Er–Yb codoped phosphate glasses with improved gain characteristics for an efficient 1.55 μm broadband optical amplifiers

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A B S T R A C T

We have investigated the optical properties of phosphate glasses codoped with Er3+−Yb3+ as a function of Yb3+ concentration in order to evaluate their potential as both glass laser systems and amplifier materials. The results of differential scanning calorimetry (DSC) measurements indicate a good thermal stability of phosphate glasses. The Judd–Ofelt (JO) model has been applied to absorption intensities of Er3+ (4f11) transitions to establish the so-called Judd–Ofelt intensity parameters: Ω4, Ω6, Ω8. With the weak spectroscopic quality factors Ω4/Ω6 (0.38), we expect a relatively prominent Infrared laser emission. The intensity parameters are used to determine the spontaneous emission probabilities of some relevant transitions, the branching ratio and the radiative lifetimes of several excited states of Er3+ and compared to the equivalent parameters for other host glasses.

Both the IR photoluminescence (PL) intensity and the PL decay time were found to largely increase with Yb3+ concentration and the maximum quantum efficiency for the 1.55 μm emission was found to be in the order of 91%. We show that the Yb3+ acts as sensitizer for Er3+ and contributes largely to the improvement of the spectroscopic properties of phosphate glasses codoped with Er3+−Yb3+.

Using McCumber method, absorption cross-section and calculated emission cross-section, for the 4I13/2 → 4I15/2 transition, were determined and compared for the doped and codoped glasses. The phosphate glasses are promising gain media for developing the solid-state 1.55 μm optical amplifiers.

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1. Introduction

The Er3+ emission at 1.53 μm has drawn particular interest for use in telecommunication applications since it is located in the third optical communication window [1]. This emission has been essential to increasing the transmission of information in Er3+ ions introduced into a relatively small volume [3–5].

In this paper, the main object is to carry out a detailed study on effects of Yb3+ contents on the spectroscopic properties of Er3+−doped phosphate glasses in order to optimise the gain and the emission cross-section of the 4I13/2 → 4I15/2 transition of Er3+ and to examine their suitability as potential optical glasses for laser and fiber amplifiers. The Yb3+ ions were introduced into the Er3+−doped phosphate glass to improve the 1.53 μm fluorescence emission of Er3+ with the help of energy transfer from Yb3+ to Er3+ ions under the excitation of 980 nm. Absorption, emission and gain cross section of 4I13/2 → 4I15/2 transition at around 1.53 μm are obtained based on the McCumber theory and absorption spectra measurement.

2. Experimental procedure

2.1. Samples preparation

Phosphate glasses were prepared according to the following compositions:

(75 − x)NaH2PO4−20ZnO−5Li2CO3−xEr2O3 (x=0.5 mol%) for doped samples (NZLE0), (74−y) NaH2PO4−20ZnO−5Li2CO3−xEr2O3−yYb2O3...
(\(x=0.5\) mol\% and \(y=0.1\) mol\%) for co-doped samples (NZLE1 and NZLE2 samples, respectively). All the starting chemical constituents are more than 99.9% purity.

Calculated quantities of the chemical components were mixed in an agate mortar and melted in an electric furnace at 900 °C for 1 h in platinum crucibles so that a homogeneously mixed melt was obtained.

Immediately after the quench, the glass was annealed at 200 °C (for 1 h) and then slowly cooled until ambient temperature. The annealing process was made with the objective of minimizing the internal mechanical stress and obtaining glasses with good mechanical stability. The obtained glasses were cut and polished carefully in order to meet the requirements for optical measurements.

DSC scans of as-cast glass specimens were carried out in Metler Toledo DSC823e. The DSC scans were recorded using 7 mg as-cast glass specimens which were powdered in order to determine the characteristic glass transition temperatures, \(T_g\), crystallization onset, \(T_c\) and the peak crystallization temperatures, \(T_p\), and heated in a platinum crucible using the same amount of alumina powder as the reference material with the heating rates of 10 °C/min between 200 and 600 °C temperatures range. The crucibles were used were matched pairs made of platinum and the temperature precision was ± 1 °C.

