Spectroscopic properties in Er^{3+}/Yb^{3+} Co-doped fluorophosphate glass*

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Using the technique of high-temperature melting, a new Er^{3+}/Yb^{3+} co-doped fluorophosphate glass was prepared. The absorption and fluorescence spectra were investigated in depth. The effect of Er^{3+} and Yb^{3+} concentration on the spectroscopic properties of the glass sample was also discussed. According to the Judd–Ofelt theory, the oscillator strength was computed. The lifetime of $^4I_{13/2}$ level (τ_m) of Er^{3+} ions was 8.23 ms, and the full width at half maximum of the dominating emission peak was 68 nm at 1.53 μm. The large stimulated emission cross section of the Er^{3+} was calculated by the McCumber theory. The spectroscopic properties of Er^{3+} ion were compared with those in different glasses. The full width at half maximum and σ_e are larger than those of other glass hosts, indicating this studied glass may be a potentially useful candidate for high-gain erbium-doped fiber amplifier.

Keywords: fluorophosphate glass, McCumber theory, Judd–Ofelt theory, fluorescence lifetime

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1. Introduction

Erbium-doped laser materials as $^4I_{13/2}$–$^4I_{15/2}$ transitions of Er^{3+} can yield eye-safe near 1.5-μm emission, which can be widely used in optical communications, medical, and military fields.[1] However, due to the development of computer networks and data transmission technology, the demand of optical transmission for communications capacity are increasing. The traditional erbium-doped silica fiber amplifier gain bandwidth (30 nm) looks smaller. It cannot meet the requirements of high-speed large-capacity information transmission.[2] In order to obtain an erbium-doped fiber amplifier with wide bandwidth, the researchers are looking for a new erbium-doped glass matrix material. Although phosphate glass can achieve large energy output, the pulse duration is longer.[3] The erbium-doped tellurite glass has broad emission bandwidth and large stimulated emission cross section, its thermal stability is poor and the up-conversion is more severe and costly. Fluoride phosphate glass is a kind of ideal dielectric material for high-gain erbium-doped fiber amplifier. It has high rare earth solubility,[4] good chemical and thermal stability, and low phonon energy. In addition, it has high gain coefficient, wide bandwidth, and low up-conversion efficiency on the merits.[5] Thus, it can be widely used in visible and infrared laser, fiber amplifier, optical data storage devices, underwater optical communications, biomedical diagnostics, and sensors, and other fields.[6−9] Compared with erbium-doped fluoride phosphate glass materials, the erbium ytterbium co-doped fluoride phosphate glass can enlarge the emission cross section and improve luminous efficiency, because it has high-sensitized ion Yb^{3+} which can enhance the absorption efficiency of the medium on the 980-nm pump light.

The spectroscopic properties of erbium ytterbium co-doped fluoride phosphate glass are researched in depth in this paper. Some spectral parameters of the fluorophosphate glasses were calculated according to Judd–Ofelt (JO) theory. These spectral parameters are transition oscillator strength, strength parameters, the spontaneous transition probability, fluorescence molecular ratio, and the stimulated emission cross section, etc. The spectral characteristics of Er^{3+} in different glass substrates were compared to investigate.

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2. Experiments

2.1. Sample preparation

The raw materials for the preparation of the fluorophosphate glass are fluorides and oxides AR, Er_2O_3 (99.999%), and Yb_2O_3 (99.999%). Glass recipe is as follows:

$$(65-m-n\%)P_2O_5-10\%RF_2-5\%AlF_3-10\%ZnO-10\%Pb_2O_33-mEr_2O_3-nYb_2O_3, \quad (1)$$

where R is the alkaline earth metals (one or several of Mg, Ca, Sr, Ba), $m = 1.0$, $n = 3$, 4, 5, 6, 7 (denoted as Er1Yb3, Er1Yb4, Er1Yb5, Er1Yb6, Er1Yb7); $n = 5$, $m = 0.5$, 1.0, 1.5 (denoted as Er0.5Yb5, Er1Yb5, Er1.5Yb5).

Said raw materials 20 g according to the recipe, were mixed well, put into the platinum crucible, then placed into the heating furnace, the silicon carbide furnace heated to 1300 °C, for 30 min. After the glass was melted completely, the glass melt was poured into the mold which was preheated in advance, and then placed into a muffle furnace. The temperature of the Muffle furnace cooled to the room temperature from 450 °C by 10 °C per hour and the glass was cut and polished after annealing.

