



# Development of bioactive silicate-based glass-ceramics from preceramic polymer and fillers

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## Abstract

Wollastonite/apatite glass-ceramics have been successfully prepared by a novel approach, consisting of the heat treatment of a silicone resin embedding micro-sized  $\text{CaCO}_3$  particles, that act as reactive fillers, and bioactive glass powder in the  $\text{SiO}_2\text{--CaO--P}_2\text{O}_5\text{--K}_2\text{O--Na}_2\text{O--MgO--CaF}_2$  system. Zn-containing silicates, such as hardystonite ( $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ ) and willemite ( $\text{Zn}_2\text{SiO}_4$ ), were also developed either by directly mixing ZnO powders with the glass, or by embedding them in the preceramic polymer, as additional fillers.

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## 1. Introduction

Preceramic polymers loaded with active filler particles offer the possibility of synthesis and near net shape manufacturing of ceramics components according to a very simple processing technique, i.e. the polymer/filler mixtures are converted into ceramics (polymer-derived ceramics, PDCs) by heating at moderate temperatures (generally below  $1400^\circ\text{C}$ ).<sup>1–4</sup> Fillers can be active, that is, react with the decomposition products of the preceramic polymer to create new phases, or passive, that is do not modify the composition of the polymer-derived ceramic phase. Favorable features of preceramic polymers, such as silicone resins, are their commercial availability, the low processing temperatures and the possibility of using polymer processing techniques for achieving complex shapes; through a control of the composition mixture, processing temperature and

heating atmosphere it is possible to produce multiphase ceramic components, including bioceramics.<sup>5–8</sup>

Apatite–wollastonite (A/W) glass-ceramics possess high bioactivity and good mechanical strength compared to the other bioactive glass-ceramics, which allows them to be used as load-bearing implants for the regeneration of hard tissue (i.e. in dental or cranio-maxillofacial surgery).<sup>9–11</sup> Kokubo et al. were the first to develop an A/W glass-ceramic, composed of apatite and wollastonite crystalline phases in a glassy matrix. The good bioactivity and strength of this material is due to the presence of wollastonite and apatite crystals.<sup>12–14</sup>

Zinc oxide has been added to the bioglass, glass-ceramics containing apatite and wollastonite, and was also incorporated in tricalcium silicate.<sup>15–17</sup> Hardystonite ( $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ , HT) ceramics are Ca–Si-based materials developed by incorporating zinc into the Ca–Si system to improve their chemical stability. The results reported in the literature suggest that  $\text{Ca}_2\text{ZnSi}_2\text{O}_7$  ceramic is conducive to the activity of both osteoblasts and osteoclasts, in turn suggesting its ability to induce proper bone remodeling, making it a candidate material for bone tissue regeneration and coatings onto currently available orthopedic and dental implants.<sup>18,19</sup>

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Table 1

The different formulations prepared for producing silicate bioactive ceramics from preceramic polymer plus filler mixtures.

Formulation	Composition (wt%)	Targeted ceramic phases
F1	80% AP40 (<25 $\mu\text{m}$ ) + 20% Wollastonite from preceramic polymer and filler (MK + $\text{CaCO}_3$ as filler)	Apatite–wollastonite
F2	40% AP40 (<25 $\mu\text{m}$ ) + 60% wollastonite from preceramic polymer and filler (MK + $\text{CaCO}_3$ as filler)	Apatite–wollastonite
H1	Hardystonite from preceramic polymer and fillers (MK + $\text{CaCO}_3$ , ZnO as fillers)	Hardystonite
H2	90% AP40 (<25 $\mu\text{m}$ ) + 10% ZnO	Apatite–wollastonite–hardystonite
H3	80% AP40 (<25 $\mu\text{m}$ ) + 20% ZnO	Apatite–hardystonite
H4	60% AP40 (<25 $\mu\text{m}$ ) + 40% hardystonite from preceramic polymer and fillers (MK + $\text{CaCO}_3$ , ZnO as fillers)	Apatite–wollastonite–hardystonite
H5	40% AP40 (<25 $\mu\text{m}$ ) + 60% Hardystonite from preceramic polymer and fillers (MK + $\text{CaCO}_3$ , ZnO as fillers)	Apatite–wollastonite–hardystonite

We already demonstrated in previous work that it is possible to produce pure wollastonite bioactive ceramics starting from preceramic polymers and fillers.<sup>4</sup> This research aimed at taking advantage of the preceramic polymer plus suitable fillers route to obtain apatite–wollastonite glass-ceramics and Zn-containing silicates. Unlike conventional apatite–wollastonite glass-ceramics, developed by a complicated process (comprising both melting and crystallization) and with limited shaping possibilities (e.g. hot pressing), the materials here presented have tunable phase assemblage and properties, while retaining the shaping possibility afforded by the presence of the preceramic polymer.