X-ray diffraction (XRD) patterns was carried out at room temperature in a Philips X’Pert system, using Cu Kα radiation (\(\lambda=1.54056\) Å), at 40 kV and 100 mA and the diffractometer setting in the 2θ range from 10° to 90° by changing the 2θ with a step size of 0.02°.

2.2. Optical measurements

The optical absorption of the polished samples was obtained in the wavelength range of 200–2000 nm, at room temperature by using a Varian 5000 UV/Vis/NIR Spectrophotometer. The absorption coefficient (\(\alpha(\lambda)\)) was calculated from the relation [6]:

\[
\alpha(\lambda) = \frac{1}{d} \ln \left( \frac{I_0(\lambda)}{I(\lambda)} \right)
\]

where \(d\) represents the thickness of the glass samples and \(\ln(I_0(\lambda)/I(\lambda))\) corresponds to absorbance.

3. Data analysis

3.1. Structure behaviour and thermal stability

Fig. 1 shows XRD patterns of monodoped and codoped glasses (NZLE0, NZLE1 and NZLE2). It can be seen that the XRD patterns of the glass samples are similar and have not any sharp diffraction peak but broad humps, the characteristic of amorphous materials [7], indicating that the synthesized glass samples under investigation maintained the amorphous state behavior.

Fig. 2 shows the DSC curves of NZLE0, NZLE1 and NZLE2 glasses. From DSC curve, the characteristic temperatures such as glass transition temperature \(T_g\), crystallization onset \(T_c\) and the peak crystallization temperatures \(T_p\) were obtained. The difference, \(\Delta T=T_p-T_g\), has been frequently used as a rough estimate of the glass stability. To achieve a large working range during operation such as fiber drawing, it is desirable to have \((T_p-T_g)\) value as large as possible [7]. The larger the \(\Delta T\), the smaller the loss of drawing fiber is [8]. The results of thermal parameters, for NZLE0, NZLE1 and NZLE2 samples, are presented in Table 1.

As shown in Table 1, both the values of \(T_g\) and the thermal stability \(\Delta T\) increase after adding \(\text{Yb}^{3+}\). It can indicate that the incorporation of \(\text{Yb}_2\text{O}_3\) into glass structure strengthens the glass network and prevents it from devitrification.

Table 1: Thermal parameters of NZLE0, NZLE1 and NZLE2 glasses.

<table>
<thead>
<tr>
<th>Samples</th>
<th>(T_g) (°C)</th>
<th>(T_c) (°C)</th>
<th>(\Delta T = T_p - T_g) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZLE0</td>
<td>271</td>
<td>427</td>
<td>156</td>
</tr>
<tr>
<td>NZLE1</td>
<td>281</td>
<td>455</td>
<td>174</td>
</tr>
<tr>
<td>NZLE2</td>
<td>290</td>
<td>473</td>
<td>183</td>
</tr>
</tbody>
</table>

3.2. Judd–Ofelt parameters

Optical absorption spectra of \(\text{Er}^{3+}\)-doped and \(\text{Er}^{3+}, \text{Yb}^{3+}\)-codoped in phosphate glass consists of 10 absorption bands peaked at 1550, 950, 790, 650, 540, 530, 490, 460, 420, and 390 nm, corresponding to the absorptions from the ground state \(^{4}I_{15/2}\) to the excited states \(^{4}I_{13/2}, ^{2}F_{5/2}, ^{2}H_{11/2}, ^{2}F_{7/2}, ^{4}F_{3/2}, ^{4}F_{5/2}, ^{4}F_{7/2}, ^{4}S_{3/2}\), and \(^2G_{9/2}\), respectively (Fig. 3 shows the optical absorption spectrum of NZLE0).

The data from the absorption spectra can be used to predict the radiative transition probabilities, the branching ratio and the radiative lifetime of different transitions, in particular from \(^{4}I_{13/2}\) to the ground state (1.55 μm) by using the Judd–Ofelt (J.O.) model. The measured absorption line strength \((S_{\text{meas}})\) for the induced
electric dipole transition of each band was determined experimentally from the area under the absorption band and can be expressed in terms of absorption coefficient α by the equation [9]:

$$S_{\text{meas}}(J \rightarrow J') = \frac{3 \chi(2l + 1) \cdot 9m}{8\pi^2 \hbar^3 N_0 (n^2 + 2)^2} \int (\alpha(\lambda) d\lambda.$$  

(2)

here, $J$ and $J'$ denote the total angular momentum quantum number of the initial and final states, respectively, $e$ is the charge of the electron, $c$ the velocity of the light in the vacuum, $h$ the Planck constant, $\lambda$ is the mean wavelength of the absorption band, $\lambda' = \alpha(\lambda) d\lambda$ is the integrated absorption coefficient as a function of $\lambda$, $N_0$ is the Er$^{3+}$ ion concentration per unit volume and $n$ is the measured refractive index. The refractive index $n$ of phosphate glasses is about 1.31 and is supposed practically unchanged with $\lambda$ [10].

