Optical and spectroscopic properties of soda-lime alumino silicate glasses doped with Er\textsuperscript{3+} and/or Yb\textsuperscript{3+}

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Abstract

A new set of soda-lime alumino silicate (SLAS) glasses doped with a fixed percentage of Er\textsuperscript{3+} and different percentages of Yb\textsuperscript{3+} ions was produced by conventional melting process. Their spectroscopic properties, namely absorption and emission spectra, radiative and experimental lifetimes, were measured and are discussed here. Planar and channel optical waveguides were produced in these glasses by ion-exchange, and their characterization is reported as well.

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1. Introduction

Due to their good chemical durability, erbium-doped soda-lime silicate glasses are attractive materials for the fabrication of low-cost integrated optical amplifiers by using the ion-exchange technique. One of the main problems associated with this kind of glass is the narrow emission bandwidth at 1.55 μm, that reduces their potential application in the WDM systems if compared with other oxide glasses, such as phosphates and tellurites. In order to overcome this intrinsic limit we have developed a new kind of soda-lime alumino-silicate (SLAS) glasses with different percentages of Al\textsubscript{2}O\textsubscript{3} and Er\textsubscript{2}O\textsubscript{3}. In a previous work we studied the effect of increasing the alumina content on the spectroscopic properties of this class of glasses, doped with Er\textsuperscript{3+} only [1]. Starting from the choice of the base composition which seemed to offer the best compromise between broad fluorescence bandwidth and long lifetime of the \textsuperscript{4}I\textsubscript{13/2} excited state, we synthesized novel SLAS glasses, co-doped with Yb\textsuperscript{3+} ions, labeled as SLASY. It is in fact well known that the presence of ytterbium significantly increases the pump efficiency and more easily leads to a net optical gain for erbium-doped waveguide amplifiers [2]. The base composition of the new set of glasses was therefore chosen as approximately corresponding to that of the sample previously labeled as AL20 [1]. Two of the three newly synthesized glasses, labeled as SLASY1 and SLASY2, contained 0.4 mol% Er\textsubscript{2}O\textsubscript{3} and were co-doped with 0.4 and 0.6 mol% Yb\textsubscript{2}O\textsubscript{3}, respectively. The third glass (SLASY3), instead, was doped with ytterbium only, in order to check the possibility of using it as a passive glass to be bonded to one of the previous Er\textsuperscript{3+}/Yb\textsuperscript{3+}-doped glasses for the realization of an integrated
lossless device \cite{3}; the term passive is used here with the meaning that the glass does not exhibit neither absorption nor fluorescence in the 1.5 μm wavelength band. In this paper the optical and spectroscopic properties of these glasses are reported and discussed.

2. Experimental

Three SLASY glasses were fabricated following a melting/cooling process similar to that described elsewhere \cite{4}. The nominal base composition of these samples was 62SiO2–12Na2O–9CaO–17Al2O3–0.3P2O5–0.5K2O mol%, close to that of AL20 glass described in a previous paper \cite{1}, while their Er\(^{3+}\) and Yb\(^{3+}\) concentrations are listed in Table 1. Moreover, in the present case, much larger batches were prepared, compared to the AL glasses \cite{1}, with the aim of obtaining a better homogeneity and a volume of glasses suitable for the fabrication of several integrated optical devices.

Each rod of glass (about 600 g weight) was cut in plates with thickness from 1 to 2 mm, which were optically polished for spectroscopic characterization and waveguide fabrication. Absorption spectra in the visible and near infrared regions were measured at room temperature on 2 mm thick plates by a double beam spectrometer with a resolution of 1 nm. The infrared fluorescence spectra under 976 nm laser diode excitation were measured using a monochromator with a resolution of 1 nm and detected with an InGaAs photodiode and lock-in technique.

Multi-mode and single-mode planar waveguides were fabricated by immersion of the samples into a diluted 1.5 mol% AgNO\(_3\) – 98.5 mol% NaNO\(_3\) melt solution at 325 °C, in order to check propagation properties. Modal measurements were carried out by a semi-automatic instrument (COMPASSO) developed in house and based on prism coupling technique and dark line spectroscopy.

Channel waveguides were first fabricated in SLASY1 glass plates by conventional photolithographic process, using a titanium mask. In order to reduce the formation of the silver clusters under the mask during the thermal ion-exchange process, we oxidized the Ti mask in a pure NaNO\(_3\) melt solution at the temperature of 380 °C for 1 h. Single-mode (at 1.55 μm) channel waveguides were realized by using the same Ag\(^+\) \(\rightleftharpoons\) Na\(^+\) ion-exchange conditions adopted for single-mode planar waveguide. Insertion losses at 1.3 μm were measured, and near-field intensity distribution images were collected by a Hamamatsu vidicon camera. Finally, preliminary measurements of optical gain in the SLASY1 samples were performed in a fiber to fiber configuration by using a 976 nm laser diode as a pump and a tunable external cavity laser diode as a signal source.

