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Investigation of Modification Effect of B_2O_3 Component on Optical Spectroscopy of Er^{3+} Doped Tellurite Glasses

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Abstract: To investigate the modification effect of the B_2O_3 component on tellurite glass, a series of glasses with a composition of xB_2O-$(80-x)TeO_2$-$10ZnO$-$10Na_2O$ (x = 0, 10, 20, 30, 40, 50, 60, 70, 80) and an additional amount of 0.5% Er_2O_3(in molar) were prepared. The refractive index, the absorption edge of the host, the J-O parameters of Er^{3+}, the fluorescent decay time, the bandwidth, and the quantum efficiency for the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition were obtained theoretically and experimentally. These results indicated that the introduction of B_2O_3 modified the performance of the tellurite glass. For example, with increasing content of B_2O_3, the refractive index of the host decreases from 1.9 to 1.5, the absorption edge of the host shifted toward the blue regime, the intensity parameter Ω_6 changed from 1.08×10^{-20}(for the pure tellurite glass) to 1.98×10^{-20} cm^2(for the pure borate glass), the bandwidth of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition increased, and the quantum efficiency of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition decreased.

Key words: Er^{3+}; glass; J-O theory; bandwidth; host absorption band gap; quantum efficiency; rare earths

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Recently, with the rapid development of the wavelength division multiplexing (WDM) system for large capacity and flexibility of information network, the broad band 1.5 μm erbium-doped fiber amplifiers (EDFAs) have become more and more important[1]. Owing to a broad bandwidth of over 70 nm, which meets the transmission capacity of WDM systems, tellurite glasses have attracted considerable attention for applications in EDFAs. The intense up-conversion emission in tellurite glass pumped at 980 nm owing to its longer fluorescent time of the $^4I_{11/2}$ level reduces the gain and the pumping efficiency for 1.5 μm emission. It is well known that pumping at 980 nm is more preferable than that at 1480 nm, since in the former case, good signal to noise ration (SNR) can be gained[2]. To enhance the 980 nm pumping efficiency and the gain at 1.5 μm, some measures have been considered. One of the most effective approaches is to introduce some favorable dopants into the glasses. For example, Choi Y G[3] has proposed Er^{3+}/Ce^{3+}-codoping to enhance the 980 nm pumping efficiency through the non-radiative energy transfer Er^{3+}: $^4I_{11/2}\rightarrow{}^4I_{13/2}$,

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Ce^{3+} : $^2F_{5/2} \rightarrow ^2F_{7/2}$. Feng X[4] has reported the addition of GeO_2 into the tellurite host to increase the phonon energy and to decrease the lifetime of the $^4I_{11/2}$ level, so that the up-conversion emission is reduced efficiently. When compared with GeO_2, B_2O_3 is a better glass-former compound and has lower price, higher stability, and larger phonon energy. Under this consideration, introducing B_2O_3 into a tellurite glass may improve the physical and chemical performance of the glass with low cost.

In this article, the dependence of the optical properties on the doping content of B_2O_3 was investigated. The glasses with alternant-changed components of B_2O_3 and TeO_2 were prepared. The refractive index, the host absorption band gap, the intensity parameters of optical transition, and the quantum efficiency of 1.5 μm emission for all the samples were obtained. It was found that with an increase of the B_2O_3 content, the refractive index of the glass decreased, the absorption gap of the host became broad, the intensity parameter Ω_6 and the bandwidth of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition increased quickly, and the quantum efficiency for the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition decreased. Based on these results, it was suggested that a small amount of B_2O_3 may be required to improve the properties of tellurite glasses. The introduction of a small amount of B_2O_3 would increase the nonradiative relaxation probability from $^4I_{11/2}$ to $^4I_{13/2}$, and thereby the 980 nm pumping efficiency would increase and the up-conversion emission depending on the metastable state $^4I_{11/2}$ absorption would reduce.

1 Experimental

1.1 Sample preparation

A series of glasses, the compositions of which are shown in Table 1, are prepared using a melt-quenching technique. All raw materials used were of analytical grade. 10 g starting materials with certain composition and additional 0.5% of Er_2O_3 (in molar) were melted at 800 ℃ for 30 min, and then quenched to room temperature in air. An annealing procedure for all these samples was performed to improve the mechanical properties. The received samples were cut and polished carefully for spectroscopic measurements.

1.2 Spectroscopic measurements

The refractive indexes for all the samples were measured using a UVISEL SPME of ellipsecopy. The absorption spectra were obtained using a Shumandzu \ VUV \ 3101pc double beam spectrophotometer in the range 200 ~ 1700 nm at room temperature. The fluorescent decays of Er^{3+} : $^4I_{13/2} \rightarrow ^4I_{15/2}$ were detected using a 980 nm pulsed output of OPO laser as an excitation light; the fluorescent signals were collected and processed via a spectrometer Triax 550 equipped with a semiconductor detector controlled by a personal computer.