2.2. The spectra

Absorption spectra were determined using a PERKIN-ELMER LAMBDA 900 UV/VIS/NIR spectrophotometer ranging from 350 nm–1700 nm with the resolution of 1 nm. Fluorescence spectra were measured on a TRIAX320 fluorescence spectrometer. The 980-nm LD was employed as the excitation source lying in the measurement range about 1400 nm–1700 nm. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Absorption spectra

Figure 1 shows the absorption spectra of Er^{3+}/Yb^{3+} co-doped fluoride phosphate glasses with different concentrations of Er^{3+}/Yb^{3+}. The measured wavelength range is 350 nm–1700 nm. As can be seen from Fig. 1, the absorption coefficient of the peak increased gradually with the concentration of Er^{3+} from 0.5 mol% to 2.0 mol%. The transition of Er^{3+} from the ground state $^4I_{15/2}$ to each excited level and the absorption transition of Yb^{3+} from the ground state $^2F_{7/2}$ to $^2F_{5/2}$ were all marked in figure.

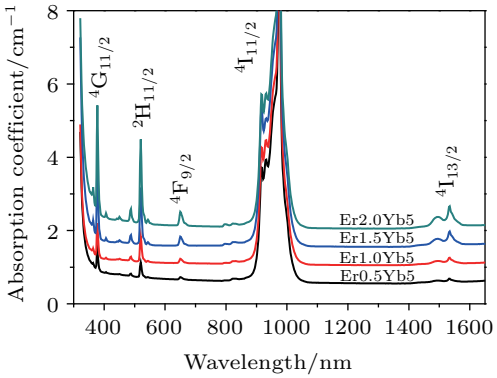


Fig. 1. (colour online) Absorption spectra of Er^{3+}/Yb^{3+} co-doped fluoride phosphate glass with different Er^{3+}-doped concentrations.

The dominating absorption peaks of Er^{3+} correspond to the energy level transitions from the state $^4I_{15/2}$ to $^4G_{11/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$ respectively. There is a very strong absorption band located at 980 nm, the absorption band should be caused by the superposition of the transitions of Er^{3+} from $^4I_{15/2}$ to $^4I_{13/2}$ and Yb^{3+} from $^2F_{7/2}$ to $^2F_{5/2}$.[10] The absorption transition $^4I_{15/2}$ to $^4I_{13/2}$ is largely influenced by the magnetic dipole transition compared to the electric dipole one, the contribution of the magnetic dipole transition was subtracted for the calculation. Meanwhile, Yb^{3+} ions, a two-energy-level system, have not only a broader absorption band but also a much larger absorption cross section than Er^{3+} ions. In addition, the Yb^{3+} concentration is usually much higher than Er^{3+} in laser glasses because of the weak concentration quenching loss. For these reasons, the absorption efficiencies of pump energy in the Yb^{3+}/Er^{3+} co-doped system is much higher than those of Er^{3+} doped singly.[11] If sensitized Er^{3+} is sensitized by Yb^{3+}, it will greatly enhance the absorption efficiency at 980 nm, which will be conducive to the bandwidth requirements of the optical fiber amplifier.

The JO theory[12] has been used mostly in evaluating the spectroscopic parameters such as strength Ω_t ($t = 2, 4, 6$), the probability of forced electric dipole transitions, branching ration, and radiative lifetime of rare-earth ions in various environments. For glasses, it has been shown that the JO parameters Ω_t are phenomenological ones including the effects of glass matrix on rare-earth ions, e.g., covalency of the rare-earth ion sites and local structures in the vicinity of rare-earth ions. Here, a short summary and the most

essential formulas will be given to make it easier to understand the following discussion.

According to the JO theory, the electric dipole transition line intensity of $4f^N$ electronic configuration can be calculated as,

$$S_{JJ'} = \sum_{\lambda=2,4,6} \Omega_\lambda |\langle 4f^N(\alpha SL)J\|U^{(\lambda)}\| \times 4f^N(\alpha' S'L')J'\rangle|^2, \quad (2)$$

where Ω_λ is the strength parameter for the line (with area dimension), $\langle 4f^N(\alpha SL)J\|U^{(\lambda)}\|4f^N(\alpha' S'L')J'\rangle$ is the reduced matrix element. Firstly, the absorption spectrum intensity $S_{JJ'}$ was measured, and then fitted line intensity parameters by the computer.