The factor $9/(n^2 + 2)^2$ in Eq. (2) represents the local field correction for the ion in the dielectric host medium, $e$ is the charge of the electron.

The values of $S_{\text{meas}}$ obtained by the numerical integration of the absorption line shapes were used to obtain the phenomenological Judd–Ofelt parameters $\Omega_i$ by fitting the experimental value with the theoretical expression derived by Judd and Ofelt [9]:

$$S_{\text{cal}}(J \rightarrow J') = \sum_{i=2,4,6} \Omega_i \langle \langle S, L | J' \mid U^{(i)} \mid (S', L') J' \rangle \rangle^2.$$  

(3)

where $\Omega_2$, $\Omega_4$ and $\Omega_6$ are the Judd–Ofelt parameters and $\langle U^{(i)} \rangle$ the doubly reduced matrix elements of the unit tensor operator of rank $i = 2, 4$ and 6 which are calculated from the intermediate coupling approximation between states characterized by the quantum numbers $(S, L, J)$ and $(S', L', J')$. The matrix elements are independent of the host material and can be easily calculated from the tables of Nielson and Koster [11]. The JO parameters, however, exhibit the influence of the host on the transition probabilities since they contain the crystal-field parameters, interconfigurational radial integrals, and the interaction between the central ion and the intermediate environment.

We have used the values of the reduced matrix elements for the chosen Er$^{3+}$ bands calculated by Carnall et al. [12].

When three absorption manifolds overlapped, the squared matrix element was taken to be the sum of the corresponding squared matrix elements and tabulated in Table 2 [12].

The values of average wavelength, integrated absorption coefficients, measured ($S_{\text{meas}}$) and calculated ($S_{\text{cal}}$) absorption line strengths for absorption transition of NZLEO are presented in Table 3.

Judd–Ofelt intensity parameters $\Omega_i$ were derived from the electric-dipole contributions of the experimental oscillator strengths using a least-square fitting approach.

The root-mean-square deviation $\Delta S_{\text{rms}}$ between the measured ($S_{\text{meas}}$) and the calculated ($S_{\text{cal}}$) oscillator strengths can be calculated based on the following relationship:

$$\Delta S_{\text{rms}} = \left[ \left(q - p \right)^{-1} \sum (S_{\text{meas}} - S_{\text{cal}})^2 \right]^{1/2}.$$  

(4)

where $q$ is the number of analysed spectral bands, and $p$ is the number of the parameters sought, which in this case are three. The calculated values of $\Delta S_{\text{rms}}$ are 0.88 × 10$^{-20}$, 0.68 × 10$^{-20}$ and 0.45 × 10$^{-20}$ cm$^2$ for Er$^{3+}$ (0.5 mol%), Er$^{3+}$/Yb$^{3+}$ (0.5/0.5 mol%) and (0.5/1 mol%), respectively. The JO intensity parameters obtained are listed in Table 4.

Table 4 shows comparisons of the Judd–Ofelt intensity parameters, $\Omega_i$ ($i = 2, 4, 6$) in various glass hosts. According to previous studies [13], $\Omega_2$ is related with the symmetry of ligand field in the glass host while $\Omega_6$ is inversely proportional to the covalency of Er–O bond. The $\Omega_6$ values of phosphate glasses are in the order that of those of other glasses. It should be mentioned here that the $\Omega_6$ values in phosphate glasses are almost nearly than those in PME19 [14], PBNEY1 [15], TZNY1 [16] glass hosts, which indicate the broader and flatter optical amplifier properties.

