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Processing and characterization of novel borophosphate glasses and fibers for medical applications

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ABSTRACT

In this paper, we investigate the effect of P_2O_5 substitution by B_2O_3 in the $(50 - x)P_2O_5 \cdot 20CaO \cdot 20SrO \cdot 10Na_2O \cdot x B_2O_3$ glass system (x from 0 to 5 mol%) on the thermal and structural properties and also on the glass reactivity in simulated body fluid. The goal is to develop new glass candidates for biomedical glass fibers. The addition of B_2O_3 at the expense of P_2O_5 increases the refractive index of the glass and also the thermal stability of the glass indicating that these glasses are promising glasses for fiber drawing. Thus, within such glass composition, the core of a core–clad fiber has a larger concentration of B_2O_3 than the clad of the fiber to enable the light to propagate inside the core. All the investigated glasses form a calcium phosphate layer at their surface when immersed in simulated body fluid. It was found that small addition of B_2O_3 (1.25 mol%) leads to a decrease in the initial dissolution rate and a delayed layer formation. However, with increasing B_2O_3 content, the chemical durability decreased slightly but was higher than for the B-free glass. In addition, formation of the calcium phosphate layer was further delayed. This suggests that small contents of B_2O_3 led to formation of P–O–B bonds and only few BO_4 units, increasing the chemical durability. At higher B_2O_3 contents, the amount of BO_4 units increases which makes the glass network slightly more prone to be hydrolyzed. Thus, formation of BO_4 units induced by the addition of B_2O_3 at the expense of P_2O_5 reduces the reactivity of the glass in SBF. Borophosphate fibers were successfully drawn from preform. As expected from the bioresponse of the bulk glasses in simulated body fluid, the reduction in the intensity of the light transmitted is less and slower in a borophosphate fiber than in a phosphate fiber upon immersion.

1. Introduction

Biomaterials are an integral and vital part of our modern health-care system. Hand in hand with more sophisticated solutions coming on the market, the demand on biomaterials based on biomedical glass fibers has increased in the past decade. Fibers based on bioactive glasses can be used for reinforcement in composite [1,2] or biosensing [3]. Due to their biocompatibility, the silica based glasses such as 45S5 [4] and S53P4 [5] are well-known candidates for different biomedical applications including bone-grafting. However, these glasses are prone to crystallize at temperatures typical for fiber drawing [6]. The problems with crystallization may, however, be solved by developing new bioactive glass compositions with thermal properties better suited for fiber drawing processes.

Phosphate glasses are good alternatives to silicate glasses in biomedical applications, such as in bone repair and reconstruction [7]. Recently, new types of bioresorbable borophosphate glasses were found to be good choices for fiber drawing due to their suitable forming properties [8]. Borophosphate glass fibers are good candidates for soft tissue engineering applications involving muscles, ligaments, and tendons. In these, the tissue has, similarly to the glass fibers a high degree of anisotropy.

Borate glasses were found to accelerate the formation of a hydroxyapatite layer and bond to bone [9]. The bioactivity of calcium phosphate glasses was favored by the addition of boron due to the ability of boron to change coordination and to attach hydroxyl groups at the surface of the glasses [10]. The incorporation of boron into the P_2O_5–CaO–Na_2O–MgO glass system showed favorable effects on the cell metabolic activity, proliferation, and morphology [11].

In our previous study, the effect of partial substitution of SrO for CaO on the thermal and bioactivity properties of phosphate glasses in the P_2O_5–CaO–SrO–Na_2O glass system was reported [12]. SrO containing

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Table 1
Thermal properties of the investigated glasses.

	Density (g/cm^3) ±0.02 g/cm^3	$T_g \pm 2$ °C	$T_x \pm 2$ °C	$\Delta T = T_x - T_g$ °C	Refractive index at ±0.001		
					633 nm	1061 nm	1312 nm
B0	2.80	444	587	143	1.538	1.530	1.527
B1.25	2.83	451	629	178	1.542	1.534	1.531
B2.5	2.85	451	662	211	1.545	1.536	1.533
B3.75	2.88	462	670	208	1.547	1.539	1.536
B5	2.90	465	672	205	1.549	1.541	1.538

glasses are of interest since traces of Sr are present in the human body [13]. Moreover, it has been shown that Sr can easily replace Ca in the mineral part of the bone to form a stronger bone [14]. In our previous study [12], we showed that SrO-containing phosphate glasses are promising glasses for fiber drawing from preforms. We also found that the addition of SrO at the expense of CaO restrains the leaching of phosphate ions while maintaining similar surface reactivity than the Sr-free phosphate glasses. Additionally, partial to full substitution of CaO for SrO has been found to enhance adhesion and proliferation of cells [15]. However, the composition of the reaction layer forming at the surface of these glasses is closer to dicalcium phosphate dihydrate (DCPD) than hydroxyapatite (HA) [12]. In order to reach Ca/P ratio closer to 1.6 and to increase the bioactivity of the phosphate-based glasses, new glasses were prepared by partially replacing P_2O_5 by B_2O_3.

In this work we study the effect of B_2O_3 addition on the thermal, structural and bioactive properties of phosphate glasses in the P_2O_5–CaO–SrO–Na_2O glass system. We also discuss the impact of the fiber drawing on those properties. Thermal properties of the glasses were measured using a differential thermal analyzer (DTA). Structural characterization of the studied glasses was performed using combination of experimental tools such as NMR, Raman and IR spectroscopies. The in-vitro testing was performed in simulated body fluid.

