High concentration Yb-Er co-doped multi-component phosphate glasses for compact eye-safe optical amplifiers

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Three different glasses, named for short YE2/1, YE4/1 and YE6/1, were obtained by doping the host material with a fixed level of $Er_2O_3$ (0.75 mol%) and an increasing level of $Yb_2O_3$ (ranging from 1.50 to 4.50 mol%). The glass samples were synthesized by conventional melt-quenching technique using high purity (99+%) chemicals.

The chemicals were weighed and mixed within a dry box to minimize the hydroxyl ions ($OH^-$) content in the glasses. The batched chemicals were melted in an alumina crucible at a temperature of 1400 °C for 1 h inside a chamber furnace under a controlled atmosphere (dry air, water content < 3 ppm) and subsequently cast into a preheated brass cylindrical mold 12 mm in diameter to obtain 10 cm-long rod preforms. The cast glasses were annealed at a temperature around the transition temperature ($T_g$) for 5 h to relieve internal stresses and finally cooled down slowly to room temperature.

Flat specimens were cut from the three preforms and optically polished to 1 mm-thick samples to be used for optical and spectroscopic characterization. Samples with thicknesses of 12 and 5 mm were used for density and coefficient of thermal expansion (CTE) measurements, respectively, and about 30 mg of fine grain sample were prepared and used for the evaluation of the glass characteristic temperatures.

### 2.2 Glass characterization

The density ($\rho$) of the glasses was measured at room temperature with an accuracy of 0.05 g/cm$^3$ by the Archimedes' method using distilled water as the immersion fluid. The concentration of the $Yb^{3+}$ and $Er^{3+}$ ions was calculated through density data in relation to the nominal composition of the glasses.

The characteristic temperatures of the glasses (glass transition temperature $T_g$ and onset crystallization temperature $T_x$) were measured using a Netzsch DSC 404 F3 Pegasus® differential scanning calorimeter with a heating rate of 5 °C/min in sealed Pt/Rh pans featuring an error of ± 3 °C. The glass stability parameter $\Delta T = T_x - T_g$ was calculated with an error of ± 6 °C.

The CTE was measured by a Netzsch DIL 402 PC horizontal alumina dilatometer operating at 5 °C/min. The measure was automatically interrupted when a shrinkage higher than 0.13% was achieved (softening point $T_s$). The CTE value was calculated in the 200 - 400 °C temperature range, featuring an error of ± 0.1 °C$^{-1}$.

The refractive index ($n$) of the glasses was measured at 5 different wavelengths (632.8, 825, 1061, 1312 and 1533 nm) by prism-coupling technique using a Metricon 2010 Prism Coupler. Ten scans were performed for each wavelength and the estimated error of the measurement was ± 0.001.

The Fourier transform infrared (FTIR) spectra were taken between 2000 and 7000 cm$^{-1}$, with a resolution of 4 cm$^{-1}$ and acquiring an average of 16 scans, using the spectrometer Alpha, Bruker Optics, working in transmission mode and equipped with a deuterated-triglycine sulphate (DTGS) detector. The content of $OH^-$ groups was evaluated through the application of the formula proposed by Ehrmann *et al.* [8], while the typical transmittance FTIR spectrum of the synthesized glasses is reported in terms of optical loss.

The continuous-wave (CW) photoluminescence spectra of the glasses were acquired in the near-infrared (NIR) region by a Jobin Yvon iHR320 spectrometer equipped with a Hamamatsu P4631-02 detector, using standard lock-in technique. The emission spectra were obtained by exciting the samples with a monochromatic light at the wavelength of 976 nm emitted by the fiber pigtailed laser diode Oclaro CM962UF76P-10R.

The fluorescence lifetimes ($\tau$) of $Er^{3+}$:$^4I_{13/2}$ level were obtained by exciting the samples with light pulses of the 976 nm laser diode. The signal was recorded by a digital oscilloscope (Tektronix TDS350) and the decay traces were fitted by single exponential. Estimated error of the measurement was ± 0.20 ms. The detector used for this measurement was a Thorlabs PDA10CS.

## 3. RESULTS AND DISCUSSION

Table 1 reports the physical, optical and spectroscopic properties of the synthesized phosphate glass samples.

*Table 1. Density ($\rho$), $Yb^{3+}$ and $Er^{3+}$ ions concentration, refractive index (n) at 1533 nm, $OH^-$ content and excited state $^4I_{13/2}$ lifetime ($\tau$) of the fabricated Yb-Er co-doped multi-component phosphate glasses.*

| Glass label | $\rho$ [g/cm$^3$] | $Yb^{3+}$ [× $10^{20}$ ions/cm$^3$] | $Er^{3+}$ [× $10^{20}$ ions/cm$^3$] | $n$ | $OH^-$ content [ppm] | $\tau$ [ms] |
|---|---|---|---|---|---|---|
| **YE2/1** | 3.43 | 3.86 | 1.93 | 1.569 | 435 | 4.60 |
| **YE4/1** | 3.43 | 7.69 | 1.92 | 1.566 | 279 | 5.50 |
| **YE6/1** | 3.43 | 11.50 | 1.92 | 1.564 | 295 | 5.50 |

It is worthwhile noting that the density of the glasses did not change by varying the $Yb^{3+}$ ions doping level, due to the fact that the doping oxide $Yb_2O_3$ was added in substitution of $Gd_2O_3$ in the host matrix, both quite close in terms of molecular weight.

