Multicomponent Rare Earth-Doped Phosphate Glasses for Compact Lasers and Amplifiers

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ABSTRACT

Thanks to its very high solubility of laser-active rare earth ions and outstanding thermo-mechanical properties, phosphate glass host represents a genuine alternative to the more traditional and employed silica glass platform to develop compact active devices, such as lasers and amplifiers. In particular, multicomponent phosphate glasses can withstand up to 10^{21} rare earth ions/cm^3, typically about 50 times more than the silica glass matrix, without showing clustering effects.

In this work we will report the ongoing activities and the recent results obtained by our research group on the design, processing and characterization of novel Er-, Nd- and Yb-doped custom phosphate glasses to be used as active medium for compact laser systems and optical amplifiers.

Keywords: phosphate glass, rare earth ion, erbium, neodymium, ytterbium, spectroscopic analysis.

1. INTRODUCTION

In recent years, phosphate glass has proved to be a promising alternative to the more traditional silica counterpart as a laser oscillator/amplifier host material thanks to its very high solubility of laser-active rare earth (RE) ions. More specifically, up to 10^{21} RE ions/cm^3 can be accommodated into multicomponent phosphate glass hosts without showing detrimental clustering effects [1,2]. This very high doping level, about 50 times higher than that commonly exhibited by the more rigid silica glass matrix, allows for the development of compact active devices with high energy storage capabilities and reduced optical nonlinearities [3,4].

Moreover, phosphate glasses display several other attractive properties with regards to photonic devices engineering. They can be processed relatively easily and they show good chemical and mechanical durability, excellent optical properties, ion-exchangeability, high cross-sections for stimulated emission, high gain, low up-conversion losses and high photo-darkening resistance [5,6].

Despite all these promising characteristics, yet phosphate glasses are far away from achieving the same competitiveness level of silica glasses in the market of laser glasses. The biggest limiting factor in this regard is represented by their thermal degradation under high-power operation [7] as a consequence of their lower thermal conductivity compared to silica glasses. A possible solution to this issue could be to develop custom phosphate glass systems featured by an increased glass transition temperature (T_g) and a reduced coefficient of thermal expansion (CTE).

Within this framework and following the above-mentioned strategy, our team has recently spent noticeable research effort towards the design of a novel phosphate glass host able to combine high RE ions solubility, high-power handling, enhanced thermal shock resistance, good thermal stability, suitability for fiber drawing and intriguing optical properties [8].

The present manuscript reports our ongoing activities and recent results regarding the design, synthesis and characterization of novel Er-, Nd- and Yb-doped custom phosphate glasses for compact laser systems and optical amplifiers.

2. EXPERIMENTAL DETAILS

2.1 Glass synthesis

A novel phosphate glass host (P_2O_5 - K_2O - Al_2O_3 - B_2O_3 - SiO_2 - PbO - La_2O_3) able to incorporate a high amount of RE ions, noticeably resistant to thermal shock and suitable for fiber drawing, was *ad hoc* designed and developed for this research.

Three different glasses, named for short EPG, NPG and YPG, were obtained by doping the host material with 1 mol% Er_2O_3, 0.3 mol% Nd_2O_3 and 2.4 mol% Yb_2O_3, respectively, with the total amount of the components being 100 mol% for all the glasses. These latter were synthesized by conventional melt-quenching technique using high purity (99+%) chemicals.

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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 with a diameter of 12 mm 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.

2.2 Glass characterization

The density (ρ) 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 immersion fluid. The concentration of the RE ions (Er^{3+}, Nd^{3+} and Yb^{3+}) 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 DTA 404 PC Eos differential thermal analyzer 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 for all the synthesized glasses.

The CTE was measured by a Netzsch DIL 402 PC horizontal alumina dilatometer operating at 5 °C/min on face parallel 5 mm-long specimens. The measure was automatically interrupted when a shrinkage higher than 0.13% was achieved (softening point T_s). CTE values were 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 refractive index experimental data were fitted using the Sellmeier's equation [9].

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 of EPG, NPG and YPG were obtained by exciting the samples with a monochromatic light at the wavelengths of 976, 785 and 915 nm emitted by the fiber pigtailed laser diodes Oclaro CM962UF76P-10R, Axcel B1-785-1400-15A and Bookham BMU8-915-01-R, respectively.

The fluorescence lifetimes (τ) of Er^{3+}:$^4I_{13/2}$, Nd^{3+}:$^4F_{3/2}$ and Yb^{3+}:$^2F_{5/2}$ levels were obtained by exciting the samples with light pulses of the 976, 785 and 915 nm laser diodes, respectively. The signal was recorded by a digital oscilloscope (Tektronix TDS350) and the decay traces were fitted by single exponential. Estimated errors of the measurement were ± 0.20 ms, ± 20 µs and ± 50 µs for EPG, NPG and YPG samples, respectively. The detector used for this measurement was a Thorlabs PDA10CS.

3. RESULTS AND DISCUSSION

Table 1 reports the physical, thermal and spectroscopic properties of the synthesized EPG, NPG and YPG samples.

