Optical Transitions of Erbium-doped Sodium Lanthanum Gallate Glasses

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Abstract—Erbium ion doped sodium lanthanum gallate glasses (Na_2O-La_2O_3-Ga_2O_3 or NLG) which are suitable for use in optical waveguide devices has been fabricated and characterized. The density, the refractive indexes, the absorption and luminescence spectra along with the luminescence decay time were measured. Using the experimental oscillator strengths, the Judd–Ofelt intensity parameters Ω_t were determined, and some important radiative properties were calculated. The emission peak of the $^4I_{13/2} \rightarrow {^4I_{15/2}}$ transition is at the 1.53-µm wavelength. The full-width at half-maximum (FWHM) bandwidth is 38 nm, which is larger than that of Er^{3+}-doped Ge/P silicate glasses (24.7nm), and comparable to that of Er^{3+}-doped Al/P silicate glasses (43.3nm). The lifetime of the $^4I_{13/2}$ level is 7.03ms and the quantum efficiency is ~100%. The results show that the NLG glass is an excellent host material for applications in fiber amplifiers and waveguide lasers.

Keywords-Fluorescence; Rare-earth ion; Gallate glass; Tran-sitions; Judd-Ofelt theory

I. INTRODUCTION

Rare-earth-doped oxide glass materials which have high chemical durability and thermal stability are broadly used in fiber amplifiers and waveguide lasers. The Er^{3+}-doped fiber amplifier (EDFA) is one of the key devices in wavelength-division-multiplexing (WDM) transmission systems. With the increasing demand for information capacity of WDM networks, the need for EDFAs with more broad and flat gain spectrum within the telecommunication window is increased. The erbium ion doped silica-based glasses can provide a narrow emission and hence a narrow gain spectrum around 1.55µm .[1-4]

Among the oxide glasses, heavy metal-oxide glasses are highly transparent in the near-infrared (NIR) regions. A heavy metal-oxide glass system as NLG does not contain any traditional glass-form oxide, such as silicon oxide. This glass system with a certain molar composition can provide good glass stability and wide transmission region. The gallate glass possesses the lowest phonon energy spectrum. Effective 1.3µm emission from Pr^{3+} and 1.5µm emission from Er^{3+} have been demonstrated in these glasses.[5,6]

In this paper we investigate the properties of Erbium-doped NLG glasses with a molar composition of 12%Na_2O-23%La_2O_3-65%Ga_2O_3 for operation at the 1.55-µm wavelength. The optical absorption, the fluorescence properties and the radiative lifetimes are measured and analyzed.

II. EXPERIMENTS

NLG glass is prepared with anhydrous lanthanum oxide (La_2O_3), gallium oxide (Ga_2O_3) and sodium carbonate (Na_2CO_3). All powders (99.5% to 99.999% purity) were obtained from Strem Chemicals Company. The glass samples used in this work has the following molar composition: 12%Na_2O, 23%La_2O_3, 65%Ga_2O_3. Er^{3+}-doped NLG glasses is prepared by doping Er_2O_3 1wt% into the glasses raw chemicals. The glasses powders are melted at 1600~1650℃ in a platinum crucible using an electrically heated furnace. The glasses were subsequently annealed at lower temperatures, and then sliced and polished to dimensions 20 mm ×20 mm ×2 mm.

The density of the glasses sample is 4.49g/cm^3. The refractive indexes were obtained using the prism coupler technique (Metricon 2010) at three wavelengths. The glass refractive indices were measured to be 1.8233, 1.7647 and 1.7338 at 414nm, 633 nm and 1550nm wavelengths, respectively.

The absorption spectrum is obtained by using Cary 5000 double-beam spectrophotometer from 350nm to 1700nm. The fluorescence spectrum is measured with a SPEX 500M manochromator and a liquid-nitrogen-cooled germanium detector. A semiconductor 980 nm laser is used as excitation source. The fluorescence lifetime of the $^4I_{15/2}$ level of Er^{3+} is measured with a 980nm laser diode light pulses and an InGaAs photodetector.