Fig. 4 shows the variations of the parameters of Judd ($\Omega_2$, $\Omega_4$, $\Omega_6$) together with the factor $\chi = \Omega_2/\Omega_6$, for different concentrations of Yb. All $\Omega_i$ parameters showed a monotonic variation suggesting low sensitivity to the environmental change of Er$^{3+}$ ion. Although the presence of Yb$^{3+}$ ions induce an important change in the values of $\Omega_i$ parameters. These changes indicate that the presence of Yb$^{3+}$ disturbs the environment around the Er$^{3+}$ ion.

The large variation in $\Omega_2$ indicates that this parameter is rather more sensitive to the environment than the other two parameters ($\Omega_4$ and $\Omega_6$). The higher $\Omega_2$ value, obtained for a concentration of 0.5 Er$^{3+}$/1Yb$^{3+}$, is indicative of high covalent bonding resulting from the relatively important doping level [17].

According to Jacobs and Weber theory [18], the erbium emission intensity could be characterized uniquely by $\Omega_2$ and $\Omega_4$ parameters. Thus, we use the so-called spectroscopic quality factor $\chi$, defined us $\chi = \Omega_2/\Omega_4$. The smaller this parameter value, the more intense the laser transition $^4I_{15/2} \rightarrow ^4I_{13/2}$ is. For Er$^{3+}$ in Phosphate glasses, this parameter is estimated to 0.38 [14] which indicate that the last transition is more efficient than in other host glasses (Table 4).

The spectroscopic quality factor $\chi$ is important in predicting the behavior of various lasing transitions in a given matrix. In this work, $\chi$ shows a decreasing tendency with the increment of the rare earth ion content. It should be noted that the presence of Yb$^{3+}$ ion as sensitizer reduces the quality factor indicating its important role in the fluorescence dynamics of the Yb$^{3+}$–Er$^{3+}$ co-doped systems [19]. This indicates that NZL glass is a promising host in the development of REs-doped transparent conducting glasses for laser and amplifier applications.
Table 3
Values of the average wavelengths, integrated absorption coefficients, experimental and calculated line strengths of NZLE glass.

<table>
<thead>
<tr>
<th>Transition from</th>
<th>λabs (nm)</th>
<th>f' (cm⁻¹)</th>
<th>Strengths</th>
<th>Scalc (10⁻²⁰ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4I₁₃/₂ to 4I₁₅/₂</td>
<td>1550</td>
<td>255.43</td>
<td>3.184</td>
<td>3.992</td>
</tr>
<tr>
<td>4I₁₁/₂</td>
<td>990</td>
<td>65.24</td>
<td>1.273</td>
<td>1.128</td>
</tr>
<tr>
<td>4F₁₀/₂</td>
<td>790</td>
<td>15.79</td>
<td>0.386</td>
<td>0.366</td>
</tr>
<tr>
<td>4F₉/₂</td>
<td>650</td>
<td>70.66</td>
<td>2.100</td>
<td>2.242</td>
</tr>
<tr>
<td>4F₉/₂</td>
<td>540</td>
<td>60.24</td>
<td>2.156</td>
<td>0.569</td>
</tr>
<tr>
<td>4H₁₁/₂</td>
<td>530</td>
<td>105.81</td>
<td>3.857</td>
<td>3.842</td>
</tr>
<tr>
<td>4F₇/₂</td>
<td>490</td>
<td>72.40</td>
<td>2.855</td>
<td>1.902</td>
</tr>
<tr>
<td>4F₇/₂</td>
<td>460</td>
<td>7.18</td>
<td>0.301</td>
<td>0.574</td>
</tr>
<tr>
<td>4F₅/₂</td>
<td>420</td>
<td>11.48</td>
<td>0.538</td>
<td>0.327</td>
</tr>
<tr>
<td>2G₂/₃</td>
<td>390</td>
<td>35.04</td>
<td>1.736</td>
<td>0.617</td>
</tr>
</tbody>
</table>

Table 4
Judd–Olfet parameters of the erbium in different host materials.

