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# Optical properties of Er<sup>3+</sup>/Yb<sup>3+</sup> co-doped phosphate glass system for NIR lasers and fiber amplifiers



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## ARTICLE INFO

### Keywords:

Phosphate glass  
Rare earth doping  
Optical properties  
Judd-Ofelt parameters

## ABSTRACT

In this research, the optical properties of Er<sup>3+</sup>/Yb<sup>3+</sup> co-doped phosphate glass have been studied to explore the potential of this glass system in laser and electronic amplifiers. The Judd-Ofelt (J-O) intensity parameter ( $\Omega_2$ ) in the J-O model was established to determine the absorption intensity of the glass. The optical properties of the glass can be evaluated by various radiation parameters such as the radiative transition probabilities ( $A_{rad}$ ), stimulated emission cross sections ( $\sigma_e$ ), branching ratios ( $\beta_{JJ}$ ), maximum half-width values ( $\Delta\lambda_p$ ), and the radiation lifetime ( $\tau_{rad}$ ) of the glass. It was found that in the case of Yb<sup>3+</sup> as a sensitizer, the spectral properties of the Er<sup>3+</sup> doped glass can be maximized. The data of  $A_{rad}$ ,  $\beta_{JJ}$ ,  $\tau_{rad}$ ,  $\sigma_e$  and  $\Delta\lambda_p$  obtained by Er<sup>3+</sup>/Yb<sup>3+</sup> co-doping can find that the Er<sup>3+</sup>-doped sample undergoes <sup>4</sup>I<sub>13/2</sub>-<sup>4</sup>I<sub>15/2</sub> transition at 1.56 μm, and the stimulated emission cross section is greatly improved. The application prospects of the glass in solid near-infrared laser and electronic communication was discussed. According to the comprehensive discussion and analysis, the glass has great application potential.

## 1. Introduction

Nowadays, rare earth ion doped glasses have been widely studied due to their excellent optical properties to meet the application requirements in solid-state lasers, optical amplifiers and three-dimensional displays [1]. Recently, in order to meet the requirements for materials in optical data transmission, detection, sensing and laser technology, phosphate glass has attracted attention due to its unique properties [2]. Compared with silicate, borate and other glass hosts, phosphate glass has unique characteristics, including low melting point, high transparency, high gain density due to high solubility of lanthanide (Ln) ions, high thermal stability, low refractive index and low dispersion [3].

In rare earth ions, Er<sup>3+</sup> and Yb<sup>3+</sup> ions are more frequently focused. The emission of Er<sup>3+</sup> at 1530 nm has attracted special attention in telecommunication applications. Because it is in the third fiber optic communication window [4]. This emission is critical for information transfer in Er<sup>3+</sup> doped fiber optical amplifiers and is often used in wavelength division multiplexing networks [2]. Although in recent years the most part of the commercial fiber optical amplifiers are made of silicate glass in a communications network, it has a very narrow bandwidth emission at 1530 nm that limits its use in broadband applications. Therefore, the need to find more efficient fiber amplifiers

and flat gain spectra led to explore more new glasses. In particular, the Er<sup>3+</sup>-doped phosphate, bismuthate and tellurite glasses, which are of interest because of their large stimulated emission cross section and a wide fluorescent band at 1530 nm. Er<sup>3+</sup>-doped glass has been widely used in a variety of optical applications, particularly in the area of glass safety lasers and optical amplifiers for optical fiber communications. Yb<sup>3+</sup> ions have a strong transmission intensity in the near-infrared domain, a high quantum yield, and a relatively long fluorescence lifetime. In addition, due to the high absorption cross section of Yb<sup>3+</sup> and the energy transfer process from Yb<sup>3+</sup> to Er<sup>3+</sup> ions, Yb<sup>3+</sup>/Er<sup>3+</sup> co-doping can enhance visible light up-conversion emission [5,6]. Among various possible host materials, phosphate glasses has excellent optical properties such as wide bandwidth emission spectrum, large diameter transmission window, high gain density and low up-conversion characteristics. Therefore, a great deal of research has been done on Yb<sup>3+</sup> doped, Er<sup>3+</sup> doped and Yb<sup>3+</sup>/Er<sup>3+</sup> co-doped phosphate, borosilicate and tellurite glasses.

In this study, doping of 50P<sub>2</sub>O<sub>5</sub>-30Sb<sub>2</sub>O<sub>3</sub>-10CaO-5Al<sub>2</sub>O<sub>3</sub>-5TeO<sub>2</sub> glasses with Er<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> were performed. The main research object is the influence of Yb<sup>3+</sup> and Er<sup>3+</sup> content on the spectral properties, structure and thermal properties of phosphate glass. The purpose of doping Yb<sup>3+</sup> is to increase the absorption cross-section of the <sup>4</sup>I<sub>13/2</sub>-<sup>4</sup>I<sub>15/2</sub> transition of Er<sup>3+</sup>, and use the Judd-Ofelt (J-O) model to

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<https://doi.org/10.1016/j.ceramint.2018.09.015>

Received 25 July 2018; Received in revised form 16 August 2018; Accepted 2 September 2018

Available online 04 September 2018

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examine its applicability as a potential optical glass laser and fiber amplifier.

