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Preparation and spectral characterization of new Er^{3+}-doped TeO_2–B_2O_3–WO_3–ZnO–ZnS glasses*

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Erbium-doped TeO_2-based oxysulfide glasses have been prepared in argon atmosphere in graphite crucibles. The results of thermal analysis and spectroscopic properties of Er^{3+} have been studied in terms of sulfide influence. As a function of composition, we have measured principally the optical absorption, spontaneous emission, and lifetime of the materials. Judd–Ofelt theory was introduced to calculate bandwidth and emission cross-section of Er^{3+}. The results demonstrate that addition of sulfide in tellurite glasses results in broad emission spectra, with high emission cross-section, slightly low emission lifetime and a comparatively high thermal stability as pure oxide glasses.

Keywords: spectral properties, Er^{3+}, laserglass
PACC: 3350D, 2320C, 4280S

1. Introduction

Tellurite glasses are of scientific and technological interest due to their relatively high refractive indices and dielectric constants and lower phonon energies compared, for instance, with the well known silicate or phosphate glasses. The refractive indices allow the utilization of these glasses as nonlinear optical materials[1] and the phonon energies have at least two important effects on improved infrared (IR) transmission (up to 6μm) and low multiphonon decay rates for rare-earth-excited states as compared with silicate and phosphate glasses. Tellurite glasses are therefore potential candidates for IR transmitting devices,[2] especially for the potential applications in the wavelength division multiplexing system of telecommunication networks.[3]

The transmission ranging from 0.5 to 10μm makes sulfide glasses a promising host for rare earth dopants.[4] Loireau-Lozac'h *et al*[5,6] verified that the addition of oxide in Ga_2S_3–La_2S_3 glasses increases the glass-forming region and reduces the critical cooling rate.[7] Researches about the rare-earth oxysulfide systems of glasses have been focused mainly on the oxysulfides of lanthanum with varying proportions of Ga_2S_3.[6,7] These glasses show much better chemical stability and are more resistant to atmospheric attack compared with the corresponding sulfide glasses.[8] The main drawback for the effective application of oxysulfide glasses is the reliability of the preparation routes in which heat treatment in a closed system is required.[9]

In this paper, we firstly report an alternative method for synthesis of TeO_2-based oxysulfide glasses in order to avoid the main difficulty in preparation. Er^{3+}-containing samples were prepared in an open tube under an argon atmosphere. For evaluating spectroscopic properties, the absorption and emission spectra are recorded and interpreted with the aid of the Judd–Ofelt (J–O) theory,[10,11] which has been successfully applied to most of the lanthanide ions. The three strength parameters Ω_t (t=2, 4, 6) are determined from the UV/visible absorption spectra of the glasses, by the best fit of calculated and observed oscillator strengths. From these parameters, the emission cross-section and lifetime can be estimated, and the results obtained are compared with those presented in the literature for other glass samples.

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2. Experiment

Commercial reagent grade powders of TeO_2, B_2O_3, WO_3, ZnO, ZnS were used as the starting materials. Glass samples were prepared according to the following compositions in mol%: $65TeO_2$–$5B_2O_3$–$10WO_3$–(20-x) ZnO–xZnS–$0.5Er_2O_3$ with the high purity of Er_2O_3 being 99.99%, where x=0, 2.5, 5, 10, 15mol%, and the samples were named as TBWZ1–5 respectively for short. Appropriate mixtures were put into a tubular furnace and heated gradually. In order to avoid volatilization of sulfur and the sulfide chemical attack of the silica tubes during the melting process, the starting materials were placed in graphite crucibles, which were placed inside a silica tube for melting under an argon atmosphere. The glasses were obtained by melting at 850°C for 20min, and then the melts were cooled down to room temperature under argon atmosphere in 48h. All the glass samples obtained were homogeneous, transparent with a dark yellow colour as seen with the naked eye. Samples for measurements of optical and spectroscopic properties were cut and polished to a size of 20mm×10mm×1mm.

