1. Introduction

Er$^{3+}$ doped telluride glass is one of the best candidates for optical communication materials owing to their high refractive index, large resistance against corrosion, high solubility of rare-earths (RE) and good transparency in the region from visible to infrared. Some effective approaches were proposed to overcome this drawback, for instance, introducing some helpful dopants such as Ce$^{3+}$ to depopulate $^4I_{11/2}$ level [3]; adopting some host adjuster such as GeO$_2$, B$_2$O$_3$ [4–6] to increase the non-radiative transition rate of $^4I_{11/2}$ level. B$_2$O$_3$ is a good host component due to its features that does not reduce the spectral bandwidth and does not deteriorate the optical, thermal or chemical durability of the glass system. Despite the great interest in the borate–tellurite glasses as the best candidate for optical communication materials, the detailed structural information regarding the Na$_2$O–ZnO–B$_2$O$_3$–TeO$_2$ system has not been reported yet. As known that glass host composition and structure affect remarkably the optical properties, it is possible for making chemical tailoring of glass according to technological need. Thus, it is essential to study systematically the structure–composition relationship and the influence of compositions on the optical properties.

In the past decades, a lot of efforts have been made to investigate the structure of the binary sodium silicate (SS), sodium borate (SB) and ternary sodium borosilicate (SBS) [7–23]. It is well known that the structural units of the SS glasses are SiO$_4$ tetrahedron linking with each other by bridging oxygen, and the non-bridging oxygen (NBO) increases proportionally to the sodium ions concentration. The SB glasses consist of B–O network, built up from planar three-coordinated boron atoms and four-coordinated boron atoms. Pure B$_2$O$_3$ contains only three-coordinated boron atoms, and some of these units are transformed into four-coordinated tetrahedral as the alkali oxide content increases. The amorphous network is built by BO$_3$ and BO$_4$ groups linked by bridging oxygen atoms. The fraction of boron atoms that is four-coordinated, N$_4$, increases with increasing alkali oxide concentration in the region over 33%, and the non-bridging oxygen (NBO) atoms are formed, N$_4$ decreases [7–19]. In the SBS glasses the structure–composition relationship is more complicated than that of the SS and SB glasses, and a lot of models were raised to explain the relationship in the past several years [20–23]. A very popular model is the one established by Dell et al. [23]. In this model the ternary system is described as the binary alkali borate system diluted in the pure silica in the compositional range $R < 0.5$ and $K < 8$ (here $R$ is the molar ratio of Na$_2$O/B$_2$O$_3$ and $K$ is the molar ratio of SiO$_2$/B$_2$O$_3$). For $R > 0.5$, a mixing of the silica and borate portions of the glasses...
starts with the formation of reedmergentite group (NaBSi2O5).
More detailed discussions have been done by Lianmeng Zhang et al. [14]. In addition, several binary tellurate glasses are reported too [24–28]. It is widely accepted that introducing small content of some modifiers into the TeO2 glass increases the fraction of the TeO2 groups as well as results in the formation of TeO2±1 polyhedron having one non-bridging oxygen atom in the TeO2 glass.

In our previous work [29], the optical transition properties of Er3+ doped xB2O3–(80–x)TeO2–10ZnO–10Na2O glasses were studied in the framework of Judd–Ofelt theory. In this present study, we investigate the glass structure, phonon sideband energy of Eu3+ doped these glasses, the non-radiative relaxation, the up-conversion and down-conversion luminescence of Er3+ doped these glasses.

2. Experimental

2.1. Sample preparation

Glasses with composition xB2O3–(80–x)TeO2–10ZnO–10Na2O and extra 0.5Er2O3 or 1Eu2O3 (here x = 10, 20, 30, 40, 50, 60, 70, 80) were prepared by using analytical grade B2O3, TeO2, ZnO, Na2CO3, Er2O3 and Eu2O3 as starting materials. According to a certain stoichiometric ratio the starting materials were weighted and mixed together. Each batch was well ground and put in an alumina crucible and then melted at 1150 °C for 0.5 h in a muffle furnace. Subsequently, the melts were poured into the pre-heated brass molds and annealed at 300 °C for 15 h. The glass samples were cut and carefully polished to meet the optical measurement. Each sample looks better transparent. According to the different composition, the samples were numbered as T[(80–x)/10]B/x/C0, where x represents the same meaning as mentioned above. A detailed preparation procedure could be found in our previous work [29].