## 2. Experimental methods

Glass samples were prepared by high temperature melting according to the following molar ratio, single doped sample  $50\text{P}_2\text{O}_5\text{-}30\text{Sb}_2\text{O}_3\text{-}10\text{CaO-}5\text{Al}_2\text{O}_3\text{-}5\text{TeO}_2\text{-}x\text{Er}_2\text{O}_3$  ( $x = 0.25, 0.5, 0.75, 1, 2$  mol%) and co-doped sample  $50\text{P}_2\text{O}_5\text{-}30\text{Sb}_2\text{O}_3\text{-}10\text{CaO-}5\text{Al}_2\text{O}_3\text{-}5\text{TeO}_2\text{-}0.5\text{Er}_2\text{O}_3\text{-}y\text{Yb}_2\text{O}_3$  ( $y = 1, 2, 3, 4, 5$  mol%). The purity of all initial components exceeds 99.7%. All chemical reagents were ground in an agate mortar, poured into a platinum crucible, and melted at a temperature of  $1100\text{ }^\circ\text{C}$  for 1 h, then poured into a previously prepared mold, annealed, held in a furnace at  $300\text{ }^\circ\text{C}$  for 1 h, and then slowly cooled to obtain a glass sample. The resulting glass was carefully cut and polished to meet the optical measurement requirements.

Prepared glass sample was measured by X-ray diffraction (Geigerflex-Rigaku Japan) to determine the amorphous structure of the glass and the phase composition of the crystallized sample. The Archimedes method was used to determine the density of all samples. The molar volume formula is  $V_m = M/\rho$ , where  $M$  is the average molar mass of the glass and  $\rho$  is the measured glass density. A high temperature horizontal thermal dilatometer (PCY, Xiangtan Co., Ltd, China) was used to determine the coefficient of thermal expansion (CTE), glass transition temperature ( $T_g$ ) and glass softening temperature ( $T_f$ ) of the glass samples. The optical absorption spectra of glass samples were measured in the wavelength range of  $300\text{--}1900\text{ nm}$  on a spectrophotometer UV-vis (Jasco-670 Japan). The emission spectra of glass samples were taken in the wavelength range of  $1400\text{--}1750\text{ nm}$  by a fluorescence spectrometer (FLS980 Britain) transition.

## 3. Results and discussions

### 3.1. XRD

The XRD pattern of single-doped and co-doped glass (Er0.25, Er0.5, Er0.5Yb1, Er0.5Yb3, Er0.5Yb4) are displayed in Fig. 1. As shown in Fig. 1, there are "amorphous peaks" with typical glass characteristics for doped samples with different contents of  $\text{Er}_2\text{O}_3$ , and there is no tendency for any crystallization, indicating that the doping of a small amount of  $\text{Er}_2\text{O}_3$  does not cause crystallization of the glass. When the glass system is co-doped with  $\text{Yb}_2\text{O}_3$  less than 3 mol%, the glass is completely transparent. It can be seen from Fig. 1 that the glass of  $\text{Yb}_2\text{O}_3$  less than 3 mol% does not have any crystallization peak,

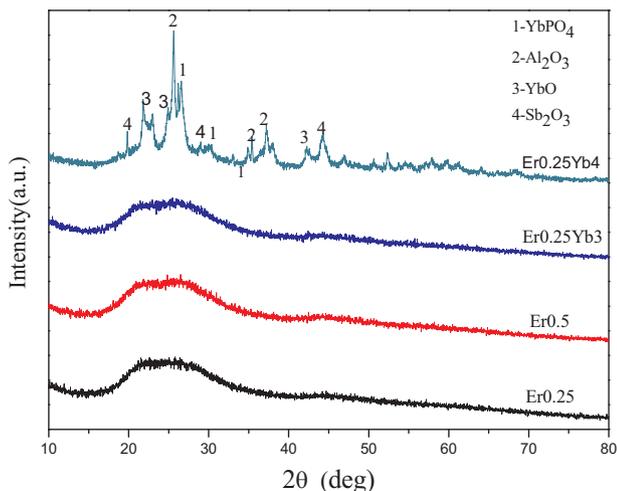


Fig. 1. X-ray diffraction patterns of Er0.25, Er0.5, Er0.5Yb1, Er0.5Yb3, Er0.5Yb4 glasses.

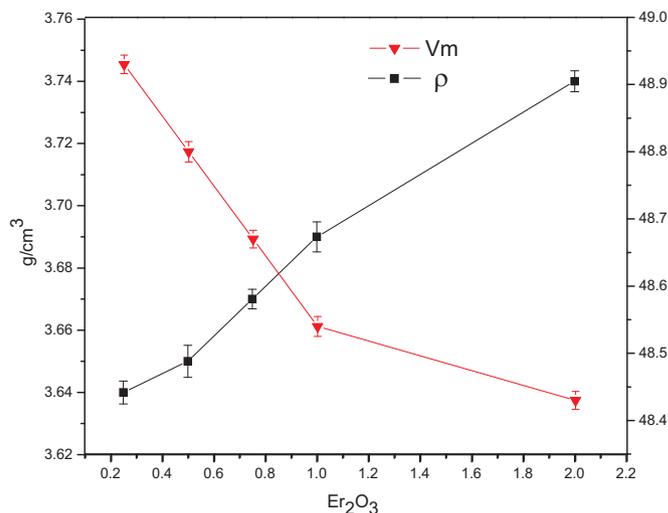


Fig. 2. The relationship of density, molar volume and composition of  $50\text{P}_2\text{O}_5\text{-}30\text{Sb}_2\text{O}_3\text{-}10\text{CaO-}5\text{Al}_2\text{O}_3\text{-}5\text{TeO}_2 + x\text{Er}_2\text{O}_3$  ( $x = 0.25, 0.5, 0.75, 1, 2$ ) glasses.

indicating that the glass is not crystallized. When the content of  $\text{Yb}_2\text{O}_3$  is 3 mol%, it can be seen that the glass is slightly milky. As can be seen from Fig. 1, the glass having a  $\text{Yb}_2\text{O}_3$  content of 3 mol% does not have any crystallization peak, indicating that the glass is stratified without crystallization. When the content of  $\text{Yb}_2\text{O}_3$  is 4 mol%, the glass is completely opaque. As can be seen from Fig. 1, the glass having a  $\text{Yb}_2\text{O}_3$  content of 4 mol% has a distinct and sharp crystallization peak, indicating that the glass begins to crystallize. These precipitated crystals are:  $\text{YbPO}_4$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{YbO}$ ,  $\text{Sb}_2\text{O}_3$ .