The transition oscillator strength is,

$$f_{\exp} = \frac{m_e c^2}{\pi e^2 N_0} \int k(\nu)\mathrm{d}\nu, \quad (3)$$

where m_e, e, c are the electron mass, electric charge, and the speed of light, respectively. N_0 is the density of Er^{3+} in unit volume (ions/cm^3). $k(\nu)$ is the absorption coefficient (cm^{-1}) of the glass samples on the wave number.

The electric dipole transition oscillator strength and magnetic dipole transition oscillator strength can be expressed as,

$$f_{\mathrm{cal}}^{\mathrm{ed}} = \frac{8\pi^2 mc\nu}{3h(2J+1)} \frac{(n^2+2)^2}{9n} S_{JJ'}, \quad (4)$$

$$f_{\mathrm{cal}}^{\mathrm{md}} = \frac{8\pi^2 mc\nu}{3he^2} \frac{n}{(2J+1)} S_{JJ'}^{\mathrm{md}}, \quad (5)$$

where ν is the center wave number of absorption lines, n is the refractive index of glass, and h is the Planck constant. And

$$f_{\exp} = f_{\mathrm{cal}}^{\mathrm{ed}} + f_{\mathrm{cal}}^{\mathrm{md}}. \quad (6)$$

According to equation (6), the parameter Ω_λ can be fitted as the following equation,

$$\sum_\lambda \Omega_\lambda U_{JJ'}^{(\lambda)} = S_{JJ'}. \quad (7)$$

These results are shown in Table 1, Tanabe[13] and other studies have indicated that Ω_t is related to materials, and no correlation with energy level transition. Ω_2 is closely related to the symmetry and regularity of ligand field and the structure of glass. The covalent properties of rare earth cations and oxygen anion are concerned with the coordination environment among the rare earth cations, which can be controlled by adjusting the composition or structure of the glass. Big Ω_2 will result in low symmetry of the coordination environment of rare earth cations, and also produce strong covalent properties of the rare earth cations and the oxygen anion. Generally, Ω_4 and Ω_6 are mainly influenced by the acidity–alkalinity of glass.

In Table 1, $K(\lambda)$ is the absorption coefficient of glass with the wavelength λ, $f_{\exp}^{\mathrm{ed}}$ is the oscillator strength of electric dipole transition, f_{md} is the oscillator strength of magnetic dipole transition, $S_{JJ\prime}$ is the intensity of spectral line. Furthermore, $\Omega_2 = 4.35 \times 10^{-20}$ cm^2, $\Omega_4 = 1.34 \times 10^{-20}$ cm^2, $\Omega_6 = 0.78 \times 10^{-20}$ cm^2, and $\delta_{\mathrm{rms}} = 0.46 \times 10^{-6}$.

Table 2 shows the comparison of the strength parameters of Er^{3+} in the matrixes. It can be seen that Ω_2 is larger in the experimental glass and belonging to the structure of glass and the symmetry ordering of ligand field. The value of Ω_2 is greater than that in the normal phosphate glass, fluorophosphate glass, bismuth glass, and alkali

Table 1. Er^{3+}-doped fluoride phosphate glass measured transition intensity of electric dipole moment $f_{\exp}^{\mathrm{ed}}$ and experimental absorption intensity $S_{JJ'}$ (Er1Yb5).