<table>
<thead>
<tr>
<th>Host materials</th>
<th>Ω₂ (10⁻²⁰ cm²)</th>
<th>Ω₄ (10⁻²⁰ cm²)</th>
<th>Ω₆ (10⁻²⁰ cm²)</th>
<th>Ω₂/Ω₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>PME19 [14]</td>
<td>5.29</td>
<td>0.53</td>
<td>1.36</td>
<td>0.38</td>
</tr>
<tr>
<td>PRNVEY [15]</td>
<td>3.2</td>
<td>2.68</td>
<td>6.54</td>
<td>0.41</td>
</tr>
<tr>
<td>T2N1Y [16]</td>
<td>5.08</td>
<td>0.97</td>
<td>1.26</td>
<td>0.77</td>
</tr>
<tr>
<td>Present work</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NZLE0</td>
<td>3.91</td>
<td>1.97</td>
<td>2.57</td>
<td>0.76</td>
</tr>
<tr>
<td>NZLE1</td>
<td>4.31</td>
<td>1.13</td>
<td>2.21</td>
<td>0.51</td>
</tr>
<tr>
<td>NZLE2</td>
<td>5.48</td>
<td>0.88</td>
<td>2.27</td>
<td>0.38</td>
</tr>
</tbody>
</table>

The emission peak position is related to the covalence degree of the Er³⁺–ligand bonds in the matrix. The more covalent these bonds, the weaker the electron–electron interaction in the 4f shell and the lower the transition energy [16]. Based on the above mentioned arguments, the obtained value of the 4I₁₃/₂ → 4I₁₅/₂ emission peak wavelength at 1.55 µm suggests that in this matrix, the Er³⁺ ion interacts strongly with its ligands. The J.O. parameters can now be applied to Eq. (3) to calculate the emission line strengths corresponding to the transitions from the upper manifold states, 4I₁₃/₂, 4I₁₁/₂, 4F₉/₂, 4S₃/₂ and 4H₁₁/₂, to their corresponding lower-lying manifold states. Using these line strengths, the radiative lifetime (τᵣ) for transitions between an excited state and the total spontaneous transition probability, Aᵣ(→f), can be calculated using the following expression [19]:

\[ Aᵣ(→f) = Aₑd + A_md = \frac{64π²r_e^2}{3h(2J+1)\lambda^2} \left[ \frac{n(n^2+2)²}{9}Sₑd + n³S_md \right] \] (5)

where Aₑd and A_md are the electric-dipole and magnetic-dipole spontaneous emission probabilities, respectively. The electric-dipole line strength, Sₑd, is calculated using Eq. (2) and presents a host dependence through the Ω₂ parameters. The magnetic-dipole line strength, S_md, can be calculated with the expression:

\[ S_md = \frac{\hbar²}{16π²r_e^2c²} |\langle S, L_y | L + 2S | S', L_y' \rangle|^² \] (6)

where |⟨S, L_y | L + 2S | S', L_y'⟩|^² are the reduced matrix elements of the operator L + 2S.

In this work, the values of A_md were calculated using the values for LaF₃ (Aₐ(βₐ)) and corrected for the refractive index difference [20]. The relationship is:

\[ A_md = \left( \frac{n}{n'} \right)^{-3} Aₐ(βₐ) \] (7)

where n and n’ are the refractive indices of erbium doped NZL and LaF₃, respectively. The radiative lifetime τᵣ of an emitting state is related to the total spontaneous transition probability for all transitions from this state by:

\[ τᵣ = \frac{1}{\sum Aᵣ(→f)} \] (8)

The fluorescence branching ratio characterize the possibility to attain stimulated emission from any specific transition and shows a host dependence trough the Ω₂ parameters.

The fluorescence branching ratios, β (→f), can be determined from the radiative decay rates by:

\[ β(→f) = \frac{Aᵣ(→f)}{\sum Aᵣ(→f)} = \frac{Aᵣ(→f)}{τᵣ} \] (9)

where the sum runs over all final states f. The luminescence branching ratio is a critical parameter to the laser designer, because it characterises the possibility of attaining stimulated emission from any specific transition. Table 5 shows the values of theoretically computed total spontaneous transition probability (A tot), fluorescence branching ratio (βₐ) and radiative lifetime (τᵣ) of various excited states of Er³⁺ in the present glassy system.