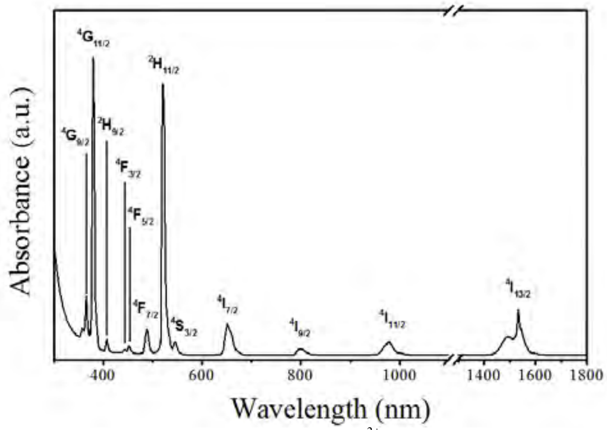

Figure 1. Absorption spectrum of Er^{3+}-doped NLG Glasses

III. Results and Discussion

Fig. 1 shows the absorption spectrum of the glasses sample and the band assignments are also indicated in the figure. There are nine absorption bands can be indentified due to the strong electronic absorption, and the appropriate electronic transitions are assigned to these bands.

By using the Judd-Ofelt approach[8,9], the radiative transitions of the Erbium ion can be analyzed. According to Judd-Ofelt theory, the experimental oscillator strengths are calculated by integrating the absorption coefficients of each band as[10]

$$f_{\exp} = \frac{mc^2}{N_0 N_A \pi e^2 \bar{\lambda}^2} \int \varepsilon(\lambda) d\lambda , \quad (1)$$

where N_0 is molar concentration of the sample, d is the thickness of the sample, $\bar{\lambda}$ is the mean wavelength of the transition, E(λ)is the absorbance, λ is the wavelength. The quantities m and e are the mass and charge of the electron, and N_A is Avogadro's number. The experimental oscillator strengths of the transitions from ground level $^4I_{15/2}$ are determined by numerical integration of the corresponding absorption bands shown in Fig. 1.

Because f_{exp} contains both the electric dipole and magnetic dipole contributions, the magnetic dipole contribution f_{md} must be subtracted from f_{exp} in order to obtain the electric dipole contribution. The magnetic dipole contribution f_{md}, is calculated from refractive index of glasses and magnetic dipole transition line strength S_{md} as[9]

$$f_{md} = n \times \frac{8\pi^2 mc}{3h\bar{\lambda}(2J+1)} S_{md} , \quad (2)$$

where h is Planck's constant, and c is the velocity of light. By using the values reported for LaF_3, the magnetic dipole line strength S_{md} is expressed as[10]

$$S_{md} = \frac{1}{4m^2c^2} \left| \langle (S,L)J \| L+2S \| (S',L')J' \rangle \right|^2 . \quad (3)$$

As the Judd-Ofelt theory shown, the electric dipole transition line strength S_{ed} from initial level $|(S,L)J\rangle$ to final level $|(S',L')J'\rangle$ can be described as[10]

$$S_{ed} = \sum_{t=2,4,6} \Omega_t \left| \langle (S,L)J \| U^{(t)} \| (S',L')J' \rangle \right|^2 , \quad (4)$$

where Ω_t are the Judd-Ofelt parameters, and are the double reduce matrix elements of unit tensor operators for the corresponding transition. The matrix elements are found to be essentially the same from host to host and we use the values in Ref. [8].

