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# Spectroscopic properties and thermal stability of $Er^{3+}/Yb^{3+}$-codoped fluorophosphate glasses*

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A comprehensive study on the thermal stability and spectroscopic properties of $Er^{3+}/Yb^{3+}$-codoped $Al(PO_3)_3$-based fluorophosphate glasses is reported of the 1.5$\mu$m fibre amplifiers in this paper. From optical absorption spectra, the Judd–Ofelt parameters of $Er^{3+}$ in the glasses and several important optical properties, such as the radiative transition probability, the branching ratio and the spontaneous emission probability, have been calculated by using Judd–Ofelt theory. The fluorophosphate glass exhibits broadband near-infrared emission at 1.53$\mu$m with a full width at half-maximum over 63nm, and a large calculated stimulated-emission cross-section of $6.85\times10^{-21}$cm$^2$.

**Keywords:** fluorophosphate glasses, Judd–Ofelt parameters, spectroscopic properties
**PACC:** 7820, 2110J, 4270C

## 1. Introduction

The rapid development of telecommunication and other data-transmitting services requires wide-band optical amplifiers and fibre laser sources. The conventional optical amplifiers in the 1.5-$\mu$m optical communication window are silica-based erbium-doped fibre amplifiers (EDFA). Although many attempts have been made on the broadening and flattening of gain spectra of silica-based EDFA in the past several years, the limitation of bandwidth and the complicated and exorbitant amplification system are still open problems in enhancing the transmission capacity.[1] Erbium-doped multi-component glasses are important active materials for 1.5-$\mu$m amplifiers and infrared(IR)-to-visible frequency converter for applications in optical telecommunications, telemetry, colour display, optical data storage, and so on.[2] Fluorophosphate (FP) glasses show relatively high thermal stability, high rare-earth (RE) ion solubility, low nonlinear refractive indices, high emission-section at around 1.5$\mu$m, and broad transmittance from the ultraviolet to the IR spectral region.[3] More recently, $Er^{3+}$-doped FP glasses containing low metaphosphate contents have demonstrated a flat gain spectrum in the range 1535–1585nm and a considerably larger laser tuning range of 1502–1606nm.[4] These special properties encourage in identifying FP glasses as attractive host materials for potential applications in high performance lasers and amplifiers.

In this paper, we report on the spectroscopic properties and thermal stability of $Er^{3+}/Yb^{3+}$-codoped $Al(PO_3)_3$-based FP glasses. The Judd–Ofelt (J-O) parameters of $Er^{3+}$ in the glasses and several important optical properties, such as the radiative transition probability, the branching ratio and the spontaneous emission probability, are calculated by using the Judd–Ofelt theory. The stimulated emission cross-section of the codoped FP glass around 1.53$\mu$m under the 977nm excitation is determined by using the McCumber theory. Frequency upconversion to the $^4F_{7/2}$ state and the $^4F_{9/2}$ state occurs simultaneously upon excitation of a 977-nm laser diode and the involved

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mechanisms are discussed.

## 2. Experimental procedure

$Al(PO_3)_3$-based FP glass samples with the composition (in mol %) of $35AlF_3$-$12RF$-$47.5MF_2$-$5Al(PO_3)_3$-$0.5ErF_{3-x}YbF_3$ ($x$=0, 0.5, 1.5, 3) (namely FPE, FPEY1, FPEY3 and FPEY6, respectively) were prepared by melting in batches of reagent-grade $RF$, $MF_2$, $AlF_3$, $Al(PO_3)_3$ ($R$=Li, Na, $M$=Mg, Ca, Sr, Ba) and rare-earth metal fluorides in an controlled atmosphere. The required amounts of batches of starting materials were melted in platinum crucibles at about 1000–1200°C for 30min in an electric furnace. The melt was cast into a preheated stainless-steel mould. After annealed at around their transition temperatures, the samples were polished and cut carefully in order to meet the requirement for spectroscopic measurements.

Absorption spectra were determined by a Perkin-Elmer Lambda-900 UV/VIS/NIR spectrophotometer in the range 350–1700nm with a resolution of 1nm. Fluorescence spectra were measured on a TRIAX320 spectrofluorimeter with 977-nm laser diode as an excitation source. Fluorescence lifetimes were measured using a modulated source and a computer-controlled digitizing oscilloscope. The densities of the glasses were measured by Archimedes' method. The $Er^{3+}$ ion concentrations were calculated from the known molar compositions and the densities of the glasses. The refractive indices of the samples were determined using a V-prism-refractometer. The glass transition temperature $T_g$ and onset crystallization temperature $T_x$ were analysed with differential thermal analyses (DTA) method on STA449/c at a heating rate of 10°C/min. All the measurements were performed at room temperature.