3. Results and discussion

3.1. Glass characterization: spectroscopic properties

Fig. 1 shows the absorption spectra in the visible and near infrared spectral regions measured on the three SLASY glasses. The spectra of the SLASY1 and SLASY2 glasses were virtually identical in the region around 1.55 μm and confirmed the broadening of the absorption/emission bandwidth that we had already measured in the Er\(^{3+}\)-doped AL20 samples \cite{1}. This is also confirmed by the analysis of fluorescence spectra; the spectrum of SLASY1 sample, peaked at 1533 nm, is compared in Fig. 2 with that of AL20 sample. It shows an effective emission bandwidth \(\Delta v_{\text{eff}}\) of 52 ± 1 nm, while for the effective

| Table 1 | Er\(^{3+}\) and Yb\(^{3+}\) concentration of the three SLASY samples |
|----------------|----------------|----------------|----------------|----------------|
| Samples       | Er\(^{3+}\) (ions/cm\(^3\)) | Yb\(^{3+}\) (ions/cm\(^3\)) | Er\(_2O_3\) (mol%) | Yb\(_2O_3\) (mol%) |
| SLASY1        | 1.80 × 10\(^{20}\) | 1.80 × 10\(^{20}\) | 0.40 | 0.40 |
| SLASY2        | 1.80 × 10\(^{20}\) | 2.70 × 10\(^{20}\) | 0.40 | 0.61 |
| SLASY3        | – | 3.60 × 10\(^{20}\) | – | 0.80 |

Fig. 1. Absorption spectra in the visible and near-infrared spectral regions of the three SLASY glasses.

Fig. 2. Comparison between Er\(^{3+}\) emission spectra of the AL20 SLAS and SLASY1 glasses.
absorption bandwidth $\Delta \lambda_{\text{abs}}^{\text{eff}}$ we measured a value of 53 ± 1 nm. In this region, the Er$^{3+}$ absorption coefficients for SLASY1 and SLASY2 glass are 1.08 ± 0.01 cm$^{-1}$ and 1.07 ± 0.01 cm$^{-1}$, respectively. So, for an Er$^{3+}$ nominal concentration of $1.8 \times 10^{20}$ ions/cm$^3$, the absorption cross-section of the $^4I_{15/2} \rightarrow ^4I_{13/2}$ transition is around $0.59 \times 10^{-20}$ cm$^2$ (± 0.02 cm$^2$), i.e., 10% lower than the value obtained for the AL20 glass.

On the other hand, in the present glasses we wanted to investigate in particular the spectroscopic features related to the presence of Ytterbium. Looking at the absorption band around 0.98 nm, we observed a very broad band with a stronger absorption peak centered at 975 nm, due to the $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition of the Yb$^{3+}$. In this spectral region, for each sample the shape of the absorption band is similar, and the differences are mainly due to the different molar concentration of Yb$_2$O$_3$ in the three glasses. The absorption coefficients of these glasses were measured to be $3.69 \pm 0.04$ cm$^{-1}$, $5.35 \pm 0.05$ cm$^{-1}$ and $6.49 \pm 0.07$ cm$^{-1}$, respectively. From the last measurement, which refers to the SLASY3 sample, containing ytterbium only, the value of Yb$^{3+}$ absorption cross-section $\sigma_{\text{abs}} = 1.80 \times 10^{-20}$ cm$^2$ (± 0.01 cm$^2$) is deduced. In the co-doped samples, the Er$^{3+}$ absorption cross-section for the $^4I_{15/2} \rightarrow ^4I_{11/2}$ transition, which overlaps with the $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition of Yb$^{3+}$, can therefore be calculated assuming that the total absorption coefficient is equal to the sum of the Er$^{3+}$ and Yb$^{3+}$ absorption coefficients. The resulting values of the Er$^{3+}$ absorption cross-section are $(0.25 \pm 0.01) \times 10^{-20}$ cm$^2$ and $(0.27 \pm 0.01) \times 10^{-20}$ cm$^2$ for the SLASY1 and SLASY2 samples, respectively. These absorption cross-sections are almost seven times smaller than the corresponding Yb$^{3+}$ absorption cross-section for the same transition.

