

Effect of B₂O₃ on the spectroscopic properties in Er³⁺/Ce³⁺ co-doped tellurite-niobium glass*

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The high phonon energy oxide of B₂O₃ is introduced into the Er³⁺/Ce³⁺ co-doped tellurite-niobium glasses with composition of TeO₂-Nb₂O₅-ZnO-Na₂O. The absorption spectra, 1.53 μm band fluorescence spectra, fluorescence lifetime and Raman spectra of Er³⁺ in glass samples are measured together with the calculations of Judd-Ofelt spectroscopic parameter, stimulated emission and absorption cross-sections, which evaluate the effect of B₂O₃ on the 1.53 μm band spectroscopic properties of Er³⁺. It is shown that the introduction of an appropriate amount of B₂O₃ can further improve the 1.53 μm band fluorescence intensity through an enhanced phonon-assisted energy transfer (ET) between Er³⁺/Ce³⁺ ions. The results indicate that the prepared Er³⁺/Ce³⁺ co-doped tellurite-niobium glass with an appropriate amount of B₂O₃ is a potential gain medium for the 1.53 μm broadband erbium-doped fiber amplifier (EDFA).

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Er³⁺-doped tellurite glass has been recognized as one of the most promising gain media for broadband erbium-doped fiber amplifier (EDFA) applied in the wavelength-division-multiplexing (WDM) communication systems^[1,2]. As a gain medium, tellurite glasses possess a series of advantages, such as good glass stability and durability, high refractive index (~2), good rare-earth ion solubility, large stimulated emission cross-section and broad fluorescence full width at half maximum (FWHM) at the 1.53 μm band^[3].

The 980 nm pumping is usually adopted by EDFA in order to achieve the low noise figure amplification of 1.53 μm band signal^[4]. However, the 980 nm pumping efficiency is relatively low for Er³⁺-doped tellurite glass due to its low phonon energy (~750 cm⁻¹) of glass matrix, which restrains the rapid multiphonon relaxation of Er³⁺ from the pump ⁴I_{11/2} level to the fluorescence ⁴I_{13/2} level. In order to improve the 980 nm pumping efficiency, it is necessary to increase the non-radiative transition rate of Er³⁺:⁴I_{11/2}→⁴I_{13/2}. To this purpose, an effective scheme involving the introduction of a suitable codopant to provoke the non-radiative decay has been proposed^[5], and the results suggest that Ce³⁺ is the most efficient ion to improve the 1.53 μm band fluorescence through the energy transfer (ET) process of Er³⁺:⁴I_{11/2}+Ce³⁺:²F_{5/2}→Er³⁺:⁴I_{13/2}+Ce³⁺:²F_{7/2}, which is shown in Fig.1.

The absorption peak of Ce³⁺:²F_{5/2}→²F_{7/2} transition appears at about 2200 cm⁻¹^[2], whereas the energy gap be-

tween Er³⁺:⁴I_{11/2}→⁴I_{13/2} emission transition is about 3600 cm⁻¹, there is an energy mismatch of about 1400 cm⁻¹ to that in Ce³⁺. Therefore, it is easily achieved that the phonon of glass host will compensate the energy difference, and then help to transfer the energy from Er³⁺:⁴I_{11/2} to Ce³⁺:²F_{5/2} level. Obviously, the glass host with larger phonon energy can be more beneficial for this energy transfer. In this paper, the high phonon energy oxide of B₂O₃ is introduced into the Er³⁺/Ce³⁺ co-doped tellurite-niobium glasses to improve the 1.53 μm band fluorescence by providing large phonon energy for Er³⁺/Ce³⁺ energy transfer process.

The Er³⁺/Ce³⁺ co-doped tellurite-niobium glasses with compositions of (73.75-x)TeO₂-10Nb₂O₅-10ZnO -5Na₂O -xB₂O₃-0.5Er₂O₃-0.75Ce₂O₃ were melted in alumina crucibles at 950 °C for about 30 min, in which x=0%, 2%, 5%, 10% and 15%, namely TNB0, TNB1, TNB2, TNB3 and TNB4, respectively. The obtained glasses were annealed to the room temperature gradually, and then were cut and well polished for further optical measurements.

