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Effect of B_2O_3 on Judd-Ofelt parameters of Er^{3+}-doped tellurite glasses*

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We have prepared Er^{3+}-doped borotellurite glasses using conventional melting and quenching method. The absorption spectrum analysis is performed on the basis of Judd-Ofelt theory. The effects of B_2O_3 on the spectroscopic parameters such as intensity parameters, line strengths of electric-dipole transitions, and spontaneous emission probability are discussed.

Keywords: Judd-Ofelt theory, tellurite glass, compositional dependence, Er^{3+} ion
PACC: 7855, 4255R, 7840

1. Introduction

Er^{3+}-doped tellurite glass shows a large stimulated emission cross section and a high full width at half maximum (FWHM) at the 1.55μm communication window and is considered as a promising material for broadband amplification. However, the upconversion emission of Er^{3+} in tellurite glass is serious due to its relative low phonon energy ($750\,cm^{-1}$),[1] which not only decreases the pumping quantum efficiency (QE) but also increases the noise figure of an amplifier. Several efforts have been made on the methods of decreasing the upconversion emission of Er^{3+} in tellurite glass. Reference [2] reported the introduction of B_2O_3, which has the largest phonon energy ($1400\,cm^{-1}$), into the tellurite glass to increase the maximum phonon energy of the glass host. Choi *et al*[3] studied the addition of energy acceptor ions such as Ce^{3+}, Eu^{3+}, and Tb^{3+} to deplete the $^4I_{11/2}$ level by nonradiative energy transfer, since their electronic transition energies are approximately resonant with the energy gap corresponding to the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition of Er^{3+}.

The Judd-Ofelt (JO) theory[4,5] has been used mostly in evaluating the probability of the forced electric-dipole transitions of rare-earth ions in various environments and is often used to calculate the spectroscopic parameters, such as JO parameters Ω_t (t=2, 4, 6), spontaneous emission probability, branching ratio, and radiation lifetime, of rare earths in various matrices. It has been shown for glasses that the JO parameters are related to local structures in the vicinity of rare-earth ions and/or the covalency of the rare-earth ion sites,[6,7] which is useful for estimating the emission properties of rare-earth-doped glasses. However, to our best knowledge, there is no detailed study of the effect of introduction of B_2O_3 on JO parameters of Er^{3+}-doped tellurite glass.

In this paper, Er^{3+}-doped borotellurite glasses are prepared and the Judd-Ofelt analysis is performed for the absorption spectra. The purpose of this work is to report the Judd-Ofelt properties of Er^{3+} ions in borotellurite glasses and to have a better understanding of the effect of B_2O_3 on the behaviour of Er^{3+} in tellurite glasses. From these data, the spontaneous emission probabilities are determined in order to evaluate the properties of Er^{3+}-doped glasses and to predict other important radiative properties, such as lifetime and branching ratios.

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2. Experimental procedures

The glasses were prepared using conventional melting and quenching method from reagent-grade powders of H_3BO_3, ZnO, La_2O_3, Er_2O_3, and high-purity powders of TeO_2 (99.999%). Samples are named as described in Table 1 in order to recognize the composition easily. About 20g batches of starting materials were fully mixed and then melted in a platinum crucibles at about 800–900°C in an electronic furnace for 30min. The melt was poured into a brass mould and cooled in air and subsequently annealed to room temperature gradually. The obtained glasses were cut and polished carefully in order to meet the requirements for optical measurements.

The refractive indices were measured on a prism by minimum deviation method. The density measurements were made by Archimedes methods with water as the immersion fluid. The Er^{3+} concentrations were calculated from the measured sample densities and initial compositions. Table 1 shows the refractive indices, densities, and Er^{3+} concentrations of the glass samples. The absorption spectra of the glasses were recorded with a PERKIN-ELMER-LANBDA 900UV/VIS/NIR spectrophotometer over a spectral range of 350–1700 nm. All the measurements were made at room temperature.

Table 1. Refractive indices, densities, and Er^{3+} concentrations of Er^{3+}-doped borotellurite glasses.

Glass sample	x/(mol%)	Density/g·cm^{-3}	Refractive index	Er^{3+} concentration / 10^{20}ion·cm^{-3}
TB0	0	6.978	2.145	1.34
TB2	2	6.758	2.112	1.39
TB4	4	6.518	2.072	1.44
TB6	6	6.234	2.030	1.50
TB8	8	5.995	1.990	1.55
TB10	10	5.648	1.945	1.59

3. Results and discussion

3.1. Absorption spectra and Judd-Ofelt analysis

Figure 1 illustrates the absorption spectra of Er^{3+}-doped $(70–x)TeO_2$-xB_2O_3-25ZnO-5La_2O_3-0.5Er_2O_3 (x=0, 2, 4, 6, 8, and 10mol%) glasses. The absorption bands can be assigned according to the excited levels of Er^{3+}. Clearly, all of the absorption peaks above 350 nm can be separated easily owing to the weak overlap of the band-gap absorption of the matrix glasses. With the substitution of B_2O_3 for TeO_2, the wavelengths of the absorption peaks almost do not change but the cut-off absorption bands shifts to longer wavelengths.