The relationship between S_{ed} and calculated oscillator strength f_{cal} is[10]

$$f_{cal} = \frac{8\pi^2 mc}{3h\bar{\lambda}(2J+1)} \frac{(n^2+2)^2}{9n} S_{ed} , \quad (5)$$

where h is the Planck's constant. The Judd-Ofelt intensity parameters Ω_t are derived from the electric dipole contribution of the experimental oscillator strengths with a least-squares fitting method. To evaluated the accuracy of the least-squares approximation, the root-mean-square (*rms*) deviation is calculated from experimental oscillator strengths f_{exp} and calculated oscillator strengths f_{cal} as

$$rms = \left[\frac{\sum \left(f_{\exp} - f_{cal} \right)^2}{no.\ of\ transition\ -\ no.\ of\ parameters} \right]^{1/2} . \quad (6)$$

Table. 1 presents the absorption-band energies, experimental and calculated oscillator strengths, S_{ed}, and Judd-Ofelt intensity parameters Ω_t of the sample. Table. 2 compares the Ω_t of Silica, ZBLAN, Phosphate, Tellurite, KBG (K_2O-Bi_2O_3-Ga_2O_3) and NLG glasses. The Ω_2 para-

TABLE I. Experimental and Calculated Oscillator Strengths, Electric Dipole Line Strength, Judd-Ofelt Intensity Parameters of Er^{3+} in NLG Glasses

Absorption	Energy (cm^{-1})	f_{exp} (10^{-6})	f_{cal} (10^{-6})	f_{md} (10^{-6})	S_{ed} (10^{-20})
$^4I_{15/2} \rightarrow {}^4I_{13/2}$	6519	1.138	0.808	0.316	1.115
$^4I_{15/2} \rightarrow {}^4I_{11/2}$	10215	0.403	0.417		0.348
$^4I_{15/2} \rightarrow {}^4I_{9/2}$	12500	0.243	0.390		0.171
$^4I_{15/2} \rightarrow {}^4F_{9/2}$	15349	1.503	1.910		0.865
$^4I_{15/2} \rightarrow {}^4S_{3/2}, {}^2H_{11/2}$	19194	9.977	9.136		4.598
$^4I_{15/2} \rightarrow {}^4F_{7/2}$	20450	1.146	1.361		0.496
$^4I_{15/2} \rightarrow {}^4F_{5/2}, {}^4F_{3/2}$	22124	0.403	0.502		0.161
$^4I_{15/2} \rightarrow ({}^2H, {}^4F, {}^2H)_{3/2}$	24540	0.405	0.441		0.146
$^4I_{15/2} \rightarrow {}^4G_{11/2}$	26316	14.713	15.654		4.946
$^4I_{15/2} \rightarrow {}^4G_{9/2}$	27322	3.360	1.384		1.088
Ω_2 ($10^{-20}cm^2$)			4.75		
Ω_4 ($10^{-20}cm^2$)			1.56		
Ω_6 ($10^{-20}cm^2$)			0.57		
Root-mean-square deviation (10^{-6})			0.849		

TABLE II. COMPARISON OF JUDD–OFELT PARAMETERS OF DIFFERENT Er^{3+}-DOPED GLASSES

Glass	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	Ω_6 (10^{-20} cm^2)	Reference
Silica	3.8	0.6	0.3	11
ZBLAN	2.20	1.40	0.91	11
Phosphate	3.73	1.00	0.72	11
Tellurite	4.12	1.81	0.85	3
KBG	3.41	1.16	0.77	7
NLG	4.75	1.56	0.57	This work