2. Experimental section

The glasses with the composition $(50 - x)P_2O_5 \cdot 20CaO \cdot 20SrO \cdot 10Na_2O \cdot x\,B_2O_3$ with $x = 0, 1.25, 2.5, 3.75$ and 5 (mol%) (labeled respectively B0, B1.25, B2.5, B3.75 and B5) were prepared using the standard melting method in a platinum crucible. $NaPO_3$, H_3BO_3, $SrCO_3$, $CaCO_3$ and $(NH_4)_2HPO_4$ were used as raw materials. $Sr(PO_3)_2$ and $Ca(PO_3)_2$ precursors were first independently prepared using a slow heating rate up to 900 °C. The precursors were mixed with the other raw materials and melted in the platinum crucible at 1200 °C. The melts were poured on a brass mold and the resulting glasses were annealed at 40 °C below their respective glass transition temperature for 4 h.

Unclad monoindex fibers were drawn by using the well-known "rod" method with a specially designed drawing tower. Before drawing, the system was purged with an Ar gas laminar flow at the rate of 3 L/min in order to lower the moisture concentration. The thermal gradient of the drawing furnace permits the softening of the preform just above its lower extremity. In order to ensure that the draw conditions do not induce either nucleation or crystallization, the temperature profiles of the draw furnace (hot zone and pre-heat zone) were precisely mapped and the dwell time in these zones was controlled prior to and during the drawing. A narrow (5 mm length) drawing furnace was used to decrease the time of presence of glass rod in the critical high-temperature zone. The preforms were drawn at 600 °C under a He gas laminar flow of 2.5 L/min to create an inert atmosphere around the preform. The fiber was then fixed on the drum in rotary motion. A computer system based on LabView software was used to control the fiber diameter and drawing tension. Fibers were drawn to a diameter of ~125 μm at a rate of 10.1 m/min with a feed rate at 2 mm/min. Nominally, 50 m of single core fiber was obtained for each drawing run. The uncoated fibers (without any protective polymer layer) were used for measurement of the thermal, structural and optical properties.

A Scanning Electron Microscope from Leo 1530 Gemini from Zeiss coupled with an Energy Dispersive X-Ray Analyzer (SEM/EDXA) from Vantage by Thermo Electron Corporation was used to analyze the oxide composition of the samples. The compositions of the as-prepared glasses were found to be in accordance with the theoretical ones, within the accuracy of measurement (~1.5 mol%).

The glass transition (T_g) and onset of crystallization (T_x) temperatures of the glasses were measured by Differential Thermal Analysis (DTA, Netzsch F1 JUPITER) at a heating rate of 15 °C·min^{-1}. The T_g was taken at the inflection point of the endotherm, as obtained by

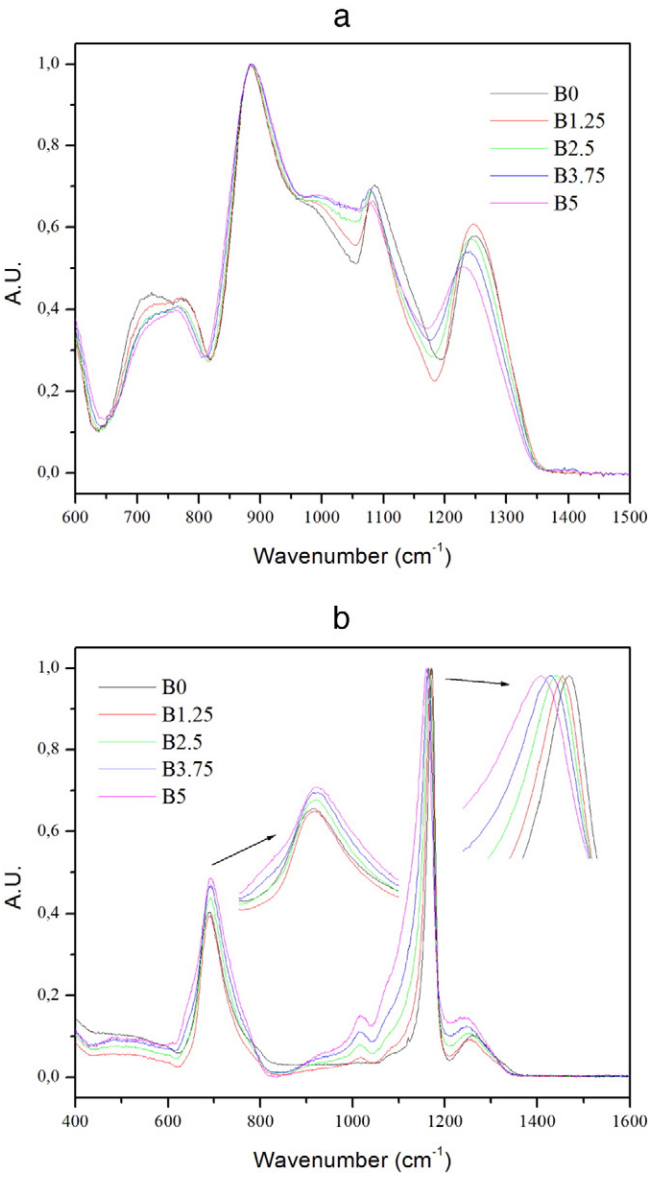

Fig. 1. IR (a) and Raman (b) spectra of the investigated glasses.