3.3. PL spectra, PL lifetimes and quantum efficiencies

The room temperature photoluminescence (PL) spectra were recorded for all the samples and are shown in Fig. 5. The emission spectra consist of the characteristic bands originated from the 4I₁₃/₂ meta-stable level to the terminal 4I₁₅/₂ and peak at 1.55 µm. The intensity of the 1.55 µm emission increases with increasing Yb³⁺ concentration in this glass (Fig. 5). The PL spectra illustrate the well-known sensitizing effect of Yb³⁺ on Er-emission intensity [21,22]. Both effects are dependent on electronic interactions between the rare earth ions.

The luminescence decay curves of the 4I₁₃/₂ → 4I₁₅/₂ transition in the Er³⁺ and Er³⁺/Yb³⁺ co-doped NZL glasses, under 976 nm excitation wavelength, have been measured at room temperature to evaluate the quantum efficiency (Fig. 6). The PL decay curves are found to be quite single exponential which gives clear evidence that the mechanism of energy transfer is homogeneous inside the network, without preferential positions regarding the excitation transfer towards sites of non-radiative decay [23,24]. When the decay curve is deviated from single exponential, it can indicate the presence of non-radiative excitation transfer.
samples. by: high rare earth doping which not the case in this work. from rare earth’s interactions. Such mechanism is manifested for high rare earth doping which not the case in this work. The measured lifetime corresponds to the mean lifetime, given by:

\[ \tau_{\text{mes}} = \frac{1}{I_0} \int \tau \, \text{d}t \quad (10) \]

**Table 5**

Calculated radiative parameters of NZLE0, NZLE1 and NZLE2 glasses.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Er(^3^+) (0.5 mol%)</th>
<th>Er(^3^+)/Yb(^3^+) (0.5/0.5 mol%)</th>
<th>Er(^3^+)/Yb(^3^+) (0.5/1 mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(A_{\text{rad}} ) (s(^{-1}))</td>
<td>(\beta_{\text{rad}} ) (%)</td>
<td>(\tau ) (ms)</td>
</tr>
<tr>
<td>(4_{13/2} \rightarrow 4_{15/2} )</td>
<td>0.132E2</td>
<td>1.00</td>
<td>7.53</td>
</tr>
<tr>
<td>(4_{11/2} \rightarrow 4_{13/2} )</td>
<td>0.140E2</td>
<td>0.84</td>
<td>6.07</td>
</tr>
<tr>
<td>(4_{11/2} \rightarrow 4_{13/2} )</td>
<td>0.239E2</td>
<td>0.14</td>
<td>20.89</td>
</tr>
<tr>
<td>(4_{13/2} \rightarrow 4_{15/2} )</td>
<td>0.138E3</td>
<td>0.90</td>
<td>0.75</td>
</tr>
<tr>
<td>(4_{13/2} \rightarrow 4_{15/2} )</td>
<td>0.5277</td>
<td>0.06</td>
<td>37.72</td>
</tr>
<tr>
<td>(4_{13/2} \rightarrow 4_{15/2} )</td>
<td>0.8052</td>
<td>0.05</td>
<td>70.88</td>
</tr>
<tr>
<td>(4_{13/2} \rightarrow 4_{15/2} )</td>
<td>0.33</td>
<td>2.48E-3</td>
<td>3.44</td>
</tr>
<tr>
<td>(4_{13/2} \rightarrow 4_{15/2} )</td>
<td>1.31E3</td>
<td>0.65</td>
<td>0.50</td>
</tr>
<tr>
<td>(4_{13/2} \rightarrow 4_{15/2} )</td>
<td>5.09E2</td>
<td>0.28</td>
<td>4.88E2</td>
</tr>
<tr>
<td>(4_{13/2} \rightarrow 4_{15/2} )</td>
<td>4.291</td>
<td>0.02</td>
<td>36.32</td>
</tr>
<tr>
<td>(4_{13/2} \rightarrow 4_{15/2} )</td>
<td>59.09</td>
<td>0.03</td>
<td>47.53</td>
</tr>
<tr>
<td>(4_{13/2} \rightarrow 4_{15/2} )</td>
<td>0.76</td>
<td>3.86E-4</td>
<td>0.65</td>
</tr>
<tr>
<td>(4_{13/2} \rightarrow 4_{15/2} )</td>
<td>3.11E3</td>
<td>0.914</td>
<td>304E3</td>
</tr>
<tr>
<td>(4_{13/2} \rightarrow 4_{15/2} )</td>
<td>80.27</td>
<td>0.02</td>
<td>66.11</td>
</tr>
<tr>
<td>(4_{13/2} \rightarrow 4_{15/2} )</td>
<td>48.62</td>
<td>0.01</td>
<td>46.37</td>
</tr>
</tbody>
</table>

Fig. 5. PL spectra relatives to \(4_{13/2} \rightarrow 4_{15/2} \) transition, under 976 nm excitation wavelength, of NZLE0 (a), NZLE1 (b) and NZLE2 (c) glasses.