The index of refraction was measured at 486.1, 589.3 and 656.3nm, with a precision V-prism refractometer (made in China) using H_2 and Na lamps as spectral source. Differential scanning calorimeter (DSC) scans were conducted with a Perkin-Elmer DSC7 instrument, at a heating rate of 10°Cmin^{-1}, between 200 and 700°C. The glass transition (T_g) and crystallization onset (T_x) temperatures were determined with an estimated error of ±4°C. The absorption spectra were measured using a Perkin-Elmer 900 spectrophotometer in the range 300–1700nm at room temperature, while the emission spectra were obtained by exciting the samples with LD980nm as a pumping laser. The fluorescence lifetimes were measured by exciting the samples with the same LD980 nm as the above and detected by a S-1 photomultiplier tube. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Density, refractive index and thermal analysis

The densities and refractive indices of the glass samples are listed in Table 1. It is shown that densities and refractive indices increase in turn with increasing ZnS content from 0 to 15mol%. As the molecular weight of S^{2-} is bigger than O^{2-}, with the gradual replacement of the O^{2-} ions by S^{2-} ions, the average molecular weight of unit volume grows, which results in the increase of densities. Consequently, the refractive indices also increase.

Table 1. Densities, refractive indices and characteristic temperatures of TBWZ1–5 glasses.

Series	x/mol%	ρ/(g/cm^3)	n_d	T_g/°C	T_x/°C	$T_x - T_g$/°C
TBWZ1	0	5.4238	1.946	392.6	549.3	156.7
TBWZ2	2.5	5.4544	1.987	395.2	554.7	159.5
TBWZ3	5	5.4867	2.042	400.8	563.5	162.7
TBWZ4	10	5.5422	2.119	404.7	569.1	164.4
TBWZ5	15	5.5902	2.198	413.9	574.6	160.7

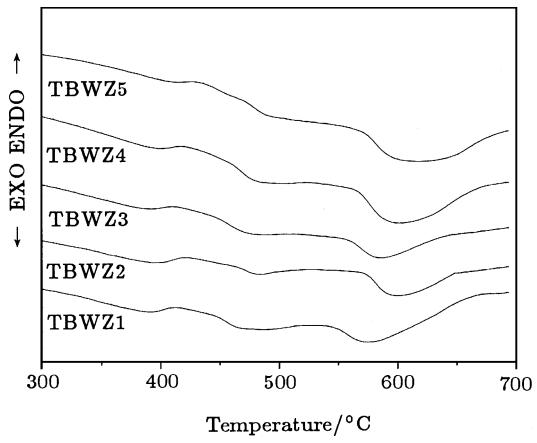


Fig.1. DSC scans of TBWZ1–5 glass samples.

Figure 1 and Table 1 show the compositional dependence of the onset crystallization temperature (T_x), the glass transition temperatures (T_g), and the difference between T_x and T_g ($\Delta T = T_x - T_g$) of TBWZ1–5 glass samples. The difference between T_x and T_g, ΔT, has been frequently used as a rough estimate of the glass formation ability or glass stability. The larger the ΔT value, the better the glass stability.[12] It is shown that, with the substitution of ZnO by ZnS from 0 to 15mol%, both the glass transition temperatures (T_g) and the crystallization onset temperatures (T_x) are gradually increased. While ΔT increases gradually from 156.7°C to 164.4°C with

the increase of ZnS from 0 to 10mol%, it begins to decrease at ZnS=15mol%. The results demonstrate that TBWZ4 has a better glass formation ability than other glasses.

3.2. Absorption spectra and Judd–Ofelt analysis

Figure 2 shows the absorption spectrum of Er^{3+} ion of TBWZ2 glass samples in the 400–1700nm region. The excited states responsible for the observed bands are assigned on the basis of the reported energy level diagram of Er^{3+} in a LaF_3 host.[13] The parts of absorption spectra corresponding to the transitions $^4I_{15/2} \rightarrow ^4I_{13/2,11/2,9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^2H_{9/2}$, have been observed. Using these absorption spectra, we have calculated the Judd–Ofelt intensity parameters Ω_t (t=2, 4, 6) by least squares fitting. According to previous studies,[14,15] the Ω_2 parameter is sensitive to the symmetry of the rare-earth site and the covalency between rare-earth ions and ligand anions; the rigidity of the network surrounding the rare-earth ion is supposed to influence the magnitude of Ω_4 and Ω_6. The covalency between Er^{3+} and ligand anions is assumed to be related with the local basicity around the rare-earth sites, which can be adjusted by changing the composition or structure of the glass host.

