

Characterization of Er³⁺-doped Na₂O-WO₃-TeO₂ glass for ion-exchanged waveguide amplifiers and lasers

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Er³⁺-doped Na₂O-WO₃-TeO₂ glass consistent with standard ion-exchange technology has been fabricated and characterized. The measured absorption and emission spectra of the glass were analyzed by the Judd-Ofelt and McCumber theories. The intensity parameters are $\Omega_2 = 7.01 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 1.80 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 1.03 \times 10^{-20} \text{ cm}^2$. The maximum emission cross-section is $0.91 \times 10^{-20} \text{ cm}^2$ at 1.533 μm , and a broad 1.5- μm emission spectrum of 65-nm full width at half-maximum (FWHM) is demonstrated. Glass transition temperature, crystallization onset temperature, density, refractive index are also reported for reference in the design and modelling of the ion-exchange process.

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In recent years, because of the use of wavelength division multiplexing (WDM) technology and the related increase in the complexity of optical networks, there has been a growing interest in integrated photonic devices. Er³⁺-doped glass waveguide devices are suitable for the manufacture of hybrid integrated optical circuit, allowing integration with other optoelectronic devices. Different technologies such as ion-exchange^[1], radio frequency (RF) sputtering^[2] have been proved valid for fabrication of waveguides on glass substrates. Among these, the ion-exchange technology is a reliable and low-cost technology, which can be tailored for most of the glass base. An extensive range of glass hosts have been investigated as hosts for ion-exchanged waveguide devices. These include phosphate, silicate, and tellurite glasses^[3-5]. Silicate glasses have superior chemical durability, but the dopant concentration of Er³⁺ is limited due to clustering^[6]. Phosphate glasses have been frequently used because of its spectroscopic characteristics and weak interaction among rare-earth ions^[7]. Recently, tellurite glasses are gaining attention since they combine good glass stability, enable relatively high rare-earth ion solubility, exhibit a good chemical durability, and have wide emission bandwidths and large stimulated emission cross-sections^[8]. These properties enable the suitability of tellurite glasses for broadband integrated photonic devices fabrication.

Na₂O-WO₃-TeO₂ (TWN) glass is developed from tungsten tellurite glass. Na₂O was added in order to make the glass suitable for the fabrication of lower loss and less stress optical waveguide devices by the ion-exchange process, since the Na⁺ and Ag⁺ ions have similar ionic radii. The glass was prepared by melting well mixed batches in alumina crucibles for 1 h at 750 °C. The melt was then cast into a pre-heated brass mold. The annealed glass sample was sliced and polished to dimensions of about 15 × 10 × 2 (mm) for optical measurements. The density of the glass was measured to be 5.57 g·cm⁻³, thus the number density of Er³⁺ ion in the glass was $4.02 \times 10^{20} \text{ cm}^{-3}$. The refractive index of the glass was measured using an ellipsometer at $\lambda = 632.8 \text{ nm}$ with $n = 2.0415$. The glass transition temperature ($T_g = 364.0 \text{ °C}$) and the crystallization onset temperature ($T_x = 413.3 \text{ °C}$)

were determined by differential thermal analysis (DTA) at a heating rate of 10 °C/min.

Absorption spectra were measured at room temperature with a Perkin-Elmer Lambda 900 UV/VIS/NIR double-beam spectrophotometer in the range of 300—1800 nm. Fluorescence spectra in the range of 1400—1700 nm were measured with a continuous-wave (CW) 970-nm pumping. Fluorescence lifetimes for the ⁴I_{13/2} level of Er³⁺ were measured with low power of 100 μs 970-nm pumping pulses. The absorption spectrum of the TWN glass is shown in Fig. 1. The band assignments are also indicated in the figure.

The Judd-Ofelt theory^[9,10] is the most useful theory in analyzing the radiative transition with the $4f^n$ configuration of rare-earth ions in various environments. The Judd-Ofelt intensity parameters Ω_t can be derived from a least-squares fitting of the theoretical oscillator strengths to the electric-dipole contributions of the experimental oscillator strengths. The Judd-Ofelt intensity parameters obtained are $\Omega_2 = 7.01 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 1.80 \times 10^{-20} \text{ cm}^2$, and $\Omega_6 = 1.03 \times 10^{-20} \text{ cm}^2$ for the Er³⁺-doped TWN glass. The measured and calculated oscillator strengths of Er³⁺ in TWN glass are presented in Table 1.

