Optical Properties of Er3+-doped Li2O-SrO-ZnO-Bi2O3 Glasses

ZhiWen Lin[a] and ShiQing Man*[b]

School of Physics and Electronic Information, Yunnan Normal University, Kunming, Yunnan, China

[a] linwen417@163.com, bman_shqing@yahoo.com

Keywords: Erbium; Bismuth Glasses; Luminescence; Optical Amplifier; Judd-Ofelt Theory

Abstract. Er^{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 Er^{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. The Raman spectrum shows three strong peaks at 255, 382, and 491cm^{-1}. The emission peak from the Er^{3+}: $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition locates around 1.53-μm with a full width at half maximum (FWHM) of ~78 nm. The theory lifetime of the $^4I_{13/2}$ level is ~2.85ms. The emission cross section is estimated to be ~9.76×10^{-21} cm^2, which is larger than those of silicate glasses. In sum, the above results indicate that the LSZB glass is a promising host material for applications in optical amplifiers.

Introduction

Glasses doped with various rare-earth ions are important materials for fluorescent display devices, optical detectors, bulk lasers, optical fibers and optical amplifiers [1-3]. Recently, the Er3+-doped SiO2-based fiber amplifier (EDFA) is widely used in tremendous capacity fiber communication system because of its some excellent characteristics, such as high gain, lower noise figure and so on. However, the bandwidth of the conventional SiO2-based EDFA is limited (~35nm), which only covers with a narrow bandwidth at 1.53μm communication window, and can not meet the demand of the modern dense wavelength division multiplexing (DWDM) optical network systems. Therefore, it is urgent to investigate new glass host which can amplify C+L band signal synchronously. Besides, as the development of the WDM technology and the miniaturization of fiber amplifier, it needs to improve unit length gain. Therefore, developing the non-silica based EDFA with broad amplifying bandwidth and high signal gain per unit length, and directly realizing the seamless amplification of (C+L)-band (1530~1610nm) region has a very important practical significance to the capacity expansion and integration of WDM communication system [4-8].

In recent years, there has been a great deal of interests in Er3+-doped bismuth-based glasses, which are considered to be a well-known promising candidate for 1.53μm broadband optical amplifiers, because they exhibit a large stimulated emission cross section and a broad emission bandwidth at the third communication window, and has a better rare earth dissolvability [9-11].

In this work, the spectroscopic properties of Er3+-doped Li2O-SrO-ZnO-Bi2O3 (LSZB) glasses were investigated for operation at the 1.55-μm wavelength. The optical absorption, the fluorescence properties, the spontaneous transition probability, and some other important parameters were measured and analyzed.

Experiments

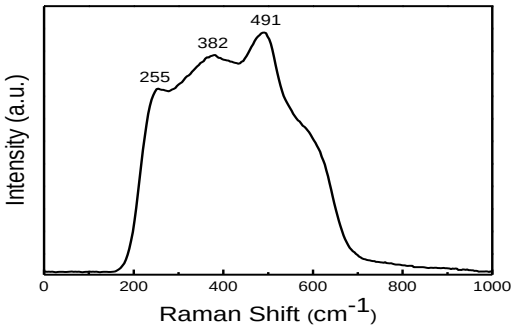
Er3+-doped LZSB glasses sample of compositions 20Li2O-3SrO-10ZnO-67Bi2O3 were prepared from high-purity anhydrous bismuth oxide (Bi2O3), zinc oxide (ZnO), strontium carbonate (SrCO3), and lithium carbonate (Li2CO3) powders. And Er2O3 was added to the starting powders to prepare glassed doped with 1wt% Er3+. 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/cm3. 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 2.3845 and 2.2748, respectively.

Raman spectra of undoped LSZB glasses were obtained at room temperature by a high sensitivity laser Raman spectrometer (Ocean Optical QE65pro, America), and a 785 nm laser was used as the excitation source. The absorption spectra of this sample were also 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 980 nm laser was used as excitation source.