2.2. Characterization

The refractive indexes for all the samples were measured by using an UVISEL SPME ellipsocopy. Glass densities were obtained by Archimedes’s method. The excitation spectra for the glass samples doped with Eu3+ were measured with a Hitachi F–4500 fluorescence spectrophotometer, monitoring the 5D0→7F2 emission at 612 nm, the phonon sideband spectra can be observed at the high energy side of 5D0→7F2 transition. The absorption spectra were obtained by using a VUV PC 3101 spectrophotometer (Shumandzu) at room temperature. The fluorescent decay curves of Er3+: 4I13/2→4I15/2 were obtained by using the 980 nm pulsed output of an OPO laser (Continue, Sunlite) with 10 ns pulse duration, 10 Hz repetition frequency as excitation light, the fluorescent signals were passed to a spectrometer Triax 550 equipped with a semiconductor detector controlled by a personal computer. In the measurement of emission intensity the same experimental conditions were kept. In order to eliminate the re-absorption effect, the samples thinner than 1 mm were used, and the excitation light was focused on the sample margin in the measurement of emission spectra of 4I13/2→4I15/2 transition.

3. Results and discussion

3.1. Density and refractive index

Fig. 1a and b show the dependence of the density ρ, molar volume Vm and the refractive index n on the glass composition. The relative uncertainties for both the density and the molar volume are estimated to be less than 1%, and the error bars were represented in Fig. 1. It is found that with increasing the B2O3 content, Vm increases first and then reaches its maximum at x = 10, after that decreases and reaches a minimum at x = 50, finally increases again. It is well known that the change of molar volume is associated with the change of the glass structure. According to Dell et al. model [23], one can confirm that for x = 10 all the Na+ ions combine with BO4 units surrounded by four TeO4 units to form the structure of NaBTe4O10 like reedmergentite in SBS glasses. So the molar volume shows a decrease because of the dense structure of NaBTe4O10, but the decrease of volume is not observed. A possible explanation for this behavior is the influence of Zn2+ ions on the different network structure of tellurite glasses. It is known that the introduction of modifier, ZnO, into the tellurite glass causes the structural transition TeO4→TeO3, and results in the formation of TeO3±1 polyhedron having one non-bridging oxygen atom [24–28]. Because of more non-bridging oxygen atoms in the glasses, only the nearly flat triangle BO3 unit with one non-bridging oxygen atom is formed. In this case, the three-dimensional structure of tellurite glass is destroyed, thus, resulting in an increase of the molar volume. With further increasing the B2O3 content, BO3 units are transformed into three-dimensional BO4, which strengthens the structure, and the molar volume decreases [18]. When x = 50, BO3 and BO4 units in the glasses begin to mix together to form BO4(B2O3)x groups, i.e., each BO4 units is linked with four BO3 units and BO4 units reach the maximum. Thereby, the glass structure becomes the densest and displays the smallest molar volume. When x > 50, the additional B2O3 form extra BO3 units which increase the molar volume.

It is known that the glass density is proportional to the average molecular weight of the glass and is inversely proportional to the molar volume. Fig. 1a shows that the fluctuation in the density va-
lue is opposite to the change in the molar volume, however, in a smaller range, the linear decrease in the average molecular weight with increasing B$_2$O$_3$ content plays an important role in modifying the density of the glasses.

Fig. 1b shows that the refractive index of the glass decreases monotonically as B$_2$O$_3$ content increases. It is well known that the refractive indexes are proportional to the electric polarizability and inversely proportional to the molar volume, as thus the high electric polarizability of Te–O bonds [24–28] has a stronger effect on the refractive index.

### 3.2. Phonon sideband spectra

In order to investigate the local structure of rare earth ions in these glasses the Eu$^{3+}$ ions were doped into the glasses, since the phonon sideband (PSB) of Eu$^{3+}$ ions is supersensitive to the evolution of the surroundings and can be clearly observed at the high energy side of $^7F_0$–$^5D_2$ transition [10]. Fig. 2 shows the dependence of phonon sideband (PSB) on the glass composition. The PSB spectra were fit to a linear combination of Gaussian’s functions. Though the detailed interpretation of the phonon sideband (PSB) of borate–tellurite glasses is not easy due to their complexity originating from the different structural units, some reliable assignments of the PSB transitions were pointed out [7,28]. In Fig. 2a, the PSB spectra of Na$_2$O–ZnO–TeO$_2$ glass (pure tellurite) consist of four main bands: Two stronger bands at 680 and 770 cm$^{-1}$ are due to the Te–O stretching vibrations of TeO$_4$ and TeO$_3$ structural units, and two weaker bands at 520 cm$^{-1}$ and 930 cm$^{-1}$ belong to the vibrations of Te–O–Te bridging bonds and Te–O$^-$ non-bridging bonds in TeO$_3$ structural units,

![Figure 2](image.png)