Table 1. Density (ρ), RE ions concentration, glass transition temperature (T_g), onset crystallization temperature (T_x), glass stability parameter (ΔT), softening temperature (T_s), coefficient of thermal expansion (CTE) and fluorescence lifetime (τ) of the fabricated Er-, Nd- and Yb-doped custom phosphate glasses.

Glass label	ρ [g/cm^3]	RE [× 10^{20} ions/cm^3]	T_g [°C]	T_x [°C]	ΔT [°C]	T_s [°C]	CTE [× 10^6 °C^{-1}]	τ [ms]
EPG	3.03	2.57	540	839	299	563	9.8	3.96
NPG	3.01	0.72	522	790	268	535	8.1	0.33
YPG	3.02	6.15	522	812	290	548	7.1	0.90

All the glasses exhibit a stability parameter ΔT above 250 °C, indicating that they are stable against crystallization and suitable for crystal-free fiber drawing. Moreover, they are characterized by T_g and CTE values respectively higher and lower than those reported in literature for other phosphate glass compositions [10], proving that they are noticeably robust and resistant to the thermal stress induced by their processing. All these features make them particularly suited as active media for the development of compact optical amplifiers and high-power laser devices.

Figure 1 reports the refractive index values of the three glasses measured at five different wavelengths and fitted with the Sellmeier's equation. EPG and YPG show similar refractive index values, while NPG displays higher values at all the wavelengths. Noteworthy, the Sellmeier's function proved to accurately fit the refractive index experimental data of all the synthesized RE-doped phosphate glasses.

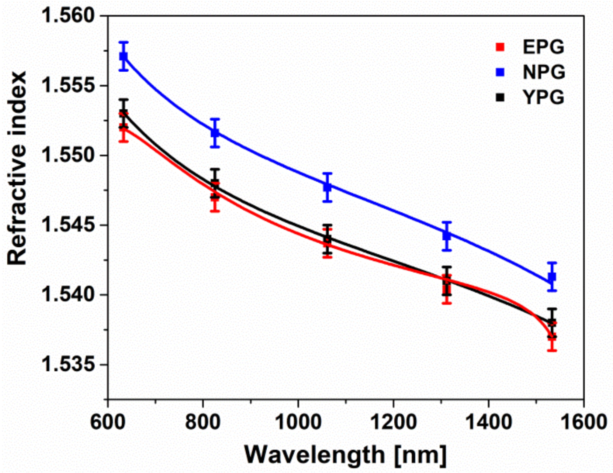

Figure 1. Refractive index values of the synthesized glasses at five different wavelengths fitted with the Sellmeier's formula. The filled squares represent the experimental data, while the continuous lines are the fitting curves.

Figure 2 shows the normalized emission spectra of EPG, NPG and YPG specimens recorded upon excitation at 976, 785, and 915 nm, respectively. The broad and intense emission peak at 1537 nm reported in Fig. 2a is assigned to the Er^{3+}:$^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition, the peak centered at 1054 nm depicted in Fig. 2b is correlated to the Nd^{3+}:$^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition and finally the emission peak at 978 nm and the band centered at 1004 nm displayed in Fig. 2c correspond to the Yb^{3+}:$^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition.

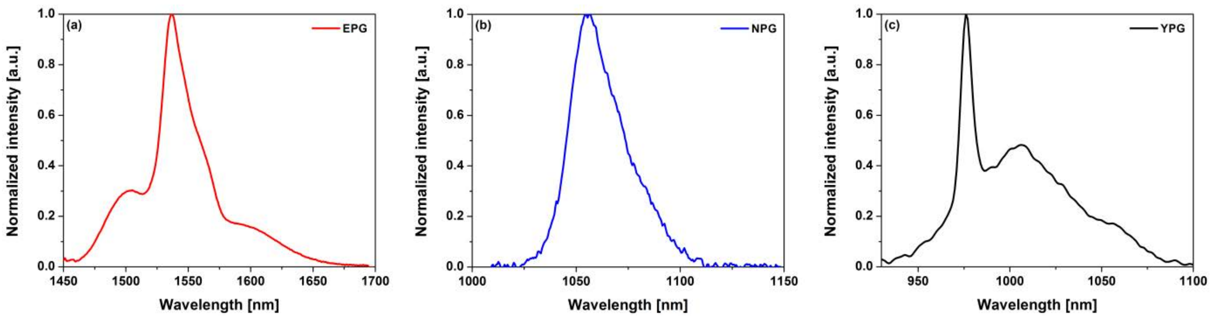

Figure 2. Normalized emission spectra of: (a) EPG, (b) NPG, and (c) YPG specimens.

4. CONCLUSIONS

This manuscript reported on the design, processing and thermal, physical, optical and spectroscopic characterization of novel Er-, Nd- and Yb-doped custom phosphate glasses. The materials were synthesized by conventional melt-quenching technique and resulted to be homogeneous, stable against crystallization and resistant to thermal shock. All these intriguing properties constitute a sound proof of the high solubility of laser-active RE ions of the starting glass host and of their suitability for crystal-free fiber drawing, thus making them particularly promising as active media for the development of compact optical amplifiers and high-power laser devices operating in the NIR region.

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