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The effect of synthesis route and magnesium addition on structure and bioactivity of sol–gel derived calcium-silicate glasses

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Abstract

Three silicate systems, i.e. pure SiO_2, SiO_2–CaO and SiO_2–CaO–MgO, were prepared via sol–gel method in two different ways: (*i*) following the acid catalysed route (noted A), and (*ii*) the quick alkali mediated route (noted Q). The thermal behaviour was investigated for the as-prepared matrices and, according to differential thermal analysis (DTA) and thermogravimetric (TGA) analyses, the calcination temperature was establish at 600 °C in order to remove the synthesis residues and to stabilise the structure. Structural, textural and morphological investigations on the heat treated samples were performed before and after immersion in simulated body fluid (SBF) by means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), N_2-adsorption and scanning electron microscopy (SEM). After 600 °C thermal treatment the samples remain mainly amorphous, only the CaO containing samples prepared by A route evidence an incipient Ca_2SiO_4 crystalline phase. The N_2-adsorption results showed that the specific surface area and the pore volume of the samples synthesised by Q route have higher values comparing with their counterparts prepared following the A route. Bioactivity tests carried out in SBF proved that the magnesium addition to the matrix obtained by Q route favours the hydroxyapatite (HA) self-assembly on the glass surface, and inhibits HA formation when it is added to the matrix obtained by A route. These results are supported by both FTIR and SEM analyses.

Keywords: D. Alkaline earth oxides; Bioactive glass; pH; Sol–gel

1. Introduction

There are two well known methods for preparing glasses and ceramics, the melt quenching and the sol–gel methods. The sol–gel method has become very popular in the last thirty years [1–10], being a chemical synthesis technique based on inorganic polymerisation reactions of metal alkoxides and metal salts precursors M(OR)*n*, where M represents the network forming element, such as Si, and R is an alkyl group C_xH_{2x+1} [11,12]. As starting materials are also used soluble metal salts in order to prepare by the sol–gel method multi-component systems which are difficult to be obtained by melting method, such as SiO_2–CaO system [10]. A main advantage in approaching the sol–gel method to obtain homogenous multi-component matrices consists in the fact that before polymerisation the components are in a homogenous solution, and the glass forming temperature is much lower than in the melt quenching method [12,13].

Jones and Fischbach [14] developed a "quick-set" process in order to obtain rapid gelation. This process consists in the adjustment of the acid sol's pH with dilute ammonium hydroxide, and leads to shortening of the gelation time from several days to a few minutes at room temperature. In the acid catalysed TEOS with excess of water solution are formed highly-branched, weakly-crosslinked clusters but the excess of water needed for complete hydrolysis of TEOS inhibits the condensation reaction [14–17]. By adding a base the gelation is induced because condensation between the ends and the middle sites of the chains is favoured [14].

Both acid catalysed and quick alkali-mediated sol–gel routes ensure accessible way to obtain bioactive materials [18] which can be used for bone repair or regeneration [19]. The capacity of these materials to form a bond with a living tissue is named

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bioactivity [20]. This ability takes place through the development of a biological apatite layer when those materials are immersed in physiological solutions [20,21].

Magnesium is an important element in the family of bioactive glasses, but is a very controversial in what regards its effects on the glass properties. Conventionally, magnesium oxide is thought to be a network modifier like calcium oxide within a silicate glass matrix [22], but some authors [23] suggest the possibility that it acts as an intermediate oxide in highly disrupted silicate glasses, and for this reason further studies are needed to clarify its structural role within a glass. Magnesium is also one of the most important elements in the human body, because it is involved in over 300 chemical reactions and can activate phagocytosis and regulate active calcium transport [22]. Therefore the magnesium ions play a significant role in the qualitative changes of bone matrix, determining the fragility of bones and, on the other hand, the depletion of magnesium adversely affects all stages of skeletal metabolism, causing cessation of bone growth [24–27].

Several studies [22,23,28,29] have reported the influence of different MgO concentrations on the properties of silicate materials. The lack of structural understanding of magnesium within glasses has led to many contradictions [22]. Further investigations are needed regarding its structural behaviour that is directly related to the bioactivity properties. To the best of our knowledge, the influence of the sol–gel preparation route (acid versus quick set) of the magnesium containing glasses was not reported before. Therefore the aim of the present work was to synthesise and characterise silicate bioactive glasses prepared by the sol–gel method following the acid catalysed and the quick alkali mediated routes, in order to compare the changes related to the addition of MgO beside CaO both in structure, morphology and bioactivity properties of the samples obtained by the two routes.

