quenching effect of OH on the $^4I_{13/2}$ levels of Er^{3+} in tungsten-tellurite glass. Systematic studies on the effect of OH groups on 1.5- μm emission of Er^{3+} can have theoretical and practical significance in developing a promising Er^{3+} doped glass for broadband optical amplifier.

Our work showed that Er^{3+} -doped $\text{TeO}_2\text{-WO}_3\text{-ZnO}$ glass would be a promising candidate for broadband optical amplifier^[7]. In this paper, the quenching effects of OH on the 1.5 μm emission of $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} in $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped $\text{TeO}_2\text{-WO}_3\text{-ZnO}$ glasses were investigated. The relationships between the 1.5 μm emission intensity, fluorescence decay rate and OH group content were discussed.

The glasses $\text{TeO}_2\text{-WO}_3\text{-ZnO-Er}_2\text{O}_3\text{-Yb}_2\text{O}_3$ were prepared from reagent grade commercial oxides. Er_2O_3 and Yb_2O_3 were of spectroscopic purity. The compositions of glass hosts were kept unchanged. Accurately weighted 50-g batches were thoroughly mixed and moved into a gold crucible. Glasses were melted at 800°C for different times while being bubbled with the mixture of carbon tetrachloride and dry oxygen gas. Then the melts were cast into a preheated stainless steel plate and then annealed near their transition temperatures for 90 mins

and cooled to room temperature. Samples for optical measurement were cut and polished to the size of about $15 \times 15 \times 1 \text{ mm}^3$.

Densities were determined following the Archimedes' principle using alcohol as immersion medium. The doping concentration of Er^{3+} was calculated according to the measured densities and the amount of Er_2O_3 added. The infrared (IR) transmission spectra were recorded with an IR spectrometer (Nicolet FTIR) in the frequency $400 - 4000 \text{ cm}^{-1}$. The emission spectra were obtained using a Jobin Yvon Triax 550 fluorescence spectrometer and exciting the samples with a CW laser diode (LD) at 970 nm. The fluorescence lifetimes were measured on a digital oscilloscope, excited by the same 970-nm LD with a pulse frequency of 20 Hz. The relative errors in these measurements are estimated to be less than 10%.

The absorption of OH groups in silicate and phosphate glasses has been extensively studied through IR transmission spectra^[8-10]. According to Scholze^[8], the fundamental stretching vibrations of OH groups experiencing different degrees of hydrogen bonding give rise to three absorption bands. The band at $3448 - 3704 \text{ cm}^{-1}$ is due to free OH groups. The band at $2632 - 3030 \text{ cm}^{-1}$ is associated with the strongly hydrogen-bonded OH groups, and the band around 2381 cm^{-1} is associated with the very strongly hydrogen-bonded OH groups^[8]. Efimov *et al.*^[9,10] have recently challenged this model. They attributed the band around 2300 cm^{-1} to the stretching modes of the OH group participating in the hydrogen bonding of a single kind. And they attributed the wide band around 3000 cm^{-1} to the stretching modes of the H_2O molecule and the higher-frequency stretching modes of the OH group participating in the hydrogen bonding of a single kind^[9,10]. Efimov *et al.* even got lower frequency hydroxyl-related absorption band up to 1500 cm^{-1} ^[9,10]. The IR transmission spectra of $\text{TeO}_2\text{-WO}_3\text{-ZnO-Er}_2\text{O}_3\text{-Yb}_2\text{O}_3$ glasses with different bubbling times were measured. Figure 1 shows the IR transmission spectra of three samples.