We had already observed a shift of the wavelength absorption peak of Er$^{3+}$ ions for the $^4I_{15/2} \rightarrow ^4I_{11/2}$ transition with an increase of the alumina content in the SLAS glasses [1]. For what concerns Yb$^{3+}$ absorption, Fig. 3 shows a comparison among the Yb$^{3+}$ absorption spectrum of SLASY1 sample and the absorption spectra of two MYx glasses [5], which again have almost the same composition of the matrix as the SLASY glasses but contain only 1 mol% Al$_2$O$_3$, with respect to 17 mol% of the latter ones. It clearly appears that a red shift occurs for the Yb$^{3+}$ absorption peak as well: the $\lambda_{\text{peak}}$ value ranged from 973 nm (in the case of MYx glasses) to 975 nm (in the case of SLASY1); moreover, it is worth noticing that the SLASY glass exhibits a much flatter profile of the absorption curve in the region between 900 nm and 970 nm in comparison with that of MYx glasses. We believe that these effects are anyway related to the high aluminum oxide concentration in the new class of glasses.

Finally, Fig. 4 compares the normalized Yb$^{3+}$ emission and absorption spectra measured on the SLASY3 glass. The two peaks are located at 977 nm and 975 nm, respectively.

A Judd–Ofelt analysis was also performed on the SLASY glasses in order to obtain the phenomenological intensity parameters $\Omega_i$ ($i = 2, 4, 6$), that are useful to calculate the spontaneous emission probabilities of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ Er$^{3+}$ transition, and also the radiative lifetimes $\tau_{\text{rad}}$ of the $^4I_{13/2}$ energy level of the Er$^{3+}$ ion. The $\Omega_i$ coefficients were found from a fit of the experimental oscillator strengths on the basis of the Judd–Ofelt parameterization scheme [6,7]. Table 2 compares the $\Omega_i$ parameters, the experimental and radiative lifetimes, stimulated emission cross section and quantum efficiency obtained for the AL20 SLAS [1] and SLASY1 glasses.

All the decay profiles were well fitted by a single exponential. Although no important differences are present in the calculated lifetimes of the two glasses, the experimental lifetimes $\tau_{\exp}$ of the metastable $^4I_{13/2}$ level are significantly different for the two samples. In particular, we observed an experimental lifetime of 4.1 ms for the SLASY1 glass while the corresponding value for the AL20 SLAS glass

![Fig. 3. Comparison among Yb$^{3+}$ absorption spectra of the MYx and SLASY1 glasses.](image1.png)

![Fig. 4. Comparison between Yb$^{3+}$ emission-absorption spectra of the SLASY3 glass.](image2.png)
Table 2  
Judd–Ofelt intensity parameters $\Omega$, stimulated emission cross section $\sigma_\text{p}$, measured and calculated lifetimes $\tau$, and quantum efficiency $\eta$ for SLASY1 and AL20 (SLAS) samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\Omega_2$ ($10^{-20}$ cm$^2$)</th>
<th>$\Omega_4$ ($10^{-20}$ cm$^2$)</th>
<th>$\Omega_6$ ($10^{-20}$ cm$^2$)</th>
<th>$\sigma_\text{p}$ (±0.2 pm$^2$)</th>
<th>$\tau$meas (±0.2 ms)</th>
<th>$\tau$calc (±0.2 ms)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLASY1</td>
<td>8.19 ± 0.58</td>
<td>1.70 ± 0.83</td>
<td>1.00 ± 0.29</td>
<td>0.70</td>
<td>4.1</td>
<td>8.71</td>
<td>0.47</td>
</tr>
<tr>
<td>AL20 (SLAS)</td>
<td>7.15 ± 0.25</td>
<td>1.95 ± 0.34</td>
<td>1.01 ± 0.12</td>
<td>0.77</td>
<td>6.2</td>
<td>8.43</td>
<td>0.74</td>
</tr>
</tbody>
</table>

was 6.2 ms. Since the measurements on the SLASY2 glass, which contains 50% more Yb atoms than SLASY1, give an even shorter value (3.4 ms), it seems that the presence of ytterbium negatively affects the lifetime of the $^1I_{13/2}$ metastable level of Er$^{3+}$. Further investigations, however, are required to clarify this point.

In the case of SLASY3, we measured the experimental lifetime of the $^3F_{3/2}$ level of Yb$^{3+}$ ions, which turned out to be around 0.7 ms, namely close to the lifetime of Yb-doped silica fibers [8] but quite shorter than specially designed Yb-doped phosphate glasses [9].

### 3.2. Waveguide characterization

The refractive index of the SLASY substrates was measured at 635 nm by the COMPASSO instrument; the indices of the three types of substrates resulted to be equal to 1.5262 ± 0.0005, 1.5276 ± 0.0005, and 1.5263 ± 0.0005, respectively.

