Effects of yttrium and ytterbium codoping on photoluminescence of erbium-doped SiO$_2$-Al$_2$O$_3$ sol-gel glass

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1. Introduction

Erbium ions (Er$^{3+}$) have several important properties that make it an excellent choice for an optical amplifier. Er$^{3+}$ has quantum levels that allow them to be stimulated to emit in the 1500 nm to 1600 nm widthband, which has the least power loss in most silica-based fiber. The future of optic amplifiers lies in the mediums used, as well as new methods of amplification. As additional bandwidth becomes necessary, the mediums used will switch to other elements that emit light at different bandwidths. In order to broaden the bandwidth, to flatten the gain and to increase the power, we performed the study on the properties of Er$^{3+}$ ions in the novel glass mediums based in Al$_2$O$_3$ - SiO$_2$ glass host doped with Y$_2$O$_3$ and Yb$_2$O$_3$.

The introduction of network modifiers such as Al$_2$O$_3$ and others ions to improve rare earth dilution and prevent micro clustering was investigated, for silica glass hosts with Er$^{3+}$, by B.J. Ainslie et al. [1]. Previous works had shown the advantage of Al$_2$O$_3$ as a homogenizing agent for the incorporation of large substitution concentrations of rare earths (up 10 times), but with a high alumina concentration, the effect of devitrification can be occur. A comparison of the relative intensities and linewidths of the Er fluorescence spectra show a clear dependence on the presence of aluminum [2,3]. The substitution of the atoms of Si$^{4+}$ by Al$^{3+}$ have an effect of extension of the Er$^{3+}$ ions in the silica network, which is concerned with the formation of non-bridging oxygen in the silica network. This non-bridging oxygen allows reduce the formation of the aggregation of Er$^{3+}$ ions by creating an Er-O-Al bonding. In this study, the proportion of Al$_2$O$_3$ and SiO$_2$ is varied from 10 to 65% in molar of Al$_2$O$_3$.

The yttrium (Y$^{3+}$) is chosen as codoping ion since their ionic radius is similar (0.0892 nm for Y$^{3+}$ and 0.0881 nm for Er$^{3+}$). Er$^{3+}$ and Y$^{3+}$ have also the same valence; therefore they can easily substitute itself and can increase the distance between two Er$^{3+}$ ions. In the case of codoping with Er$^{3+}$ and Y$^{3+}$, the formation of Er-O-Y-O-Er may be take place.
instead of Er-O-Er which explains the reducing of the quenching effect dealing with the Er$^{3+}$ ions concentration. With the use of ytterbium (Yb$^{3+}$) as a sensitize for Er$^{3+}$, a mechanism based on an energy transfer through $^3\text{F}_{5/2}\text{(Yb)} \rightarrow ^4\text{I}_{11/2}\text{(Er)}$ has been known for a long time and offers attractive alternatives to optical amplifier materials doped only with Er$^{3+}$.

Up to now, there is no systematically investigation on the glass of the composition (1-x) SiO$_2$ - xAl$_2$O$_3$ - yY$_2$O$_3$: 0.65Er$_2$O$_3$ (mol %), x varies from 0 to 65, Y$_2$O$_3$ from 0 to 4 mol%. Only sample up to 10 mol% of Al$_2$O$_3$ was investigated by M. Nogami at al. [4] and for 50 mol% by Nedelec at al. [5]. A first report on binary SiO$_2$–Al$_2$O$_3$ system but only on xerogel and aerogels (not on glass) as a function of the Si to Al molar ratio was done and shown that with high Al content the octahedral coordination dominated [6]. Very recently (2003) a study on Er/Yb co-activated silica-alumina monolithic glasses was published, but the advantage of a specific Er/Yb/Al glass composition for the spectroscopy properties at 1.53 $\mu$m was not yet identify [7].

This work is a first attempt to make a new sol-gel glass host based on SiO$_2$, Al$_2$O$_3$, and Y$_2$O$_3$ doped with Er$^{3+}$ ions. For this aim, at first, we must find the optimal proportion of Al$_2$O$_3$ and SiO$_2$ for the Er emission in the glasses. All these samples were doped with 0.65 mol% Er$^{3+}$ concentration which is the optimal in SiO$_2$ sol-gel glass [2,3,8,9]. Then, Y$_2$O$_3$ is added to the glass and last, we added Yb$_2$O$_3$ to these glass hosts. We observe the emission of Er$^{3+}$ under the influence of these parameters. Some new spectroscopy properties of Er$^{3+}$ ions in these glasses will be present.