The absorption spectrum of the glass sample was recorded by a Perkin-Elmer-Lambda 950 UV/VIS/NIR spectrophotometer. The near-infrared fluorescence spectrum was measured by a Jobin Yvon Triax550 spectrophotometer under the excitation of 975 nm LD. The fluorescence lifetime was measured by light pulse excitation of a 975 nm LD, and the fluorescence decaying curve was recorded by a digital oscilloscope (Tektonix TDS

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1012, 100 MHz) after averaging 128 times. The Raman spectra were measured by Renishaw micro-Raman instrument.

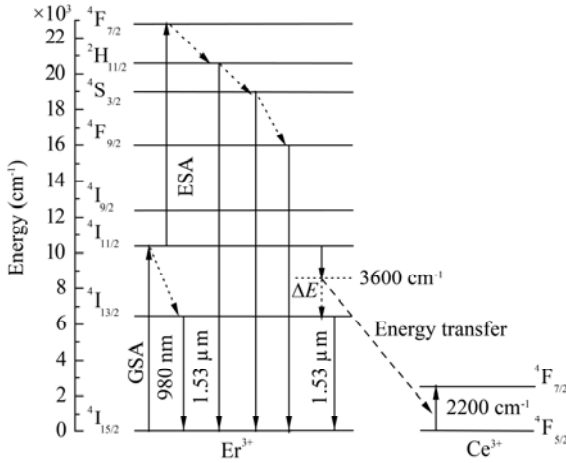


Fig.1 The energy level diagram of Er³⁺ and Ce³⁺ and relevant transitions in tellurite glass pumped at 980 nm

Fig.2 shows the measured Raman spectra of the TNB0–TNB4 samples in the frequency range from 350 cm⁻¹ to 1650 cm⁻¹. It can be seen from the Raman spectra that for tellurite-niobium glass, there are three sharp peaks located at 445 cm⁻¹, 675 cm⁻¹ and 760 cm⁻¹ corresponding to the symmetric stretching and bending vibration of Te-O-Te bond, asymmetric stretching vibration of Te-O bond in [TeO₄] trigonal bipyramid structural groups and bending vibration of Te-O bond and Te=O double bonds in [TeO₃] triangular pyramid and distortion [TeO₃₊₁] triangular pyramid structural groups, respectively^[6,7], while the scattering peak located at 875 cm⁻¹ is ascribed to the stretching vibration of Nb-O bonds in [NbO₆] octahedral structural group^[8]. It is shown that the Raman spectra of TNB1–TNB4 glass samples containing B₂O₃ all exhibit 1420 cm⁻¹ characteristic peak which is due to the stretching vibration of B-O bond in [BO₃] structural group^[9], and the peak intensity increases with the increase of B₂O₃ amount. Obviously, the maximum phonon energy of glass host increases from 875 cm⁻¹ to 1420 cm⁻¹ with the introduction of B₂O₃ oxide. Therefore, the energy mismatch between the emission transition of Er³⁺:⁴I_{11/2}→⁴I_{13/2} and the absorption transition of Ce³⁺:²F_{5/2}→²F_{7/2} can be compensated requiring only one host phonon in the tellurite-niobium glass host containing B₂O₃ oxide, which indicates that an enhanced energy transfer can be expected.

Fig.3 displays the measured absorption spectra of Er³⁺/Ce³⁺ co-doped TNB0–TNB4 glass samples in the wavelength range from 400 nm to 1650 nm. Due to the intensive inter-configurational absorption transition of Ce³⁺ in the visible-ultraviolet band^[10], only six absorption peaks can be observed in the spectrum, which are originated from the absorption transitions between the ground state, ⁴I_{15/2} and various excited states of ⁴I_{13/2}, ⁴I_{11/2}, ⁴I_{9/2},

⁴F_{9/2}, ⁴S_{3/2} and ²H_{11/2} of Er³⁺, respectively.

