Design, processing and characterization of custom phosphate glasses for photonic and biomedical applications

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ABSTRACT

Phosphate glasses (PGs) are promising host materials for the development of compact fiber amplifiers and lasers thanks to their good chemical durability, easy processing, outstanding optical properties, no clustering effect and very high solubility of rare-earth (RE) ions. Furthermore, some particular calcium-phosphate glasses exhibit unique dissolution properties in aqueous media with degradation rates that can be tailored by properly designing the glass composition. This feature makes them attractive biomaterials and allows the engineering of novel biomedical devices for deep-tissue diagnosis and therapy.

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 custom phosphate glasses for both photonic and biomedical applications.

Keywords: phosphate glass, rare-earth ion, optical material, biomaterial, bioresorbable optics, spectroscopic analysis.

1. INTRODUCTION

Recently, phosphate glasses have attracted increasing attention as laser oscillator/amplifier host materials thanks to their good chemical and mechanical durability, ion-exchangeability, high cross-sections for stimulated emission, high gain, low concentration quenching, no clustering effects, low upconversion losses, very high solubility for rare-earth ions and high photodarkening resistance [1,2]. These features allow the introduction of large concentrations of active ions into relatively small volumes, thus resulting in smaller laser devices with high energy storage capabilities [2].

Over the years, phosphate glasses have also been studied extensively as potential candidate materials for a wide range of biomedical applications, such as hard and soft tissue regeneration [3] and deep-tissue photodynamic therapy (PDT) [4], due to their unique dissolution properties in aqueous fluids with degradation rates that can be tailored by properly designing the glass composition [5].

For many years, the two research fields regarding the phosphate glasses for optics and photonics and the bioresorbable calcium-phosphate glasses for biomedical applications have been considered to be apart, with very little interaction between them. Indeed, only few researchers have investigated the optical properties of bioresorbable calcium-phosphate glasses (CPGs) [6] and even less have tried to combine bioresorbability and optical functionalities together.

Within this framework and in view of fulfilling this lack targeting this new type of materials, our group has recently spent noticeable research effort towards the manufacturing of a novel CPG able to combine for the first time in a vitreous material solubility in aqueous media, good thermal stability, intriguing optical features and low intrinsic attenuation loss [7]. Even more recent research by our group has led to the fabrication of bioresorbable RE-doped CPGs. The aim is to exploit the fluorescence and stimulated emission of different lanthanides for novel applications in therapy and diagnostics by using resorbable/disposable devices that do not need explant after use.

The present manuscript reports the ongoing activities and the recent results obtained by our research group on the design, processing and characterization of Nd- and Yb-doped phosphate glasses for compact fiber amplifiers and lasers and of undoped and Yb-Er co-doped bioresorbable calcium-phosphate glasses for biomedical applications.

2. EXPERIMENTAL DETAILS

2.1 Glasses fabrication

The PG (P_2O_5 - K_2O - Al_2O_3 - B_2O_3 - SiO_2 - PbO - La_2O_3) and CPG (P_2O_5 - Na_2O - B_2O_3 - CaO - SiO_2 - MgO) hosts studied in this work were fabricated by melt-quenching technique using chemicals with high purity level (99+%). Based on the PG and CPG compositions, respectively, a Nd-doped and a Yb-doped phosphate glass labelled as Nd-PG (Nd^{3+} ions concentration $7.2 \times 10^{+19}$ cm^{-3}) and Yb-PG (Yb^{3+} ions concentration $6.2 \times 10^{+20}$ cm^{-3}) and a Yb-Er co-doped calcium-phosphate glass named Yb-Er CPG (Yb^{3+} ions concentration $4.7 \times 10^{+20}$ cm^{-3} and Er^{3+} ions concentration $1.6 \times 10^{+20}$ cm^{-3}) were successfully synthesized. The chemicals were weighted and mixed within a dry box and they were subsequently melted in an alumina crucible in a vertical furnace under controlled atmosphere to minimize the hydroxyl ions (OH^-) content in the glasses. The melting process was carried out for a time interval of 1 h at the temperatures of 1400 and 1200 °C for the PG and CPG based compositions, respectively. The melt was cast into a preheated cylindrical brass mould, then 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. The obtained glasses were cut and optically polished to 1 mm-thick samples for optical and spectroscopic characterizations.