From Fig. 1, it is clear that the absorption bands around 2300 cm^{-1} and 3000 cm^{-1} exist in the studied glasses. They appear as two broad absorption bands in the transmission spectra. One is in $2500 - 3650 \text{ cm}^{-1}$ in the three samples, which is due to the combination of the

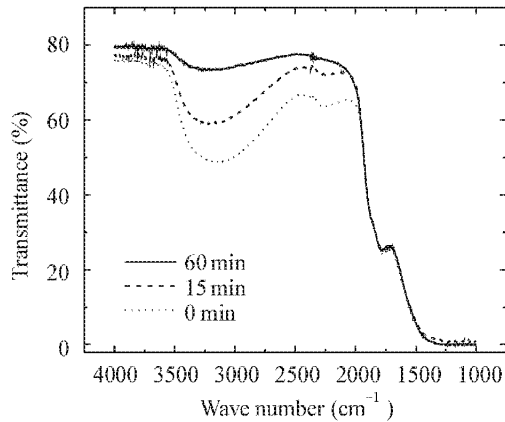


Fig. 1. IR transmission spectra of the glass samples with different bubbling times. The thickness of the samples is 0.95 mm.

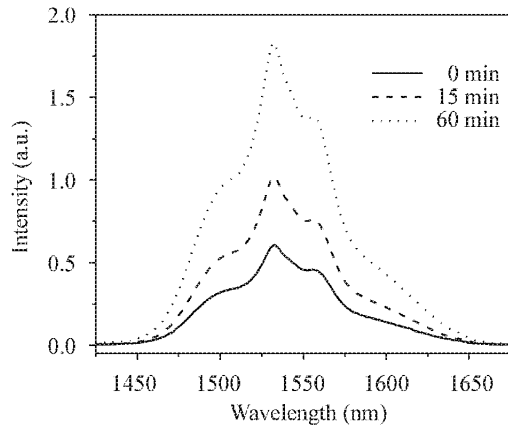


Fig. 2. Emission spectra of Er^{3+} at $1.5 \mu\text{m}$ in tungsten-tellurite glasses with different bubbling time. Er^{3+} concentration is 3.21×10^{20} ions/ cm^3 .

absorption of the free OH groups and the strong hydrogen-bonded OH groups, or the stretching modes of the H_2O molecule and the higher-frequency stretching modes of the OH group participating in the hydrogen bonding of a single kind. The other is in $2040\text{--}2380 \text{ cm}^{-1}$ only in the two samples with short bubbling time, which is due to the absorption of the very strongly hydrogen-bonded OH groups or the stretching modes of the OH group participating in the hydrogen bonding of a single kind. With the increase of bubbling time, the IR transmittance of samples in $2000\text{--}3650 \text{ cm}^{-1}$ band increases, which means the decrease of the OH groups and/or the H_2O molecule in the glasses. Moreover, the absorption band in $2040\text{--}2380 \text{ cm}^{-1}$ can be fully eliminated, which means that the very strongly hydrogen-bonded OH groups or the stretching modes of the OH group participating in the hydrogen bonding of a single kind can be removed completely after a long time bubbling while they cannot be wholly removed in germanotellurite glass^[6]. There are still a part of these OH groups left in the glasses, which is more difficult to remove. So the OH radicals removing process is needed to improve.

OH groups are known to have great influence on the IR emission of rare earth ions. Figure 2 shows the $1.5\text{-}\mu\text{m}$ emission spectra of Er^{3+} in $\text{TeO}_2\text{-WO}_3\text{-ZnO-Er}_2\text{O}_3\text{-}$

Yb_2O_3 glass samples with different bubbling times. It is seen that, through bubbling the melt with the mixture of carbon tetrachloride and dry oxygen gas, the fluorescence intensity of Er^{3+} at $1.5 \mu\text{m}$ increases more than two times. As is shown in Fig. 1, the content of OH groups in glass samples is largely reduced through bubbling. The longer the bubbling time, the less the OH groups remained in the glass. By bubbling, the quenching effects of OH groups upon the $1.5\text{-}\mu\text{m}$ emission of Er^{3+} become weaker. As a result, the fluorescence intensity of Er^{3+} at $1.5 \mu\text{m}$ increases. It is also seen that the $1.5\text{-}\mu\text{m}$ emission bandwidths are large. The full width at half maximum (FWHM) is $\sim 72 \text{ nm}$ for all samples.