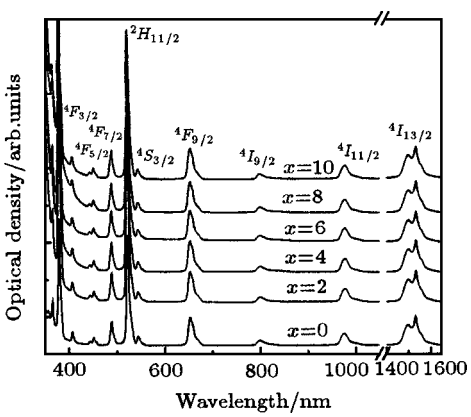


Fig.1. Absorption spectra of Er^{3+}-doped borotellurite glasses.

According to the Judd-Ofelt theory, the transitions between two states of $4f^N$ configuration of rare-earth ions, which are forbidden when the ions are free, become allowed in the crystal field by mixing into the $4f^N$ configuration with another configuration having opposite parity.[6] The line strength for the transitions between the ground state J manifold $|(S,L)J\rangle$ and a final J' manifold $|(S',L')J'\rangle$ can be calculated by

$$S_{JJ'} = 0.22 \times 10^3 \times \frac{1}{(n^2+2)^2} \times \frac{n(2J+1)}{\lambda \times N \times l} \int \mathrm{OD}(\lambda)\mathrm{d}\lambda, \quad (1)$$

where n is the refractive index of a glass host, N is the concentration of the rare-earth ion, l is the absorption length of the glass sample, J is the total angular momentum of the initial manifold, λ is the mean wavelength of the absorption band, and $\mathrm{OD}(\lambda)$ is the absorption coefficient.

The line strength of electric-dipole transition is written as

$$S_{\mathrm{ed}} = \sum_{t=2,4,6} \Omega_t | < 4f^N(SL)J \| U^{(\lambda)} \| 4f^N(S'L')J' > |, \quad (2)$$

where $\Omega_t s$ (t=2, 4, 6) are strength parameters and $||U^{(\lambda)}||s$ are the reduced matrix elements of the unit tensor operators provided in Ref.[8], which is independent of glass matrix. The intensity parameters, Ω_t (t=2, 4, 6), are usually obtained experimentally from the absorption spectra by a least-square fitting approach using at least three absorption bands, which should not contain the contribution of magnetic dipole transition. In order to increase the accuracy of JO calculation as possible as we can, eight absorption bands corresponding to the transitions from the ground state $^4I_{15/2}$ level to the excited levels $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4F_{5/2}$, and $^4F_{3/2}$ are used for the fitting. Figure 2 illustrates the intensity parameters of Er^{3+} in the glass samples. It can be seen that all of the three parameters increase with an increase of B_2O_3 content, but the Ω_2 parameter changes much more sensitive than Ω_4 and Ω_6 parameters. Previous study[9] has shown that Ω_2 is closely related to the hypersensitive transitions of rare-earth ions and the structure change of the rare-earth ion sites in the glass host. The most striking effect on the hypersensitive transitions of rare-earth ions is expected to be the highly polarized and asymmetric environment around rare-earth ions. The higher the polarization and asymmetry of the environment, the higher the hypersensitive transition and the larger the Ω_2 value.[6] B_2O_3 is a known glass former with a strong glass forming ability. When B_2O_3 was introduced into the glass composition, B will coordinate with three or four oxygen ions and thus form $[BO_3]$ trigonal and $[BO_4]$ tetrahedron units in the glass structure, while only tellurite groups $[TeO_3]$, $[TeO_{3+\delta}]$, and $[TeO_4]$ exist with the absence of B_2O_3.[10] Since the borate groups and the tellurite groups show different influence on the environment around Er^{3+} sites, the polarization and asymmetry of the environment become increasing with an increase of B_2O_3 content, and consequently the Ω_2 value increases. Tanabe *et al*[11] measured the isomer shift of ^{151}Eu as a probe and concluded that Ω_6 of Er^{3+} increases with decrease of the covalency of Er—O bonds in oxide glasses, which is related to the local basicity of the glass. With the substitution of B_2O_3 for TeO_2, the number of the borate groups $[BO_3]$ trigonal and $[BO_4]$ tetrahedral units in the network structure increases. Therefore, much more of the non-bridge oxygen ions, which tend to coordinate with Er^{3+}, will contribute to the coordination with glass former cation ions. The nonbridging oxygen ions in the glass structure decreases due to increasing the glass former ions, which lead to decreasing the basicity of the glass.[12] Consequently, the covalency of Er—O bond decreases and the Ω_6 value increases. The Ω_6 value only increases slightly, which indicates that the addition of B_2O_3 has weak influence on the covalency of Er—O bond.

