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Effect of B_2O_3 on luminescence of erbium doped tellurite glasses

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Abstract

The B_2O_3 was introduced into the Er^{3+} doped TeO_2–ZnO–Na_2O glass to increase the phonon energy of the host. The effect of B_2O_3 on the non-radiative rate of the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition of Er^{3+}, the lifetime of the $^4I_{11/2}$ and $^4I_{13/2}$ levels, the green and red upconversion emissions intensity, and the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission intensity was discussed. The results show that the phonon energy of boro-tellurite glass is close to that of germanate glass and is quite smaller than that of borate glass. The lifetime of $^4I_{11/2}$ level and the upconversion emissions decrease with increasing B_2O_3 concentration. The higher OH group concentration presented in the boro-tellurite glass may shorten the lifetime of $^4I_{13/2}$ level and also reduce the quantum efficiency of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission. The future dehydrating procedures are suggested to enhance the efficiency of amplification at 1.5 μm band.

Keywords: Tellurite glass; Erbium; Phonon energy; Upconversion; Optical amplifier

1. Introduction

Recently, Er^{3+} doped tellurite glass has been received much attention because it was considered to be a promising candidate for developing 1.5 μm broadband optical fiber amplifier [1,2]. For designing laser glasses with high performance, it is necessary to know the relationship between the host composition and radiative (or non-radiative) characters of the Er^{3+} ions.

The laser system of erbium at 1.5 μm band can be considered as a three level system when pumped with a 980 nm laser diode (LD). The $^4I_{11/2}$ level gets populated first, then non-radiates to the initial emission level $^4I_{13/2}$. The 1.5 μm emission occurs when the population inverts between the $^4I_{13/2}$ and $^4I_{15/2}$ levels. To ensure and optimize this process it is necessary to obtain a rapid non-radiative rate from the $^4I_{11/2}$ to $^4I_{13/2}$ level to shorten the lifetime of $^4I_{11/2}$ level. Otherwise, the probability of the excited state absorption (ESA) from erbium $^4I_{11/2}$ level to higher energy excited states, such as the $^4F_{7/2}$ level, becomes large and decreases the efficiency of the 1.5 μm amplification. TeO_2-based glass has the lowest phonon energy among the oxide glasses. Therefore, strong green upconversion emission is observed in Er^{3+} doped tellurite glasses even the excitation power is as lower as 30 mw [3].

The multiphonon decay rate for rare earths in crystals and oxide glasses observes the energy gap law [4], which is strongly depended on the maximum phonon energy of the host and the energy gap between two excited levels. Since the energy gap between the $^4I_{11/2}$ and $^4I_{13/2}$ level of Er^{3+} is nearly unchanged, the phonon energy of the host may play the key role of determining the multiphonon decay rate. In order to increase the multiphonon decay rate of $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition, it is necessary to enhance the phonon energy of the glass host.

In this paper, the B_2O_3 was introduced into the TeO_2–ZnO–Na_2O (TZN) glass because of its high phonon energy. The effect of B_2O_3 on upconversion emission intensity, 1.5 μm emission intensity, and lifetime of the $^4I_{11/2}$ and $^4I_{13/2}$ levels of Er^{3+} in these glasses have been investigated.

2. Experimental procedures

Er^{3+} doped boro-tellurite glasses with composition $70TeO_2$–$(15-x)$ZnO–$15Na_2O$–xB_2O_3–1 wt.% Er_2O_3 (x = 0, 4, 8, 12, and 15 mol%) were melted in alumina crucibles at 800–900 °C for about 45 min. The obtained glasses were annealed to room temperature gradually, and then were cut and well polished for optical measurements.