The Judd-Ofelt intensity parameters are important for investigating the local structure and bonding in the vicinity of rare-earth ions. The Ω_2 parameter is closely

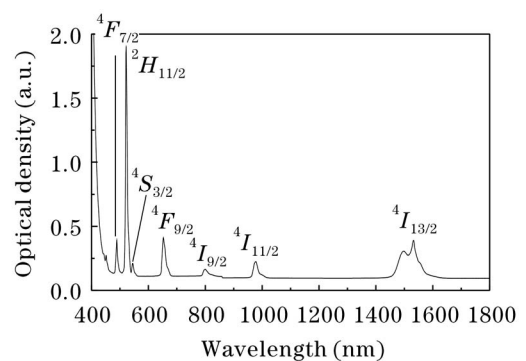


Fig. 1. Absorption spectrum of Er³⁺-doped TWN glass.

Table 1. Experimental and Calculated Oscillator Strengths of Er³⁺ in TWN Glass

Absorption	Energy (cm ⁻¹)	P_{exp} (10 ⁻⁶)	P_{calc} (10 ⁻⁶)
${}^4I_{15/2} \rightarrow {}^4I_{13/2}$	6527	2.464	1.918 (P_{ed}) 0.629 (P_{md})
${}^4I_{15/2} \rightarrow {}^4I_{11/2}$	10230	0.886	0.867
${}^4I_{15/2} \rightarrow {}^4I_{9/2}$	12500	0.476	0.563
${}^4I_{15/2} \rightarrow {}^4F_{9/2}$	15314	3.158	3.080
${}^4I_{15/2} \rightarrow {}^4S_{3/2}$	18349	0.552	0.584
${}^4I_{15/2} \rightarrow {}^2H_{11/2}$	19157	15.657	15.657
${}^4I_{15/2} \rightarrow {}^4F_{7/2}$	20450	2.409	2.613
Root Mean-Square Deviation ($\times 10^{-7}$)			1.3

Table 2. Judd-Ofelt Intensity Parameters in Er³⁺-Doped Glasses

Glass	Ω_2 ($\times 10^{-20}$ cm ²)	Ω_4 ($\times 10^{-20}$ cm ²)	Ω_6 ($\times 10^{-20}$ cm ²)
TWN	7.01	1.80	1.03
Phosphate ^[12]	6.65	1.52	1.11
Germanate ^[12]	5.81	0.85	0.28
Silicate ^[12]	4.23	1.04	0.61
Fluoride ^[12]	2.91	1.27	1.11

Table 3. Predicted Spontaneous-Radiative Transition Rates and Lifetimes of Er³⁺ in TWN Glass

Transition	Average Frequency (cm ⁻¹)	A_{ed} (s ⁻¹)	A_{md} (s ⁻¹)	β	τ_{rad} (ms)
${}^4I_{13/2} \rightarrow {}^4I_{15/2}$	6527	229.8	77.9	1.000	3.25
${}^4I_{11/2} \rightarrow {}^4I_{15/2}$	10230	329.0		0.843	2.56
${}^4I_{13/2}$	3703	43.7	17.4	0.112	
${}^4I_{9/2} \rightarrow {}^4I_{15/2}$	12500	384.6		0.785	2.04
${}^4I_{13/2}$	5973	100.8		0.206	
${}^4I_{11/2}$	2270	2.0	2.5	0.004	
${}^4F_{9/2} \rightarrow {}^4I_{15/2}$	15314	3141.5		0.898	0.286
${}^4I_{13/2}$	8787	177.5		0.051	
${}^4I_{11/2}$	5084	150.2	12.2	0.043	
${}^4I_{9/2}$	2814	13.0	5.3	0.004	
${}^4S_{3/2} \rightarrow {}^4I_{15/2}$	18349	2115.6		0.655	0.310
${}^4I_{13/2}$	11822	917.1		0.284	
${}^4I_{11/2}$	8119	69.7		0.022	
${}^4I_{9/2}$	5849	125.7		0.039	

related to the hypersensitive transitions, and takes large values when rare-earth ions exist in polarized and asymmetric sites. On the other hand, the Ω_4 and Ω_6 parameters are related to the basicity of the medium in which the ions are situated^[11]. Table 2 shows a comparison of the Judd-Ofelt intensity parameters in TWN glass and in other glasses. The Ω_2 parameter in TWN glass is larger than those in other glasses, indicating a greater degree of polarization and asymmetry of Er³⁺ ions ligand due to the structure mixing of various tellurite and tungstate groups.