## 3. Results and discussion

Figure 1 illustrates the DTA curve of the $Er^{3+}/Yb^{3+}$-doped FPEY3 glass. The values of $T_x$, $T_g$, and $\Delta T = T_x - T_g$ for the glass are shown in Table 1. The glass densities, $D$, the refractive indices, $n_d$, of the $Er^{3+}$-doped FP glass (FPE) and $Er^{3+}/Yb^{3+}$-codoped FP glass were also summarized in Table 1. The difference $\Delta T$ is commonly used as a rough evaluation of the glass stability. It is desirable for a glass host to have $\Delta T$ as large as possible, because fibre drawing is a reheating process and any crystallization during the process will increase the scattering loss of the fibre and downgrade the optical properties. To the fluoride glass introducing a certain amount of metaphosphate, the value of $\Delta T$ increases from 118 to 144°C, as shown in Table 1. This indicates that the introduction of a small quantity metaphosphate into fluoride glass can significantly improve the glass stability against devitrification.

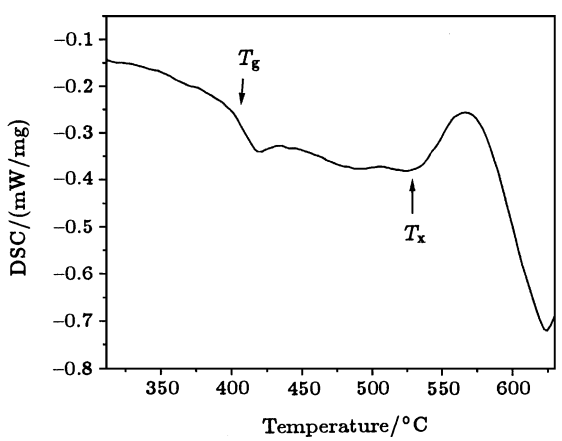



**Fig.1.** DTA curves of the FPEY3 glass.

**Table 1.** Values of $T_g$, $T_x$, and $\Delta T = T_x - T_g$ for the FPEY glass and densities, refractive indices and RE ion concentrations of two samples.

| Sample | $n_d$ | $D$/(g/cm$^3$) | $N_{Er}/10^{20}$cm$^{-3}$ | $N_{Yb}/10^{20}$cm$^{-3}$ | $Yb^{3+}/Er^{3+}$ | $T_g$ | $T_x$ | $\Delta T$ |
|---|---|---|---|---|---|---|---|---|
| FPE[thiswork] | 1.4706 | 3.52 | 1.11 | 0 | 0 | – | – | – |
| FPEY1[thiswork] | 1.4712 | 3.54 | 1.11 | 1.11 | 1 | – | – | – |
| FPEY3[thiswork] | 1.4726 | 3.63 | 1.12 | 3.36 | 3 | 389 | 533 | 144 |
| FPEY6[thiswork] | 1.4758 | 3.68 | 1.11 | 6.66 | 6 | – | – | – |
| Fluoride[5] | – | – | – | – | – | 430 | 548 | 118 |

The optical absorption spectra of the FPEY3 and FPE samples in the 350–1700 nm spectral range are presented in Fig.2. The inhomogeneously broadened bands are assigned to the transitions from the $^4I_{15/2}$ ground state to the excited states of $Er^{3+}$ ions and to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition corresponding to $Yb^{3+}$ ions. Both samples demonstrate short wavelength cutoff of 360 nm. The absorption band of $Yb^{3+}$ for the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ optical transition overlaps that of $Er^{3+}$ for the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition. Com-

pared with $Er^{3+}$, the absorption of $Yb^{3+}$ at around 980nm is predominant as shown in Fig.2. Because of the large spectral overlap between $Yb^{3+}$ emission ($^2F_{5/2} \rightarrow ^2F_{7/2}$) and $Er^{3+}$ absorption ($^4I_{15/2} \rightarrow ^4I_{11/2}$) as well as the short lifetime of $^4I_{11/2}$ state ($Er^{3+}$) in the FP glass, it is educible that a phonon-assisted energy transfer (PAET) from $Yb^{3+}$ to $Er^{3+}$ has a high efficiency in the FP glass. The PAET process can be described as: $Er^{3+}$ ($^4I_{15/2}$)+$Yb^{3+}$ ($^2F_{5/2}$) $\rightarrow$ $Er^{3+}$ ($^4I_{11/2}$)+$Yb^{3+}$ ($^2F_{7/2}$), which acts as indirect pumping of $Er^{3+}$. The PAET efficiency ($\eta$) can be expressed as: $\eta = 1-\tau_{Yb}/\tau^0_{Yb}$,[6] where $\tau_{Yb}$ and $\tau^0_{Yb}$ are the $^2F_{5/2}$ lifetimes of $Yb^{3+}$ ions with and without $Er^{3+}$ ions, respectively. Based on the measured $^2F_{5/2}$ lifetime, the highest value of the calculated PAET efficiency is 82% belonging to the FPEY3 sample in this work.