Results and Discussion

Fig. 1 shows the Raman spectrum of undoped LSZB glasses at room temperature. As can be seen from Fig. 1, the Raman spectrum composed of three bands which peak at 255, 382 and 491cm-1, respectively.



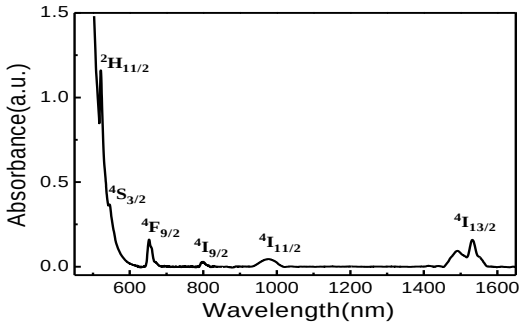


Fig. 1 Raman Spectrum of Undoped Li_2O-SrO-ZnO-Bi_2O_3 Glasses. Fig. 2 Absorption Spectrum of Er^{3+}-doped Li_2O-SrO-ZnO-Bi_2O_3 Glasses.

Fig. 2 shows the optical absorption spectrum of Er3+-doped LSZB glasses at room temperature. The absorption spectrum consists of six absorption bands that are also indicated in this figure. The assignments of absorption bands corresponding to the transitions from ground state 4I15/2 to the excited states.

The radiative transitions within the 4fn configuration of a rare earth ion can be analyzed by using the Judd-Ofelt theory. The line strength Sed of the electric dipole transition between two J states can be given by the following equation in Judd-Ofelt theory [12, 13].

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

where J and J' specify the total angular momentum of initial and final states, respectively. Ωt (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. [14].

The experimental oscillator strengths fexp of the transitions was calculated from the following equation:

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

where N0 is molar concentration of the sample, NA is Avogadro's number, $\bar{\lambda}$ is the mean wavelength of the transition, $\varepsilon(\lambda)$ 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 fexp contains both the electric-dipole fed and the magnetic-dipole fmd contributions, it can be written by

$$f_{\exp} = f_{ed} + f_{md} \tag{3}$$

The magnetic-dipole contribution of oscillator strength fmd can be calculated from the refractive index of the glasses n and the line strength Smd of the magnetic dipole transition. The formula is

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

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 $n=A+B/\lambda^2$, where A=2.2457, B=53326.8 nm^2.

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

$$S_{md} = \frac{1}{4m^2c^2} \left| \left\langle (S,L)J \| L + 2S \| (S',L')J' \right\rangle \right|^2 . \tag{5}$$

where m is the electron mass and c is the velocity of light. The values for the matrix elements in Eqs.(1) and (5) can be calculated according to the reported of LaF_3 [15]. The electric-dipole contribution of oscillator strength over an absorption band then can be written as

$$f_{cal}(J,J') = \frac{8\pi^2 mc}{3h\bar{\lambda}(2J+1)} \frac{(n^2+2)^2}{9n} S_{ed} \,, \tag{6}$$

According to the Eqs.(1)-(6), the experimental oscillator strengths $f_{\exp}$, the dipole line strengths S_{ed} and the calculated oscillator strengths f_{cal} were calculated. Besides, the three Judd-Ofelt intensity parameters Ω_t were also calculated by a least-square fitting approach. All the results of Er^{3+}-doped Bi_2O_3-ZnO-SrO-Li_2O glasses are summarized in Table 1.

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 [14]

$$rms = \left[\frac{\sum (f_{exp} - f_{cal})^2}{no.\,of\ transition - no.\,of\ parameter} \right]^{1/2} . \tag{7}$$

Table 1 Measured and Calculated Oscillator Strengths, Judd-Ofelt Parameters and Electric-dipole Line Strengths of Er^{3+} in LSZB Glasses.