2.2 Glasses characterization

The density of the glasses was measured at room temperature by the Archimedes' method using distilled water as immersion fluid with an estimated error of 0.05 g cm^{-3}. The concentrations of the RE ions (Er^{3+}, Nd^{3+} and Yb^{3+}) were 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 with an error of ± 3 °C using a Netzsch DTA 404 PC Eos differential thermal analyzer with a heating rate of 5 °C/min in sealed Pt/Rh pans. The glass stability parameter $\Delta T = T_x - T_g$ was calculated with an error of ± 6 °C for all the fabricated glasses.

The coefficient of thermal expansion (CTE) was measured by a horizontal alumina dilatometer (Netzsch, DIL 402 PC) operating at 5 °C min^{-1} 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 of the Nd-PG and Yb-PG and of the CPG and Yb-Er CPG samples was measured at 1061 and 1533 nm, respectively, by prism coupling technique using a Metricon 2010 Prism Coupler. Estimated error of the measurement was ± 0.001.

The absorption spectrum was measured on the Yb-Er CPG sample in order to identify the Yb^{3+} and Er^{3+} main absorption peaks. The measurement was performed at room temperature for wavelengths ranging from 300 to 1700 nm using a double beam scanning spectrophotometer (Varian Cary 500).

The continuous-wave (CW) photoluminescence spectra of Nd-PG and Yb-PG specimens in the near-infrared region were acquired by a Jobin Yvon iHR320 spectrometer equipped with a Hamamatsu P4631-02 detector, using standard lock-in technique. The emission spectrum of Nd-PG was obtained by exciting the sample with a monochromatic light at the wavelength of 785 nm, emitted by the fiber pigtailed laser diode Axcel B1-785-1400-15A, while the emission spectrum of Yb-PG was obtained by exciting the sample with a monochromatic light at the wavelength of 915 nm, emitted by the fiber pigtailed laser diode Bookham BMU8-915-01-R.

The fluorescence lifetimes 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 Yb-Er CPG, Nd-PG and Yb-PG samples, respectively. The detector used for this measurement was a Thorlabs PDA10CS.

3. RESULTS AND DISCUSSION

3.1 Rare-earth doped phosphate glasses for compact fiber amplifiers and lasers

Table 1 reports the thermal, physical, optical and fluorescence properties of the manufactured Nd-PG and Yb-PG samples.

Table 1. Glass transition temperature (T_g), onset crystallization temperature (T_x), glass stability parameter (ΔT), coefficient of thermal expansion (CTE), density, refractive index and fluorescence lifetime of the manufactured RE-doped phosphate glasses.

Glass label	T_g (°C)	T_x (°C)	ΔT (°C)	CTE ($°C^{-1}$) × 10^6	ρ (g cm^{-3})	n @ 1061 nm	Fluorescence lifetime [µs]
Nd-PG	522	790	268	8.1	3.01	1.548	329
Yb-PG	522	812	290	7.1	3.02	1.544	900

The glass stability parameter above 200 °C and the relatively low coefficient of thermal expansion exhibited by both glasses make them suitable for preform fabrication and crystal-free fiber drawing and promising active media for compact high-power laser devices.

Fig. 1 depicts the normalized emission spectra of Yb-PG and Nd-PG specimens in the region between 940 nm and 1110 nm recorded upon excitation at 915 nm and 785 nm, respectively. The emission peaks at 978 nm and 1004 nm correspond to the Yb^{3+}:$^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition, while the peak centered at 1054 nm is correlated to the Nd^{3+}:$^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition.

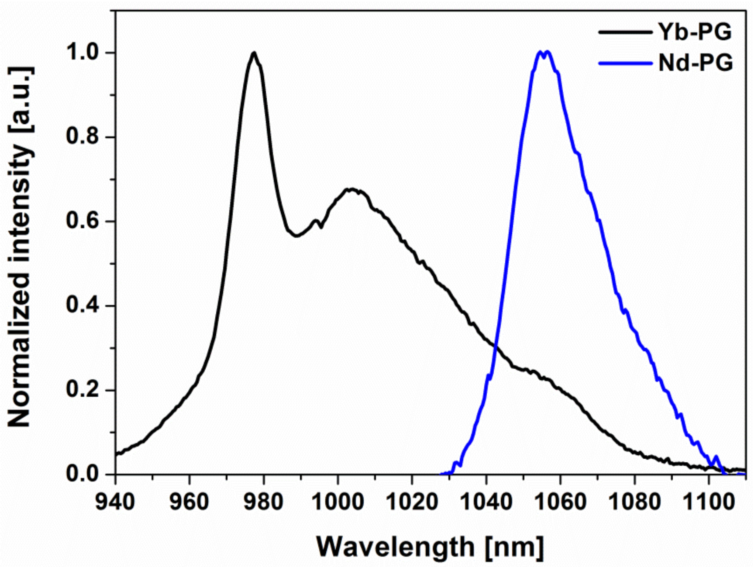

Figure 1. Normalized emission spectra of Yb-PG and Nd-PG specimens.