The OH radicals in glass are effective quenchers of the IR emission of Er^{3+} $^4I_{13/2}$ level. As is shown in Fig. 1, the higher vibration frequencies of OH groups occur in the range of $2500\text{--}3650 \text{ cm}^{-1}$, which are much higher than other vibration frequencies in the glass. Therefore, energy transfer from the $^4I_{13/2}$ level to OH groups plays an important role in the glasses. The energy gap between the $^4I_{13/2}$ level and $^4I_{15/2}$ level is $\sim 6500 \text{ cm}^{-1}$. So, only two or three phonons are required for non-radiative de-excitation of the $1.5\text{-}\mu\text{m}$ emission of Er^{3+} . At the same time, OH groups can also quench the $^2F_{5/2}$ level of Yb^{3+} . Thus, the efficiency of energy transfer from Yb^{3+} ($^2F_{5/2}$) to Er^{3+} ($^4I_{13/2}$), and the efficiency of Er^{3+} emission corresponding to $^4I_{13/2} \rightarrow ^4I_{15/2}$ will be decreased. Therefore, decreasing OH content is important to enhance the emission of Er^{3+} at $1.5 \mu\text{m}$.

The absorption coefficient of the OH vibration band at peak wavenumber, α_{OH} , is used as a measure of the OH content^[11]. α_{OH} is calculated by^[9,10,12]

$$\alpha_{\text{OH}} = L^{-1} \ln(T_0/T), \quad (1)$$

where L is the thickness of the sample, T_0 is the transmittance of glass at the wavenumber 4000 cm^{-1} without OH groups absorption, and T is the transmittance at peak wavenumber of the absorption of OH groups.

For understanding the effect of OH content on fluorescence decay rate of the IR emission of Er^{3+} , the fluorescence lifetimes of the $^4I_{13/2}$ level of Er^{3+} , τ_m , were measured for all samples bubbling with different times. Figure 3 shows the dependence of the fluorescence decay rate, $1/\tau_m$, on the absorption coefficient of OH groups, α_{OH} . It is seen that the measured decay rate increases nearly linearly with α_{OH} .

Considering the energy transfer from the $^4I_{13/2}$ level to OH groups, the total decay rate, $1/\tau_m$, of the $^4I_{13/2}$ level, which is defined as the reciprocal of the measured fluorescence lifetime, is given by

$$1/\tau_m = A_{\text{rad}} + W_{\text{OH}} + W_{\text{other}}, \quad (2)$$

where A_{rad} is the sum of all radiative decay rates of $^4I_{13/2}$ level, W_{OH} is the rate of energy transfer to OH groups and W_{other} is the other non-radiative decay rate including cross-relaxation, multiphonon relaxation, etc.

The energy transfer rate to OH groups, W_{OH} , which is proportional to the acceptor and donor concentration^[13], can be expressed as

$$W_{\text{OH}} = k_{\text{OH-Er}} N_{\text{Er}} \alpha_{\text{OH}}, \quad (3)$$

where $k_{\text{OH-Er}}$ is a constant, N_{Er} is the Er^{3+} concentration (donor concentration), α_{OH} is the measure of OH

groups content (acceptor concentration).

Because of the linear correlation between the total decay rate $1/\tau_m$ and α_{OH} as shown in Fig. 3, the total decay rate can be described as

$$1/\tau_m = m_{OH}\alpha_{OH} + 1/\tau_0, \quad (4)$$

where m_{OH} is the slope of the fitting curve and $1/\tau_0$ is the decay rate in the absence of OH groups. From Eqs. (2) – (4), we can get

$$m_{OH} = k_{OH-Er}N_{Er}, \quad (5)$$

$$1/\tau_0 = A_{rad} + W_{other}, \quad (6)$$

$$1/\tau_m = k_{OH-Er}N_{Er}\alpha_{OH} + 1/\tau_0. \quad (7)$$

From these considerations, it can be concluded that k_{OH-Er} is a constant determined by the strength of the interactions between Er^{3+} ions and OH groups in the case of energy migration, independent of the concentration of Er^{3+} and OH. According to Eq. (7) and Fig. 3, the constant k_{OH-Er} for Er^{3+} in the tungsten tellurite glass was calculated. The value of k_{OH-Er} is about $17.0 \times 10^{-20} \text{ cm}^4/\text{s}$, which is comparable to that for Er^{3+} in Yb^{3+}/Er^{3+} co-doped phosphate glasses^[12].