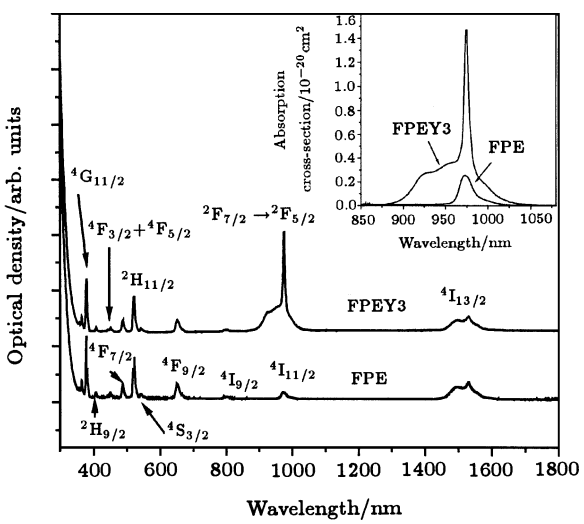



**Fig.2.** Room-temperature absorption spectra of the FPEY3 and FPE samples. Inset shows the absorption cross-sections at around 980nm of two samples.

The absorption cross-section $\sigma_{abs}$ was determined from the absorption spectrum, and is given by: $\sigma_{abs} = \frac{2.303\log(I_0/I)}{N_0 d}$, where $\log(I_0/I)$ is the optical density of the absorption spectrum, $d$ is the sample thickness and $N_0$ is the active ion concentration. The calculated absorption cross-sections of the samples with and without $Yb^{3+}$ ions in the wavelength range of 850–1100nm are illustrated in the inset of Fig.2. Obviously, the absorption cross-section of the codoped sample is much higher than that of the single-doped sample with the same $Er^{3+}$ concentrations. It can be seen that the maximum absorption cross-section of the codoped sample is 5.78 times higher than that of the single-doped sample. Higher absorption cross-section will result in better pumping efficiency and better sensitization.[7] So the $Er^{3+}/Yb^{3+}$-codoped FP glass can be pumped more efficiently than $Er^{3+}$ single-doped one by a 977-nm laser diode.

The J-O theory[8,9] is the most useful theory to estimate the probability of the forced electric-dipole (ED) transitions, the fluorescence branching ratio, and the radiative lifetime, of RE ions in various hosts. According to the J-O theory, three intensity parameters $\Omega_t s$ ($t$=2,4,6) were determined by the standard procedure described elsewhere[10] and summarized in Table 2 together with the root-mean-square $\sigma_{rms}$ values for evaluating the validity of the $\Omega_t s$. The matrix elements given by Weber[13] and Carnall *et al*[14] were employed in the calculation. The values of the $\Omega_t$ parameters are very close to the values obtained from alkaline and alkaline-earth fluorophosphate glass doped with 0.5 mol % $ErF_3$.[11]

**Table 2.** J-O parameters of $Er^{3+}$ in the investigated glasses and their root-mean-square values $\sigma_{rms}$.

| Sample | $\Omega_2/10^{-20}$cm$^2$ | $\Omega_4/10^{-20}$cm$^2$ | $\Omega_6/10^{-20}$cm$^2$ | $\sigma_{rms}/10^{-7}$ |
|---|---|---|---|---|
| FPE[thiswork] | 3.56 | 1.89 | 1.42 | 1.3 |
| FPEY1[thiswork] | 3.02 | 1.71 | 1.27 | 1.3 |
| FPEY3[thiswork] | 3.41 | 1.69 | 1.31 | 1.4 |
| FPEY6[thiswork] | 3.31 | 1.62 | 1.35 | 1.5 |
| Fluorophosphate[11] | 3.25 | 1.41 | 1.49 | 2.3 |
| Phosphate[12] | 5.02 | 1.27 | 0.92 | 2.33 |
| Aluminate[10] | 5.6 | 1.60 | 0.61 | – |
| Silicate[10] | 4.23 | 1.04 | 0.61 | – |
| Germanate[10] | 5.81 | 0.85 | 0.28 | – |

According to the J-O theory, for the transitions satisfying the selection principles $\Delta S = \Delta L$=0, $\Delta J$=0, $\pm$1, there exist the contributions of magnetic-dipole (MD) transitions. Larger relative contributions of ED transition will result in broader and flatter emission spectrum.[15] The MD line strength $S_{md}$ is independent of the ligand field and is characteristic of the transition determined by the quantum numbers.

