

# Sol–gel synthesis, structure, sintering and properties of bioactive and inert nano-apatite–zirconia glass–ceramics

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## Abstract

We synthesized four glasses of the system  $61.2\text{SiO}_2-(24.3-x)\text{CaO}-4.5\text{P}_2\text{O}_5-10\text{ZrO}_2-x\text{K}_2\text{O}$  ( $x=0, 2, 4, 6$  mol% = Ca replaced by K) using a sol–gel route and compared their properties with a  $68\text{SiO}_2-27\text{CaO}-5\text{P}_2\text{O}_5$  (mol%) Zr-free base glass. Their structure, sintering and crystallization behavior were investigated with the aim of converting the gel-glasses into dense glass–ceramics. Then, the *in vitro* bioactivity and mechanical properties of the optimized sintered samples were characterized. The structure of the gel-glasses was investigated by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR) and high-resolution transmission electron microscopy (HR-TEM). The sintering and crystallization kinetics of the glasses were studied by hot stage microscopy (HSM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The microstructures of the resulting glass–ceramics were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) coupled with energy dispersive spectroscopy (EDS). The apatite-forming ability of the sintered glass–ceramics in simulated body fluid (SBF) was investigated using FTIR spectroscopy and SEM. The three-point bending strength, Vickers microhardness and fracture toughness were also measured. Structural analysis by NMR and FTIR revealed that Zr acts as a glass former and K is a modifier, as expected. The  $\text{K}_2\text{O}$  addition strongly improved the material's sinterability, e.g., 2 mol%  $\text{K}_2\text{O}$  decreased the optimum sintering temperature from 1300 °C to 1050 °C. Uniformly dispersed  $\text{ZrO}_2$  nano-crystals, with particle sizes of 25–55 nm, were precipitated in the glass–ceramics. *In vitro* bioactivity tests confirmed that the  $\text{K}_2\text{O}$ -free glass–ceramics (partially sintered at 1000 °C) were bioactive and hydroxycarbonate apatite (HCA) grew on their surface after 24 h in SBF. However, the > 90% dense glass–ceramics with various contents of  $\text{K}_2\text{O}$  exhibited low solubility and a much smaller tendency toward HCA formation. Improvement of some mechanical properties was observed for the sample containing 2 mol%  $\text{K}_2\text{O}$ , in which apatite and zirconia crystallized. The 3p-bending strength and fracture toughness of the 94% dense sample were approximately 140 MPa and  $2 \text{ MPa m}^{1/2}$ , respectively. We propose that crack deflection by the  $\text{ZrO}_2$  crystals and the presence of Zr ions in the residual glass network are prevalent for improving the materials' mechanical properties. Some potential applications, such as bioactive scaffolds, are suggested for these glass–ceramics.

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## 1. Introduction

Glasses and glass–ceramics are promising materials for various applications, such as commodity products or parts of

sophisticated electrical, biomedical and optical devices [1,2]. Most monolithic glasses are produced via the classical melting–quenching process, and some can be converted into glass–ceramics by controlled heat-treatments. Such treatments are usually performed at relatively low temperatures, not far from the glass transition,  $T_g$ , to induce internal nucleation, followed by a second stage at a somewhat higher temperature to promote crystallization of different phases [3–5].

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Another, less frequent, process based on powder processing is sometimes used, in which glass powders are shaped and then sintered and simultaneously crystallized. The processing parameters are selected in such a way that the glass softens prior to crystallization and undergoes viscous flow and densification before the crystallization process is completed. Sintering and crystallization usually proceed concurrently, and the free surfaces of the glass frits encourage crystallization; hence, precise control of the chemical composition, frit particle size, temperature and time are essential [3–5].

Over the past thirty years, the synthesis of different glasses via the sol–gel route has attracted the attention of many researchers [6–8]. This method allows for low-temperature chemistry-based synthesis, where a sol containing chemical precursors gellifies under certain pH and concentration conditions near room temperature. Gels are wet inorganic networks of silica, which can then be dried and heated, e.g., at 600–700 °C, and are converted into a glass. In principle, sol–gel-derived glass powders exhibit higher purity and greater chemical homogeneity than melt-derived powders [6–9].

Among the numerous glass types prepared by the sol–gel method, many studies on bioactive glasses with the base composition  $\text{SiO}_2\text{--CaO--P}_2\text{O}_5$  have been performed, mainly because nano-porous glasses with high surface area containing hydroxyl groups can be easily synthesized by this procedure [9–15]. Nano-porous glasses are usually highly bioactive even if they have relatively high silica content, more than 60 mol% [8–10]. Therefore, extensive efforts have been made towards the synthesis of powders, porous particulates and mesoporous glasses for scaffold development, bone regeneration, drug delivery, and treatment of hypersensitive teeth, etc. [9–15].