2 Results and Discussion

Fig. 1 depicts the dependence of the refractive indexes on the wavelengths for all the samples. The refractive indexes data are well fitted to the experiential equation $n = n_0 + A/\lambda^2 + B/\lambda^4$ (here n, and n_0 are the refractive indexes at λ and $\lambda \rightarrow \infty$, respectively, and A and B are the constants for a certain sample) to the experimental data. It is seen that with an increase of the B_2O_3 content, the refractive index decreases. Based on this fact, it can be concluded that B_2O_3 is a good chemical component for modifying the refractive index of glass.

Table 1 Compositions for all the glass samples (%, mol fraction)

Compositions	TeO_2	B_2O_3	ZnO	Na_2O	Er_2O_3
T0B8	0	80	10	10	0.5
T1B7	10	70	10	10	0.5
T2B6	20	60	10	10	0.5
T3B5	30	50	10	10	0.5
T4B4	40	40	10	10	0.5
T5B3	50	30	10	10	0.5
T6B2	60	20	10	10	0.5
T7B1	70	10	10	10	0.5
T8B0	80	0	10	10	0.5

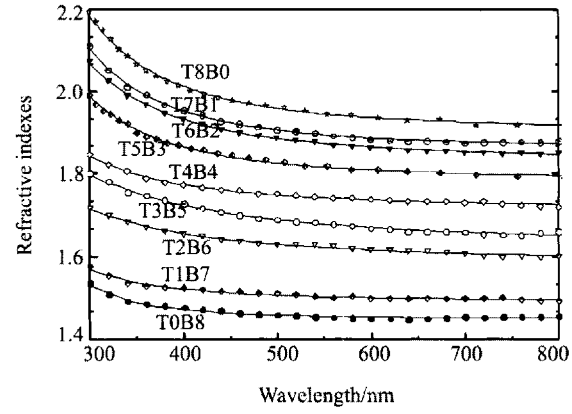

Fig. 1 Dependence of refractive index on wavelength for all samples (the symbols describe the experimental measurement data, and continuous solid lines represent the fitting curves)

Judd-Ofelt's theory[5,6] provided a very clear description of the optical transitions of rare earths in solid materials. Judd-Ofelt's calculation procedure was often used for characterizing transparent materials doped with rare earths and became a standard method[7,8]. In this study, the standard calculation procedure has also been followed to calculate the optical transition intensity parameters for all the samples of Er^{3+} doped borate tellurite glasses. To clearly describe and discuss, only the most basic equations in the Judd-Ofelt's theory are mentioned here.

The electric-dipole line strength S_{ed} and the magnetic dipole line strength S_{md} can be expressed by the following equations:

$$S_{ed} = \frac{e^2}{4\pi\varepsilon_0} \sum_{\lambda = 2, 4, 6} \Omega_\lambda | < f^N \psi J | U^{(\lambda)} | f^N \Psi' J' > |^2 \quad (1)$$

$$S_{md} = S \frac{e^2}{16\pi m^2 c^2 \varepsilon_0} | < f^N \psi J \| L + 2S \| f^N \Psi' J' > \|^2 \quad (2)$$

The theoretical oscillator strength f_{cal} and the experimental oscillator strength for f_{meas} for certain transition can be written as:

$$f_{cal} = 4\pi\varepsilon_0 \frac{8\pi^2 mv}{3h(2J+1)e^2}[x_{ed}S_{ed} + x_{md}S_{md}] \quad (3)$$

$$f_{meas} = 4\pi\varepsilon_0 \frac{nc}{\pi e^2} \int \sigma_A(\nu) d\nu \quad (4)$$

The intensity parameters $\Omega_\lambda (\lambda = 2, 4, 6)$ for the optical transition of trivalent rare earths can be derived from Eqs. 1 ~ 4. The spontaneous radiative transition probability can be obtained from the following equation:

$$A_{ab} = \frac{64\pi^4 \nu^3}{3hc^3(2J+1)}(x'_{ed}S_{ed} + x'_{md}S_{md}) \quad (5)$$