Absorption	Energy [cm^{-1}]	f_{exp} [10^{-6}]	f_{cal} [10^{-6}]	f_{md} [10^{-6}]	S_{ed} [10^{-20}]
$^4I_{15/2} \rightarrow {}^4I_{13/2}$	6527	2.019	1.362	0.7184	1.231
$^4I_{15/2} \rightarrow {}^4I_{11/2}$	10215	0.983	0.642		0.361
$^4I_{15/2} \rightarrow {}^4I_{9/2}$	12516	0.250	0.565		0.253
$^4I_{15/2} \rightarrow {}^4F_{9/2}$	15326	3.251	3.074		1.087
$^4I_{15/2} \rightarrow {}^4S_{3/2}$,	18332	0.156	0.551		0.156
$^4I_{15/2} \rightarrow {}^2H_{11/2}$	19175	9.778	9.801		2.613
Ω_2 [10^{-20} cm^2]				2.75	
Ω_4 [10^{-20} cm^2]				1.42	
Ω_6 [10^{-20} cm^2]				0.71	
Root-mean-square deviation [10^{-6}]				0.526	

Because the Judd-Ofelt parameters Ω_t do not depend on the transition states, the total spontaneous emission probabilities of the excited states of Er^{3+} is expressed by the equation [15]

$$A[(S,L)J;(S',L')J'] = A_{ed} + A_{md} = \frac{64\pi^4 e^2}{3h(2J+1)\bar{\lambda}^3} \times \left[\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md} \right], \quad (8)$$

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 $|(S,L)J\rangle$ to lower level $|(S',L')J'\rangle$ is given by [16]

$$\beta[(S,L)J;(S',L')J'] = \frac{A[(S,L)J;(S',L')J']}{\sum_{S',L',J'} A[(S,L)J;(S',L')J']}. \quad (9)$$

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

$$\tau_{rad} = \left\{ \sum_{S',L',J'} A[(S,L)J;(S',L')J'] \right\}^{-1} = A_{total}^{-1}. \quad (10)$$

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

Table 2 Calculated spontaneous emission probabilities, fluorescence branching ratios,and radiative lifetimes of Er^{3+} in the LSZB glasses.

Transition	Energy [cm^{-1}]	A_{ed}[s^{-1}]	A_{md}[s^{-1}]	A_{total}[s^{-1}]	β	τ_{rad} [ms]
$^4I_{13/2} \rightarrow {}^4I_{15/2}$	6527	231	120	351	1	2.85
$^4I_{11/2} \rightarrow {}^4I_{13/2}$	3688	36	33	69	0.18	2.65
$^4I_{11/2} \rightarrow {}^4I_{15/2}$	10215	308		308	0.82	
$^4I_{9/2} \rightarrow {}^4I_{11/2}$	2301	1	7	8	0.02	1.90
$^4I_{9/2} \rightarrow {}^4I_{13/2}$	5989	92		92	0.17	
$^4I_{9/2} \rightarrow {}^4I_{15/2}$	12516	426		426	0.81	
$^4F_{9/2} \rightarrow {}^4I_{9/2}$	2801	6	4	10	0	0.20
$^4F_{9/2} \rightarrow {}^4I_{11/2}$	5111	133	79	212	0.04	

$^4F_{9/2}\rightarrow{}^4I_{13/2}$	8799	204	204	0.04	
$^4F_{9/2}\rightarrow{}^4I_{15/2}$	15326	4506	4506	0.92	
$^4S_{3/2}\rightarrow{}^4F_{9/2}$	3006	1	1	0	0.24
$^4S_{3/2}\rightarrow{}^4I_{9/2}$	5816	129	129	0.03	
$^4S_{3/2}\rightarrow{}^4I_{11/2}$	8117	77	77	0.02	
$^4S_{3/2}\rightarrow{}^4I_{13/2}$	11805	1026	1026	0.24	
$^4S_{3/2}\rightarrow{}^4I_{15/2}$	18332	3003	3003	0.71	
$^2H_{11/2}\rightarrow{}^4I_{15/2}$	19175	18905		-	-

Fig. 3 shows the fluorescence spectrum of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition under 980 nm excitation. The FWHM of 1.53 μm emission band is ~78nm, which is much wider than those of Er^{3+}-doped Ge/P silicate glasses (24.7 nm) [17].