Transition $^4I_{15/2}$ $(S',L')J'$	ν/cm^{-1}	λ/nm	$K(\lambda)$ $\int K(\lambda)\mathrm{d}\lambda$	$f_{\exp}^{\mathrm{ed}}$ (10^{-6})	$S_{JJ'}$ (10^{-20})	f_{md} (10^{-6})
$^4I_{15/2} \rightarrow (S',L')J'$	6527	1532	22.939	0.766	1.117	0.535
$\rightarrow^4 I_{13/2}$	10267	974	467.350	65.613	60.800	
$\rightarrow^4 I_{11/2}$	12531	798	2.520	0.527	0.400	
$\rightarrow^4 I_{9/2}$	15385	650	4.378	1.380	0.854	
$\rightarrow^4F_{9/2}$	18382	544	0.899	0.405	0.210	
$\rightarrow^4S_{3/2}$	19231	520	13.104	6.455	3.193	
$\rightarrow^2H_{11/2}$	20492	488	2.686	1.502	0.697	
$\rightarrow^4F_{7/2}$	22222	450	0.455	0.299	0.128	
$\rightarrow^4F_{5/2}$	22624	442	0.100	0.068	0.029	
$\rightarrow^4F_{3/2}$	24631	406	0.881	0.712	0.275	
$\rightarrow^2H_{9/2}$	26455	378	14.552	13.564	4.878	
$\rightarrow^4G_{11/2}$	27473	364	2.192	2.204	0.763	

borate glass, respectively. It indicated that the effect of the polarization on Er^{3+} is strong by the surrounding ions in the Er^{3+}-doped fluorine phosphate glass. The asymmetry of Er^{3+} surroundings is higher, and the covalent property of the Er–O bond will be stronger. The coordination symmetry of rare earth ions is lower, so they are more likely to be stimulated. Ω_6 is much smaller than that in the germanium silicate glass, fluoride phosphate glass, and the alkali borate glass, indicating that the alkaline is lower in the recipe for fluoride phosphate glass. The stability of the glass will be enhanced with fewer non-bridging oxygen ions.

Table 2. Comparison of strength parameters of Er^{3+} ions in different matrixes.

Glass	$10^{20}\Omega_2/\mathrm{cm}^2$	$10^{20}\Omega_4/\mathrm{cm}^2$	$10^{20}\Omega_6/\mathrm{cm}^2$	Ref.
Phosphate glass	3.89	1.01	0.55	[14]
Germanosilicate glass	5.81	0.85	0.28	[14]
Fluorophosphate glass	2.91	1.63	1.26	[14]
Silicate glass	4.23	1.04	0.61	[14]
Tellurate glass	5.41	1.55	1.45	[15]
Bismuthate glass	3.86	1.52	1.17	[14]
Alkali borate	3.90	1.84	1.46	[16]
Fluorine phosphate	4.35	1.34	0.78	this article

According to JO theory, using strength parameters Ω_λ and spectral line intensity formula, and combining with the reduced matrix element $U^{(\lambda)}_{J''J'}$, the intensity of light line $S_{J''J'}$ can be obtained. The spontaneous emission transition probability $A_{J''J'}$, radiative lifetimes τ, and fluorescence ratio per β are calculated as follows:

$$A_{J''J'} = \frac{64\pi^4\nu^3e^2}{3hc^2}\cdot\frac{1}{2J''+1}\cdot\frac{n(n^2+2)^2}{9}S_{J''J'}, \quad (8)$$

$$\tau = \frac{1}{\sum\limits_{J'} A_{J''J'}}, \quad (9)$$

$$\beta = \frac{A_{J''J'}}{\sum\limits_{J'} A_{J''J'}}. \quad (10)$$

The fluorescence lifetime of Er^{3+} $^4I_{13/2}$ is defined as the time of the peak fluorescence intensity decreasing to $1/e$. It is necessary to point out that the lifetime is an important amplifier parameter. Fluorescence lifetime was determined by the phonon energy of the glass substrate. If the phonon energy of the glass substrate increases, the transition probability of non-radiative transition will enlarge, and the lifetime will shrink at the same time. It can be seen from Table 3 that the fluorescence lifetime of glass ($^4I_{13/2} \rightarrow ^4I_{15/2}$) is 8.23 ms. The results show that the fluoride phosphate has a long fluorescence lifetime. Furthermore, the necessary pump energy to achieve high population inversion will diminish, which is due to the long lifetime.[17]

Table 3. Spontaneous transition probability, fluorescence ratio per β', and fluorescence lifetime in Er^{3+}-doped fluoride phosphate glasses.

