Optical Properties of 1.47-μm Emission in Tm^{3+}-doped Li_2O-SrO-ZnO-Bi_2O_3 Glasses

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Abstract. Tm^{3+}-doped Li_2O-SrO-ZnO-Bi_2O_3 (LSZB) glasses that are suitable for optical amplifier applications have been fabricated through the conventional melt-quenching method, and the spectroscopic properties of Tm^{3+} in the glasses were characterized. The density, the refractive indices, the optical absorption, the Judd–Ofelt parameters Ω_t, and the spontaneous transition probabilities of the glasses were measured and calculated. Using the least-squares fitting method, the Judd–Ofelt intensity parameters Ω_t were found to be $\Omega_2=4.29\times10^{-20}cm^2$, $\Omega_4=1.16\times10^{-20}cm^2$, and $\Omega_6=0.84\times10^{-20}cm^2$. Intense 1.47-μm fluorescence was observed in these glass systems under 785-nm excitation. The emission peak from the Tm^{3+}: $^3H_4\rightarrow{}^3F_4$ transition locates around 1.47-μm with a bandwidth is ~112 nm, which is significantly wider than the bandwidth of Tm^{3+}-doped ZBLAN at 80nm but smaller than that in KBG glasses. The results indicate that Tm^{3+}-doped LSZB glasses is a promising host material for applications in optical amplifiers.

Keywords: Fluorescence; Rare-earth ion; Bismuth glass; Judd-Ofelt theory; Optical amplifier

I. INTRODUCTION

Glasses doped with various rare-earth ions are important materials for fluorescent display devices, optical detectors, optical fibers, bulk lasers and optical amplifiers [1,2]. There has been an ever growing demand for optical fiber communication capacity and system integration, driven mainly by the rapid growth of the Internet. Erbium-doped fiber amplifier (EDFA) and wavelength-division multiplexing (WDM) technology enable the transmission of information in long distance and great capacity[3,4]. However, with the further development of the Internet, conventional silica-based Erbium-doped fiber amplifiers, most of which work in the C-band (1530nm~1565nm), cannot meet the requirement of the growing fiber system any more. Consequently, much more attention has been paid to light amplification in the S-band and S+-band (1450nm~1520nm)[5-7]. Since it is impractical to achieve the above amplification using Erbium ions, investigating other rare earth ions' luminescence properties is becoming increasing important[8].

Rare earth doped bismuth-based glasses are being studied for use as laser and amplifier device materials[9]. In the last years, Tm^{3+} doped glasses have been generated a great deal of attention due to the interesting spectroscopic properties of their 1.47 infrared emission, which is important to achieve a band extension in the spectral range corresponding to the S-band amplifier region. Therefore it is urgent to develop a new optical amplifier at S band [10-12]. At the same time, there has been a great deal of interest in Tm^{3+}-doped bismuth-based glasses, which were considered to be a promising candidate for the optical amplifiers at S band, because they exhibit a good glass stability, rare-earth ion solubility, slow corrosion rate, lower phonon energy spectrum among oxide glass formers, high refractive index, and high nonlinear refractive index[13].

In this work, the spectroscopic properties of Tm^{3+}-doped Li_2O-SrO-ZnO-Bi_2O_3 (LSZB) glasses were investigated for operation at the 1.47-μm wavelength. The optical absorption, the fluorescence properties, the spontaneous transition probability, and some other important parameters were measured and investigated.

II. EXPERIMENTS

Tm^{3+}-doped LZSB glasses sample of compositions $20Li_2O$-3SrO-10ZnO-$67Bi_2O_3$ were prepared from high-purity (99.999-99.5%) anhydrous bismuth oxide (Bi_2O_3), zinc oxide (ZnO), strontium carbonate ($SrCO_3$), and lithium carbonate (Li_2CO_3) powders. And Tm_2O_3 was added to the starting powders to prepare glassed doped with 1.0 wt.% Tm^{3+}. The mixed powders were melted using a platinum crucible with a closed lid in an electrically heated furnace at 1000 ℃ for 30 min. The glasses were subsequently annealed at lower temperatures and then cut and polished to dimensions 20 mm×20 mm×2 mm.

The density of this sample is 8.168 g/cm^3. The refractive indices were measured through the prism coupler technique (Metricon 2010). The refractive indices of LSZB glasses at 635.9 and 1547.9 nm wavelengths are

2.3847 and 2.2747, respectively.