### 3.2. Density and thermal properties

Fig. 2 is the relationship of density, molar volume and composition of  $50\text{P}_2\text{O}_5\text{-}30\text{Sb}_2\text{O}_3\text{-}10\text{CaO-}5\text{Al}_2\text{O}_3\text{-}5\text{TeO}_2 + x\text{Er}_2\text{O}_3$  ( $x = 0.25, 0.5, 0.75, 1, 2$ ) glasses. It can be seen that the density of the glass gradually increases as the  $\text{Er}_2\text{O}_3$  content increases. Because the relative molecular mass of  $\text{Er}_2\text{O}_3$  is relatively larger, and the addition of a small amount of  $\text{Er}_2\text{O}_3$  has little effect on the glass physical characteristics, the density of the glass increases with the increase of the content of  $\text{Er}_2\text{O}_3$ . Fig. 3 is the transition temperature ( $T_g$ ), softening temperature ( $T_f$ ) and coefficient of thermal expansion (CTE) of a glass sample. As shown in Fig. 3, as the content of  $\text{Er}_2\text{O}_3$  increases, the  $T_g$  and  $T_f$  of the glass also gradually

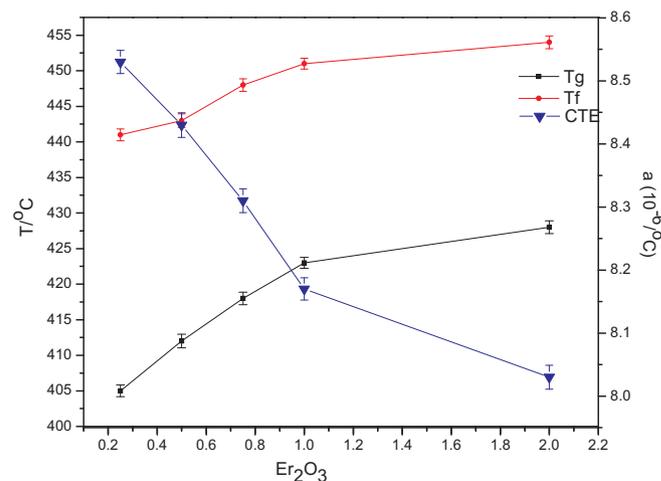


Fig. 3. The relationship of thermal properties ( $T_g$ ,  $T_f$ , CTE) and composition of erbium-glasses.

increase. The thermal properties of the material depend on the composition and structure of the glass network. When the network structure of the glass becomes tight, the  $T_g$  and  $T_f$  are increased. When the melting temperature of the components in the glass network increases,  $T_g$  and  $T_f$  also rise. When the content of  $\text{Er}_2\text{O}_3$  increases, the glass network becomes more compact, resulting in a decrease in the coefficient of thermal expansion of the glass system.  $\text{Er}_2\text{O}_3$  can be used as a glass modification, and its effects on  $T_g$ ,  $T_s$  and CTE are closely related to their field strength. The field strength ( $F$ ), the binding ability of the modified cation and the non-bridged oxygen can be calculated by  $F = Z_1 Z_2 e_2 / r_2$ , where  $Z_1$ ,  $Z_2$  represent the valence of oxygen and cation,  $e$  represents the electron charge, and  $r$  represents the cation and the distance of oxygen ions. In general, the greater the field strength, the greater the network modification.  $\text{Er}^{3+}$  has a higher field strength and its stronger binding ability to non-bridged oxygen, thereby enhancing the network strength of phosphate. Therefore, as the  $\text{Er}^{3+}$  in the composition increases, it has a higher field strength, resulting in an increase in  $T_g$ ,  $T_s$ , and a decrease in CTE.

### 3.3. FT-IR analyses

The FT-IR spectra provides information about the vibrations of various molecules and the rotation of covalent bonds in the network structure. We all know that the O/P ratio in phosphate glass has a great influence on its structure and properties. As the O/P ratio increases, the cross-linked  $\text{Q}^3$  unit phosphate network depolymerizes (O/P = 2.5) in the linear  $\text{Q}^2$  unit (O/P = 3), further depolymerizing into  $\text{Q}^1$  units (O/P = 3.5), and finally into an isolated  $\text{Q}^0$  unit (O/P = 4) [7].