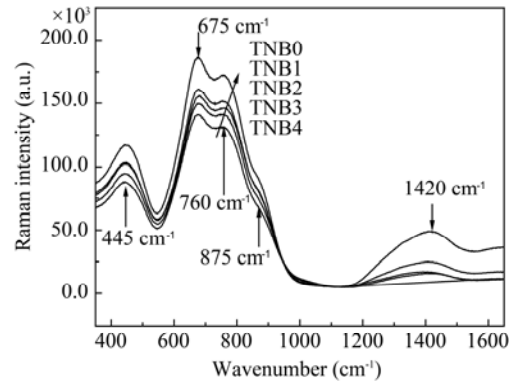


Fig.2 Raman spectra of TNB0–TNB4 glass samples

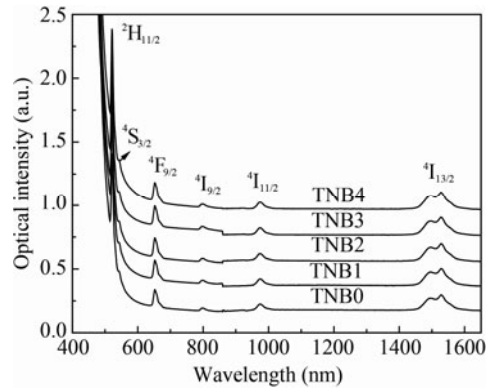


Fig.3 Absorption spectra of TNB0–TNB4 glass samples

According to the Judd-Ofelt theory^[11,12], the three Judd-Ofelt intensity parameters Ω_t ($t=2, 4, 6$) can be determined by least-square fitting approach. The obtained intensity parameters of TNB0 and TNB1 glass samples together with the other glass hosts are summarized in Tab.1. The Judd-Ofelt intensity parameters give the indirect information on the glass symmetry and the covalent bonding of rare-earth ions. The parameter Ω_2 is sensitive to glass symmetry at the Er³⁺ sites, and a large Ω_2 represents a low symmetry of glass network, while the parameter Ω_6 is insensitive to the local structure but inversely proportional to the covalency of Er-O bond^[13]. The Er-O bond is related with the local basicity around the rare-earth sites, which can be adjusted by the composition or structure of the glass hosts. With the introduction of B₂O₃ oxide into the tellurite-niobium glass, the structure units [BO₃] and [BO₄] gradually participate in the glass network as a network former, which increases the glass structure disorder or lowers the glass structure symmetry, and in turn leads to an increase of the value of Ω_2 . Meanwhile, the number of the non-bridging oxygen ions in the glass network decreases, and then leads to an increase of Ω_6 . Glass hosts with higher ratios of Ω_4/Ω_6 , which are known as the spectroscopic quality factors, can induce the strong stimulated emission^[14]. Tab.1 also presents the different Ω_4/Ω_6 values of Er³⁺ in various glass

hosts. The relatively high values of Ω_4/Ω_6 for TNB glasses indicate their effectiveness for 1.53 μm band luminescence.

Tab.1 Judd-Ofelt parameters Ω_t ($t=2, 4, 6$) of Er^{3+} in various glass hosts

Glass host	Ω_2	Ω_4	Ω_6	Ω_4/Ω_6
TNB0	6.18	1.08	0.58	1.86
TNB1	6.27	1.23	0.73	1.68
$\text{TeO}_2\text{-ZnO-K}_2\text{O-CaO}^{[5]}$	6.81	1.75	0.94	1.81
Silicate ^[15]	4.23	1.04	0.61	1.70
Phosphate ^[15]	6.65	1.52	1.11	1.37
Fluoride ^[16]	2.91	1.27	1.11	1.14

The obtained three Judd-Ofelt intensity parameters can be applied further to calculate the radiative transition probability, fluorescence branching ratio and radiative lifetime of Er^{3+} . The radiative transition probability of $\text{Er}^{3+}:^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition in TNB1 glass sample is calculated to be 226.9 s^{-1} , which is much larger than that in phosphate glass (118 s^{-1})^[15]. The large transition probability is beneficial for achieving intense 1.53 μm fluorescence emission.