For a three-level gain system such as Er^{3+} ions operating at 1550 nm wavelength, both the stimulated emission σ_e. and the absorption cross section σ_a play an important role in determining the performance of a device. Cross sections quantify the ability of an ion to absorb and emit light. The theory of McCumber is used to calculate the emission cross section from the measured absorption spectrum[18].

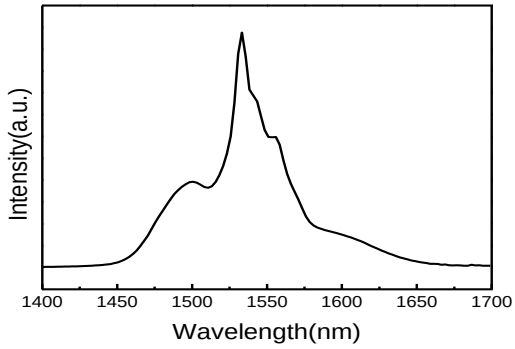


Fig.3 Fluorescence spectrum of $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition of Er^{3+}-doped Li_2O-SrO-ZnO-Bi_2O_3 glasses.

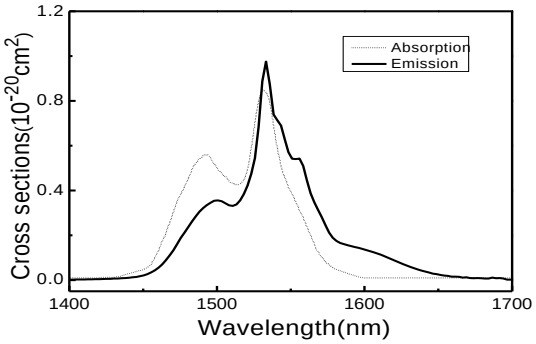


Fig.4 Absorption and stimulated emission cross sections of Er^{3+}-doped Li_2O-SrO-ZnO-Bi_2O_3 glasses.

In the theory of McCumber, the absorption cross section spectrum $\sigma_a(\nu)$ for transitions between an upper and lower manifold of levels is related to the stimulated emission cross section spectrum $\sigma_e(\nu)$ for transitions between the same two manifolds by

$$\sigma_e(\nu) = \sigma_a(\nu)\exp[(\varepsilon - h\nu)/kT]. \quad (11)$$

where k is Boltzman's constant, T is the temperature, and ε is the net free energy required to excite one ion from the to level. The ε was determined using the procedure provided in Ref. [19]. The absorption and the stimulated emission cross-sections of Er^{3+}-doped LSZB glasses shown in Fig. 4.

The peak of stimulated emission cross-section σ_e is 9.76×10^{-21} cm^2. The value is larger than those of silicate glasses [20].

Conclusions

Er^{3+}-doped LSZB glasses have been fabricated and characterized and are shown to be suitable for operation at the 1.55-μm wavelength. The Judd–Ofelt parameters Ω_t were determined, and some other important radiative properties and lifetimes were calculated. The Raman spectrum shows three

strong peaks, at 255, 382, and 491cm^{-1}. The FWHM of the emission from the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition at the 1.53-μm wavelength was ~78 nm and this value is much larger than that of silicate-based glasses (~30-40 nm). The theory lifetime of the $^4I_{13/2}$ level is ~2.85ms. Emission cross section at 1.53-μm is estimated to be ~9.76×10^{-21} cm^2, which is much larger than those of silicate glasses. Our results show that Er^{3+}-doped LSZB glass is a promising host material for broadband optical amplifier in the WDM systems.

Acknowledgment

This work is supported by the National Natural Science Foundation of China (NSFC) (Grant No. 21171072 and Grant No. 21361028).