**Fig. 2.** The phonon sideband (PSB) spectra for the glasses with different compositions. Fig. 2a–i are corresponding to the samples T8B0–T0B8. The sample number is marked in each figure.
respectively. The PSB spectra of Na₂O–ZnO–B₂O₃ glass (pure borate) consist of five bands centered at about 1414, 1299, 1075, 870, 735 cm⁻¹ (see Fig. 2i). The band centered at 1299 cm⁻¹ and 1414 cm⁻¹ can be attributed to the BO₃ units stretching vibrations, which are associated with the vibrational mode inside the various borate rings and the non-bridging B–O bonds, respectively. The lowest frequency band, 735 cm⁻¹, can be assigned to the bending vibration of the B–O–B linkage with the network, and the other two bands at 870, 1075 cm⁻¹ are due to B–O stretching vibrations of tetragonal BO₄ units in the different structural groups. There is no new band appearing in the other glasses. The more detailed assignments of the various bands for other samples to the mode vibration are shown in Fig. 2b–h.

According to the research results by Y. Shimizugawa et al. [25], 930 cm⁻¹ vibration band can be assigned to Te–O non-bridging bonds of TeO₃ units originating from modifying oxides ZnO. When x is larger than 10, the band responsible for the shift of non-bridging oxygen atoms disappears in the borate groups. The stronger vibration band of 770 cm⁻¹ reflects that more TeO₃ units coupling with Eu³⁺ ions still exist in the glass host. As known that Eu³⁺ ions have a strong affinity towards the tellurite groups [25], 930 cm⁻¹ vibration band can be assigned to Te–O bonds, which are associated with the vibrational mode inside the various tellurite groups. The vibration band of BO₄ units appearing at x = 50 is attributed to the increasing BO₄ units, which are transformed from BO₃ units as the B³⁺ ions increase. In Na₂O–ZnO–B₂O₃ glass, the band at about 1400 cm⁻¹ can be assigned to the vibration of B–O non-bridging bonds of BO₃ units, thus indicating more non-bridging oxygen ions exist in the borate glass. Tanabe et al. [10] have pointed out that B–O-bonds are formed by an introduction of Eu³⁺ itself dominantly coordinate Eu³⁺ instead of a large number of boroxal rings.

3.3. Radiative, non-radiative relaxation rates and lifetimes

In our previous work [29], the optical transition calculations for all the samples doped with Er³⁺ ions were carried out based on the Judd–Ofelt (J–O) theory [30–34]. The dependency of optical transition intensity parameters on the glass composition was studied. This section is focused on the radiative, non-radiative relaxation and quantum efficiency of level ⁴I₁³/₂ of Er³⁺.

According to J–O theory the radiative relaxation rate for ⁴I₁₃/₂ → ⁴I₁₅/₂ can be expressed as follows [35]:

\[
A_{\text{rad}} = \frac{16\pi^2\hbar^2}{3\hbar^2\omega_0^2(2J+1)} \left[ \frac{n(n^2 + 2)^2}{9} (0.0192 \Omega_2 + 0.118 \Omega_4 + 1.462 \Omega_6) 
+ \frac{n^2}{4m^2c^2} \{ \langle \delta n^2 \rangle L + 2S[\delta \psi^2] \} \right] 
\]  

(1)

Because of the little contribution of Ω₂, Ω₄ to the value of \( A_{\text{rad}} \) Eq. (1) can be simplified as
The up-conversion emission intensity can be obtained by using the normalized-thermal-lens method developed by Jacinto et al. [39,40]. The quantum efficiency can also be obtained from the following formula:

\[ \eta = \frac{1}{\tau A_{\text{rad}}} \]  

(6)

where \( \tau \) is lifetime and \( A_{\text{rad}} \) is the radiative transition rate. The quantum efficiencies of level \( ^4I_{13/2} \) for all the samples were calculated by using formula (6) and reported in our previous work [29]. The quantum efficiency decreases as the B\(_2\)O\(_3\) content increases. In general, the introduction of B\(_2\)O\(_3\) would improve the glass mechanical performance and its chemical stability. However, this is on the base of immobilating partial quantum efficiency. It is also found that when introducing 10 mol\% of B\(_2\)O\(_3\), the quantum efficiency goes down to about 70%. Usually, 100% quantum efficiency is preferable, but the quantum efficiency is not the only factor under consideration. If this decrease in quantum efficiency is acceptable in the practical application, the introduction of B\(_2\)O\(_3\) would be helpful for increasing glass host performance.