2. Experimental

2.1. Sample preparation

Using a sol-gel method, a series of glasses samples: (100-x)SiO$_2$ - xAl$_2$O$_3$ - yY$_2$O$_3$: 0.65Er$_2$O$_3$ (mol %), x varies from 0 to 10, 20, 30, 40, 50, 65; y = 0, 2, and 4 molar, were prepared. Volume ratios of reactants were chosen in order to realize a known total of Al (mol% SiO$_2$ + mol% Al$_2$O$_3$ = 1). The chemical precursors of Si and Al used in this study were Si(OC$_2$H$_5$)$_4$ (TEOS) 98% and Al(OC$_4$H$_9$)$^\text{sec}$ 98% from Merck. The solvent was isopropanol (i-PrOH) 99.7%. The used rare earth salts were ErCl$_3$.6H$_2$O, Y$_2$(CO$_3$)$_3$ and YbCl$_3$ from Aldrich. The Si(OC$_2$H$_5$)$_4$ was first hydrolyzed for 1 h at room temperature with a solution of H$_2$O, isopropanol and HCl in the molar ratios 1 : 2 : 0.0027 per mole of Si(OC$_2$H$_5$)$_4$. Al(OC$_4$H$_9$)$^\text{sec}$$_3$ , diluted in i-PrOH and ethylacetocetate, added to the above solution and followed by a stirring for 1h at room temperature. ErCl$_3$.6H$_2$O (or Y$^{3+}$, Yb$^{3+}$) dissolved in i-PrOH and H$_2$O was added and stirred for 1h. Adding the mixed solution of H$_2$O, i-PrOH and HCl, hydrolyzed the resultant homogeneous solution. In this reaction, the molar ratio was maintained at 4: 2: 0.015 per mole of metal alkoxide. In this preparation, we used a drying control chemical additive (DCCA), that is dimethylformamide (DMF), and the silica colloidal in order to minimize cracking during drying by reducing shrinkage and increasing strength. This mixture was added in the final solution at the last step of the preparation, similar as reported in [2,9,10].

After the solution had been stirred for 1h, it was left for about 10 days to form a stiff gel of $26 \times 230$ mm. The stiff gel was dried at room temperature for 15 days. After that, the dried gel was heated in air for 2 h at 900°C to form glass. In order to completely hydrolyze the alkoxydes, the gel can be heated to 150°C in a tightly sealed vessel for 24h. Resulting gel was heated in air at 50°C/h and kept for 2 h at temperature ranging 100 to 900°C.
2.2. Measurement of fluorescence properties

The IR emitted light from the sample, collected by an optical fiber located at 10 mm from the sample surface, was analyzed on the same side as the excitation with a TRIAX 320 Spectrometer (Jobin-Yvon) and a near IR array detector Hamamatsu (256 pixel). This setup has a resolution of 1 nm/point for a slit $\leq 50$ µm. To compare the intensity of the samples, the measurement of the emission relative intensities were realized on the glass powder samples.

3. Results and discussion

3.1. Effect of the proportion of Al$_2$O$_3$ / SiO$_2$ on the luminescence of Er$^{3+}$ ions in the glasses

Figs.1 and 2 show the photoluminescence spectra (PL) corresponding to the transition from the $^4$I$_{13/2}$ state to the $^4$I$_{15/2}$ state multiples of Er$^{3+}$ in glasses with different proportions of Al$_2$O$_3$/SiO$_2$ in which Al$_2$O$_3$ varies from 0 to 65 mol% (fig.1) and theirs normalized PL intensities to show the bandwidth of the emission (fig.2). The main peak at 1530 nm with a shoulder at about 1550 nm is observed. A shift 3 nm to shorter wavelengths is observed. A little increase of the intensity of this shoulder is observed (fig.2). Some changes are observed in the shape of emission band. The largest spectral bandwidth is about 59.5 nm. The strongest intensity is reached with amount of Al$_2$O$_3$ is 50 %. The more Al-doped glass exhibits the flatter band.

When the aluminum ions are added in the SiO$_2$ glass host, they could be incorporation in two local bonding configurations, such as AlO$_4$/2 groups, as a network former, and an octahedral coordination of oxygen atoms, such as AlO$_6$/2 groups, as a network modifier [7].