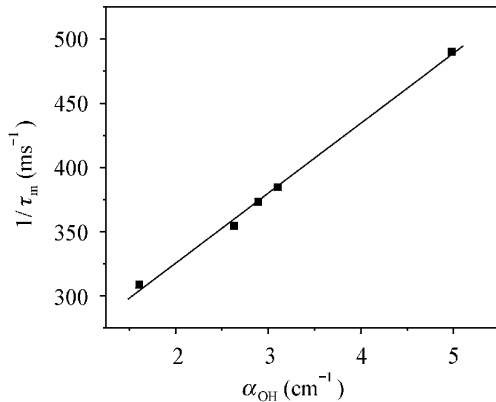


Fig. 3. The dependence of decay rate, $1/\tau_m$, of ${}^4I_{13/2}$ level of Er^{3+} on the absorption coefficient of OH groups, α_{OH} , in tungsten-tellurite glasses.

To sum up, in $TeO_2-WO_3-ZnO-Er_2O_3-Yb_2O_3$ glasses, the very strongly hydrogen-bonded OH groups can be completely eliminated, while the free and the strong hydrogen-bonded OH groups are more difficult to remove. OH groups have great influence on the $1.5\text{-}\mu\text{m}$ emission of Er^{3+} . Decreasing the OH content in glass can largely increase the emission intensity of Er^{3+} at $1.5\text{-}\mu\text{m}$. The fluorescence decay rate of the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} increases linearly with the OH content. The constant, k_{OH-Er} , which represents the strength of the interactions between Er^{3+} ions and OH groups is about $17.0 \times 10^{-20} \text{ cm}^4/\text{s}$, which is comparable to that in Yb^{3+}/Er^{3+} co-doped phosphate glasses.

We would like to thank Youyu Fan and Shunguang Li for the optical tests. J. Li's e-mail address is jiachengli2001@yahoo.com.cn.

References

1. A. Mori, Y. Ohishi, and S. Sudo, *Electron. Lett.* **36**, 863 (1997).
2. S. Shen, M. Naftaly, and A. Jha, *Opt. Commun.* **205**, 101 (2002).
3. E. Snokes, P. G. Kik, and A. Polman, *Opt. Mater.* **5**, 159 (1996).
4. Y. Yan, A. J. Faber, and H. Waal, *J. Non-Cryst. Solids* **181**, 283 (1995).
5. J. M. Jewell and I. D. Aggarwal, *J. Non-Cryst. Solids* **181**, 189 (1995).
6. X. Feng, S. Tanabe, and T. Hanada, *J. Non-Cryst. Solids* **281**, 48 (2001).
7. J. C. Li, S. G. Li, H. F. Hu, and F. X. Gan, *Chin. Phys. Lett.* **21**, (2004) (to be published).
8. H. Scholze, *Glass Ind.* **47**, 546 (1966).
9. A. M. Efimov, F. Gkostyreva, and G. A. Sycheva. *J. Non-Cryst. Solids* **238**, 124 (1998).
10. A. M. Efimov and V. G. Pogareva. *J. Non-Cryst. Solids* **275**, 189 (2000).
11. H. E.-Heidepriem, W. Seeber, and D. Ehri, *J. Non-Cryst. Solids* **163**, 74 (1993).
12. Z. P. Liu, S. X. Dai, C. H. Qi, L. L. Hu, and Z. H. Jiang, *Acta Photon. Sin.* (in Chinese) **30**, 1413 (2001).
13. H. E.-Heidepriem, W. Seeber, and D. Ehrt, *J. Non-Cryst. Solids* **183**, 191 (1995).