Table 2 presents the compositional dependence of parameters Ω_t (t=2, 4, 6) of Er^{3+}-doped $65TeO_2$–$5B_2O_3$–$10WO_3$–$(20\text{-}x)ZnO$–$xZnS$ (x=0, 2.5, 5, 10, 15mol%) glass samples. Apparently, all of the three parameters Ω_t (t=2, 4, 6) increase monotonically with increasing content of sulfide in the host matrix. The decrease of Ω_2 caused by the sulfide content follows this trend and can be explained by the predominant increase of the degree of covalency in rare-earth sites in accordance with Ref.[16]. The growing content of sulfide in the host matrix, which presents a relatively big polarizability, increases the global optical basicity of the network. As the ZnS content increases, the presence of S^{2-} around Er^{3+} probably results in a greater increase of the covalency between Er^{3+} and ligand anions, which also results in the rise of Ω_2. Indeed, the increase of the S^-/O^{2-} leads to the alteration of the tellurium network in which the covalent character increases. In our glasses series, the observed change of Ω_6 shows a slight increase when the ZnS content grows. According to J–O theory,[10,11] the calculated $^4I_{13/2} \rightarrow ^4I_{15/2}$ radiative decay rates in Er^{3+} emission transition, which is expressed by S_{ed} [$^4I_{13/2}$; $^4I_{15/2}$]=$0.0188\Omega_2+0.1176\Omega_4+1.4617\Omega_6$ (where S_{ed} is electronic dipole transitions),[17] depend on the value of parameters Ω_t and among them mostly by Ω_6, and so does the bandwidth of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition. It can be presumed that the bandwidth of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition increases with the increase of sulfide content from TBWZ1 to TBWZ5 in turn.

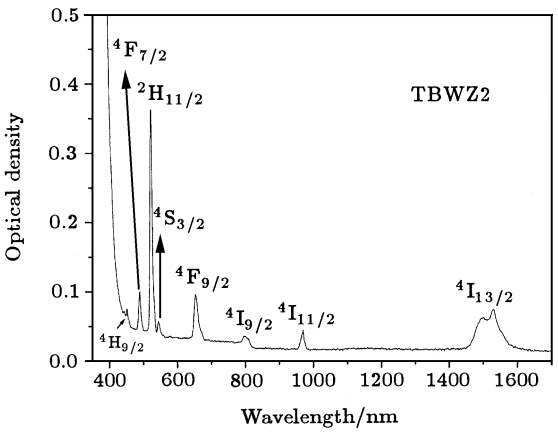


Fig.2. Spectral absorption curves for the TBWZ2 glass samples studied.

Table 2. Judd–Ofelt intensity parameters Ω_2, Ω_4, Ω_6 for glasses TBWZ1–5.

Series	x/mol%	$\Omega_2/10^{-20}cm^2$	$\Omega_4/10^{-20}cm^2$	$\Omega_6/10^{-20}cm^2$
TBWZ1	0	5.71	1.81	0.98
TBWZ2	2.5	5.77	1.82	0.97
TBWZ3	5	5.91	1.84	0.99
TBWZ4	10	6.27	1.87	1.01
TBWZ5	15	6.49	1.93	1.04

3.3. Full width at half maximum (FWHM) and emission cross-section

Figure 3 shows the normalized emission spectra of Er^{3+} in the glass samples. Because of the differences of the emission spectra in different glass hosts, FWHM is often used as a semiquantitative indication of the bandwidth. Figure 4 illustrates the compositional dependence of FWHM of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} in the glass samples. Obviously, the FWHM increases monotonically with increasing ZnS content,

which is in agreement with the results obtained with Ω_6. The results suggest that for these glasses, the increase of sulfide content results in the variation of ligand fields around Er^{3+} sites, which leads to a more inhomogeneous distribution of Er^{3+} sites, and then to a more inhomogeneous broadening of the emission spectra.