Transition $^4I_{15/2} \rightarrow (S',L')J'$	ν/cm^{-1}	A_r/s^{-1}		$\sum A_r/\mathrm{s}^{-1}$	β	τ/ms
		A_{ed}	A_{md}			
$\rightarrow ^4I_{13/2}$	6519	77.750	43.280	121.040	1.000	8.260
$\rightarrow ^4I_{11/2}$	10256	92.960	0.000	115.530	80.470	8.660
$\rightarrow ^4I_{9/2}$	3609	11.470	11.100		19.530	
$\rightarrow ^4F_{9/2}$	12516	78.780	0.000	103.730	75.950	9.640
$\rightarrow ^4S_{3/2}$	5768	22.860	0.000		22.040	
$\rightarrow ^2H_{11/2}$	2159	0.000	2.084		2.010	
$\rightarrow ^4F_{7/2}$	15361	821.000	0.000	1051.500	78.080	0.950
$\rightarrow ^4F_{5/2}$	8635	47.630	0.000		4.530	
$\rightarrow ^4F_{3/2}$	5036	44.540	0.000		4.240	
$\rightarrow ^2H_{9/2}$	2867	3.294	135.000		13.150	
$\rightarrow ^4G_{11/2}$	18353	224.700	0.000	361.940	62.080	2.760
$\rightarrow ^4G_{9/2}$	11852	105.400	0.000		29.110	

3.2. Fluorescence spectrum

Figure 2 shows the Er^{3+}/Yb^{3+} co-doped fluorescence spectra. It can be seen from Fig. 2 that the fluorescence intensity enlarged when the Er^{3+} concentration increased from 0.5 mol% to 1.0 mol%. This is mainly due to the increasing Er^{3+} on $^4I_{13/2}$. Accordingly, the Er^{3+}-involved in fluorescence emission in 1.53 μm will grow. However, when the Er^{3+} concentration is increased from 1.0 mol% to 2.0 mol%, the fluorescence intensity is reduced drastically. This is mainly attributed to several reasons, such as (i) the Er^{3+} concentration is increased; (ii) the interaction between rare earth ions is enhanced; (iii) the non-radiative transition probabilities are increased; (iv) the concentration quenching effect occurrs. The full width at half maximum (FWHM) at peak 1532 nm is about 68 nm, which is much larger than that ever reported, for example, silicate glass (40 nm) and phosphate glass (37 nm).[18,19] These results represent a significant step toward the application of broadband fiber amplifier.

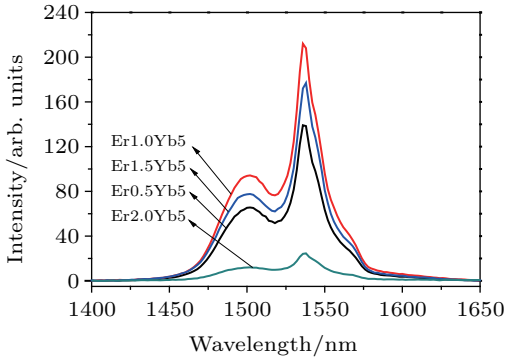


Fig. 2. (colour online) The fluorescence spectra of the Er^{3+}/Yb^{3+} co-doped fluoride phosphate.

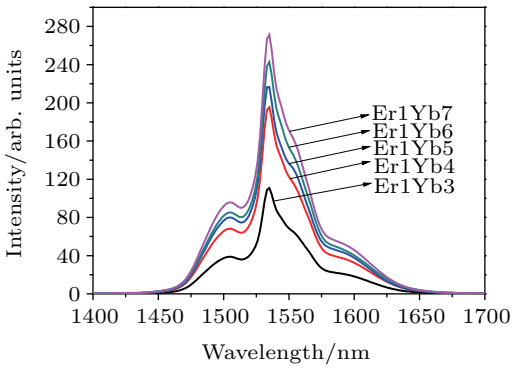


Fig. 3. (colour online) The fluorescence spectra of the Er^{3+}/Yb^{3+} with different Yb^{3+} ion concentrations.

Due to the fact that the maximal fluorescence intensity with the Er^{3+} content is about 1.0 mol%, the Er^{3+} concentration is a constant 1.0 mol% and Yb^{3+} concentration is considered as a variable quantity. Figure 3 shows the dependence of Er^{3+} fluorescence intensity of the fluoride phosphate glass on the Er^{3+} concentration. The 980-nm LD was used as the excited source. It can be seen from Fig. 3 that, the fluorescence effect of fluorophosphate glasses strengthens gradually with the increasing of Yb^{3+} content. This was attributed to Yb^{3+}:$^2F_{5/2}$ + Er^{3+}:$^4I_{15/2}$ = Yb^{3+}:$^2F_{7/2}$ + Er^{3+}:$^4I_{11/2}$, and the transformation of energy will result in the increasing number of particles on $^4I_{11/2}$. Partly due to the instability of $^4I_{11/2}$, and rapid transition to $^4I_{13/2}$, these will result in enhancing the number of Er^{3+}, which is related to the emission intensity located at 1.53-μm wavelength.