Fig. 4 shows the FT-IR spectra of single-doped and co-doped glass. The FT-IR spectra indicated that the absorption peak at  $522\text{ cm}^{-1}$  is formed by the overlap of two peaks of  $480\text{ cm}^{-1}$  and  $574\text{ cm}^{-1}$ , mainly due to the vibration mode of the  $(\text{PO}_4)^{3-}$  group in the  $\text{Q}^0$  unit and bending vibration of the O–P–O bond in the  $\text{Q}^1$  unit [8]. The peak at  $745\text{ cm}^{-1}$  is attributed to the symmetric stretching vibration of P–O–P bond [9], and the peak at  $914\text{ cm}^{-1}$  is attributed to the asymmetric stretching vibration of the P–O–P bond [10]. There is a wide and large band at  $1040\text{ cm}^{-1}$  due to the stretching vibration of the P–O tetrahedron. In addition, the peak at  $1144\text{ cm}^{-1}$  is attributed to the anti-symmetric stretching vibration of the O–P–O bond in the  $\text{Q}^1$  unit. The band at  $1385\text{ cm}^{-1}$  is considered to be a symmetric stretching vibration of the P=O bond. The absorption peak at  $630\text{ cm}^{-1}$  is related to the presence of the P–O–Sb bond [11]. The position of the peak indicates the structural environment around the chemical bond. It can be seen from Fig. 4, there is no significant change in the position and intensity of the peaks with the change of  $\text{Er}_2\text{O}_3$  and  $\text{Yb}_2\text{O}_3$  content, which indicates that  $\text{Er}_2\text{O}_3$  and  $\text{Yb}_2\text{O}_3$  do not significantly affect the structure of the glass or the structure changes very small due to too little doping

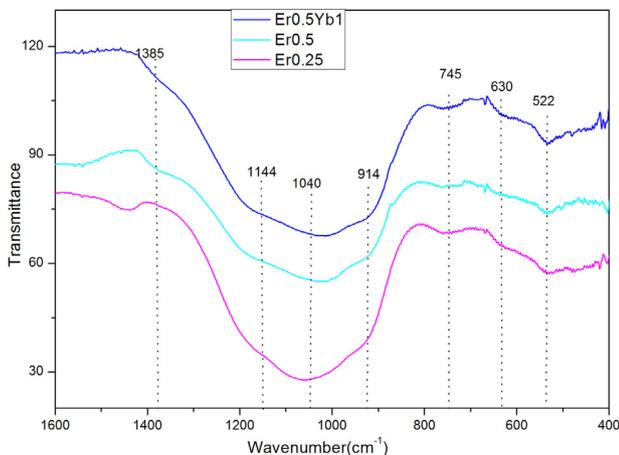


Fig. 4. The FT-IR spectra of Er0.25, Er0.5 and Er0.5Yb1 glasses.

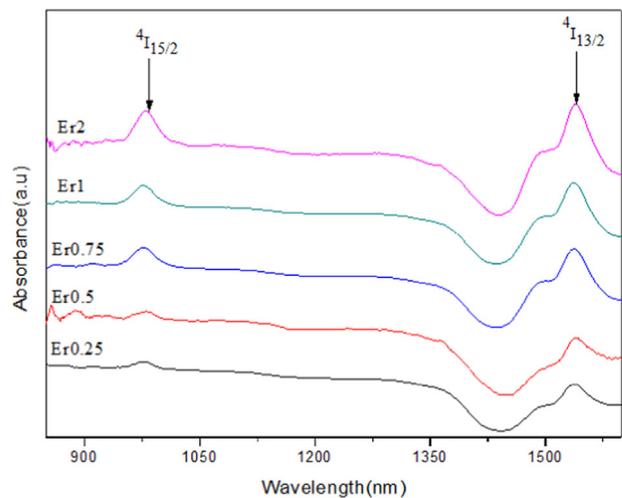
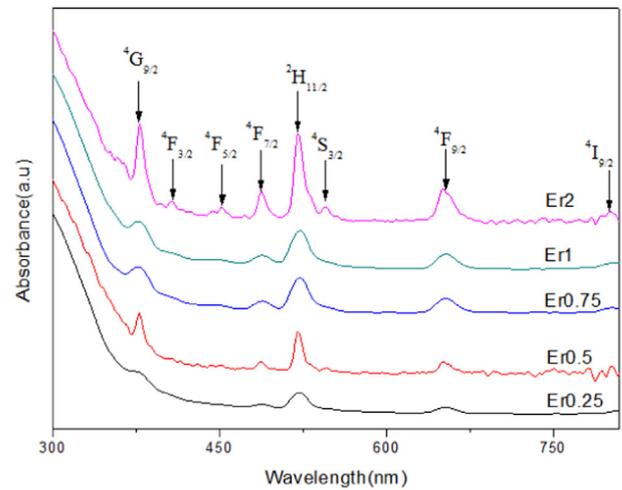


Fig. 5. Absorption spectra of  $\text{Er}^{3+}$  single doped phosphate glasses.

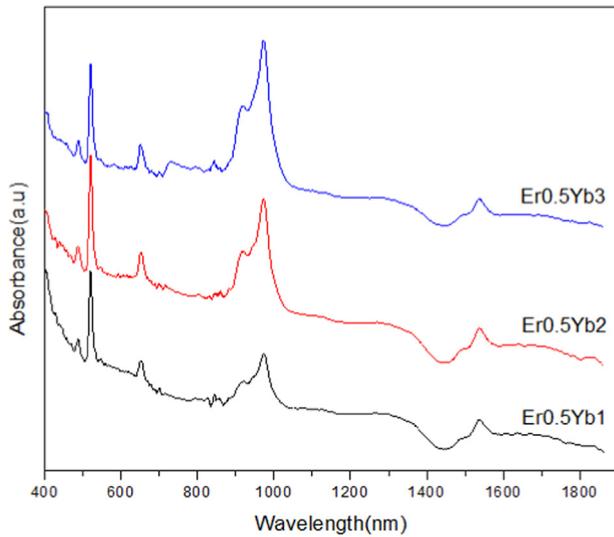
amount of rare earth.