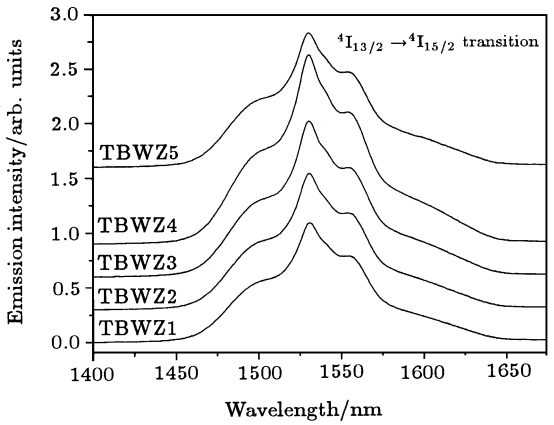


Fig.3. Compositional dependence of the normalized emission spectra of Er^{3+} ions in TBWZ1–5 glass samples.

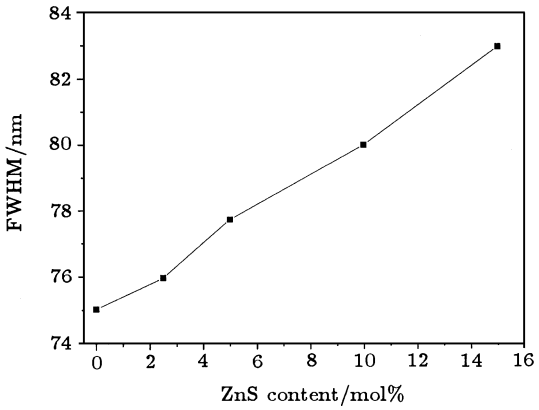


Fig.4. Compositional dependence of FWHM of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} in $65TeO_2$–$5B_2O_3$–$10WO_3$–(20-x)ZnO–xZnS (x=0, 2.5, 5, 10, 15mol%) glass samples.

According to the McCumber theory,[18] the stimulated emission cross-section (σ_e) of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} can be calculated from the measured absorption cross-section (σ_a), which is related by

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

where h is the Planck constant, k is the Boltzmann constant, and ε is the net free energy required to excite one Er^{3+} from the $^4I_{15/2}$ state to $^4I_{13/2}$ state at temperature T. The values of σ_a and ε can be calculated according to the experimentally obtained absorption spectra and the simplified procedure provided in Ref.[18], respectively. Figure 5 demonstrates the absorption cross-section and the emission cross-section for the 1.53μm transition band of Er^{3+} in TBWZ2 glass. The stimulated emission cross-section is proportional to the refractive index of the glass host [$\sigma \sim (n^2+2)^2/n$].[19] Since the index increases with the increase of ZnS, it is expected that the stimulated emission cross-section at the 1.53μm band improves from TBWZ1 to TBWZ5 glasses gradually.

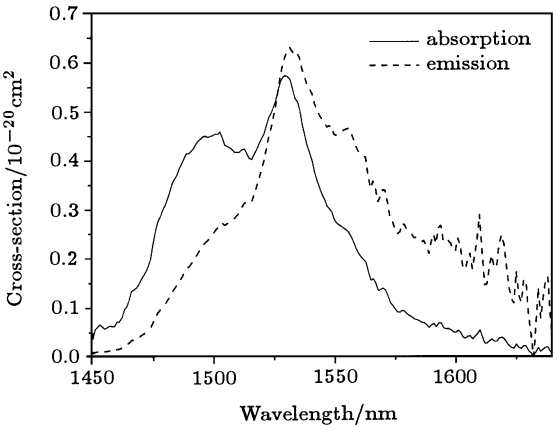


Fig.5. Absorption and emission cross-section spectra of Er^{3+} for the 1.5μm band.