The absorption spectra of this sample were measured at room temperature with a Cary 5000 double-beam spectrophotometer from 300 nm to 2600 nm. The fluorescence spectra were recorded with a SPEX 500M monochromator and a liquid-nitrogen-cooled germanium detector, and a semiconductor 785nm laser was used as excitation source.

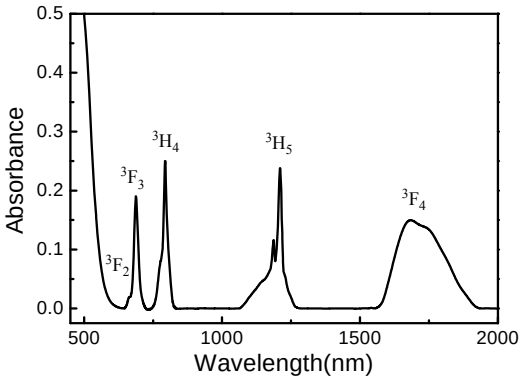

Figure 1. Absorption spectrum of Tm^{3+}-doped LSZB glasses.

III. Results and Discussion

The optical absorption spectrum of Tm^{3+}-doped LSZB glasses at room temperature is shown in Figure 1., from which an energy-level diagram of Tm^{3+} is constructed (Figure 2.). The absorption spectrum consists of five absorption bands that are also indicated in this figure. The assignments of absorption bands corresponding to the transitions from the ground state $^3H_6$ to the excited states of the Tm^{3+} ion. The absorption spectra show wavelengths that may be used as pump lights for laser and optical amplifiers. There possible pump transitions are $^3H_6 \rightarrow {}^3F_2$ (658 nm), $^3H_6 \rightarrow {}^3F_3$ (688 nm) and $^3H_6 \rightarrow {}^3F_4$ (793 nm).

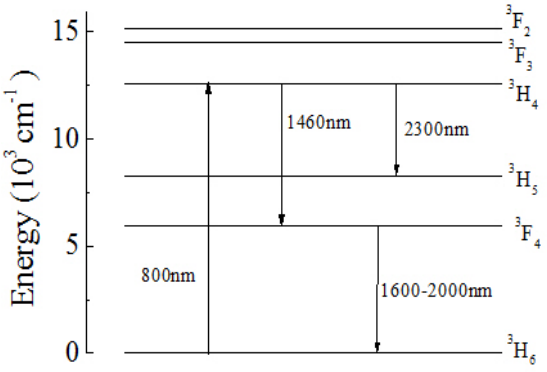

Figure 2. Energy level diagram of Tm^{3+}-doped LSZB glasses

The radiative transitions within the $4f^n$ configuration of a rare earth ion can be analyzed by using the Judd-Ofelt theory. The line strength S_{ed} of the electric dipole transition between two J states can be given by the following equation in Judd-Ofelt theory [14,15].

$$S_{ed}(J;J') = \sum_{t=2,4,6} \Omega_t \left| \left\langle (S,L)J \left\| U^{(t)} \right\| (S',L')J' \right\rangle \right|^2, \quad (1)$$

where J and J' specify the total angular momentum of initial and final states, respectively. Ω_t (t=2,4,6) are the Judd-Ofelt parameters, *(S,L)J* and *(S',L')J'* represent the initial and final states of the transition, and the elements $U^{(t)}$ are the unit tensor operators for the corresponding transition and we used the values in Ref [16].

The experimental oscillator strengths f_{exp} of the transitions was calculated from the following equation:

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

where N_0 is molar concentration of the sample, N_A is Avogadro's number, $\bar{\lambda}$ is the mean wavelength of the transition, ε (λ)is the absorbance at the wavelength λ. The quantities m and e are the mass and charge of the electron, and c is the speed of light.

Since the experimental oscillator strengths f_{exp} contains both the electric-dipole f_{ed} and the magnetic-dipole f_{md} contributions, it can be written by

$$f_{\exp} = f_{ed} + f_{md}, \quad (3)$$

The magnetic-dipole contribution of oscillator strength f_{md} can be calculated from the refractive index of the glasses n and the line strength S_{md} of the magnetic dipole transition. The formula is

$$f_{md} = n \times \frac{8\pi^2 mc}{3h\bar{\lambda}(2J+1)} S_{md}, \quad (4)$$

where h is Planck's constant, c is the velocity of light. For each wavelength, and the refractive index of the glasses sample was calculated by the Cauchy's equation

$$n = A + \frac{B}{\lambda^2}, \quad (5)$$

where A=2.2523, B=53535.98 nm^2.