To compute the intensity parameters of the optical transitions, the absorption spectra for the Er^{3+} doped glasses with different compositions were measured, as shown in Fig. 2. Slight changes in the absorption spectra of Er^{3+} were observed for different samples. The integrated absorption cross sections for all the transitions in different samples were calculated carefully in aid of some software tools. Following the Judd-Ofelt's calculation procedure, programming was done using the QBASIC language, and the intensity parameters were obtained, which are listed in Table 2. For each sample, the relative root mean square (rms) is less than 5%, which ensures that the calculation results are reliable. From the calculation results, it is found that with an increase of the B_2O_3 content, the intensity parameter Ω_6 increases from 1.08 to 1.98. Ω_2 also increases when B_2O_3 changes in the lower content range. For the transition ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$, according to Eq. 2, the magnetic dipole part of the line strength S_{md} is constant; with reference to Eq. 1, the electric-dipole part of the line strength S_{ed} can be written in the following form, while considering the reduced matrix elements[9,10]:

$$S_{ed} = [{}^4I_{13/2} : {}^4I_{15/2}] = 0.019 \times \Omega_2 + 0.118 \times \Omega_4 + 1.462 \times \Omega_6 \quad (6)$$

According to Eqs. 5 and 6, it can be stated that the radiative transition probability for the transition ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ lies on both the refractive index and the intensity parameter Ω_6, since the reduced matrix elements of Ω_2 and Ω_4 are less than that of Ω_6. For the as-prepared samples, the refractive index decreases and the intensity parameter Ω_6 increases as the B_2O_3 content increases. The results of the radiative transition probability (listed in Table 3) for ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition show a decreased trend with the increase of the B_2O_3 content. This fact implies that in these samples, the change in the refractive index influences the radiative probability for the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition more effectively than the change in the intensity parameter Ω_6. It is well known that Ω_2 is more sensitive to the environment than the rest among the J-O parameters and is also a measure of the covalency of the rare earth-ligand bond and the disorder degree of environment surrounding the rare earth[11]. The large Ω_2 indicates that the site occupied by Er^{3+} has high covalency and environment disorder. As seen in Table 2, when the B_2O_3 content is less than 50%, its influence is not prominent; when it increases up to 60%, it plays an obvious role; the host may be considerably disordered and Ω_2 becomes the largest. It is not surprising that while

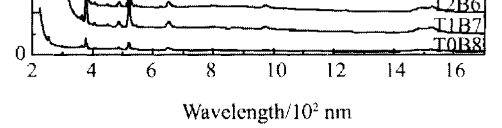

Fig. 2 Absorption spectra for all samples measured at room temperature

Table 2 J-O parameters for all the samples

Samples	T0B8	T1B7	T2B6	T3B5	T4B4	T5B3	T6B2	T7B1	T8B0
$\Omega_2/10^{-20}$	4.91	7.26	7.17	6.23	6.90	5.97	6.05	6.22	6.15
$\Omega_4/10^{-20}$	1.77	2.13	1.58	1.52	1.79	1.52	1.64	1.66	1.57
$\Omega_6/10^{-20}$	1.98	1.75	1.73	1.30	1.35	1.12	1.05	1.09	1.08

the TeO_2 is absent, Ω_2 is decreased for the sample T0B8, since the host is a borate glass.

Fig. 3 shows a comparison of the normalized spectral line shape for the emission $^4I_{13/2}\rightarrow{}^4I_{15/2}$ for all samples. It is found that the spectral bandwidth increases when the B_2O_3 content increases. Based on this fact, it can be concluded that B_2O_3 is of great benefit to broaden the bandwidth of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition.

The optical absorption edge is an important parameter for describing solid state materials. It is necessary to realize the effect of the B_2O_3 content doped into tellurite glasses on the optical properties. The optical absorption edge for disordered materials is interpreted in terms of indirect transitions across an optical band gap. For the absorption by indirect transitions, the absorption coefficient, $\alpha(\omega)$ is given by[12]

$$\alpha(\omega)=\frac{A(h\omega-E_{\mathrm{OPT}})^2}{h\omega} \qquad (7)$$

where, $\alpha(\omega)$ is the absorption coefficient, A a constant, E_{OPT} the optical band gap, and $h\omega$ the photo energy of the incident radiation. The optical energy gap is obtained by extrapolating from the linear region of the plots of $h\omega$. Fig. 4 shows the dependence of $(\alpha h\omega)^{1/2}$ on $h\omega$ and the value of the absorption edge is derived and signed there. From the change of the absorption edge of the host, it is found that with the increase of B_2O_3, the absorption edge strongly shifts toward the blue regime. This fact suggests that introducing a small amount of B_2O_3 can control the absorption edge of the host. To observe the shorter wavelength emission, the host absorption edge must be higher than the interested emission wavelength. In that case, introducing B_2O_3 will be of help without doubt.