The absorption spectra of the glasses were recorded with a PERKIN-ELMER-LAMBDA 950 UV-VIS-NIR spectrophotometer over a spectral range of 400–1700 nm. The

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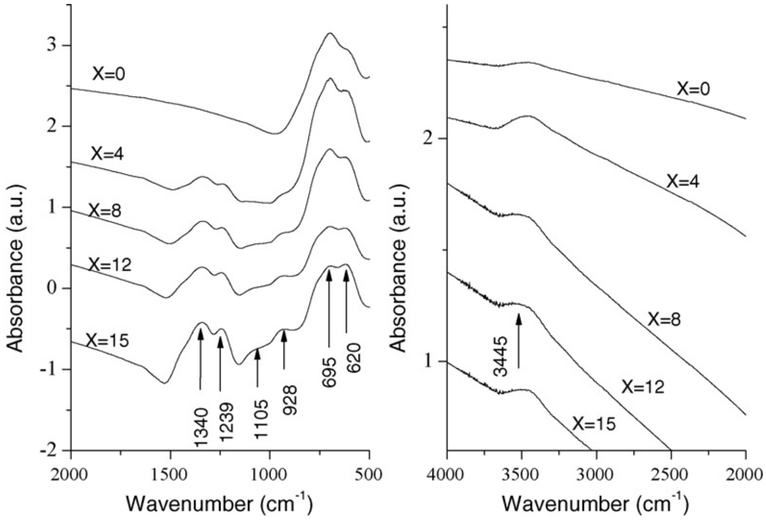

Fig. 1. The FT-IR absorption spectra of $70TeO_2$–$(15 - x)$ZnO–$15Na_2O$–xB_2O_3–1 wt.% Er_2O_3 ($x = 0$, 4, 8, 12, and 15 mol%) glasses.

luminescence spectra were obtained with a TRIAX 550 spectrofluorimeter upon excitation of the 975 nm. In order to compare the luminescence intensity of different samples as accurate as we can, the position and power of the pumping beam and the width (1 mm) of the slit to collect the luminescence signal were fixed under the same condition, and the samples was set at the same place in the experimental set-up. The fluorescence decay curves of 980 and 1532 nm, which were pumped by a modulated 800 and 980 nm LD, respectively, are recorded by a digital oscilloscope (Tektonix TDS 1012, 100 MHz) after averaging 128 times to avoid noise. Infrared transmission measurement was done with a FT-IR spectroscopy (Thermo Nicolet, nexus 470) in the range of 400–4000 cm^{-1}. All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the FT-IR spectra of glasses $70TeO_2$–$(15 - x)$ ZnO–$15Na_2O$–xB_2O_3–1 wt.% Er_2O_3 ($x = 0$, 4, 8, 12, and 15 mol%). It can be seen that each spectrum consists of a major band in the range of 600–800 cm^{-1}. This band was mainly assigned to vibrations due to tellurium–oxygen polyhedra in contrast with assignments by [5]. The band around 620 cm^{-1} is assigned to a vibration of the continuous networks composed of TeO_4 tetragonal bipyramids (tbp). The band around 695 cm^{-1} is assigned to antisymmetric vibrations of Te–O–Te linkages constructed by two unequivalent Te–O bonds [6]. As expected, the addition of B_2O_3 into the tellurite glasses appears a broad absorption band in the 1150–1500 cm^{-1} range. The peak centered at 1340 cm^{-1} is associated with the B–O(B) stretching vibrations of polymerized BO_3 groups [7,8]. The shoulder at 1239 cm^{-1} is assigned to the stretching vibration of $B–O^-$ bond in isolated BO_3 groups. In addition, with increasing B_2O_3 concentration, two weak shoulders at 928 and 1105 cm^{-1} increase gradually, which are ascribed to the asymmetrical stretching of =B–O–B≡ or =B–O– bonds [9]. Moreover, except the TZN glass, the boro-tellurite glass samples obviously contain an absorption band peaked at 3445 cm^{-1}, which is ascribed to the vibration of OH groups. A possible reaction of producing OH group in the glass can be expressed as $H_3BO_3 \rightarrow B_2O_3 + H_2O$, since H_3BO_3 was acted as a starting material in the samples preparation process.