Fig.4 shows the measured 1.53 μm band fluorescence emission spectra of $\text{Er}^{3+}/\text{Ce}^{3+}$ co-doped glass samples of TNB0–TNB4 in the wavelength range from 1400 nm to 1700 nm. The inset gives the variation of 1.53 μm band peak fluorescence intensity with B_2O_3 amount in the glasses. As shown in Fig.4, compared with the TNB0 glass without B_2O_3 oxide, the 1.53 μm band infrared fluorescence is further improved when 2% B_2O_3 is introduced. The improvement of the fluorescence intensity can be attributed to the increase of the maximum phonon energy of glass matrix. The larger the phonon energy, the less the phonons needed to bridge the existing energy difference between $\text{Er}^{3+}:^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ and $\text{Ce}^{3+}:^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transitions. As a result, the non-radiative transition rate of $\text{Er}^{3+}:^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ is further increased due to the enhanced energy transfer, the Er^{3+} ions accumulated at $^4\text{I}_{13/2}$ level should be denser, and thus a much stronger 1.53 μm band fluorescence can be anticipated. However, when the B_2O_3 amount is further increased, the 1.53 μm band fluorescence intensity does not continue to increase as expected. On the contrary, it decreases significantly. The decrease of fluorescence intensity can be attributed to the OH groups incorporated in the prepared tellurite glass coming from the chemicals and the fabrication atmosphere. It is known that the OH group in the glass sample can easily become the fluorescence quenching center of the $\text{Er}^{3+}:^4\text{I}_{13/2}$ level, because the absorption peak of second harmonic vibration of OH group has a great degree of overlap with the 1.53 μm band fluorescence spectrum.

The stimulated emission cross-section of Er^{3+} can be obtained by the McCumber theory^[17]:

$$\sigma_e(\lambda) = \sigma_a(\lambda) \exp[(\varepsilon - h\nu) / kT], \quad (1)$$

where h is the Planck constant, k is the Boltzmann constant, and ε is the net free energy^[18]. The absorption cross-section of Er^{3+} is obtained from the measured absorption spectrum by

$$\sigma_a(\lambda) = \frac{2.303}{NL} OD(\lambda), \quad (2)$$

where $OD(\lambda)$ is the optical density, L is the thickness of glass sample, and N is the doped concentration. Fig.5 gives the calculated stimulated emission cross-section of σ_e , absorption cross-section of σ_a and the difference curve of $\sigma_e - \sigma_a$ corresponding to the $\text{Er}^{3+}:^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transitions for the TNB1 glass sample. According to Ref.[19], the gain spectrum profile of EDFA strongly depends on the difference spectrum $\sigma_e - \sigma_a$, and the longer peak wavelength of $\sigma_e - \sigma_a$ is corresponding to the better gain profile. The compositional dependence of peak wavelength is shown in the inset of Fig.5. It is easily found that the peak wavelength of $\sigma_e - \sigma_a$ in the TNB1 and TNB2 glasses is longer, indicating the better gain profile can be achieved in these glasses.

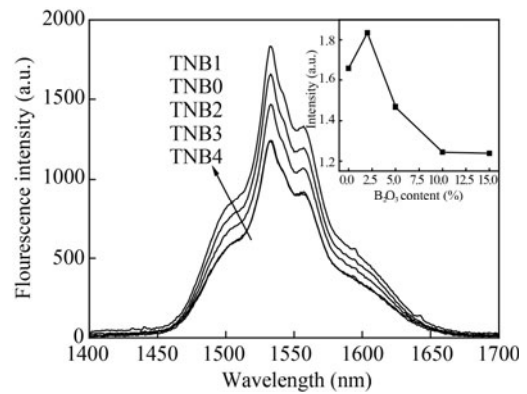


Fig.4 1.53 μm band fluorescence emission spectra of Er^{3+} in TNB0–TNB4 glass samples (The inset is the variation of 1.53 μm band peak fluorescence intensity with B_2O_3 amount in the glasses.)