### 3.4. Absorption spectra

Fig. 5 shows the optical absorption spectra of a single doped  $\text{Er}^{3+}$  phosphate glass containing 10 absorption peaks at 1537, 976, 797, 651, 541, 520, 487, 450, 406 and 370 nm, respectively. Corresponding absorption from the ground state  $^4\text{I}_{15/2}$  to the excited state  $^4\text{I}_{13/2}$ ,  $^4\text{I}_{11/2}$ ,  $^4\text{I}_{9/2}$ ,  $^4\text{F}_{9/2}$ ,  $^4\text{S}_{3/2}$ ,  $^4\text{H}_{11/2}$ ,  $^4\text{F}_{7/2}$ ,  $^4\text{F}_{5/2}$ ,  $^4\text{H}_{9/2}$  and  $^4\text{G}_{11/2}$ , as shown in Fig. 5. It is found that all the absorption bands are the same for  $\text{Er}^{3+}$  single-doped and  $\text{Yb}^{3+}/\text{Er}^{3+}$  co-doped glass except for some differences in the spectral bands. It can be seen from Fig. 6,  $\text{Yb}^{3+}/\text{Er}^{3+}$  co-doped phosphate glass has broad and strong absorption of  $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$  at 976 nm, due to the large spectral overlap between  $\text{Er}^{3+}$  absorption ( $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ ) and  $\text{Yb}^{3+}$  emission ( $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ ), so it has a strong absorption coefficient.

The J-O intensity parameter can be obtained by analyzing the absorption spectrum to predict the radiative transition probabilities, branching ratios, and radiation lifetimes for different transitions. Particularly, the value of the ground state to  $^4\text{I}_{13/2}$  (1.55  $\mu\text{m}$ ) can be predicted using the Judd-Ofelt model. The absorption band within the experimental area determines the measured intensity of the absorption line of the induced dipole transitions in each band. The experimental line strength  $S_{\text{exp}}$  can be expressed by the following formula (1) [12]:

$$S_{\text{exp}}(J \rightarrow J') = \frac{3ch(2J+1)}{8\pi^3\lambda e^2 N_0} \left[ \frac{9n}{(n^2+2)^2} \right] \int a(\lambda) d\lambda \quad (1)$$



**Fig. 6.** Absorption spectra of 50P<sub>2</sub>O<sub>5</sub>–30Sb<sub>2</sub>O<sub>3</sub>–10CaO–5Al<sub>2</sub>O<sub>3</sub>–5TeO<sub>2</sub>–0.5Er<sub>2</sub>O<sub>3</sub> + xYb<sub>2</sub>O<sub>3</sub> (x = 1, 2, 3 mol) glasses.

where  $J$  and  $J'$  in the formula respectively are the number of initial and final states of the total angular momentum quantum, respectively.  $H$  is Planck's constant,  $C$  is the speed of light in vacuum,  $\lambda$  is the wavelength of each absorption band,  $e$  is the charge of electrons,  $N_0$  is the concentration of Er<sup>3+</sup> ions per unit volume,  $n$  is the refractive index at the relative wavelength and does not change with  $\lambda$ . The factor  $[9n/(n^2 + 2)^2]$  in the formula is the local field correction of the ions in the dielectrics,  $T = \int a(\lambda)d\lambda$  represents the integral absorption coefficient of  $\lambda$ .

The value of  $S_{exp}$  obtained by numerical integration of the shape of the absorption line was used to obtain the Judd-Ofelt parameter  $\Omega_t$ , which is fitted using experimental data using the theoretical expressions of the Judd and Ofelt (2) [13].

$$S_{cal}(J \rightarrow J') = \sum_{t=2,4,6} \Omega_t |(S, L)J||U^t|| (S', L')J'|^2 \quad (2)$$

where  $\Omega_2, \Omega_4, \Omega_6$  in the formula are the Judd-Ofelt parameter,  $||U^t||$  ( $t = 2, 4$  and  $6$ ) represents the bi-matrix of the unit tensor operator, which is derived from the state-characteristic quantum numbers ( $S, L, J$ ) and ( $S', L', J'$ ) intermediate coupling approximate calculations. The elements of the matrix can be easily estimated from the data in the Nielson and Koster tables, and the matrix material has no effect on it [14,15]. The  $J$  parameters show the probability of matrix transfer because they contain crystal field parameters, radial integration between configurations, and interactions between the intermediate environment and the central ions [16,17].

When the three absorption peaks overlap, the square matrix element is summed from the matched square matrix elements in Table 1.

The average wavelength values of Er/Yb (0.5/0) and Er/Yb (0.5/1) glasses, The experimental line strengths ( $S_{exp}$ ) and the calculated line strengths ( $S_{cal}$ ) are shown in Table 2. The J-O strength parameter  $\Omega_t$  ( $t = 2, 4, 6$ ) is obtained using the least squares method by assuming  $S_{exp} = S_{cal}$ . The calculated line strengths can be evaluated by the root mean

**Table 1**  
Values of the reduced matrix elements for the absorption transitions of Er<sup>3+</sup>.

Transition from <sup>4</sup> I <sub>15/2</sub> to	(U <sup>(2)</sup> ) <sup>2</sup>	(U <sup>(4)</sup> ) <sup>2</sup>	(U <sup>(6)</sup> ) <sup>2</sup>
<sup>4</sup> I <sub>13/2</sub>	0.0195	0.1173	1.4316
<sup>4</sup> I <sub>11/2</sub>	0.0282	0.0003	0.991
<sup>4</sup> F <sub>9/2</sub>	0.0	0.5354	0.4618
<sup>4</sup> H <sub>11/2</sub>	0.7125	0.4125	0.0925
<sup>4</sup> F <sub>7/2</sub>	0.0	0.1469	0.6266

**Table 2**

Values of the average wavelengths, experimental and calculated line strengths of Er/Yb(0.5/0) and Er/Yb(0.5/1) glasses.