2. Materials and methods

Bioactive materials belonging to SiO_2, SiO_2–CaO, SiO_2–CaO–MgO systems were prepared by the sol–gel method with acid catalysed (A) and quick-set (Q) routes. The compositions in mol % of the prepared glasses are presented in Table 1: pure SiO_2, i.e. $100SiO_2$ (referred hereinafter as Si_A) synthesised following the acid catalysed route, and Si_Q as quickly prepared using the acid catalysed base condensed method, $75SiO_2 \cdot 25CaO$ (SiCa_A and SiCa_Q), $64.5SiO_2 \cdot 21.5CaO \cdot 14MgO$ (SiCaMg_A and SiCaMg_Q). The reagents used were tetraethoxysilan $SiC_8H_{20}O_4$ (TEOS) – precursor for SiO_2, calcium nitrate tetrahydrate $Ca(NO_3)_2 \cdot 4(H_2O)$ – precursor for CaO, magnesium nitrate hexahydrate $Mg(NO_3)_2 \cdot 6(H_2O)$ – precursor for MgO.

Table 1
The sample's acronym related to composition and synthesis route.

Acronym	Composition	Synthesis route
Si_A	$100 \cdot SiO_2$	**A**
Si_Q	$100 \cdot SiO_2$	**Q**
SiCa_A	$75SiO_2 \cdot 25CaO$	**A**
SiCa_Q	$75SiO_2 \cdot 25CaO$	**Q**
SiCaMg_A	$64.5SiO_2 \cdot 21.5CaO \cdot 14MgO$	**A**
SiCaMg_Q	$64.5SiO_2 \cdot 21.5CaO \cdot 14MgO$	**Q**

In order to obtain $100 \cdot SiO_2$ samples, tetraethylorthosilicate, distilled water and nitric acid (as a hydrolysis catalyst) were mixed (pH ~ 1.5) and the mixture was allowed to react for 30 min under continuous stirring for the acid hydrolysis of TEOS. Then half of the solution was left for gelation (Si_A) and to the other half ammonia solution was added drop wise under continuous steering for quick gelation (Si_Q). In the case of multicomponent glasses ($75SiO_2 \cdot 25CaO$ and $64.5SiO_2 \cdot 21.5CaO \cdot 14MgO$) the appropriate amounts of reagents, dissolved previously in distilled water, were added to the 1.5 pH TEOS solution under continuous steering. Following the same procedures as for the Si_A and Si_Q syntheses, SiCa_A, SiCa_Q, SiCaMg_A and SiCaMg_Q systems were obtained. The samples prepared by A route had different gelation times: 1 day Si_A, 2 days SiCa_A, 4 days SiCaMg_A. The solvent was removed from the resulted gels by drying for 24 h at 110 °C. Further, the samples were stabilized by heat treatment at 600 °C for 1 h, according to thermal analysis results obtained on the dried powders (xerogels).

The thermal behaviour was investigated with a Shimadzu differential thermal analyzer DTG-60H which simultaneously measures TG and DTA, in air, using alumina crucibles, with heating rate of 10 °C/min, from room temperature up to 850 °C. The structural properties of the samples were analyzed with a Shimadzu XRD-6000 diffractometer, using Cu Ka radiation ($\lambda = 1.5418$ Å), with Ni-filter with a speed of 2°/min, in the 10–80° range (2θ), and a JASCO FT/IR 6200 spectrometer in absorption mode in 1400–400 cm^{-1} spectral domain with a spectral resolution of 4 cm^{-1} using KBr pellet technique. Textural properties were investigated with surface area analyser Qsurf Series M1. The surface area of the samples was determined by measuring nitrogen adsorption/desorption isotherms at 77 K, using the Brunauer, Emmett and Teller (BET) equation. Scanning electron microscopy (SEM) images were taken with a FEI Quanta 3D FEG dual beam microscope. In order to amplify the secondary electrons signal, the powders were metallised with a gold thin layer of 5 nm in a Q150R ES automatic Sputter Coater, in argon atmosphere. Chemical analysis of local area was carried out by energy dispersive X-ray spectroscopy (EDS) measurements performed on the same microscope.

For in vitro bioactivity evaluation equal amounts of samples were incubated in simulated body fluid (SBF) obtained according to Kokubo's protocol [30], at 37 °C under static conditions, up to 14 days and the HAp layer formation on the glass surface was evaluated. The SBF solution was renewed every four days.

3. Results and discussion

The DTA curves (Fig. 1) reveal an initial endothermic process around 100 °C for all the samples, accompanied by weight loss, as observed in the TG runs. These events can be