One important drawback of the sol–gel synthesis over the melt process is that it is very difficult to obtain crack-free glass monoliths with diameters in excess of  $\sim 1$  cm [6,7]. One solution is to partially sinter gel-glass powders to a desirable density for particular applications, such as scaffolds, coatings and bone grafts. In this process, crystallization may be encouraged in some cases, depending on the intended application and whether the considered crystals are bioactive [8,12–14]. However, very few research results addressing the sintering process of bioactive gel-glasses have been reported. This apparent lack of reports may be due to the fact that gel-derived glass powders are highly porous and exhibit a great tendency toward incipient crystallization, which normally deteriorates their sinterability. This problem was predicted by one of us in 1992 [16]: “*Due to the intrinsic nature of gels (high OH-content, residual carbon, high fictive state), sol–gel glasses crystallize faster than melt-derived glasses at any temperature. Additionally, gels must be (in general) slowly heated from room temperature to approximately half the liquidus temperature to densify to a glass. That is a riskier path than quenching from the liquid state because the nucleation region is crossed on heating, allowing crystal growth from a plethora of nuclei* [16]”.

Our group has developed a bioactive  $68\text{SiO}_2\text{--}27\text{CaO--}5\text{P}_2\text{O}_5$  (mol%) gel-glass powder. We previously reported that this powder exhibits poor sinterability and maximum densification

is only reached at temperatures above 1300 °C. The resulting crystalline phases—crystoballite and pseudo-wollastonite—are neither bioactive nor suitable for good mechanical properties [17]. One solution for overcoming this problem would be to modify the composition by including “fluxing” agents such as  $\text{Na}_2\text{O}$ ,  $\text{B}_2\text{O}_3$ ,  $\text{K}_2\text{O}$  or  $\text{CaF}_2$  in the gel-glass composition [18–22]. In this regard, sintering with concurrent crystallization can be employed to convert the gel-glass powders into dense glass–ceramics.

Potassium oxide ( $\text{K}_2\text{O}$ ) belongs to the alkaline oxides group, which, in general, acts as a glass network modifier. This oxide reduces the viscosity and, for some compositions, helps to improve the sinterability of glass powder compacts [3]. Despite extensive studies performed on the biological performance of a companion oxide,  $\text{Na}_2\text{O}$ -containing gel-glass, only a few published studies are available on the effect of  $\text{K}_2\text{O}$  on the properties of gel-derived bioactive glasses [21–23]. It has been reported that replacement of  $\text{Na}_2\text{O}$  by  $\text{K}_2\text{O}$  increases the crystallization temperature in a  $\text{SiO}_2\text{--CaO--P}_2\text{O}_5\text{--Na}_2\text{O}$  glass [23], and its substitution for  $\text{CaO}$  improves sinterability [21].

In addition, for many years, researchers have been trying to incorporate  $\text{ZrO}_2$  into numerous glass and glass–ceramic compositions to benefit from its (potential) toughening aptitude. Their aims were to develop bone graft substitutes, bone cements and bioactive materials with improved mechanical properties and durability [24–31]. For example, inert and durable glass–ceramics containing  $\text{ZrO}_2$  are applicable for dental restoration build-up on a zirconia core (IPS Cosmo® is a commercial example) [2,24]. Reinforced bioactive glass–ceramics by  $\text{ZrO}_2$  particles have been studied for more than 20 years [25–31]. These materials are usually made by sintering or melting processes, which have some limitations. For instance, in the course of melting, zirconia often results in an increased melting temperature and viscosity of the liquid [24–27]. Through the sintering route, the zirconia powder can be mixed with a glass frit, and the pressed mixture must then be densified and crystallized. However, in this case, zirconia particles tend to agglomerate during mixing and also increase the sintering temperature [28–31]. Therefore, it is clear that fabrication of glasses and glass–ceramics with a high content of  $\text{ZrO}_2$  is difficult when conventional sintering or melting is employed.

The sol–gel process has been used as an alternative route to incorporate high contents of  $\text{ZrO}_2$  in glasses, and it appears that zirconium addition can be performed at room temperature, thus avoiding high melting and sintering temperatures [32–37]. We have recently reported on the cell proliferation and *in vitro* bioactivity of a new gel-glass powder in the  $\text{SiO}_2\text{--CaO--P}_2\text{O}_5\text{--ZrO}_2$  system [37]. We demonstrated that a simple sol–gel route can be used to synthesize a bioactive  $\text{SiO}_2\text{--CaO--P}_2\text{O}_5$  glass powder containing 10 mol%  $\text{ZrO}_2$ . In that article, we focused on the biological performance of the  $\text{ZrO}_2$ -containing bioactive glass and its glass–ceramic derivative powders (apatite–wollastonite–zirconia glass–ceramic). The addition of  $\text{ZrO}_2$  into the base glass composition reduced the rate of HCA formation from one day to three days. However, surprisingly, hydroxyapatite formed more rapidly on the crystalline powder surface than on the glass particles. We have demonstrated that  $\text{ZrO}_2$  can be employed

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