The resulting PL decay times are collected in Table 6. The PL lifetime becomes more longer after Yb\(^3^+\) adding which can prove the efficient excitation transfer from Yb\(^3^+\) to Er\(^3^+\). It is explained from the overlapping between the emission band of the \(2F_{5/2}\) excited state relative to Yb\(^3^+\) and the absorption one corresponding to the \(4_{15/2} \rightarrow 4_{13/2}\) transition in Er\(^3^+\).

The quantum efficiency (\(\eta\)) is calculated from the radiative lifetime \(\tau_{\text{rad}}\), obtained from Judd–Ofelt theory, and the measured experimental lifetime \(\tau_{\text{mes}}\), as given by:

\[ \eta(\%) = \frac{\tau_{\text{mes}}}{\tau_{\text{rad}}} \quad (11) \]

The results show a significant increase of the quantum efficiency after co-doping with Yb\(^3^+\) ions. The obtained quantum efficiency is compared to others results reported in Table 7. It indicates that this glassy system could be considered as a good candidate for the eye-safe laser emission at 1.55 \(\mu\)m.

### 3.4. Cross-section at 1.55 \(\mu\)m

The emission cross-section of the \(4_{13/2} \rightarrow 4_{15/2}\) transition has been obtained from the line shape of the emission spectrum. Its expression is [26]:

\[ \sigma_{\text{e}} = \frac{\lambda_{\text{em}}^2 A_{\text{tot}}}{8\pi cn\Delta\lambda_{\text{eff}}} \quad (12) \]

where \(\lambda_{\text{em}}\) is the peak emission, \(n\) is the refractive index, \(A_{\text{tot}}\) is the total spontaneous transition probability and \(\Delta\lambda_{\text{eff}}\) is the effective bandwidth.

The effective bandwidth is an important parameter for the Er\(^3^+\)-doped fiber amplifier (EDFA) used in the wavelength division multiplexing (WDM) network system of optical communication. The definition of the effective bandwidth according to...
Weber et al. [27] is:

$$\Delta \lambda_{\text{eff}} = \frac{\int |I(\lambda)| d\lambda}{I_{\text{max}}}$$  \hspace{1cm} (13)

where \(I(\lambda)\) is the emission intensity at the wavelength \(\lambda\), and \(I_{\text{max}}\) is the intensity at the peak wavelength \(\lambda\). As can be seen in Table 8, \(\Delta \lambda_{\text{eff}}\) increases from 65.41 to 70.02 nm and the FWHM increases from 43.84 to 65.76 nm after adding 1 mol% of Yb2O3. The broadening of the luminescence band in this glass is mainly due to the variation of local structure and coordination numbers surrounding Er3+ ions site.

These values are larger than those reported for materials commonly used for optical amplifiers, such as 37 nm and 44 nm for other phosphate glasses [28,29], 40 nm for silicate glasses [30] and in the same order of magnitude for tellurite glass doped Er–Yb (54–63 nm) [16]. However, these values are less than those reported for tellurite-phosphate glasses (71–78 nm) [16].

Generally, inhomogeneous broadening is dominant for the bandwidth broadening of Er3+ in glasses caused by variations of ligand fields of Er3+ from site to site. \(\Delta \lambda_{\text{eff}}\) does change significantly in our glass samples, suggesting that the increase of Yb2O3 concentration effectively affects the differences in the ligand field of Er3+ from site to site and thus lead to larger inhomogeneous broadening of the emission spectra. The larger value of \(\Delta \lambda_{\text{eff}}\) could be interesting for wavelength-division multiplexing applications.