Fig. 2 illustrates the lifetime of $^4I_{11/2}$ and $^4I_{13/2}$ levels as a function of B_2O_3 concentration. As expected, the $^4I_{11/2}$ level lifetime decreases dramatically with increasing of B_2O_3 concentration. In particular, when 4 mol% ZnO was substituted by the B_2O_3, the lifetime drops from 180 to 120 μs. It indicates the phonon energy of these glasses is enhanced. However, the $^4I_{13/2}$ level lifetime decreases slightly and remains unchanged when the B_2O_3 concentration is larger than 12 mol%. Previous study shows that the free OH is a dominant quenching centers in Er^{3+} doped glasses for the lifetime of the $^4I_{13/2}$ level [10], since only two or three phonons are required for non-radiative decay of the Er^{3+} ions at these two levels.

For a given excited state level, the multiphonon decay rate (MPR) W_{MPR} can be expressed by

$$W_{MPR} = \frac{1}{\tau_{exp}} - \sum A - W_{ET} \quad (1)$$

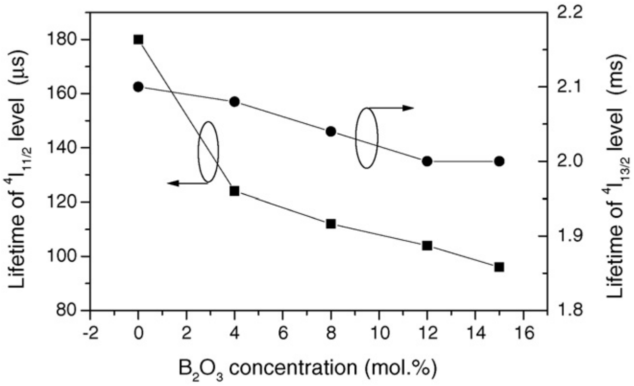

Fig. 2. The lifetime of Er^{3+}:$^4I_{11/2}$ and $^4I_{13/2}$ level as function of B_2O_3 concentration in $70TeO_2$–$(15 - x)$ZnO–$15Na_2O$–xB_2O_3–1 wt.% Er_2O_3 ($x = 0$, 4, 8, 12, and 15 mol%) glasses.

Table 1
Spontaneous emission probabilities of Er^{3+}:^4I_J levels ($J = 11/2,13/2$) in $70TeO_2–(15 − x)ZnO–15Na_2O–xB_2O_3$–1 wt.% Er_2O_3 ($x = 0$, 4, 8, 12, and 15 mol%) glasses

Transition	A_{ed} (s^{-1})	A_{md} (s^{-1})	A_{tol}	ΣA_{tol} (ms)
$70TeO_2–15ZnO–15Na_2O$–1 wt.% Er_2O_3				
$^4I_{11/2} \rightarrow {}^4I_{13/2}$	53.8	17.7	71.5	251.3
$^4I_{15/2}$	179.8	0	179.8	
$70TeO_2–11ZnO–15Na_2O–4B_2O_3$–1 wt.% Er_2O_3				
$^4I_{11/2} \rightarrow {}^4I_{13/2}$	49.2	15.8	65	227.5
$^4I_{15/2}$	162.5	0	162.5	
$70TeO_2–7ZnO–15Na_2O–8B_2O_3$–1 wt.% Er_2O_3				
$^4I_{11/2} \rightarrow {}^4I_{13/2}$	46.2	13.7	59.9	212.1
$^4I_{15/2}$	152.2	0	152.2	
$70TeO_2–3ZnO–15Na_2O–12B_2O_3$–1 wt.% Er_2O_3				
$^4I_{11/2} \rightarrow {}^4I_{13/2}$	39.6	11.8	51.4	183.3
$^4I_{15/2}$	131.9	0	131.9	
$70TeO_2–15Na_2O–15B_2O_3$–1 wt.% Er_2O_3				
$^4I_{11/2} \rightarrow {}^4I_{13/2}$	41.7	10.9	52.6	188.4
$^4I_{15/2}$	135.8	0	135.8	