Transition from <sup>4</sup> I <sub>15/2</sub> to	$\lambda_{abs}$ (nm)	$S_{exp}$ (10 <sup>-20</sup> cm <sup>2</sup> )	$S_{cal}$ (10 <sup>-20</sup> cm <sup>2</sup> )
<sup>4</sup> I <sub>13/2</sub> (Er/Yb(0.5/0))	1550	2.680	3.471
<sup>4</sup> I <sub>11/2</sub>	990	0.871	0.991
<sup>4</sup> F <sub>9/2</sub>	650	2.432	2.347
<sup>4</sup> H <sub>11/2</sub>	530	4.196	4.791
<sup>4</sup> F <sub>7/2</sub>	460	2.551	1.719
		$\Delta S_{rms} = 0.85 \times 10^{-20}$	
<sup>4</sup> I <sub>13/2</sub> Er/Yb(0.5/1)	1550	3.567	3.491
<sup>4</sup> I <sub>11/2</sub>	990	1.046	2.351
<sup>4</sup> H <sub>11/2</sub>	530	4.406	4.599
<sup>4</sup> F <sub>7/2</sub>	460	1.603	1.648
<sup>4</sup> F <sub>9/2</sub>	650	2.013	1.943
		$\Delta S_{rms} = 0.74 \times 10^{-20}$	

square deviation  $\Delta S_{rms}$ , which is calculated using the following expression (3) [18]:

$$\Delta S_{rms} = [(q - p)^{-1} \sum (S_{exp} - S_{cal})^2]^{1/2} \quad (3)$$

Here  $q$  and  $p$  are the number of analysis bands and the number of parameters, respectively. Here  $p$  is 3. The  $\Delta S_{rms}$  values of Er0.5Yb0 and Er0.5Yb1 are very small, which are  $0.85 \times 10^{-20}$  and  $0.74 \times 10^{-20}$ , respectively. This indicates that the experimental line strength and the theoretical line strength fit well, and this experiment can be applied to the J-O theory.

Table 3 shows the Judd-Ofelt parameters ( $\Omega_2, \Omega_4, \Omega_6$ ) and the factor  $\chi = \Omega_4/\Omega_6$  at different Yb<sup>3+</sup> concentrations. All  $\Omega_t$  ( $t = 2, 4, 6$ ) parameters exhibit monotonic changes with low sensitivity to changes in Er<sup>3+</sup> ions. However, the concentration of Yb<sup>3+</sup> causes a significant change in the value of the  $\Omega_t$  parameter. These phenomena prove that the concentration of Yb<sup>3+</sup> affects the environment around Er<sup>3+</sup>. At same time, Table 3 shows the comparison of J-O strength parameters ( $\Omega_2, \Omega_4, \Omega_6$ ) in different glass matrices. Based on the Jacobs and Weber theory [19,20], the  $\Omega_4$  and  $\Omega_6$  parameters can be used to describe Er<sup>3+</sup> luminescence. Therefore,  $\Omega_4/\Omega_6$  can be used to represent the spectral quality factor  $\chi$ . If its parameter value is small, it indicates that the laser conversion <sup>4</sup>I<sub>13/2</sub>–<sup>4</sup>I<sub>15/2</sub> is strong. When the Er<sup>3+</sup> in the phosphate glass is 0.5 mol% and the Yb<sup>3+</sup> is 3 mol%, this parameter is 0.48. The spectral quality factors  $\chi$  are very important in predicting the various laser transition behaviors of a given organization matrix. In this work,  $\chi$  decreased as the content of rare earth ions increased. It should be noted here that the presence of Yb<sup>3+</sup> as a sensitizer reduces the quality factor. It is shown to be very important in the fluorescence kinetics of the Yb<sup>3+</sup>/Er<sup>3+</sup> co-doped system. The lower spectral quality factor indicates that the phosphate glass of this system has a promising future in rare earth-doped transparent optical glass, which can be applied to glass lasers and amplifiers.

The spectral intensity of each transition can be obtained by the calculation of the J-O intensity parameter, and then the spectral intensity is used to calculate the spontaneous transition probability ( $A_{rad}$ ), the radiation lifetime ( $\tau_{rad}$ ) and the branching ratio ( $\beta_{JJ'}$ ) of each corresponding transition. The calculation expression are as follows (4):

$$A_{rad}[J, J'] = \frac{64\pi^4 e^2}{3h(2J+1)\pi^3} \times [\chi_{ed} S_{ed} + \chi_{md} S_{md}] \quad (4)$$

**Table 3**  
Judd-Ofelt parameters of the erbium in different host materials.

Host materials	$\Omega_2$	$\Omega_4$	$\Omega_6$	$\chi = \Omega_4/\Omega_6$
Er/Yb(0.5/0)	4.98	2.53	2.15	1.18
Er/Yb(0.5/1)	4.98	1.71	2.23	0.77
Er/Yb(0.5/2)	5.13	1.32	2.16	0.61
Er/Yb(0.5/3)	5.32	0.98	2.04	0.48

The experimental line strengths are the sum of the electrical dipole transitions ( $S_{ed}$ ) and the magnetic dipole transitions ( $S_{md}$ ). In the theoretical calculation, only the electrical dipole transitions are involved, so if there is a magnetic dipole transition, then the intensity of this part should be subtracted. The formula is as follows (5) and (6):

$$S_{exp} = S_{ed} + S_{md} \tag{5}$$

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

It can be seen from the formula that if there is a magnetic dipole transition, the magnetic dipole transition strength is independent of the nature of the rare earth ion matrix, so the common magnetic dipole transition strength can be queried by the literature.