The magnitude of the emission cross-section σ_e, bandwidth FWHM, and FWHM $\times\sigma_e$, which are useful optical properties, can be estimated from the Judd–Ofelt parameters and are listed in Table 3. The FWHM and σ_e values are very important for an optical amplifier to realize broadband and high-gain amplification. The gain bandwidth of an amplifier can be evaluated by the product FWHM $\times\sigma_e$. The bigger the product, the better the property. From Table 3, both FWHM and σ_e increase gradually with the increase of sulfide. It is obvious that the optical properties of glass TBWZ5 is better than that of the other glasses as a host material for an Er^{3+}-doped optical fibre amplifier. Compared with tellurite glass,[20] it can be shown that it is beneficial for bandwidth and emission cross-section with addition of appropriate amount of sulfide in tellurite glasses.

Table 3. FWHM, σ_e and FWHM $\times\sigma_e$ in TBWZ1–5 and tellurite glasses.

Series	FWHM/nm	$\sigma_e/10^{-21}$cm^2	FWHM$\times\sigma_e$
TBWZ1	75.03	5.7	427.7
TBWZ2	75.96	6.5	493.7
TBWZ3	77.71	6.9	536.2
TBWZ4	79.97	7.4	591.8
TBWZ5	82.92	8.3	688.2
Tellurite[19]	65	7.5	487.5

3.4. Fluorescence lifetime

Figure 6 shows the measured lifetime of the $^4I_{13/2}$ level of Er^{3+} in $65TeO_2$–$5B_2O_3$–$10WO_3$–(20-x)ZnO–xZnS (x=0, 2.5, 5, 10, 15mol%) glass samples. Obviously, with the increase of ZnS from 0 to 15mol%, the lifetime decreases slightly from 2.9 to 2.7ms. This trend can be explained as follows: the radiative lifetime calculated by the Judd–Ofelt theory is inversely proportional to the refractive index of the glass host, so is the measured lifetime. With the increase of ZnS, the refractive indices increase, which results in the decrease of radiative lifetime. Moreover, due to the presence of hydroxyl groups, the $^2I_{13/2}$ level will be quenched effectively, which leads to a short lifetime of Er^{3+}. In addition, the effect of composition is a potent factor. The conversion of sulfide-oxide depends basically on experimental conditions such as melting temperature and pressure. Therefore, the composition could be tuned in order to obtain the optical properties and other properties which are dependent on the sulfur/oxygen ratio, such as stability against crystallization and chemical resistance. These aspects will be studied in future work.

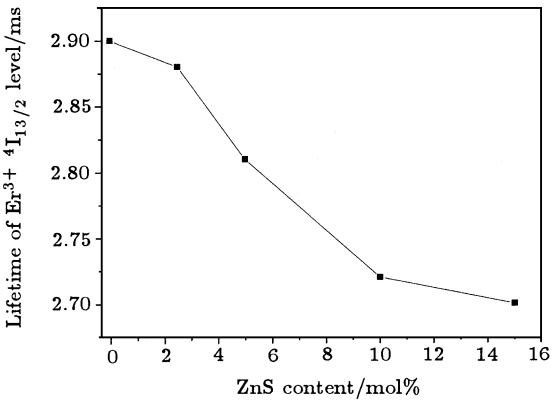


Fig.6. Compositional dependence of the lifetime of the $^4I_{13/2}$ level of Er^{3+} in $65TeO_2$–$5B_2O_3$–$10WO_3$–(20-x)ZnO–xZnS (x=0, 2.5, 5, 10, 15mol%) glass samples.

4. Conclusion

A new method has been introduced to prepare TeO_2-based oxysulfide glasses. Homogeneous and transparent glasses were prepared in a dry argon atmosphere in graphite crucibles. The samples have been characterized by DSC, absorption and emission spectroscopy. The spectroscopic properties have been analysed based on the Judd–Ofelt theory. The results indicate that glass samples with composition of $65TeO_2$–$5B_2O_3$–$10WO_3$–$5ZnO$–$15ZnS$–$0.5Er_2O_3$ have better bandwidth and emission cross-sections and slightly lower lifetime. But the thermal stability does not change notably with introducing S^{2-} ions. These results suggest that the glass TBWZ5 displays favourable properties concerning IR optical applications. Future work is in progress with stability against crystallization, chemical resistance and other optical properties, and also the investigation of upconversion phenomenon by tuning the compositions and experimental conditions.

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