After obtaining the Judd-Ofelt intensity parameters, some important radiative properties can now be calculated. The values of the predicted spontaneous radiative transition rates ($A = A_{\text{ed}} + A_{\text{md}}$), the branching ratios β , and the radiative lifetime τ_{rad} of Er³⁺ in TWN glass are

listed in Table 3. The branching ratios for the transitions ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ are 66% and 90%, respectively. Thus, it is possible to obtain efficient green and red emissions in the glass under suitable excitation conditions.

The fluorescence spectrum of the TWN glass is shown in Fig. 2. The peak wavelength is centered around 1.532 μm due to the transition from ${}^4I_{13/2}$ to ${}^4I_{15/2}$ level in Er³⁺, and the full width at half-maximum (FWHM) is ~ 65 nm. This value is wider than that of Er³⁺, Yb³⁺ co-doped phosphate glass, and comparable to that of Er³⁺ doped Na₂O-ZnO-TeO₂ glasses. The measured lifetime τ_{meas} of the ${}^4I_{13/2}$ level is ~ 4.0 ms. It should be noted that the measured lifetime was longer than the calculated radiative lifetime. This is possibly due to the reabsorption phenomena (samples are about 2 mm thick). For

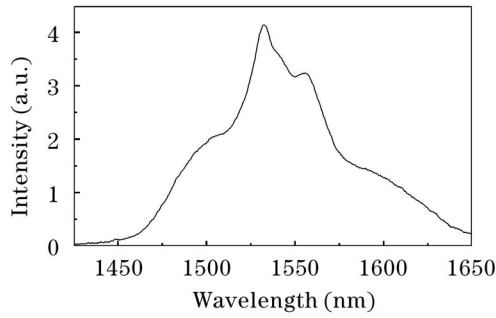


Fig. 2. Fluorescence spectrum of Er³⁺-doped TWN glass.

tellurite glasses, which usually possess high refractive indices (> 2.0), the influence of reabsorption will be significant, and now thinner samples are being prepared to verify the dependence of the measured value on the sample thickness.

The absorption cross-sections were determined from the absorption spectra and the peak value is $0.81 \times 10^{-20} \text{ cm}^2$ at $1.532 \mu\text{m}$. The stimulated emission cross-sections are calculated according to the McCumber theory^[13]. Since the stimulated emission cross-sections calculated by the McCumber theory are just obtained from the measured absorption spectrum, reabsorption is not involved in the calculation procedure; consequently, the calculated emission spectrum reflects the intrinsic $1.5\text{-}\mu\text{m}$ emission line shape free from reabsorption. Figure 3 illustrates the calculated absorption and stimulated emission cross-sections for the ${}^4I_{15/2}\text{-}{}^4I_{13/2}$ transition of Er³⁺ in the TWN glass. The maximum stimulated emission cross-section is $0.91 \times 10^{-20} \text{ cm}^2$ at $1.533 \mu\text{m}$. This value is 26% higher than the value of $0.72 \times 10^{-20} \text{ cm}^2$ in phosphate glass^[14]. The very high value is due to the high value of the refractive index, since the stimulated

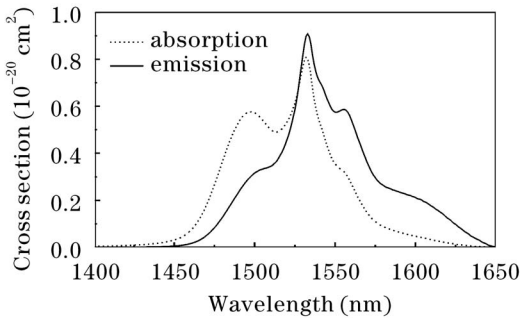


Fig. 3. Absorption and stimulated emission cross-sections of Er³⁺-doped TWN glass.

emission cross-section of rare-earth ions increases with the refractive index as $(n^2 + 2)^2/n$ for electric-dipole transitions, and as n for magnetic-dipole transitions^[8].

In conclusion, the TWN glass has high and broadband absorption and stimulated emission cross-sections at $1.5 \mu\text{m}$. The maximum emission cross-section is $0.91 \times 10^{-20} \text{ cm}^2$ at $1.533 \mu\text{m}$, and a broad $1.5\text{-}\mu\text{m}$ emission spectrum of 65-nm FWHM is demonstrated. The TWN glass should be practical for the ion-exchanged waveguide fabrication because of its higher glass transition temperature ($T_g = 364.0 \text{ }^\circ\text{C}$), which is higher than the temperature of commonly used Ag⁺-Na⁺ ion-exchange processes. Our primary experimental results indicate that the TWN glass is a promising glass host for development of ion-exchanged broadband waveguide devices. Research is in progress to further improve its basic and spectroscopic properties.

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