The formula for calculating the radiation lifetime ( $\tau_{rad}$ ) is as follows (7):

$$\tau_{rad} = \left\{ \sum_{S',L',J'} A_{rad} |(S, L)J; (S', L')J'| \right\}^{-1} \tag{7}$$

The fluorescence branching ratio ( $\beta_{JJ'}$ ) can be used as a useful parameter for predicting laser performance. Its expression is as follows (8):

$$\beta_{JJ'} [(S, L)J; (S', L')J'] = \frac{A [(S, L)J; (S', L')J']}{\sum_{S',L',J'} A [(S, L)J; (S', L')J']} \tag{8}$$

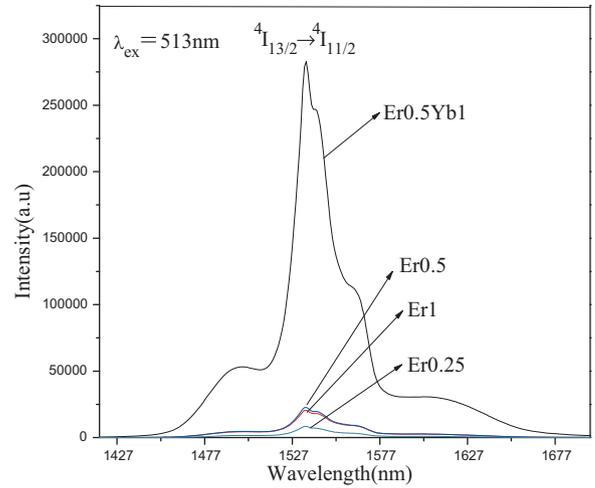
Table 4 shows the calculated values of  $A_{rad}$ ,  $\tau_{rad}$  and  $\beta_{JJ'}$  for the Er0.5 and Er0.5Yb1 doped glass samples. This indicates that the Er0.5-doped glass has a lower radiation lifetime than the Er0.5Yb1-doped glass sample, demonstrating that there is an efficient energy transfer between  $Yb^{3+}$  and  $Er^{3+}$ .

### 3.5. Emission spectra at room temperature

Fig. 7 shows the emission spectrum of the  $Er^{3+}/Yb^{3+}$  co-doped phosphate glass in the 1400–1750 nm wavelength range at 980 nm excitation. The emission spectrum shows the effect of  $Yb^{3+}$  concentration on the radiation intensity. There is a distinctly broad emission band at 1564 nm (1.56  $\mu$ m), which corresponds to the transition of the  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  energy level of  $Er^{3+}$ . When the concentration of  $Er^{3+}$  is less than 0.5 mol%, the transition intensity of  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  increases with the increase of  $Er^{3+}$ . When the concentration is greater than 0.5 mol%, the transition intensity decreases with the increase of  $Er^{3+}$  due to the photo quenching effect. The quenching of light is mutual, and non-radiative energy conversion is included in the  $Er^{3+}$  doping. This phenomenon can also be called the self-concentration quenching, because at high concentrations of  $Er^{3+}$ , the interaction is very strong due to the small ion spacing, which leads to the formation of ion clusters and non-radiative processes, thereby increasing the non-radiative rate to cause luminescence quenching [21]. In addition, the gradually increasing concentration quenching effect will result in weaker emission intensity. Fig. 7 shows that the emission intensity of the co-doped sample is much greater than the emission intensity of the

**Table 4**  
Radiative properties of  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  transitions in  $Er^{3+}$  doped and  $Er^{3+}-Yb^{3+}$  co-doped phosphate glasses.

Radiative properties	Er0.5	Er0.5Yb1
Peak emission wavelength ( $\lambda_p$ , nm)	1560	1560
Effective linewidth ( $\Delta\lambda_p$ , nm)	106	183
Radiative transition probability ( $A_{rad}$ , s <sup>-1</sup> )	152	743
Fluorescence branching ratio ( $\beta_{JJ'}$ )	1	1
Stimulated emission cross section ( $\sigma_e$ , 10 <sup>-20</sup> cm <sup>2</sup> )	0.51	2.68
Gain band width ( $\sigma_e \times \Delta\lambda_p$ , 10 <sup>-25</sup> cm <sup>3</sup> )	0.54	2.74
Optical gain parameter ( $\sigma_e \times \tau_{rad}$ , 10 <sup>-25</sup> cm <sup>2</sup> s)	186.51	271.28
Radiative lifetime ( $\tau_{rad}$ , ms)	4.62	1.24



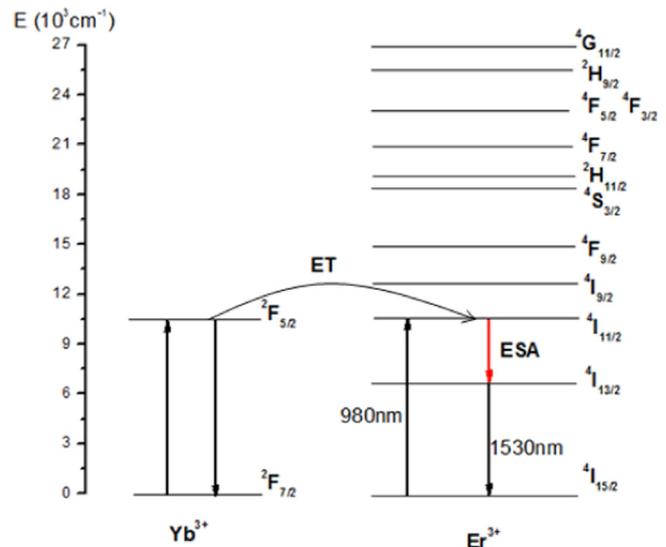
**Fig. 7.** Emission spectra of  $Er^{3+}$  doped and  $Er^{3+}/Yb^{3+}$ -codoped glasses.