These groups could act as solvation shells in the glass network for rare-earth ions. In the case of the AlO$_{4}$/2, due to charge compensation, the Er$^{3+}$ ions are preferentially accommodated near to the aluminum sites and the formation of tetrahedral coordinated Al is considered to play an important role in homogeneous dispersion of Er in aluminosilicate.
3.2. Effect of Y₂O₃ on the luminescence of Er³⁺ ions in the glasses

Figs. 3 presents the integrated intensity of the emission band of \( ^4I_{13/2} \rightarrow ^4I_{15/2} \) transition in the three kinds of the composition glass host: the first one is the aluminosilicate with the increasing of Al₂O₃ amount from 0 to 65 mol%, second codoped with 2 mol% of Y₂O₃ and the last codoped with 4 mol% of Y₂O₃.

![Fig. 3](image)

The integrated intensity is reached maximum in the composition host with 65 mol% Al₂O₃ and 4 mol% Y₂O₃. We have observed, in this glass sample co-doped with 65%Al₂O₃ and 4 mol%Y₂O₃, the emission intensity at 1550 nm two times higher than that in the glass not codoped. As presented above, a shift of 3 nm to shorter wavelengths is observed. The study on spectral broadening of 1500 nm emission of Er³⁺ doped these various glasses is performed. Fig. 4 shows the normalized emission spectral profiles. The little broadening of the emission bandwidth is observed. The full width at half maximum (FWHM) increases from about 56 nm (in the sample without Y₂O₃) to 59.5 nm in the sample with 4 Y₂O₃ (fig.4). We find an increase in the flatness and in the broadening of the emission band for the Al-Y-doped glass (bandwidth of 59.5 nm) and larger than those in silica glass (around 30 nm).

3.3. Effect of ytterbium codoping on photoluminescence of Er ions in the glass

The Yb³⁺ is chosen as codoping ions for Er³⁺ by the basic principle of Yb-Er energy transfer through \( ^2F_{5/2} (\text{Yb}^{3+}) \rightarrow ^4I_{11/2} (\text{Er}^{3+}) \). The \( ^2F_{7/2} \rightarrow ^2F_{5/2} \) transition of Yb³⁺ in the near infrared (~980 nm) has a high absorption cross section and, in combination with efficient
Yb → Er energy transfer, may allow for a considerable reduction of Er\(^{3+}\) concentration while maintaining sufficient pump-light absorption, making it possible to design short optic communication devices requiring only low excitation intensities.

**Fig.5.** Normalized PL spectra of Er\(^{3+}\) for a constant Er amount of 0.65 mol% (curve 2) and with 0.65 mol% Yb\(_2\)O\(_3\) (curve 3) in (1-x)SiO\(_2\)-xAl\(_2\)O\(_3\) (x=10 and 11 mol\%) glasses, under 980 nm excitation.

**Fig.6.** Normalized emission intensity of Er\(^{3+}\) in SiO\(_2\)-Al\(_2\)O\(_3\) different glasses.

Figs. 5 and 6 present the normalized PL of Er\(^{3+}\) ions, in the glass host of 10 and 11 mol\% Al\(_2\)O\(_3\) with and without Yb\(^{3+}\) doping. For the two samples with the same composition of 11 mol\% Al\(_2\)O\(_3\), doped with 0.65 mol\% Er\(_2\)O\(_3\) and co-doped with 0.65 mol\% Yb\(^{3+}\) (fig. 5), we observe an increase in the PL intensity at 1531 nm for the sample codoped with 0.65 mol\% Yb\(_2\)O\(_3\). Their flatness and bandwidth of 55 nm was similar (fig.6). This means the Yb\(^{3+}\) ions are not affect to broad the emission spectral band, they should transfert nonradiatively their energy to the Er\(^{3+}\) ions.

### 4. Conclusions

From the spectroscopy results obtained, we can show that the strongest emission intensity of Er\(^{3+}\), with the same amount, is reached in the glass composition of 0.35SiO\(_2\)-0.65Al\(_2\)O\(_3\)-0.04Y\(_2\)O\(_3\):0.65Er\(_2\)O\(_3\). A shift of 3 nm to shorter wavelengths is observed. In this glass composition, the FWHM is largest and the value of bandwidth is 59.5 nm. An increase in the flatness and in the broadening of the emission band for the 0.35SiO\(_2\)-0.65Al\(_2\)O\(_3\)-0.04Y\(_2\)O\(_3\):0.0065Er\(_2\)O\(_3\) glass host were observed and larger than those in sol-gel silica glass.

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References