According to the McCumber[20] theory, the emission cross section of $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition can be obtained by the absorption cross section of $^4I_{15/2} \rightarrow ^4I_{13/2}$ transition, such as the following type

$$\sigma_e(\lambda) = \sigma_a(\lambda) \exp[(\varepsilon - h\nu)/kT], \tag{11}$$

where $\sigma_\alpha(\lambda)$ is the absorption cross section, it can be calculated by,

$$\sigma_a(\lambda) = \frac{2.303}{N_0 l} \lg(I_0/I), \tag{12}$$

where $\lg(I_0/I)$ is the optical density, L is the sample thickness, N_0 is the doping concentration of rare earth, h is the Planck constant, ν is the laser emission frequency, k is the Boltzmann constant, T is the test temperature of the sample, and ε is the average transition energy from $^4I_{15/2}$ to $^4I_{13/2}$. We calculated Er1Yb5 by the McCumber theory and the stimulated emission cross section of the main peak of 1.53 μm was obtained to be $\sigma_e = 0.83 \times 10^{-20}$ cm^2.

Table 4. σ_e, FWHM, and FWHM $\times\sigma_e$ of $I_{15/2} \rightarrow ^4I_{13/2}$ transition with Er^{3+} in different glass matrixes.

Glass	$10^{21}\sigma_e$/cm^2	FWHM/nm	10^{21} FWHM$\times\sigma_e$ /(cm$^2\times$nm)
Silicate	5.50	40.00	220.00[18]
Phosphate	6.40	37.00	236.80[19]
Fluorophosphate (this article)	8.30	68.00	578.00

The FWHM of the fluorescence emission and the stimulated emission cross section are two very important parameters for fiber amplifier realizing broadband and high gain amplification. Usually by using the product of FWHM $\times\sigma_e$ to measure the amplification

character of fiber amplifier gain medium, which may be enlarged by improving the two parameters as mentioned above.[21,22] Table 4 shows the stimulated emission cross section and fluorescence FWHM of the different glass substrates. Er^{3+}-doped fluorophosphate glasses in this paper have a large σ_e and FWHM values. The FWHM $\times\sigma_e$ is greater than that of silicate and phosphate, which is very beneficial for the optical fiber amplifier to realize amplification.

4. Conclusions

In this paper, we investigated spectral properties of the fluorophosphate glass doped with Er^{3+}/Yb^{3+}. The fluorescence intensity increased firstly and then decreased with the increasing Er^{3+} concentration. When the Yb^{3+} concentration was changed from 3 mol% to 7 mol%, the fluorescence intensity has been increased, and the optimum doping concentration is Er^{3+} = 1.0 mol% and Yb^{3+} = 7.0 mol% repectively. According to the Judd–Ofelt theory, the spectral parameters of the fluorophosphate glass such as the transition oscillator strength, strength parameters, the spontaneous transition probability, fluorescence molecular ratio, and the stimulated emission cross section were all studied. The FWHM of the emission peak from Er^{3+4} $I_{13/2}$ $\rightarrow{}^4I_{15/2}$ is 68 nm. The fluorescence lifetime of the energy level is 8.23 ms. The strength parameters are $\Omega_2 = 4.35 \times 10^{-20}$ cm^2, $\Omega_4 = 1.34 \times 10^{-20}$ cm^2, $\Omega_6 = 0.78 \times 10^{-20}$ cm^2, and the stimulated emission cross section near the peak 1.53 μm is 0.83×10^{-20} cm^2. The properties of Er^{3+} are compared in different glass substrates. These results indicate that the glass has a wide FWHM of the fluorescence and larger stimulated emission cross section. The product of FWHM $\times\sigma_e$ was larger than that of erbium-doped silicate glass and phosphate glass, and the glass is a kind of ideal dielectric material for high gain erbium-doped fiber amplifier.

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