where τ_{exp} is the measured lifetime of the excited state level, ΣA is the total spontaneous emission probability, and W_{ET} is the energy transfer (ET) rate, which is strongly depended on rare earth (RE) concentration. When rare earth concentration is lower than 0.5 at.%, the W_{ET} is generally negligible [11]. Since the Er^{3+} concentration is sufficiently low (<0.13 at.%) in our experiment, therefore, the contribution from energy transfer was ignored in the formula (1) and the W_{MPR} can be given by

$$W_{MPR} = \frac{1}{\tau_{exp}} - \sum A \tag{2}$$

For the Er^{3+}:$^4I_{11/2}$ level, the ΣA contains the spontaneous emission probabilities from $^4I_{11/2} \rightarrow {}^4I_{13/2}$ and $^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition, and A can be calculated from

$$A = \frac{(2J+1)8\pi cn^2}{(2J'+1)\rho_N \lambda_m^4} \int k(\lambda)\,d\lambda \tag{3}$$

where J and J' are the total momentums for the upper and lower levels, the ρ_N is the number of Er^{3+} ions per unit volume, the $k(\lambda)$ is the absorption coefficient, n, c and λ_m are the refractive index, the light velocity and the mean emission wavelength, respectively. Table 1 lists the values of A for the $^4I_{11/2}$ to the lower-lying levels $^4I_{13/2}$ and $^4I_{15/2}$.

The inset of Fig. 3 shows the compositional dependence on the multiphonon decay rate for Er^{3+}:$^4I_{11/2}$ level in our glass samples. It can be seen that the W_{MPR} increases monotonously with increasing B_2O_3 concentration. This agrees well with the shortening lifetime of $^4I_{11/2}$ level as shown in Fig. 2, since the lifetime of $^4I_{11/2}$ level is mainly depended on the W_{MPR} and the A is inconsiderable. Taking the TZN glass as an example, the value of ΣA is only $\sim$250 s^{-1}, while the W_{MPR} can reach to 5300 s^{-1}, the quantum efficiency of this level is lower than 5%. Fig. 3 shows the multiphonon decay rate of Er^{3+}:$^4I_{11/2}$ level as a function of phonon energy for various glass hosts. The W_{MPR} of borate, phosphate, silicate, germanate, and fluoride glass are data reported in Ref. [12] and used for comparison. It suggests that the decay rate is strongly depended on the glass host. The fast decay for the $^4I_{11/2}$ level is borate glass, following in order by phosphate, silicate, germanate, tellurite and fluoride. The decay rate for tellurite glass is approximately 10^{-3} and 10^{-1} times the corresponding rate in borate and silicate glass, respectively. When the 15 mol% B_2O_3 is introduced into the TZN glass, the W_{MPR} of $^4I_{11/2}$ level is considerably enhanced. It is about twice larger than that of TZN glasses. However, W_{MPR} of $^4I_{11/2}$ level for boro-tellurite glass is only comparable to that of germanate glass, and is quite smaller than that of borate glass in spite of the their comparable maximum phonon energy. Previous studies indicate that the energy of local vibrational modes coupled to the Er^{3+} centers could be smaller than that of the maximum phonon energy of glass network [13]. Therefore, it indicates the phonon energy of glass of boro-tellurite is similar to that of the germanate glass.