single-doped sample, indicating the effective energy transfer between  $Yb^{3+}$  and  $Er^{3+}$ . Initially,  $Yb^{3+}$  excited from  ${}^2F_{7/2}$  ground state to  ${}^2F_{5/2}$  under 980 nm laser excitation. Under this condition,  $Yb^{3+}$  doping is a photosensitizer and energy transmitter for  $Er^{3+}$  in the  ${}^4I_{15/2}$  ground state. After the energy is absorbed,  $Er^{3+}$  is excited to  ${}^4I_{11/2}$ , and then the non-radiative decay [ ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$  ( $Er^{3+}$ )] occurs rapidly, causing  ${}^4I_{13/2}$  to become metastable. In addition, the  ${}^4I_{11/2}$  excited state of  $Er^{3+}$  is similar to the  $Yb^{3+}$  excited state [22,23]. The energy transfer mechanism described above is shown in Fig. 8.

These factors facilitate the energy transfer process and increase the luminescence intensity of the doped glass. Here, the J-O intensity parameter is used to determine the important radiation characteristics in the  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  transition, such as  $\lambda_p$ ,  $A_{rad}$ ,  $\sigma_e$ ,  $\Delta\lambda_p$ , and  $\beta_{JJ'}$ .

For optical fiber amplifiers, the effective bandwidth is a very important parameter. The synergistic effect of the local structure and the ions surrounding of the  $Er^{3+}$  in this glass sample is an important factor in the enlargement of the luminescent band. Normally, non-homogeneous expansion of  $Er^{3+}$  is dominant in glass. This widening of the bandwidth is due to re-absorption/self-absorption, which usually causes the absorption and emission spectra to overlap in the ternary systems [24].

The change of  $\Delta\lambda_p$  in the glass doped with different concentrations of  $Yb^{3+}$  is very significant, which proves that the change of the



**Fig. 8.** Energy level diagram of Er0.5Yb1 glass.

coordination field of  $\text{Er}^{3+}$  is affected by the doping of  $\text{Yb}^{3+}$ , resulting in the non-uniform broadening of the emission spectrum. Besides, the full width at half maximum ( $\Delta\lambda_p$ ) of the Er0.5 and Er0.5Yb1 glasses is 106 nm and 183 nm, which is very large for the application of wavelength division multiplexing (WDM). The larger  $\Delta\lambda_p$  value is extremely helpful in WDM applications [25]. For the application of the amplifier, the importance of the stimulated emission cross section in the conversion is second only to the line width. Therefore,  $\sigma_e$  and  $\Delta\lambda_p$  are extremely useful parameters in achieving bandwidth, high-gain amplification in optical amplifiers. The radiation-induced transition can be enhanced by doping with  $\text{Yb}^{3+}$ , which will significantly increase the values of  $\sigma_e$  and  $\Delta\lambda_p$ . The optical gain is evaluated by analyzing the bandwidth gain ( $\sigma_e \times \Delta\lambda_p$ ) and optical gain ( $\sigma_e \times \tau_{\text{rad}}$ ) of the optical amplifier. Large bandwidth and optical gain are required for the optical amplifier, because the energy bandwidth is lower for large bandwidths [26]. Table 4 shows the calculation of the radiation and the optical properties of the Er0.5 and Er0.5Yb1 glass samples. These values indicate that this glass can be well applied in the manufacture of fiber amplifiers because of its greater  $\tau_{\text{rad}}$ ,  $\sigma_e$ , and  $\Delta\lambda_p$  values than the reported glass [27,28]. Therefore, this glass is a good carrier for doping  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$ .

#### 4. Conclusions

Rare earth doped phosphate glasses ( $50\text{P}_2\text{O}_5\text{-}30\text{Sb}_2\text{O}_3\text{-}10\text{CaO-}5\text{Al}_2\text{O}_3\text{-}5\text{TeO}_2\text{-}x\text{Er}_2\text{O}_3\text{-}y\text{Yb}_2\text{O}_3$ ) was successfully prepared by high temperature melting method. It is found that when the glass system is doped with more than 3 mol% of  $\text{Yb}_2\text{O}_3$ , some crystals will precipitate in the glass. The Judd-Ofelt parameters of  $\Omega_t$  ( $t = 2, 4, 6$ ) are largely sensitive to the codoping of  $\text{Yb}^{3+}$ , and the spectral quality factor  $\chi$  decreases with  $\text{Yb}_2\text{O}_3$  doping. At the same time,  $\text{Yb}^{3+}/\text{Er}^{3+}$  co-doping results in an increase in the emission intensity of  ${}^4\text{I}_{13/2}\text{-}{}^4\text{I}_{15/2}$ , which showed an effective energy transfer between  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$ . The optical properties of  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped phosphate glasses were comprehensively studied and analyzed using the radiative transition probabilities ( $A_{\text{rad}}$ ), stimulated emission cross sections ( $\sigma_e$ ), branching ratios ( $\beta_{J,J'}$ ), maximum half-width values ( $\Delta\lambda_p$ ), and the radiation lifetime ( $\tau_{\text{rad}}$ ) of the glass. The comprehensive research results indicate that  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped phosphate glass has great application prospects in solid-state NIR lasers and fiber amplifiers.

#### Acknowledgments

This work was financially supported by the Priority Academic Program Development of Jiangsu Higher Education Institutions and Jiangsu Collaborative Innovation Center For Advanced Inorganic Function Composites.

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