For magnetic dipole transitions, the line strength S_{md} is given by

$$S_{md} = \frac{1}{4m^2c^2} \left| \left\langle (S,L)J \left\| L + 2S \right\| (S',L')J' \right\rangle \right|^2, \quad (6)$$

where m is the electron mass and c is the velocity of light. The values for the matrix elements in (1) and (5) can be calculated according to the values reported in Ref.17. The electric-dipole contribution of oscillator strength over an absorption band then can be expressed as

$$f_{cal}(J,J') = \frac{8\pi^2 mc}{3h\bar{\lambda}(2J+1)} \frac{(n^2+2)^2}{9n} S_{ed}, \quad (7)$$

Where h is Planck's constant, n is the refractive indexes of

TABLE I. MEASURED AND CALCULATED OSCILLATOR STRENGTHS, JUDD-OFELT PARAMETERS, AND ELECTRIC-DIPOLE LINE STRENGTHS OF Tm^{3+} IN LSZB GLASSES.

Transition	Energy (cm^{-1})	f_{exp} (10^{-6})	f_{cal} (10^{-6})	f_{md} (10^{-6})	S_{ed} (10^{-20})
$^3H_6 \rightarrow {}^3F_4$	5959	4.1515	4.1654		3.3421
$^3H_6 \rightarrow {}^3H_5$	8258	3.0558	2.2127	0.6370	1.2623
$^3H_6 \rightarrow {}^3H_4$	12610	4.4927	4.5705		1.6410
$^3H_6 \rightarrow {}^3F_{3,2}$	14535	4.0590	4.2257		1.2863
Ω_2 (10^{-20} cm^2)			4.29		
Ω_4 (10^{-20} cm^2)			1.16		
Ω_6 (10^{-20} cm^2)			0.84		
Root-mean-square deviation (10^{-6})			0.610		

TABLE II. CALCUIATED SPONTANEOUS EMISSION PROBABILITIES, FLUORESCENCE BRANCHING RATIOS, AND RADIATIVE LIFETIMES OF Tm^{3+} IN THE LSZB GLASSE

Transition	Energy (cm^{-1})	A_{ed}(s^{-1})	A_{md}(s^{-1})	A_{total} (s^{-1})	β_{ij}	τ_{rad} (μs)
$^3F_2 \rightarrow {}^3F_3$	390	0	0	0	0	103
$^3F_2 \rightarrow {}^3H_4$	2315	36.3		36.3	0.004	
$^3F_2 \rightarrow {}^3H_5$	6667	463.4		463.4	0.047	
$^3F_2 \rightarrow {}^3F_4$	8966	1855.6		1855.6	0.191	
$^3F_2 \rightarrow {}^3H_6$	14925	7365.5		7365.5	0.758	
$^3F_3 \rightarrow {}^3H_4$	1925	9.3		9.3	0.001	154
$^3F_3 \rightarrow {}^3H_5$	6277	1025.0		1025.0	0.158	
$^3F_3 \rightarrow {}^3F_4$	8576	133.6	197.3	330.9	0.051	
$^3F_3 \rightarrow {}^3H_6$	14535	5138.2		5138.2	0.790	
$^3H_4 \rightarrow {}^3H_5$	4352	52.0	30.8	82.8	0.021	256
$^3H_4 \rightarrow {}^3F_4$	6651	265.6		265.6	0.068	
$^3H_4 \rightarrow {}^3H_6$	12610	3557.8		3557.8	0.911	
$^3H_5 \rightarrow {}^3F_4$	2299	5.9		5.9	0.007	1239
$^3H_5 \rightarrow {}^3H_6$	8258	622.3	179.2	801.5	0.993	
$^3F_4 \rightarrow {}^3H_6$	5959	762.9		762.9	1	1311

the glass host, $\bar{\lambda}$ is the mean wavelength of the transition. From the integrated absorbance, three intensity parameters Ω_t (t=2,4,6) were determined by using a least-square fitting approach.

A method of the fitting is given by the root-mean-square (rms) deviation between the measured and the calculated oscillator strengths, and the relationship is expressed as

$$rms = \left[\frac{\sum (f_{\exp} - f_{cal})^2}{no.\,of\ transition - no.\,of\ parameters} \right]^{1/2} \quad (8)$$

According to the (1)-(8), the experimental oscillator strengths f_{exp}, the electric-dipole line strengths S_{ed} and the calculated oscillator strengths f_{cal} were calculated. All the results of Tm^{3+}-doped Li_2O-SrO-ZnO-Bi_2O_3 glasses are summarized in Table. 1. It had been reported that the Ω_2 parameter is affected by the covalent chemical bonding, the Ω_4 and the Ω_6 parameters are related to the rigidity of the medium in which the ions are situated. Using the least-squares fitting approach, the Ω_t parameters were found to be Ω_2 =4.29 × 10^{-20} cm^2, Ω_4 =1.16 × 10^{-20} cm^2 and Ω_6 =0.84 × 10^{-20} cm^2.