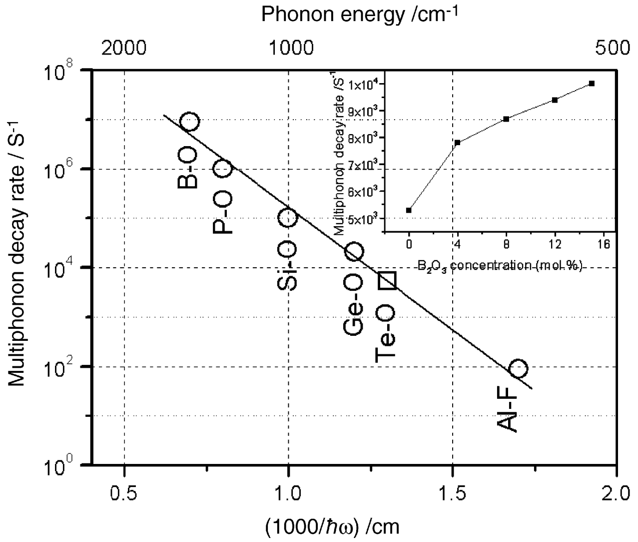

Fig. 3. Multiphonon decay rate of Er^{3+}:$^4I_{11/2}$ level as a function of phonon energy for various glass host. The inset figure is componential dependence of multiphonon decay rate of Er^{3+}:$^4I_{11/2}$ level in $70TeO_2–(15 − x)ZnO–15Na_2O–xB_2O_3$–1 wt.% Er_2O_3 ($x = 0$, 4, 8, 12, and 15 mol%) glasses.

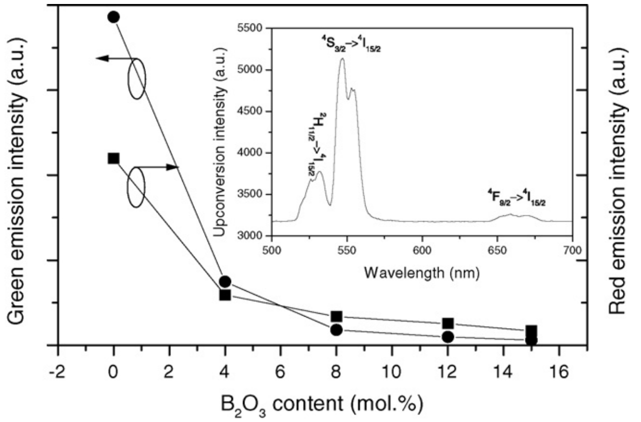

Fig. 4. Green- and red-upconversion emission intensity as function of B_2O_3 concentration in $70TeO_2$–$(15-x)$ZnO–$15Na_2O$–xB_2O_3–1 wt.% Er_2O_3 ($x=0$, 4, 8, 12, and 15 mol%) glasses. The inset figure is upconversion fluorescence in $70TeO_2$–15ZnO–$15Na_2O$–1 wt.% Er_2O_3 glass under 975 nm excitation.

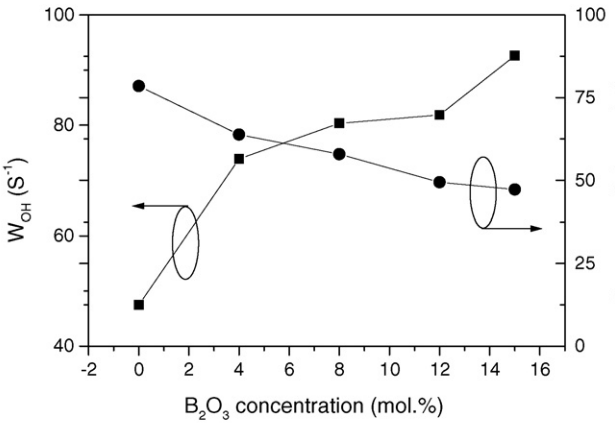

Fig. 6. The energy transfer rate between Er^{3+} and OH and the quantum efficiency of $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition as function of B_2O_3 concentration in $70TeO_2$–$(15-x)$ZnO–$15Na_2O$–xB_2O_3–1 wt.% Er_2O_3 ($x=0$, 4, 8, 12, and 15 mol%) glasses.

The inset of Fig. 4 shows the upconversion emission of Er^{3+} doped TZN glass under 980 nm excitation. The strong green emissions at 546 and 531 nm are ascribed to the $^4S_{3/2}\rightarrow{}^4I_{15/2}$ and $^2H_{11/2}\rightarrow{}^4I_{15/2}$ transitions, respectively. The red emission at 665 nm is assigned to the $^4F_{9/2}\rightarrow{}^4I_{15/2}$ transition. The upconversion process involved in the population of the relevant excited-state emitting levels ($^4S_{3/2}$, $^2H_{11/2}$ and $^4F_{9/2}$) of Er^{3+} doped glass has been well explained [2,14]. As be expected, the green and red emissions decrease with the increase of B_2O_3 concentration as shown in Fig. 4. The reason may be ascribe to the shortening lifetime of the $^4I_{11/2}$ level, since the probability of upconversion excitation is expected to be proportional to the lifetime of the intermediate level $^4I_{11/2}$.