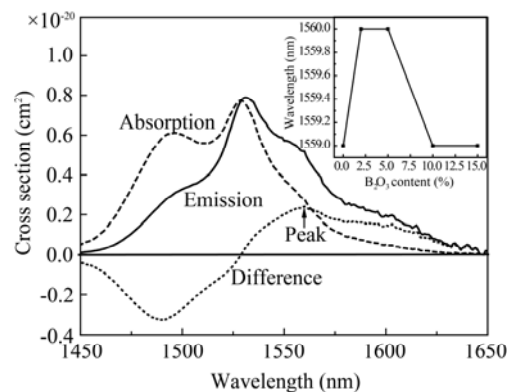


Fig.5 Absorption and emission cross-sections of Er^{3+} in TNB1 glass sample (The inset is the compositional dependence of peak wavelength.)

The Er^{3+} lifetime of $^4\text{I}_{13/2}$ level and quantum efficiency of $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition are directly related to the laser

performance and treated as key parameters in the spectroscopic analysis^[20]. Fig.6 shows the compositional dependence of the measured lifetime (τ_m) and the radiative lifetime (τ_{rad}) of $^4I_{13/2}$ level, and the quantum efficiency ($\eta = \tau_m / \tau_{rad}$) of $Er^{3+}: ^4I_{13/2} \rightarrow ^4I_{15/2}$ transition for the TNB glasses. It can be found that the fluorescence lifetime decreases roughly, while the quantum efficiency first increases to 58.1% in TNB1 glass, and then decreases with the increase of B_2O_3 amount, which is in good accordance with the measured 1.53 μm band fluorescence intensity. When introducing B_2O_3 oxide into the Er^{3+}/Ce^{3+} co-doped tellurite-niobium glasses, the energy transfer from $Er^{3+}: ^4I_{11/2}$ level to $Ce^{3+}: ^2F_{7/2}$ level is enhanced due to the increased maximum phonon energy, which is more suitable to bridge the existing energy mismatch on the one hand, and on the other hand, the quenching effect on the 1.53 μm fluorescence aroused by residual OH groups also aggravates accordingly. When the amount of B_2O_3 increases to a certain extent, the latter begins to dominate the 1.53 μm fluorescence emission.

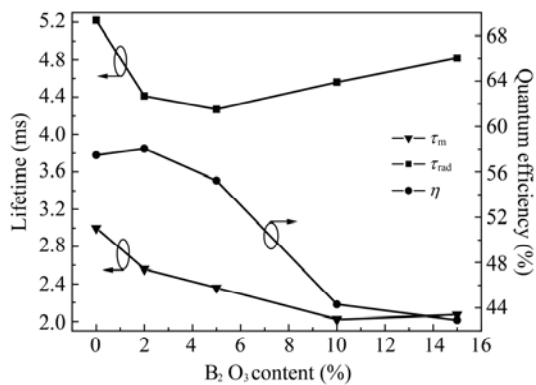


Fig.6 Compositional dependence of lifetime of the $^4I_{13/2}$ level and quantum efficiencies of $Er^{3+}: ^4I_{13/2} \rightarrow ^4I_{15/2}$ transition in TNB0-TNB4 glass samples

It is found that introducing 2% amount of B_2O_3 oxide into the Er^{3+}/Ce^{3+} co-doped tellurite-niobium glass with composition of $TeO_2-Nb_2O_5-ZnO-Na_2O$ can further improve the 1.53 μm band fluorescence intensity, which is attributed to the enhanced energy transfer process between Er^{3+}/Ce^{3+} ions. Therefore, as a low phonon energy glass host applied for the 1.53 μm band broad EDFA, B_2O_3 as a high phonon-energy oxide can be selectively introduced into the Er^{3+}/Ce^{3+} co-doped tellurite glass, and meanwhile the dehydrating

procedure is adopted.

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