The absorption cross-section determined from absorption spectrum was used to calculate the emission cross-section based on the McCumber theory [31]:

$$\sigma_{\text{ef}}(\nu) = \sigma_{\text{ex}}(\nu) \exp \left( \frac{(\nu - \nu_0)}{K T} \right)$$ \hspace{1cm} (14)

\(\nu\) is the photon frequency, \(h\) the Planck constant, \(k\) the Boltzmann constant, and \(\epsilon\) the net free energy required to excite one Er3+ ion from the \(4I_{15/2}\) to \(4I_{13/2}\) state at temperature \(T\). By using the method proposed by Miniscalco and Quimby [32], the energy \(\epsilon\) is estimated to 6474.17 cm\(^{-1}\) for NZLE2 sample. This value is comparable to that reported for tellurite glass (6548 cm\(^{-1}\)) [33]. The emission cross-section \(\sigma_e\) and absorption cross-section \(\sigma_a\) are shown in Fig. 7.

Emission cross-section \(\sigma_e\) and the FWHM are important parameters in optical amplifier’s achieving broadband and high-gain amplification. The bandwidth properties of the optical amplifier can be evaluated from the product FWHM \times \sigma_e. Larger values for the FWHM \times \sigma_e product and longer experimental lifetimes \(\tau_{\text{mes}}\) imply wider gain bandwidth and lower pump threshold power.

Radiative excitation transfer can enhance since co-doping the glass with Er and Yb shows an effective increase of \(\sigma_e\).

**Table 7**

<table>
<thead>
<tr>
<th>Host materials</th>
<th>TZNY1 [16]</th>
<th>PME14 [18]</th>
<th>Tellurite glass TZNE (0.5%) [25]</th>
<th>Present work NZLE2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\eta (%))</td>
<td>91</td>
<td>86</td>
<td>100</td>
<td>91</td>
</tr>
</tbody>
</table>

**Table 8**

The effective width \(\Delta \lambda_{\text{eff}}\), FWHM, emission cross-section \(\sigma_e\) and \(\sigma_{\text{ex}}\) FWHM for PL band at 1.55 \(\mu\)m.

<table>
<thead>
<tr>
<th>Er3+/Yb3+ (mol%)</th>
<th>0.5/0</th>
<th>0.5/0.5</th>
<th>0.5/1</th>
<th>Aluminosilicate glass [34]</th>
<th>PBGG [35]</th>
<th>SBS1 [36]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FWHM (nm)</td>
<td>43.842</td>
<td>44.839</td>
<td>65.764</td>
<td>43</td>
<td>38</td>
<td>88</td>
</tr>
<tr>
<td>(\Delta \lambda_{\text{eff}}) (nm)</td>
<td>65.411</td>
<td>65.177</td>
<td>70.025</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(\sigma_e) ((\times 10^{-21} \text{cm}^2))</td>
<td>7.7</td>
<td>6.2</td>
<td>7.2</td>
<td>5.7</td>
<td>8.9</td>
<td>6.8</td>
</tr>
<tr>
<td>(\sigma_{\text{ex}}) \times FWHM ((\times 10^{-21} \text{nm/cm}^2))</td>
<td>337.5</td>
<td>278</td>
<td>473.5</td>
<td>245.1</td>
<td>338.5</td>
<td>598.4</td>
</tr>
</tbody>
</table>

**4. Conclusion**

The spectroscopic properties of Er3+/Yb3+ co-doped phosphate glasses were thoroughly investigated. The \(\Omega_r\) (\(r=2, 4, 6\)) intensity parameters, the radiative rates, the branching ratios and radiative lifetimes were successfully calculated based on the experimental absorption spectrum and Judd–Ofelt theory. All these parameters were found to be largely sensitive to Yb3+ codoping.

Longer PL lifetimes and high quantum efficiencies, up to 91%, were reported after Yb3+ codoping which can indicate the presence of an efficient excitation transfer from Yb3+ to Er3+. The peak stimulated emission cross-sections have been predicted from McCumber’s theory and are found comparable with the measured emission cross-section values. Large gain bandwidth and high stimulated emission cross-section are obtained for the \(4I_{13/2} \rightarrow 4I_{15/2}\) transition.

These results indicate that the Er3+/Yb3+ doped NZL phosphate glasses are good candidates for the fabrication of optical amplifiers and lasers.

**Fig. 7.** Absorption cross-section and calculated emission cross-section for the 1.55 \(\mu\)m emission band and the case of NZLE2 glass sample.
References