So the ED transition related to the glass composition and structure is one of the important factors modifying the emission properties. The ED line strength $S_{ed}$ of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of $Er^{3+}$ is related with three $\Omega_t s$ and reduced matrix elements[13] by: $S_{ed}[^4I_{13/2}; {}^4I_{15/2}] = 0.0188\Omega_2 + 0.1176\Omega_4 + 1.4617\Omega_6$, the $\Omega_6$ plays the most important role in the cross-section of the 1.53-$\mu$m band among the three $\Omega_t s$. As shown in Table 2, the $\Omega_6$ values in the FP samples are obviously larger than the oxide glasses, which means the broader and flatter optical amplifying properties.

The J-O intensity parameters allow the calculation of the total spontaneous emission probability $A$, fluorescence branching ratio $\beta$ and radiative lifetimes $\tau_{rad}$ of the most important excited states of the $Er^{3+}$ ions by the procedure outlined in Ref.[16]. These are summarized in Table 3.

**Table 3.** Predicted spontaneous radiation transition rates, fluorescent branch ratios and radiative lifetimes of $Er^{3+}$ in the RE-doped FP glasses.

| Initial state | Final state | Average energy/$cm^{-1}$ | $A/s^{-1}$ | | $\beta$ | $\tau_{rad}/\mu s$ |
|---|---|---|---|---|---|---|
| | | | $A_{ed}$ | $A_{md}$ | | |
| FPE: $^4I_{13/2}$ | $^4I_{15/2}$ | 6533 | 96 | 33 | 1.00 | 7743 |
| $^4I_{11/2}$ | $^4I_{15/2}$ | 10267 | 121 | | 0.83 | |
| | $^4I_{13/2}$ | 3751 | 16 | 9.6 | 0.17 | 6809 |
| $^4I_{9/2}$ | $^4I_{15/2}$ | 12500 | 113 | | 0.74 | |
| | $^4I_{13/2}$ | 5958 | 40 | | 0.26 | 6537 |
| $^4F_{9/2}$ | $^4I_{15/2}$ | 15368 | 1281 | | 0.91 | |
| | $^4I_{13/2}$ | 8835 | 64 | | 0.05 | |
| | $^4I_{11/2}$ | 5084 | 55 | | 0.04 | |
| | $^4I_{9/2}$ | 2877 | 2 | | 0.00 | 713 |
| $^4S_{3/2}$ | $^4I_{15/2}$ | 18484 | 1046 | | 0.67 | |
| | $^4I_{13/2}$ | 11951 | 431 | | 0.28 | |
| | $^4I_{11/2}$ | 8200 | 33 | | 0.02 | |
| | $^4I_{9/2}$ | 5993 | 55 | | 0.04 | 639 |
| $^2H_{11/2}$ | $^4I_{15/2}$ | 19194 | 4105 | | | |
| FPEY3: $^4I_{13/2}$ | $^4I_{15/2}$ | 6533 | 89 | 33 | 1.00 | 8193 |
| $^4I_{11/2}$ | $^4I_{15/2}$ | 10267 | 113 | | 0.82 | |
| | $^4I_{13/2}$ | 3751 | 15 | 9.7 | 0.18 | 7279 |
| $^4I_{9/2}$ | $^4I_{15/2}$ | 12484 | 101 | | 0.73 | |
| | $^4I_{13/2}$ | 5958 | 37 | | 0.27 | 7236 |
| $^4F_{9/2}$ | $^4I_{15/2}$ | 15368 | 1164 | | 0.91 | |
| | $^4I_{13/2}$ | 8835 | 58 | | 0.05 | |
| | $^4I_{11/2}$ | 5084 | 51 | | 0.04 | |
| | $^4I_{9/2}$ | 2877 | 2 | | 0.00 | 784 |
| $^4S_{3/2}$ | $^4I_{15/2}$ | 18484 | 969 | | 0.67 | |
| | $^4I_{13/2}$ | 11951 | 399 | | 0.28 | |
| | $^4I_{11/2}$ | 8200 | 31 | | 0.02 | |
| | $^4I_{9/2}$ | 5993 | 51 | | 0.03 | 690 |
| $^2H_{11/2}$ | $^4I_{15/2}$ | 19194 | 3883 | | | |

