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In situ thermal and structural characterization of bioactive calcium phosphate glass ceramics containing TiO_2 and MgO oxides: High temperature – XRD studies

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Abstract

This study aims to develop glass ceramics in the calcium phosphate system that exhibit suitable properties to be used for biomedical applications. Calcium phosphate glasses with the incorporation of small additions of MgO and TiO_2 oxides were prepared in the pyro-and orthophosphate regions. The glass ceramics were prepared by a controlled powder sintering process through heat-treatment at different temperatures, as defined by results from differential thermal analysis (DTA). The composition of the crystalline phases precipitated in the glassy matrix as a result of heat treatments at different temperatures, ranging from 681 to 725 °C, was determined from X-ray diffraction data. The sequence of phase crystallization in the mother glass was also studied in situ using high temperature X-ray diffraction (HT-XRD) analysis. Results showed that the first phases that precipitated in the glass matrix were α- and β-$Ca_2P_2O_7$ at 620 °C. A small amount of $CaTi_4(PO_4)_6$ appeared at 630 °C. At 650 °C the three phases α-$Ca_2P_2O_7$, β-$Ca_2P_2O_7$ and $CaTi_4(PO_4)_6$ were clearly presented with a small amount of TiP_2O_7 and finally at 660 °C all four phases were observed. Glass ceramics were also characterized using Raman and X-ray photoelectron spectroscopy. This study demonstrates that, by altering the heat treatment cycle, it is possible to prepare glass ceramics in the calcium phosphate system that contains different bioactive and biocompatible phases.

1. Introduction

Calcium phosphate glasses have been considered as prospective materials for the reconstruction and repair of bone as a consequence of their biocompatibility and bioactivity, which are of enormous interest in the development of bioabsorbable material for bone healing applications. Therefore, a biocompatible resorbable material with increased resorption rates may be useful; this rate can be high and controllable in some calcium phosphate glass ceramics. Due to this feature and the fact that the composition of glass ceramics may resemble the mineral phase of bone, calcium phosphate glass ceramics may be tailored to be used as a cavity filler for maxillofacial surgery or as a drug delivery carrier, among other applications. However, a balance between

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their degradation rate and the bone remodeling time must be considered, as some glass systems are too soluble for some purposes. It is well known that by modifying the composition of these glass ceramics, the degradation rate can be controlled, and this can be considerably reduced by the incorporation of some metallic oxides in the glass network, such as TiO_2 [1–6]. Previous reports of the preparation of glass and glass ceramics in the $CaO–P_2O_5–TiO_2$ system have indicated that biocompatible and bioactive phases may be produced [7,8]. With this composition a new family of phosphate glass ceramics appears, with a mixture of soluble and less soluble crystalline phases, such as β-$Ca_2P_2O_7$ and $CaTi_4(PO_4)_6$, respectively [9–11].

The aim of this work is to study the crystallization of the glass in the system $CaO–P_2O_5–MgO–TiO_2$ prepared between the pyrophosphate (Q^1) and orthophosphate (Q^0) region ($3.5 < O/P < 4.0$). A heat treatment, defined by the results obtained from differential thermal analysis (DTA), was used to achieve nucleation and bulk crystallization. This heat treatment was studied in situ using high temperature X-ray diffraction (HT-XRD). Various other properties of the glass ceramics were studied by Raman and X-ray photoelectron spectroscopy and correlated to the changes in the glass structure after heat treatment.

2. Materials and methods

2.1. Glass ceramic preparation

The calcium phosphate glass was prepared with the composition of $37P_2O_5–45CaO–5MgO–13TiO_2$ in mol% (MT13) by the conventional melting technique, using the following analytical chemicals: $CaCO_3$, $MgHPO_4 \cdot 3H_2O$, TiO_2 and H_3PO_4. Briefly, after water quenching, the glass particles were dried and then pulverized in a ball mill pot by a wet-method using methanol to a mean particle size less than 10 μm [12]. This powder was firstly uniaxially pressed at 185 MPa to obtain disc shaped compacts followed by sintering/crystallization cycles at different temperatures. The heat treatment temperatures used to obtain the glass ceramics were based on the previous differential thermal analysis (DTA) results, as described elsewhere [12]. Briefly, these results showed that the values obtained for glass transition temperature, T_g, was 637 °C and the onset of crystallization was at 726 °C. Four different heat treatment temperatures (659, 681, 703 and 725 °C) that lay between these two values were chosen, Table 1.

Table 1
Heat treatment cycle applied to amorphous glass to obtain glass ceramics

Heat treatment	Temperature (°C)	Glass ceramic
NC	659	MT13NC
A	681	MT13A
B	703	MT13B
C	725	MT13C

2.2. Materials characterization

High temperature X-ray diffraction (HT-XRD) analysis was performed on the mother glass to study the sequence of phase crystallization. For HT-XRD, glass samples were analyzed using a Bruker D8 Advance diffractometer, with flat plate geometry and Cu-Kα radiation. Data were collected using a scintillation counter with primary and secondary Goebel mirrors from 20° to 50° (2θ), with a step size of 0.02° and a counting time of 1.7 s per step. The analysis was performed each 10 °C from 600 to 740 °C with a heating rate of 4 °C/min and a dwell time of 45 min per scan.

The heat-treated samples as prepared in the Section 2.1 were analyzed by X-ray diffraction (XRD) in order to identify and to quantify the percentage of crystalline phases that precipitated in the microstructure at the different treatment temperatures. For the X-ray diffraction measurements glass ceramics were ground to a fine powder and data were collected from 10° to 70° (2θ), with a step size of 0.02° and a counting time of 5 s per step. Satisfactory quantitative phase analysis of these samples using the Rietveld method, using the software GSAS, was not possible due to the complex powder patterns, in particular the presence of four different phases with differing peak widths/shapes, significant overlapping of peaks, and an amorphous phase. The weight fraction of each crystalline phase that precipitated for the different heat treatments was calculated from an equation that accounts for the scale factor of each phase and the density of each phase [13]. The purpose of these calculations was not to determine definitive values of the phase compositions of these samples, as it is acknowledged that such methods make numerous assumptions. In particular, they will not account for varying degrees of crystallinity of the different phases and preferred orientation effects. However, for the purpose of following trends in the evolution of the crystallization of the four phases with increasing temperature this model is adequate. For each diffraction pattern, a background was fitted and subtracted, using the Bruker DIFFRAC^{plus} EVA software. The uncertainty associated with the composition was less than 5%.

To identify functional groups, the glass and glass ceramic samples were analyzed by FT-Raman spectroscopy (transmission mode) using a system 2000 FTIR spectrometer (Perkin Elmer). The resolution used was 4 cm^{-1} and the number of scans was 200 for each analysis.