## 2. Experimental procedure

The preceramic polymer used in the present research was polymethylsiloxane, SILRES<sup>®</sup> MK (Wacker-Chemie GmbH, München, Germany) that is known to be converted, after the heating in air, into amorphous silica ( $\text{Si}_2\text{O}$ ) with a ceramic yield of 84 wt%. The MK silicone resin, in powder form, was dissolved in isopropyl alcohol under magnetic stirring for 10 min, then mixed with micro and nano-sized active and passive fillers, followed by sonication to obtain homogenous dispersions which were left to dry overnight at 60 °C in air. The active fillers consisted of micro-sized  $\text{CaCO}_3$  (<10  $\mu\text{m}$ , Sigma–Aldrich Ltd., Gillingham, UK) and nano-sized ZnO (30 nm, Inframat<sup>®</sup> Advanced Materials, Manchester, CT, USA) to obtain wollastonite and hardystonite-based ceramics; the passive filler was represented by a proprietary glass powder (AP40, BAM, Berlin, Germany; density 2.799 g/cc) that crystallizes into an apatite/wollastonite (A/W) glass ceramic upon heating. The AP40 glass powder (of composition (wt%): 44.30  $\text{SiO}_2$ , 31.89  $\text{CaO}$ , 11.21  $\text{P}_2\text{O}_5$ , 0.20  $\text{K}_2\text{O}$ , 4.60  $\text{Na}_2\text{O}$ , 2.80  $\text{MgO}$ , 5.00  $\text{CaF}_2$ ) was prepared by mixing pure raw materials for 2 h in a tubular mixer followed by melting process for 3 h at 1550 °C in a platinum crucible. After cooling, the glass frit was milled by means of a jaw crushing machine, by gradually decreasing the gap between the jaws; the resulting powders were carefully sieved to different size ranges: G (<25  $\mu\text{m}$ ), G1 (25–45  $\mu\text{m}$ ), G2 (45–90  $\mu\text{m}$ ) and G3 (90–100  $\mu\text{m}$ ).

The crystallization of the AP40 glass powder was assessed by using differential thermal analysis (DTA, Netzsch STA 429, Selb, Germany) at 10 °C/min in air. The effect of AP40 glass particle size on the crystallization behavior was studied using powders with different particle size. For the apatite/wollastonite

glass-ceramic formation, the AP40 glass powder was heat treated at different temperatures (720 and 900 °C) that cover the crystallization range of AP40 and were also used for crystallizing bulk samples in previous works.<sup>20,21</sup> The heating rate was 2 °C/min and the holding time was 1 h or 5 h; then the furnace was turned off and the samples subjected to natural cooling. Some experiments were also conducted using a two-step heating, with holding time at 720 °C of 1 or 5 h followed by heating at 900 °C for 1 or 5 h.

Stoichiometric formulations consisting of the MK polymer and fillers (Table 1) were used to obtain the different silicate-based bioactive ceramics. After drying of the mixtures of MK resin and fillers, the solid residues were manually ground into fine powders (sieved below 300  $\mu\text{m}$ ). The powders were uniaxially pressed in a cylindrical steel die, applying a pressure of 20 MPa for 30 s without any binder. Disk specimens with 16 mm diameter and 3 mm thickness were obtained and heated with 2 °C/min heating rate in the 900–1200 °C range for 1 h at maximum temperature, followed by cooling in the furnace.

The crystalline phases evolution was investigated using X-Ray diffraction (XRD, Bruker AXS-D8 advance, Karlsruhe,

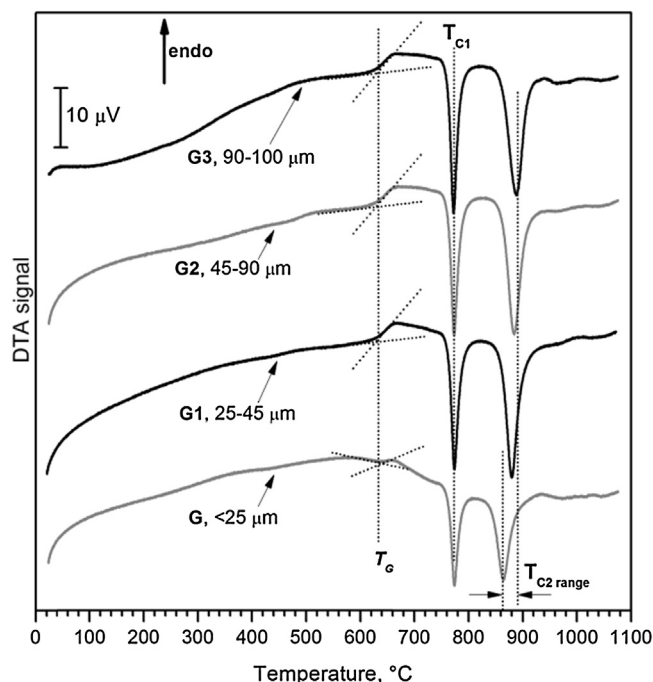


Fig. 1. DTA curves for AP40 glass in different particle sizes.

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