The inset of Fig. 5 depicts the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ emission of Er^{3+} doped TZN glass. As the B_2O_3 concentration increases, the fluorescence full width at half maximum (FWHM) is hardly affected. However, as shown in Fig. 5, the emission intensity decreases at first, and then remains nearly unchanged when the B_2O_3 concentration increases. This trend is not in agreement with the previous analysis. Indeed, as discussed above, the increasing of multiphonon decay rate for the $^4I_{11/2}$ level should allow the population of the $^4I_{13/2}$ level more densely. As a result, the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ emission intensity should get much stronger. The decrease of intensity may attribute to the large quantity of OH group present in the boro-tellurite glass. Therefore, it is necessary to estimate the OH content in the glasses and the non-radiative decay rate between the excited level $^4I_{13/2}$ and ground state $^4I_{15/2}$.

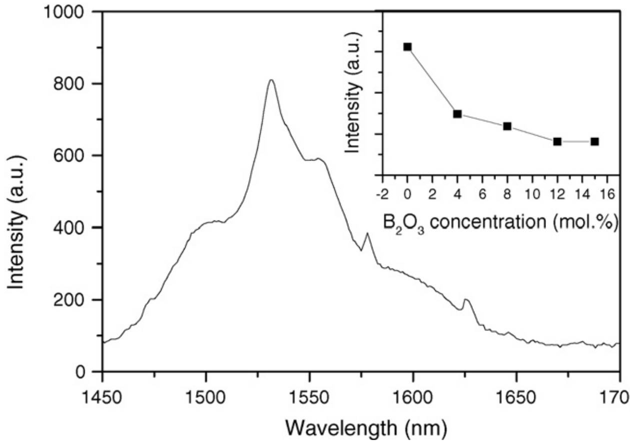

Fig. 5. The emission spectrum of $70TeO_2$–15ZnO–$15Na_2O$–1 wt.% Er_2O_3 glass under 975 nm excitation, the inset figure is mission intensity as function of B_2O_3 concentration in $70TeO_2$–$(15-x)$ZnO–$15Na_2O$–xB_2O_3–1 wt.% Er_2O_3 ($x=0$, 4, 8, 12, and 15 mol%) glasses.

The free OH concentration can be estimated from the absorption coefficient at the peak absorption band [10]. In this work, the absorption coefficient of the OH vibration band at 3445 cm^{-1} is 1.4, 2.3, 2.6, 2.7 and 3.1 cm^{-1}, respectively, when the B_2O_3 concentration increases from 0 to 15 mol%. According to [10], the free OH content N_{OH} (ions/cm^3) can be expressed as

$$N_{OH}=\frac{N}{\varepsilon L}\ln\frac{1}{T} \quad (4)$$

where N is the Avogadro constant, L the glass thickness, T the transmittance, and ε is molar absorptivity of the free OH groups in the glass, here we take the $\varepsilon=49.1\times10^3$ cm^2/mol [15]. The calculated N_{OH} in our glasses is about 1.72, 2.82, 3.19, 3.31 and 3.8×10^{19} ions/cm^3, respectively. This result is in accordance with the result of Feng et al. [10] in erbium-doped germanotellurite glasses. Previous investigation has demonstrated that the higher is the OH concentration presented in the glass sample, the lower is quantum efficiency of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ emission [16]. The energy transfer rate between Er^{3+} and OH can been obtained by [16]:

$$W_{OH}=8\pi C_{Er-Er}N_{Er}N_{Er-OH}=8\pi C_{Er-Er}N_{Er}(\alpha N_{OH}) \quad (5)$$

where C_{Er-Er} is an Er–Er interaction constant, $\alpha(0<\alpha<1)$ is the Er–OH couple probability, and the N_{OH} and N_{Er} are the concentrations of the free OH groups and Er^{3+} ions, respectively. In Ref. [17], it is reported that the value of α and C_{Er-Er} for tellurite glasses is about 15% and 46×10^{-40} cm^6 s^{-1}, respectively. Thus, we estimated the W_{OH} in our glasses and the results are depicted in Fig. 6. Fig. 6 also shows the quantum efficiency