The luminescent decays of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition for all the samples were recorded and are shown in Fig. 5. These data well fit to a mono-exponential function, and indicate that with an increase of the B_2O_3 content, the decay time becomes shorter and shorter. The quantum efficiency h of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition was estimated according to the relation below[13]

$$h=A_{\mathrm{ab}}\tau_{\mathrm{f}} \qquad (8)$$

where, A_{ab} is the radiative transition probability, which can be derived from Eq. 5, and τ_{f} is the fluorescent lifetime . The calculation results are listed in Table 3 together with A_{ab}. Table 3 shows that the quantum efficiency becomes lower while the content of B_2O_3 increases. From this fact, it is concluded that the required content of B_2O_3 for improving the performance of tellurite glasses will be lesser to maintain high adequate quantum efficiency.

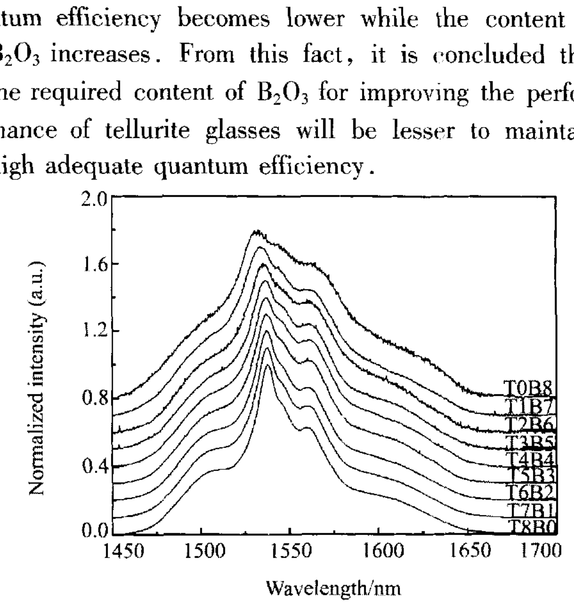

Fig. 3 Normalized emission spectral line shapes for all samples

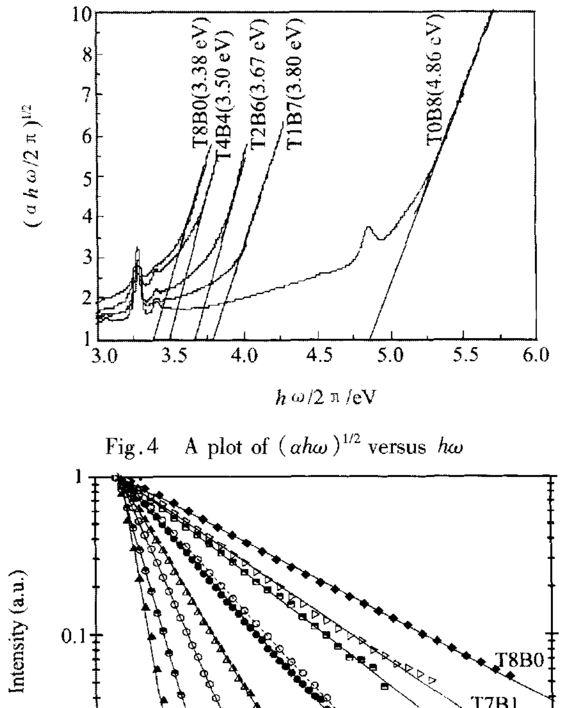

Fig. 4 A plot of $(\alpha h\omega)^{1/2}$ versus $h\omega$

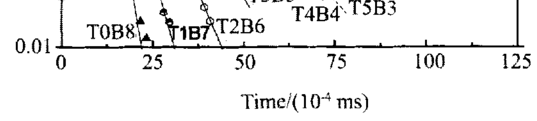

Fig. 5 Fluorescence decays for all the studied samples

Table 3 Radiative probabilities and the quantum efficiency of $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition for all the samples

Sample	T0B8	T1B7	T2B6	T3B5	T4B4	T5B3	T6B2	T7B1	T8B0
A_{ab}	156.46	150.82	198.14	186.48	213.73	225.32	251.2	266.59	292.22
η	6.1	8	16	20.1	34.6	37.8	60	68.8	99.4

3 Conclusion

In summary, several glass-samples of varied contents of B_2O_3 and TeO_2 with Er^{3+} were prepared using the melt-quenching technique. It was found that B_2O_3 was a very useful component for modifying tellurite glasses. The increase of the B_2O_3 content can result in some interesting changes of the properties of the glasses, for instance, increase of the intensity parameter Ω_6(from 1.08×10^{-20} to 1.98×10^{-20} cm^2), broadening of the line width of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition, decrease of the refractive index of the host, moving of the host absorption edge toward blue, increase of the nonradiative relaxation probability between $^4I_{11/2}$ and $^4I_{13/2}$, and lowering of the quantum efficiency of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition.

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