References

[1] W.T. Camall, P.R. Eields and K. Rajnak. Electronic energy levels in the trivalent lanthanide aquo ions. I. Pr3+, Nd3+, Pm3+, Sm3+, Dy3+, Ho3+, Er3+, and Tm3+ [J]. Chem. Phys., 1968, 49 (10): 4424~4442

[2] J.S. Wang, E.M. Vogel and E. Snitzer. Tellurite glass: a new candidate for fiber devices [J]. Opt. Mater., 1994, 3 (3):187~203

[3] H. Lin, E. Y. B. Pun, X. J. Wang, et al. Intense visible fluorescence and energy transfer in Dy3+, Tb3+, Sm3+ and Eu3+ doped rare-earth borate glasses [J]. Alloy. Compd., 2005, 390:197~201

[4] H. Ono, K. Nakagawa, M. Yamada, S. Sudo. Er3+-doped fluorophosphate glasses fibre amplifier for WDM systems [J]. Electron. Lett., 1996, 32:1586~1587

[5] M. Yamada, T. Kanamori, Y. Terunuma, K. Oikawa, M. Shimizu, S. Sudo and K. Sagawa. Fluoride-based erbium doped fiber amplifier with inherently flat gain spectrum [J]. IEEE Photonics Technol. Lett., 1996, 8:882~884

[6] Y. Ohishi, A. Mori, M. Yamada, H. Ono, Y. Nishida, and K. Oikawa. Gain characteristics of tellurite-based erbium doped fiber amplifiers for 1.5-μm broadband amplification [J]. Opt. Lett., 1998, 28:274~276

[7] P. Blixt, J. Nilsson, T. Carlnas, and B. Jaskorzynska. Concentration-dependent upconversion in Er3+-doped fiber amplifiers: experiments and modeling [J]. IEEE Photonics Technol. Lett., 1991, 3:996~998

[8] S.Q. Man, E.Y.B. Pun, and P.S. Chung. Praseodymium-doped alkali bismuth gallate glasses [J]. Opt. Soc. Am., 2000, 17:23~27

[9] T.F. Xu, X. Shen, Q.H. Nie, et al. Spectral properties and thermal stability of Er3+/Yb3+ codoped tungsten-tellurite glasses [J]. Opt. Mater., 2006, 28 (3):241~245

[10] H. Lin, K. Lin, E.Y.B. Pun, et al. Infrared and visible fluorescence in Er3+-doped gallium tellurite glasses [J]. Chem. Phys. Lett., 2004, 398:146~150

[11] H.T. Amorim, M.V.D. Vermelho, A.S. Gouveia-Neto, et al. Red-green-blue upconversion emission and energy-transfer between Tm3+ and Er3+ ions in tellurite glasses excited at 1.064 mm [J]. Solid State Chem., 2003, 171:278~281

[12] B.R. Judd. Optical absorption intensities of rare-earth ions. Phys Rev., 1962, 127 (13): 750~761

[13] G.S. Ofelt. Intensities of crystal spectra of rare earth ions [J]. Chem. Phys., 1962, 37:511~520

[14] M.J. Weber, J.D. Myers, and D.H. Blackburn. Optical properties of Nd3+ in tellurite and phosphotellurite glasses [J]. Appl. Phys., 1981, 52:2944~2949

[15] M.J. Weber. Probabilities for radiative and nonradiative decay of Er3+ in LaF3. Phys. Rev., 1967, 157:262~276

[16] R. Jacobs, M. Weber. Dependence of the 4F3/2→4I11/2 induced-emission cross section for Nd3+ on glass composition [J]. IEEE., 1976, 12:102~111

[17] W.J. Miniscalco. Erbium-doped glasses for fiber amplifiers at 1500 nm [J]. Lightwave Technol., 1991, 9:234~250

[18] D.E. McCumber. Theory of phonon terminated optical masers. Phys. Rev., 1964, 134: A299~A306

[19] T.J. Whitley, C.A. Millar, R. Wyatt, M.C. Brierley, and D.Szebesta. Upconversion pumped green lasing in erbium doped fluorozirconate fibre. Electron. Lett., 1991, 27:1785~1786

[20] W.J. Miniscalco, R.S. Quimby. General procedure for the analysis of Er3+ cross sections. Opt. Lett., 1991, 16:258~261