TABLE III. CALCULATED SPONTANEOUS RADIATIVE TRANSITION RATES AND LIFETIMES OF Er^{3+} IN NLG GLASSES

Transition	Average Frequency (cm^{-1})	$A_{ed}(s^{-1})$	$A_{md}(s^{-1})$	β	τ_{rad} (ms)
$^4I_{13/2} \to {}^4I_{15/2}$	6519	93.5	52.7	1	6.84
$^4I_{11/2} \to {}^4I_{13/2}$	3696	15.5	12.1	0.17	6.22
$\to {}^4I_{15/2}$	10215	133.1		0.83	
$^4I_{9/2} \to {}^4I_{11/2}$	2385		2.0	0.009	4.39
$\to {}^4I_{13/2}$	5981	34.7		0.152	
$\to {}^4I_{15/2}$	12500	191.3		0.839	
$^4F_{9/2} \to {}^4I_{9/2}$	2849	4.6	3.4	0.004	0.50
$\to {}^4I_{11/2}$	5134	60.8	8.2	0.035	
$\to {}^4I_{13/2}$	8830	100.0		0.051	
$\to {}^4I_{15/2}$	15349	1767.5		0.910	
$^4S_{3/2} \to {}^4I_{9/2}$	5832	55.0		0.043	0.77
$\to {}^4I_{11/2}$	8117	29.0		0.022	
$\to {}^4I_{13/2}$	11813	350.0		0.271	
$\to {}^4I_{15/2}$	18332	858.5		0.664	
$^2H_{11/2} \to {}^4I_{15/2}$	19212	10165.7		-	-
$^4F_{7/2} \to {}^4I_{15/2}$	20450	2669.7		-	-
$^4F_{5/2} \to {}^4I_{15/2}$	22124	984.9		-	-
$^4F_{3/2} \to {}^4I_{15/2}$	22548	336.7		-	-
$^2H_{9/2} \to {}^4H_{11/2}$	5328		1.3	~0	0.24
$\to {}^4F_{9/2}$	9191	42.3	56.5	0.02	
$\to {}^4I_{9/2}$	12040	33.8	1.3	0.01	
$\to {}^4I_{11/2}$	14325	741.0	49.0	0.19	
$\to {}^4I_{13/2}$	18021	1915.1		0.45	
$\to {}^4I_{15/2}$	24540	1377.9		0.33	

meter is affected by the covalent chemical bonding, the Ω_4 and the Ω_6 para-meters are related to the rigidity of the medium in which the ions are situated.[12] Ω_2 of NLG glass is larger than those of all other glasses, which indicates the NLG glasses have a higher covalent degree. Ω_4 of NLG glass is smaller than Tellurite glass but larger than those of other glasses. And Ω_6 of NLG glass is larger than Silica glass but smaller than those of other glasses. These differences are in good agreement of with the experi-mental data on the rigidity and viscosity of the melts.

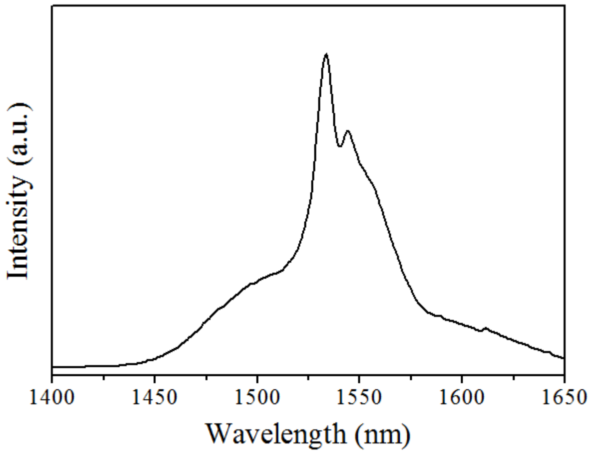

Figure 2. Fluorescence Spectrum of Er^{3+}-doped NLG Glasses

According to the Judd-Ofelt theory, using the values of Ω_t, some of the important radiative properties can be calculated. The spontaneous-transition probability is given by[13]

$$A[(S,L)J;(S',L')J'] = A_{ed} + A_{md} = \frac{64\pi^4 e^2}{3h\bar{\lambda}(2J+1)} \times \left[\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md}\right], \quad (7)$$

where A_{ed} and A_{md} are the respective electric dipole and magnetic dipole contribution.