Because the Judd-Ofelt parameters Ω_t do not depend on the transition states, the total spontaneous emission probabilities of the excited states of Tm^{3+} is expressed by the equation[18]

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

where A_{ed} and A_{md} are the electric-dipole and magnetic-dipole spontaneous emission probabilities, respectively.

The fluorescence branching ratio β of transitions from initial level |(S,L)J〉 to lower level |(S′,L′)J′〉 could be

calculated as

$$\beta[(S,L)J;(S',L')J'] = \frac{A[(S,L)J;(S',L')J']}{\sum_{S',L',J'} A[(S,L)J;(S',L')J']}, \quad (10)$$

And the radiative lifetime τ_{rad} of each excited state is defined as

$$\tau_{rad} = \left\{ \sum_{S',L',J'} A[(S,L)J;(S',L')J'] \right\}^{-1} = A_{total}^{-1}. \quad (11)$$

Table. 2 presents the calculated values of the spontaneous emission probabilities, the branching ratios, and the calculated lifetimes for the main emitting states in Tm^{3+}-doped LSZB glasses.

The fluorescence spectrum of Tm^{3+}-doped LSZB glass in the range of 1300-1650 nm is shown in Figure 3. Fluorescence bands at 1.47 μm ($^3H_4 \rightarrow {}^3F_4$) was observed from the glass doped with 1.0 wt.% Tm_2O_3. Because of limitations of the spectrometer, only part of the spectrum of the $^3F_4 \rightarrow {}^3H_6$ transition in the 1600–2000 nm can be observed. The bandwidth of the $^3H_4 \rightarrow {}^3F_4$ transition is ~112 nm, which is significantly wider than the 80 nm bandwidth of Tm^{3+}-doped ZBLAN but smaller than that in KBG glasses [19,20].

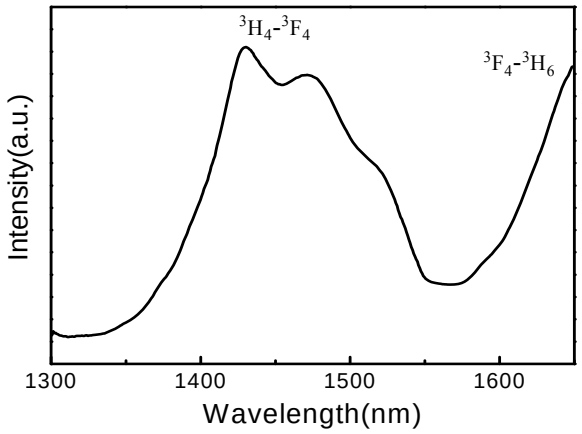

Figure 3. Fluorescence spectrum of Tm^{3+}-doped LSZB glass in the range of 1300-1650 nm.

IV. CONCLUSIONS

In conclusion, the optical properties of Tm^{3+} doped bismuth-based glass with composition of $20Li_2O$-3SrO-$10ZnO$-$67Bi_2O_3$ (mol%) are investigated. The Judd-Ofelt intensity parameters, radiative properties and lifetimes were calculated by using the Judd-Ofelt theory. Using the least-squares fitting approach, the Judd–Ofelt intensity parameters Ω_t were found to be $\Omega_2=4.29\times10^{-20}cm^2$, $\Omega_4=1.16\times10^{-20}cm^2$, and $\Omega_6=0.84\times10^{-20}cm^2$. The bandwidth of the $^3H_4 \rightarrow {}^3F_4$ transition is ~112 nm, which is significantly wider than the 80 nm bandwidth of Tm^{3+}-doped ZBLAN but smaller than that in KBG glasses. The theory lifetimes of the $^3H_5 \rightarrow {}^3F_4$ and $^3F_4 \rightarrow {}^3H_6$ could reach to 1.239 and 1.311 ms respectively. The present results indicate that Tm^{3+}-doped LSZB glasses are promising host materials for use in lasers and optical amplifiers operating in the 1.47 μm wavelength range.

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