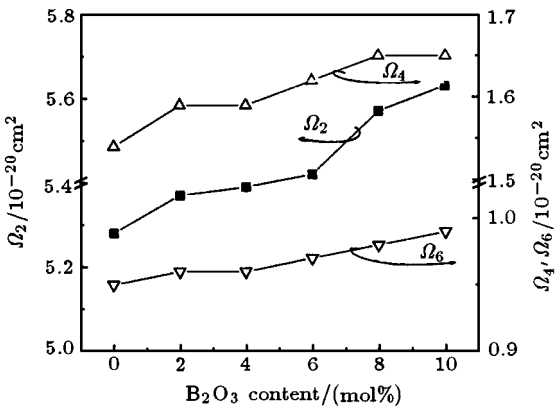


Fig.2. Compositional dependence of JO parameters, Ω_t (t=2, 4, 6), of Er^{3+} in borotellurite glasses.

3.2. Line strengths for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}

Besides the importance of intensity parameters Ω_t (t=2, 4, 6) in evaluating the local structure in the vicinity of rare-earth ions and/or the covalency of the rare-earth ion sites in glasses, the three parameters are often used to calculate the line strength of electric-dipole transitions of rare-earth ions since the Ω_t parameters do not depend on the transition levels. For the transitions between states which meet the transition selective rules $\Delta S = \Delta L = 0$, $\Delta J = 0, \pm 1$, there exists the contribution of magnetic dipole transition ($S_{\rm md}$). The magnetic dipole transition is independent of the glass structure and composition, which is given by

$$S_{\rm md} = \frac{1}{4m^2c^2}| < (S,L)J||L+2S||(S',L')J' > |^2; \quad (3)$$

the $M = | < (S,L)J||L+2S||(S',L')J' > |$ matrix elements between SLJ states are
for $J' = J-1$,

$$M = \hbar\{[(S+L+1)^2 - J^2][J^2-(L-S)^2]/4J\}^{1/2};$$

for $J' = J$,

$$M = \hbar[(2J+1)/4J(J+1)]^{1/2}[S(S+1) - L(L+1) + 3J(J+1)];$$

for $J' = J + 1$,

$$M = \hbar\{[(S+L+1)^2 - (J+1)^2][(J+1)^2 - (L-S)^2]/4(J+1)\}^{1/2},$$

where $\hbar = h/2\pi$, h is the Planck constant, J is the total angular momentum, L is the orbit angular momentum, and S is the total spin-orbit angular momentum.

For the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}, the line strength of the electric-dipole component can be expressed as

$$S_{ed}[^4I_{13/2}; {}^4I_{15/2}] = 0.0188\Omega_2 + 0.1176\Omega_4 + 1.4617\Omega_6. \quad (4)$$

It was considered to be an effective way to increase the relative contribution of electric-dipole transition in order to obtain broadband and flat emission spectrum.[12] According to Weber *et al*,[13] the ligand fields in different Er^{3+} sites can affect differently the amount of Stark splitting and/or the strengths of transitions between Stark sublevels. In the case of different Er^{3+}-doped glasses, the energies of Stark sublevels involved in the 1.55μm emission remain approximately constant, and variations in spectra are caused primarily by changes in transition intensities. Table 2 lists the line strengths of electic- and magnetic-dipole transitions of Er^{3+} in the glass samples. It can be seen that the S_{ed} and $S_{ed}/(S_{ed} + S_{md})$ increase slightly with increasing B_2O_3 content, suggesting that increasing B_2O_3 content cannot lead to increasing the variations of ligand fields around Er^{3+} sites effectively, and thus cannot lead to increasing the bandwidth of the emission spectrum of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition.

Table 2. The line strengths of electric- and magnetic-dipole parameters of Er^{3+} in the glass samples.