The fluorescence branching ratio β of transitions from initial level |(S, L) J⟩ to lower level |(S′, L′) J′⟩ is given by[13]

$$\beta[(S,L)J;(S',L')J'] = \frac{A[(S,L)J;(S',L')J']}{\sum_{S',L',J'} A[(S,L)J;(S',L')J']}, \quad (8)$$

and the radiative lifetime τ_{rad} of an emitting state is related to the total fluorescence emission probability of all

TABLE IV. COMPARISON OF THE PEAK VALUES OF THE EMISSION CROSS SECTIONS OF DIFFERENT GLASSES

Glass	Measured peak σ_e (10^{-21}cm)	Reference
Al/P silica	5.7	16
Silicate (L22)	7.27	16
Fluorophosphate (L11)	7.16	16
Fluorophosphate (L14)	5.79	16
KBG	11.7	7
NLG	7.29	This work

emissions from this state by[14]

$$\tau_{rad} = \left\{ \sum_{S',L',J'} A[(S,L)J;(S',L')J'] \right\}^{-1}. \quad (9)$$

Table. 3 shows calculated spontaneous radiative transition probabilities, branching ratios and lifetimes of Er^{3+} in NLG glasses. The ratios of transition $^4F_{9/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ are 91% and 66.4%, respectively. Which means the glasses is possible to emit efficient green and red fluorescence under suitable excitation conditions.

The performance of a three level gain system as Er^{3+} ions operating at 1550nm wavelength can be determined by the stimulated emission cross section σ_e. It plays important roles in quantifying the ability of a rare earth ion to absorb and emit light.

σ_e can be determined by the measured emission line shape function. The peak value of σ_e can be calculated as[15]

$$\sigma_e = \frac{A_{ed}\lambda^2}{8\pi cn^2} \frac{I_e(v)}{\int I_e(v)dv}, \quad (10)$$

where v is the frequency and I is the emission intensity. The final state of the Er^{3+} emission at the 1.55μm wavelength is the ground state. The only possible emission of 1550nm wavelength is from the $^4I_{13/2}$ state, and the ground state is $^4I_{15/2}$.

Fig. 2 shows the photoluminescence spectrum of Er^{3+}-doped NLG glass pumped at 980nm wavelength. The peak wavelength is at ~1533nm and is due to the $^4I_{13/2}$ to $^4I_{15/2}$ transition. The measured peak value of σ_e of Er^{3+}-doped NLG glass is ~7.29×10^{-21} cm^2. Table. 4 present comparison of the peak values σ_e of different glasses. It indicates the σ_e of Er^{3+}-doped NLG glass is comparable to the silicate (L22) glasses (7.27×10^{-21} cm^2) and Fluorophosphate (L11) glasses (7.16×10^{-21} cm^2), larger than the Al/P silicate glasses (5.7×10^{-21} cm^2) but smaller than the KBG glasses (11.7×10^{-21} cm^2) [16].

The full-width at half-maximum (FWHM) bandwidth of NLG glass is 38nm, and this measured value is larger than that of Er^{3+}-doped Ge/P silicate glasses (24.7nm), and comparable to that of Er^{3+}-doped Al/P silicate glasses (43.3nm)[17]. The measured lifetime τ_{mea} is ~7.03ms and the radiative quantum efficiency is ~100%.

IV. CONCLUSIONS

The Er^{3+}-doped NLG glasses have been fabricated and characterized. It is shown to be suitable for operation at 1.533μm wavelength. Using Judd-Ofelt theory, the Judd-Ofelt intensity parameters, radiative properties and lifetimes are calculated. The emission from the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition is at 1.533μm wavelength with a spectral bandwidth of ~ 38nm. This value is larger than that of Er^{3+}-doped Ge/P silicate glass (24.7nm), and comparable to that of Er^{3+}-doped Al/P silicate glass (43.3nm). The lifetime of the $^4I_{13/2}$ state is ~7.03ms and the quantum efficiency is ~100%. The measured peak value of σ_e is ~7.29×10^{-21}cm^2, and this value is comparable to the silicate (L22) glasses (7.27×10^{-21} cm^2) and Fluorophosphate (L11) glasses (7.16×10^{-21} cm^2), larger than the Al/P silicate glasses (5.7×10^{-21} cm^2) but smaller than the KBG glasses (11.7×10^{-21} cm^2). The results show that the Er^{3+}-doped Na_2O-La_2O_3-Ga_2O_3 glass is an excellent material for applications in fiber amplifiers and waveguide lasers.

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