As a first step, multi-mode planar waveguides were fabricated in all three types of substrates by Ag$^+$ ion-exchange at 325 °C, with a diffusion time of 90 min. In the case of SLASY1 and SLASY2 glasses we found that the increase of Yb$^{3+}$ concentration decreased the diffusion constant $D_\text{Ag}^+$, which was determined to be equal to $(4.2 ± 0.1) \times 10^{-3}$ μm$^2$/s and $(3.7 ± 0.1) \times 10^{-3}$ μm$^2$/s, respectively. On the other hand, in the case of the SLASY3 sample, doped with Yb$^{3+}$ ions only, the diffusion process is faster than in the previous ones $[D_\text{Ag}^+ = (4.8 ± 0.1) \times 10^{-3}$ μm$^2$/s]. Fig. 5 shows the refractive index profiles of the three SLASY multi-mode planar waveguides, as reconstructed from the measured effective indices by a new method based on a combination of two analytical functions [10].

Subsequently, a single-mode planar waveguide at 1.55 μm was obtained in the SLASY1 sample with a diffusion time of 12 min: the corresponding diffusion depth was $3.3 ± 0.1$ μm. Using the same exchange parameters and conventional photolithographic patterning, single mode channel waveguides, having widths between 4 μm and 8 μm, were fabricated in the same type of substrate. Propagation losses below 0.4 dB/cm were measured at 1.3 μm, and insertion losses around 3 dB were achieved in a 4 cm long and 5 μm wide waveguide. The coupling losses (about 0.7 dB per facet) are mostly due to the geometrical mismatch between the mode in the optical fiber and the mode in the channel waveguide: the latter one exhibits a small spot size of $4.8 \times 3.0$ μm$^2$ (width × height) at 1.55 μm, as a consequence of the high index change caused by Ag$^+$ ↔ Na$^+$ ion-exchange.

Finally, a signal enhancement of 2 dB/cm was measured by detecting the power of the 1.534 μm laser signal at the output of the waveguide when the pump laser at 977.8 nm was switched on and off. The corresponding pump power, measured at the end of the input fiber, was 110 mW. No net gain was achieved, and the reason of this is still under investigation. We believe that it could be due, in large part, to the not-optimal pumping scheme: the pump wavelength is very close to the Yb$^{3+}$ absorption peak, and so a fast pump absorption occurs along the waveguide. Moreover, the experimental tests made evident a strong green light that decayed very quickly with the distance, due to up-conversion phenomena, which limit the gain factor of the amplifier [11]. On the other hand, reducing the insertion losses with a burial ion-exchange step can increase the performance of the amplifier and improve the optical gain [12].

### 4. Conclusion

We have tested a set of new Er$^{3+}$/Yb$^{3+}$ co-doped soda-lime alumino silicate (SLAS) glasses, designed for the fabrication of waveguide amplifiers through the ion exchange process. The choice of silicate glasses rather than phosphates was mainly motivated by the superior chemical resistance of silicates and by their greater adaptability to different fabrication processes for the manufacturing of integrated optical devices.

Their spectroscopic characterization confirmed the interesting values of the effective absorption/emission band-
widths that we had recently measured in SLAS glasses with virtually equal base composition, but doped with Er$^{3+}$ only. Moreover, thanks to the co-doping with Yb$^{3+}$ ions, the absorption cross-section at around 980 nm was largely increased, leading the way to a more efficient pumping scheme of the amplifier.

In comparison with other soda-lime silicate glasses previously investigated, labeled as MYx glasses [5], which again had the same multi-component formulation as SLASY glasses, but contained 1 mol% Al$_2$O$_3$ only, the new samples, due to their high alumina content, showed, together with the almost doubled effective luminescence bandwidth (52 nm), a 2 nm shift of the Yb$^{3+}$ absorption peak (at 975 nm). Unfortunately, the measured lifetimes of the $^4$I$_{13/2}$ Er$^{3+}$ level were significantly reduced in the new glasses, giving a quantum efficiency lower than 50%. At this moment, this behavior cannot be attributed to a specific reason (even the possible presence of Fe impurities related to the introduction of Yb could be considered), and further investigations are definitely required to clarify this point.

Multi-mode slab waveguides were fabricated by Ag$^+$ $\leftrightarrow$ Na$^+$ ion-exchange in order to reliably assess the diffusion parameters and the produced refractive index profile. Single-mode channel waveguides with quite low propagation losses at 1.3 $\mu$m (<0.4 dB/cm) were fabricated by a standard photolithographic process. Preliminary gain measurements have shown a signal enhancement of 2 dB/cm; since burying of the channel waveguide may lead to a substantial decrease of insertion losses, we can conclude that these glasses have a good potential for the development of ion-exchanged integrated optical active devices.

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