Glass sample	$S_{ed}/10^{-20}cm^2$	$S_{md}/10^{-20}cm^2$	$(S_{ed}+S_{md})/10^{-20}cm^2$	$S_{ed}/(S_{ed}+S_{md})$
TB0	1.685	0.723	2.408	0.700
TB2	1.691		2.414	0.700
TB4	1.691		2.414	0.700
TB6	1.710		2.433	0.703
TB8	1.731		2.454	0.705
TB10	1.747		2.470	0.707

Figure 3 illustrates the $S_{ed}/(S_{ed} + S_{md})$ ratios of Er^{3+} in different glasses as a function of Ω_6. Obviously, the $S_{ed}/(S_{ed} + S_{md})$ value increases with Ω_6. The $S_{ed}/(S_{ed} + S_{md})$ value in tellurite glass is smaller than that in bismuth-based glass, but much larger than those in other glass hosts, indicating that tellurite- and bismuth-based glasses are preferable for Er^{3+}-doped to realize broadband and flat emission.

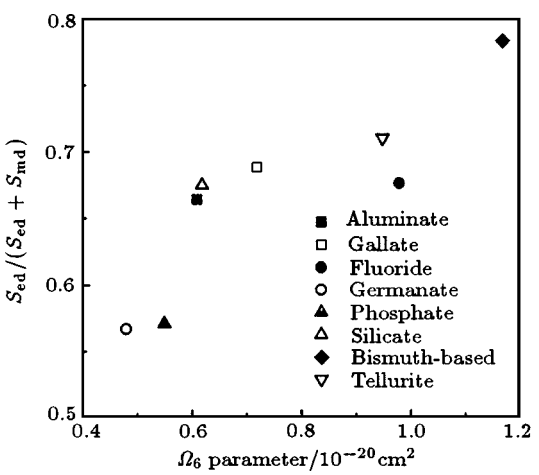


Fig.3. $S_{ed}/(S_{ed} + S_{md})$ values of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} in borotellurite glasses.

3.3. Spontaneous emission probability

The spontaneous emission probability can be calculated from the Judd-Ofelt theory, using the equation

$$A[(S,L)J;(S',L')J'] = A_{ed} + A_{md} = \frac{64\pi^4 e^2}{3h\lambda^3(2J+1)} \times \left[\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md}\right]. \quad (5)$$

Table 3 lists the emission probabilities for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ and $^4I_{11/2} \rightarrow {}^4I_J$ (J=13/2,15/2) transitions of Er^{3+}. The emission probability is important for the evaluation of the property of the laser glass. Besides, it is also used to predict other important radiative properties, such as lifetime and branching ratios.[14] From Eq.(5), we can see that the large emission probability results from the large refractive index of the glass host. Weber *et al*[13] studied the ratio of the effective field E_{eff} at the ion site in the glass to the applied field E_0 in the usual simple isotropic tight binding approximation, which results in a factor of $n(n^2+2)^2/9$ in the spontaneous emission probability. With the replacement of TeO_2 by B_2O_3, the refractive index of the glass decreases monotonically, which leads

to decreasing the emission probability. On the other hand, Takebe *et al*[14] reported that the spontaneous emission probability is also affected by the covalency of the rare-earth ion sites. The emission probability of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} increases with decreasing covalency of rare-earth ion sites. Since the introduction of B_2O_3 into the tellurite glass cannot change the covalency of rare-earth sites significantly, consequently, the refractive index of the glass host has much more influence on the emission probability than the covalency of rare-earth ion sites.

Table 3. Spontaneous emission probability for Er^{3+}-doped borotellurite glasses.

Glass sample	Spontaneous emission probability/s^{-1}						
	$^4I_{13/2} \rightarrow {}^4I_{15/2}$			$^4I_{11/2} \rightarrow {}^4I_J$			
				$^4I_{13/2}$		$^4I_{15/2}$	
	A_{ed}	A_{md}	A_{total}	A_{ed}	A_{md}	A_{ed}	A_{total}
TB0	204.2	86.8	291.0	33.8	24.7	285.0	0.771
TB2	200.6	85.2	285.8	32.7	24.1	279.0	0.774
TB4	196.3	83.7	280.0	31.9	23.6	273.0	0.779
TB6	193.7	82.1	275.8	31.5	23.2	269.1	0.771
TB8	191.5	80.5	272.0	31.2	22.7	266.7	0.779
TB10	188.7	78.9	267.6	30.7	22.3	262.8	0.782

4. Conclusions

We have shown the effects of B_2O_3 on spectroscopic properties of Er^{3+} in borotellurite glasses. Though the nonbridging oxygen ions in the glass structure decreases due to increasing the glass former ions with increasing B_2O_3 content, the addition of B_2O_3 cannot decrease the local basicity of the glass effectively due to the similarity of coordination structure between TeO_2 and B_2O_3. The $S_{ed}/(S_{ed} + S_{md})$ ratio for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition only changes slightly, indicating that B_2O_3 cannot lead to a much more inhomogeneous distribution of Er^{3+} sites. The spontaneous emission probability for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition decreases monotonically, resulting from decreasing refractive index of the glass host.

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