3.2 Bioresorbable calcium-phosphate glasses for biomedical applications

Table 2 reports the thermal, physical, optical and fluorescence properties of the manufactured CPG and Yb-Er CPG samples.

Table 2. Glass transition temperature (T_g), onset crystallization temperature (T_x), glass stability parameter (ΔT), coefficient of thermal expansion (CTE), density, refractive index and fluorescence lifetime of the synthesized undoped and Yb-Er co-doped bioresorbable calcium-phosphate glasses.

Glass label	T_g (°C)	T_x (°C)	ΔT (°C)	CTE (°C^{-1}) × 10^6	ρ (g cm^{-3})	n @ 1533 nm	Er^{3+}:$^4I_{13/2}$ fluorescence lifetime [ms]
CPG	435	658	223	12.4	2.61	1.514	n.a.
Yb-Er CPG	447	674	227	11.3	2.77	1.526	5.20

Both glasses prove to be stable against crystallization ($\Delta T > 200$ °C) and suitable for fiber drawing. Furthermore, they exhibit good thermo-mechanical compatibility and sufficient refractive index mismatch for effective light guiding. All these features make Yb-Er CPG and CPG particularly suited as core and cladding materials, respectively, for the development of a bioresorbable eye-safe fiber laser source operating at 1550 nm.

Fig. 2 shows the UV-Vis absorption spectrum of Yb-Er CPG sample in the region between 300 and 1700 nm. The absorption peaks related to the Yb^{3+}:$^2F_{5/2} \rightarrow {}^2F_{7/2}$ and Er^{3+}:$^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions, located respectively at around 1000 and 1550 nm, are clearly distinguishable.

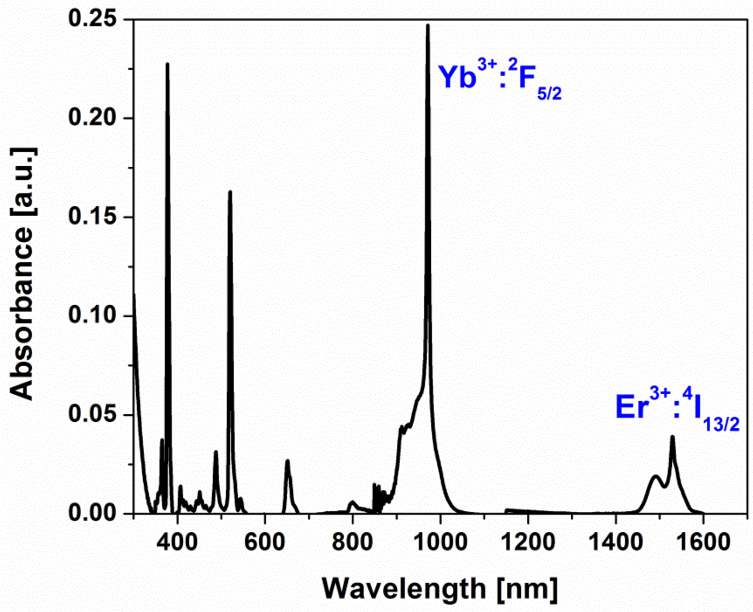

Figure 2. UV-Vis absorption spectrum of Yb-Er CPG sample. The Yb^{3+}:$^2F_{5/2}$ and Er^{3+}:$^4I_{13/2}$ levels are labeled.

4. CONCLUSIONS

This paper reports the design, processing and thermal, physical, optical and spectroscopic characterization of novel custom phosphate and calcium-phosphate glasses for photonic and biomedical applications. All synthesized materials were homogeneous, stable against crystallization and thus suitable for fiber drawing. In detail, Nd-PG and Yb-PG samples revealed to be promising active media for compact high-power laser devices, while Yb-Er CPG and CPG specimens proved to be particularly suited as core and cladding materials, respectively, for the development of a bioresorbable eye-safe fiber laser source operating at 1550 nm.

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