According to the McCumber theory,[17] the stimulated emission cross-section $\sigma_{emi}$ and the absorption cross-section are related by: $\sigma_{emi} = \sigma_{abs}\exp[(\varepsilon - h\nu)/kT]$, where $\nu$ is the photon frequency, $k$ the Boltzmann constant. $\varepsilon$ is the net free energy required to excite one erbium ion from the ground state to the excited state at temperature $T$, and the value was calculated using the procedure provided by Ref.[18]. The calculated absorption and emission cross-sections of the FPEY3 glass in the wavelength range of 1420–1630nm under the 977-nm excitation are illustrated in Fig.3. Owing to Stokes shift and shape variations, it can be observed that the $\sigma_{abs}$ is larger than the $\sigma_{emi}$ for wavelengths shorter than the peak wavelength, while the reverse situation arises for wavelengths longer than the peak wavelength. And

the $\sigma^P_{emi}$ is larger than the $\sigma^P_{abs}$ at the peak wavelength. In this work, the obtained $\sigma^P_{emi}$ of the FPEY3 glass is $6.85\times10^{-21}$cm$^2$, which is much higher than that of the silicate glasses[10] and equivalent to that in the phosphate glasses and commercialized Kigre samples.[19] Figure 4 shows the fluorescence spectrum of the FPEY3 sample in the wavelength range of 1440–1650nm at 977-nm excitation. The FPEY3 sample exhibits broadband near-infrared emission at 1.5-$\mu$m with a full width at half-maximum (FWHM) over 63 nm. Larger values of the FWHM $\times\sigma_{emi}$ product imply wider gain bandwidth. In this work the $\sigma^P_{emi}$ and FWHM $\times\sigma^P_{emi}$ of the FP glasses are much higher than those of the silicate and phosphate glasses.[10,20]

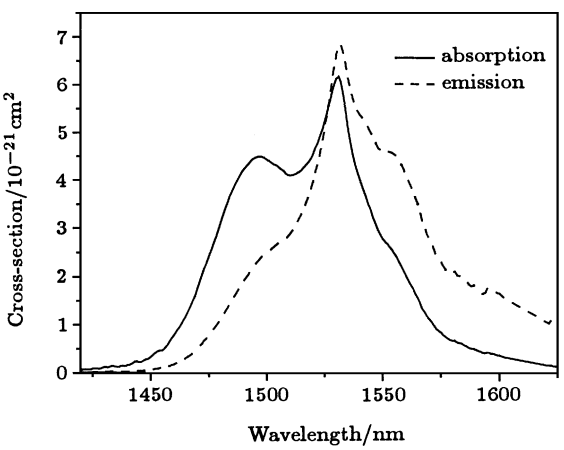



**Fig.3.** The calculated absorption cross-section, stimulated emission cross-section of the FPEY3 sample around 1.53$\mu$m at 977-nm excitation at room temperature.

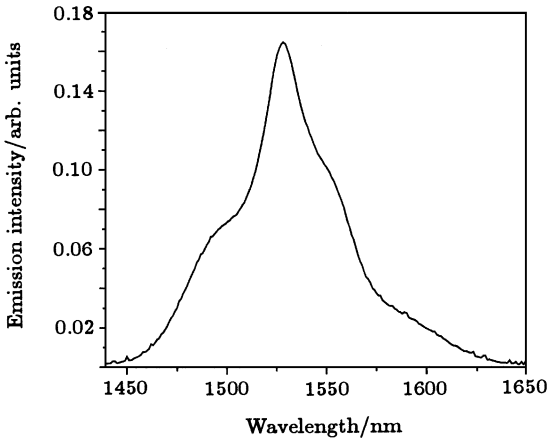



**Fig.4.** 1.53-$\mu$m emission spectrum relative to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of the FPEY3 sample at 977-nm excitation.

## 4. Conclusion

In summary, the spectroscopic properties and thermal stability of the $Er^{3+}/Yb^{3+}$-codoped $Al(PO_3)_3$-based fluorophosphate glass have been investigated. The FP glasses studied exhibit a $\Delta T$ over 100°C, indicating that the glasses are quite stable against devitrification. The $\Omega_6$ values of the FP glass samples studied are larger than that of the conventional oxide glasses, which indicates the broader and flatter 1.5-$\mu$m optical amplifying properties. The FPEY3 glass exhibits a broadband near-IR emission at 1.53$\mu$m with a FWHM over 63nm, and a large calculated stimulated-emission cross-section of $6.85\times10^{-21}$cm$^2$. This paper shows that $Er^{3+}/Yb^{3+}$-codoped fluorophosphate glasses could be promising materials for achieving high optical performance EDFA.

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