(η) of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition. It can be clearly seen that the η decreases monotonously because of the increasing of W_{OH} in the glasses. Therefore, dehydrating procedures are strongly suggested to enhance the quantum efficiency of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition.

4. Conclusions

We have investigated the effect of B_2O_3 on the spectra of Er^{3+} doped TZN glasses. The phonon energy of boro-tellurite glass is close to that of germanate glass, and quite smaller than that of borate glass. The multiphonon decay rate for $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition increases with increase of B_2O_3 content. As a result, the lifetime of $^4I_{11/2}$ level and the upconversion emissions decrease accordingly. The reaction of $H_3BO_3 \rightarrow B_2O_3 + H_2O$ leads to the higher OH group concentration presented in the boro-tellurite glass, thus the lifetime of $^4I_{13/2}$ level may be shortened. The existence of OH group also reduces the quantum efficiency of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission. It is expected that the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission intensity will be enhanced if the dehydrating procedures are adopted. The results presented in this study provide useful information for further development of optical fiber amplifiers or lasers at 1.5 μm band.

Acknowledgements

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References

[1] A. Jha, S. Shen, M. Naftaly, Phy. Rev. B 62 (2000) 6215.

[2] Q. Nie, Y. Gao, T. Xu, X. Shen, Spectrochim. Acta A 61 (2005) 1939.

[3] J. Yang, L. Zhang, L. Wen, S. Dai, L. Hu, Z. Jang, J. Appl. Phys. 95 (2004) 3020.

[4] C.B. Layne, W.H. Lowdermilk, M.J. Weber, Phy. Rev. B 16 (1977) 11.

[5] T. Sekiya, N. Mochida, A. Soejima, J. Non-Cryst. Solids 191 (1995) 115.

[6] T. Kosuge, Y. Benino, V. Dimitrov, R. Sato, T. Komatsu, J. Non-Cryst. Solids 242 (1998) 154.

[7] K. Blaszczak, W. Jelonek, A. Adzmczyk, J Mol. Struct. 511/512 (1999) 163.

[8] K. Blaszczak, A. Adzmczyk, J. Mol. Struct. 596 (2001) 61.

[9] L. Petit, T. Cardinal, J.J. Videau, G. Le Flem, Y. Guyot, G. Boulon, M. Couzi, T. Buffeteau, J. Non-Cryst. Solids 298 (2002) 76.

[10] X. Feng, S. Tanabe, T. Hanada, J. Non-Cryst. Solids 281 (2001) 48.

[11] J.P. van der ziel, L.G. Van Uitert, W.H. Grodkiewicz, R.M. Mikulyak, J. Appl. Phys. 60 (1986) 4262.

[12] S. Tanabe, J. Non-Cryst. Solids 256&257 (1999) 282.

[13] S. Todoroki, X. Kirao, N. Soga, J. Non-Cryst. Solids 143 (1992) 46.

[14] X. Shen, Q. Nie, T. Xu, Y. Gao, Spectrochim. Acta A 61 (2005) 2827.

[15] L. Nemec, J. Gotz, J. Am. Ceram. Soc. 53 (1970) 526.

[16] S. Dai, J. Zhang, C. Yu, G. Zhou, G. Wang, L. Hu, Mater. Lett. 59 (2005) 2333.

[17] S. Dai, C. Yu, G. Zhou, J. Zhang, G. Wang, L. Hu, J. Lumin. 117 (2006) 39.