### 3.4. Up-conversion and down-conversion luminescence

Usually, up-conversion emission is in competition with the infrared down-conversion emission in Er\(^{3+}\) doped materials while upon 980 nm excitation. Effective elimination of the up-conversion luminescence may be benefit to the infrared down-conversion emission. The up-conversion fluorescent spectra for all the samples were measured upon 980 nm excitation and shown in Fig. 4. The most intense up-conversion emission is observed from the sample T8B0 (pure tellurite glass), and its intensity is about 40 and 100 times more intense than that of the sample T7B1 and T6B2, respectively. The up-conversion emission intensities for other samples are very weak. The dependence of integrated up-conversion emission intensity on the content of B\(_2\)O\(_3\) was derived and plotted in a single log coordinate as the insert of Fig. 4. The intensity of up-conversion emission extremely decreases as the B\(_2\)O\(_3\) content increases. It is also observed that the green emission is stronger than that of the red emission, thus indicating the energy transfer between Er\(^{3+}\) ions is weak [41] at the present doping level.

The down-conversion emission spectra for \( ^4I_{13/2} \rightarrow ^4I_{15/2} \) transition were also measured for all the samples. The integrated emission intensities were calculated and the dependence of integrated emission intensity on the B\(_2\)O\(_3\) content is shown in Fig. 5. It is observed that the integrated emission intensity of \( ^4I_{13/2} \rightarrow ^4I_{15/2} \) transition decreases extremely with increasing the B\(_2\)O\(_3\) content. The insert in Fig. 5 displays the normalized emission spectra for the samples with different contents of B\(_2\)O\(_3\).

Fig. 3. Dependence of the radiative transition rate \( A_{\text{rad}} \) for the transition \( ^4I_{13/2} \rightarrow ^4I_{15/2} \). the summation \( W_{\text{MP}} + W_{\text{ET}} \) (\( W_{\text{MP}} \) is multiphonon relaxation rate, \( W_{\text{ET}} \) is energy transfer rate), and \( 1/\tau \) (\( \tau \) is lifetime of level \( ^4I_{13/2} \)) on the content of B\(_2\)O\(_3\).

Fig. 4. The up-conversion emission spectra for the samples T8B0 (■), T7B1 (▲) and T6B2 (○); insert represents the relationship between integrated up-conversion emission intensity and the B\(_2\)O\(_3\) content.
bandwidth of $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition increases with increasing the $B_2O_3$ content. The effective spectral bandwidth $\Delta_{\text{eff}}$ can be estimated by using following formula:

$$\Delta_{\text{eff}} = \frac{\int I(\lambda) d\lambda}{I_p(\lambda)}$$ (7)

where $I_p(\lambda)$ is the maximum intensity at the peak wavelength $\lambda$. The effective spectral bandwidths of sample T8B0 (pure tellurite glass) and T0B8 (pure borate) are estimated to be 61.1 and 89.6 nm, respectively. The effective spectral bandwidth of the other sample disperses between these two values, and increases with increasing the $B_2O_3$ content. Compared to the evolution trends of up-conversion and down-conversion emission intensities in Figs. 4 and 5, we can conclude that the up-conversion emission intensity attenuates more quickly than the intensity of $^4I_{13/2} \rightarrow ^4I_{15/2}$ does. A similar phenomenon is also observed in Yb$^{3+}$/Er$^{3+}$ co-doped silicate–borate glasses [42]. Therefore, introducing $B_2O_3$ into the tellurite glasses may be a better way to obtain a glass system with an increasing infrared spectral bandwidth, an emission efficiency of satisfying the practical application, and low up-conversion emission efficiency. It is worthwhile to mention that introducing $B_2O_3$ is probably not the direct reason causing an increase in the non-radiative transition rates between trivalent erbium levels. $B_2O_3$ introduction may increase OH$^-$ content, which is an effective quencher for the Er$^{3+}$ in the glasses, thus, the OH$^-$ may be responsible for the increased non-radiative transition rates. This may be a further issue in our research work.

4. Conclusion

It was found that when a smaller content of $B_2O_3$ is introduced, $B_2O_3$ is transformed into BO$_3$ units because of large number of non-bridging oxygen ions from modifying oxides ZnO. No structure of NaBO$_2$Te$_2$O$_{10}$ exists in the glass host. As the $B_2O_3$ content continues to increase the BO$_4$ units and BO$_3$ units begin to constitute BO$_4$(BO$_3$)$_3$ structures. When $x = 50$, BO$_4$ units reach maximum and all B$^{3+}$ ions enter the structure of BO$_4$(BO$_3$)$_3$ to form the firmest structure. Rest B$^{3+}$ ions will form BO$_3$ unit. We also investigated the dependence of radiative and non-radiative relaxation rate, lifetime and transition intensity of $^4I_{13/2}$ level as well as up-conversion emission on the glass composition. It is observed that the up-conversion emission intensity is more sensitive to the $B_2O_3$ content than that of 1.5 $\mu$m emission.

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