The glasses showed typical $T_g$, $T_s$, $T_x$, and CTE values equal to 502 °C, 533 °C, 762 °C, and 11.87 × $10^{-6}$ $°C^{-1}$, respectively. The higher $T_g$ and lower CTE than those reported in literature for other phosphate glass compositions [9] prove that they are markedly robust and resistant to the thermal stress induced by their processing. Moreover, a typical glass stability parameter $\Delta T$ of 260 °C was assessed, thus indicating that the synthesized glasses are stable against devitrification and suitable for crystal-free fiber drawing.

Fig. 1 reports a typical IR spectrum of the manufactured glass samples in the region between 2500 and 4000 $cm^{-1}$. The broad and intense $OH^-$ vibration band centered at around 3000 $cm^{-1}$ provides useful information on the concentration of $OH^-$ groups inside the glasses [10]. Free $OH^-$ groups are regarded as effective quenchers of the IR radiation in Yb-Er co-doped phosphate glasses, resulting in a noticeable decrease of the $Er^{3+}$:$^4I_{13/2}$ lifetime.

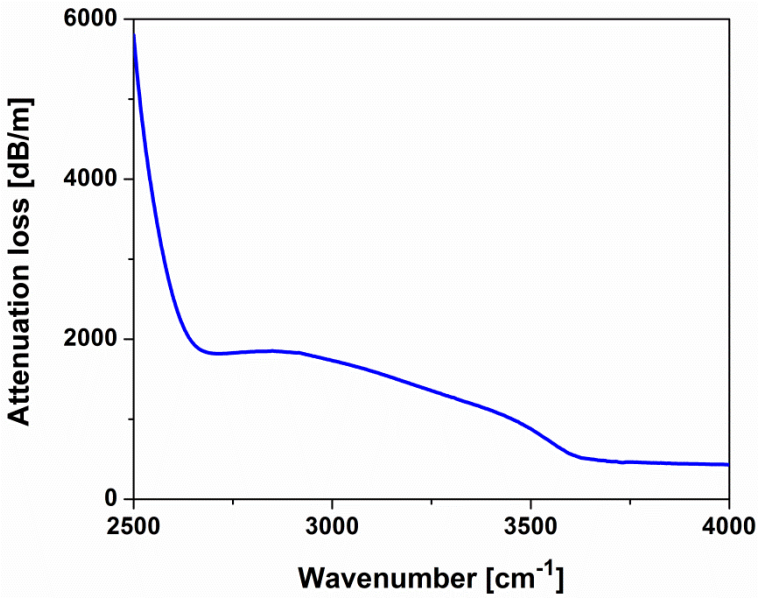


*Figure 1. IR spectrum of the YE4/1 glass showing the broad $OH^-$ vibration band at 3000 $cm^{-1}$ .*

The YE2/1 glass exhibited a greater $OH^-$ groups content and consistently a shorter excited state $Er^{3+}$:$^4I_{13/2}$ lifetime compared to the YE4/1 and YE6/1 glasses, as evident from the data reported in the last two columns of Table 1. This experimental evidence can possibly be ascribed to a higher absorption of water molecules readily during its weighing and/or melting processes.

Fig. 2 shows the emission spectra of the Yb-Er co-doped phosphate glasses in the wavelength range between 1470 and 1630 nm recorded upon excitation at 976 nm.

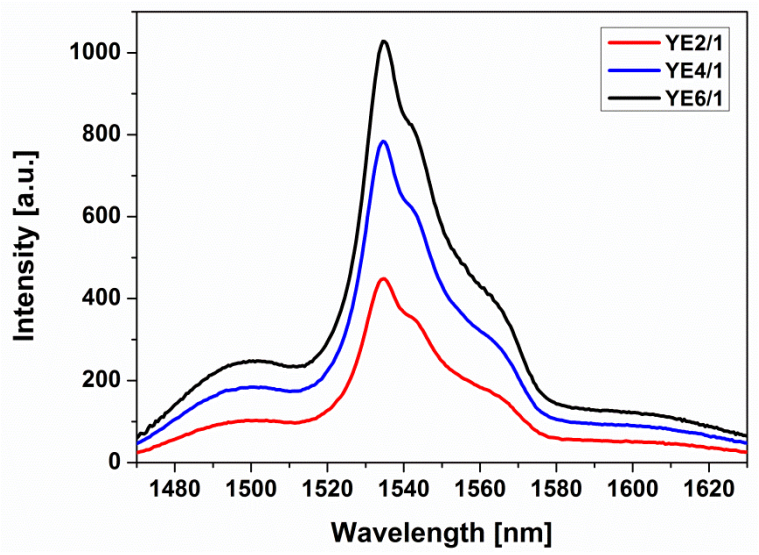


*Figure 2. Fluorescence emission spectra of the synthesized glass samples under excitation at 976 nm.*

The broad and intense emission peak at around 1535 nm is assigned to the $Er^{3+}$:$^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition and features a full width at half maximum (FWHM) of about 35 nm. It can be observed that the peak height of the emission increases steadily with rising $Yb^{3+}$ ions concentration, due to the increasing absorption of the pump source.

## 4. CONCLUSIONS

This paper reported on the design, processing and physical, thermo-mechanical, optical, and spectroscopic characterization of novel Yb-Er co-doped phosphate glasses. The glass host developed for this research was able to incorporate up to $10^{21}$ $Er^{3+}$ and $Yb^{3+}$ ions/$cm^3$ without clustering, while the RE-doped glasses resulted to be stable against crystallization and therefore suitable for fiber drawing, resistant to thermal shock and they also showed promising optical and fluorescent properties. In light of all these features, the synthesized phosphate glasses can be profitably employed as active media for the development of compact optical amplifiers for high-power and eye-safe LIDAR sources.

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