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Nanocrystalline apatite formation on bioactive glass in a sol–gel synthesis

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ABSTRACT

The goal of this study was to understand the process involved in the formation of a nanocrystalline apatite phase during bioglass formation via a sol–gel process. X-ray diffraction, Rietveld refinement and transmission electron microscopy were employed to evaluate the structural changes and ordering processes that occur during glass formation. The presence of nanocrystalline apatite domains was observed after thermal treatment at temperatures lower than T_g. The formation of this phase was directly related to the initial segregation of calcium nitrate and triethylphosphate from the amorphous silicate clusters during the drying process. After thermal treatment at 300 °C, the calcium nitrate decomposed, and calcite formed. Calcite was further decarbonized, and the remaining phosphate groups reacted with calcium, increasing the quantity of nanocrystalline apatite domains. Higher than T_g, these domains acquire a higher crystallinity that was easily identified among the other crystallization products, such as combeite and β-cristobalite, following independent events. Therefore, the sol–gel process generates suitable conditions for apatite crystallization even during the initial formation of a bioglass at low temperatures and without being in contact with biological fluids.

1. Introduction

Bioactive glasses have been widely investigated and employed as implants and grafts due to their ability to form effective bonds with bone tissue [1,2]. When in contact with biological fluids, the bioglass surface tends to react with several ions present in the biological fluid, which generates a carbonated apatite layer similar to that found in the mineral phase of bones [3–5]. This apatite layer is responsible for the high biocompatibility associated with these ceramics. However, this apatite phase can be crystallized even during glass formation without previous contact with a biological fluid [6,7].

There are several types of bioactive glasses, including silicate-, phosphate- and borate-based glasses [8,9]. The best known bioactive glass composition is based on the SiO_2–Na_2O–CaO–P_2O_5 quaternary system [8]. As expected, the main crystalline phases generated during its crystallization process are silicates and phosphates [10,11]. The glasses crystallize at temperatures above the glass transition temperature (T_g), and they exhibit a typical amorphous structure at lower temperatures. However, regions with short-range ordering exist in the glass structure even below T_g [12].

The crystalline-like ordering in melt-derived glasses has been extensively studied over the years [13,14]. Several theories, concepts and models have been employed to explain the glass structure [13,15]. Currently, modern experimental techniques allow for the confirmation of the presence of short-range crystalline or nanocrystalline domains along the vitreous structure [16]. Gupta [15] suggested that the short-range ordering in a solid glass must be similar to that observed in its liquid phase.

Alkaline- and alkaline earth-containing glasses are more susceptible to forming nanocrystalline domains from the vitreous state because their ionic character promotes interruption of the glass network [12,17]. The weakness of the bond between the alkali/non-bridging oxygen allows for greater atomic mobility and consequently for the segregation of alkali elements forming the so-called modifier channels in the glass structure [17]. These channels are very reactive and cause susceptible regions to order.

Poorly ordered apatite domains have been identified in sol–gel--derived bioactive glasses using X-ray diffraction [6,7]. However, the intensity of the broad diffraction peaks embedded in the amorphous background from the vitreous phase does not allow for precise structural studies using conventional diffraction techniques. It is necessary to improve the acquisition conditions to obtain evidence of these nanocrystalline domains and to understand their real nature. Consequently, these broad peaks were not taken into account in several studies and have been assumed to be an amorphous background resulting from the vitreous structure [18–22].

In fact, these broad peaks are not observed in melt-quench-derived glasses at relatively low temperatures, which means that they are less susceptible to order and form these nanocrystalline domains [23,24,9,25]. Therefore, the mechanism for the formation of nanocrystalline apatite phases during glass formation at low temperatures has never

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Table 1
Theoretical (above) and experimental (below) compositions of the bioactive glasses measured by wavelength-dispersive X-ray fluorescence (WDXRF).

Sample	Composition (mol%)				
	SiO_2	P_2O_5	Na_2O	CaO	MgO
BV 0.0% MgO	64.00	5.00	5.00	26.00	0.00
	69.75 ± 0.82	2.06 ± 0.38	8.29 ± 0.84	19.72 ± 1.73	–
BV 1.2% MgO	64.00	5.00	5.00	25.00	1.00
	69.85 ± 0.91	2.04 ± 0.35	8.46 ± 0.17	19.41 ± 0.67	1.22 ± 0.01
BV 3.9% MgO	64.00	5.00	5.00	23.00	3.00
	64.62 ± 2.53	2.45 ± 0.62	7.78 ± 0.41	21.26 ± 2.21	3.87 ± 0.33

been studied in detail, particularly using X-ray diffraction with Rietveld refinement.

In a recent work [26], we investigated the partial replacement of CaO by MgO, SrO and ZnO on the properties of a SiO_2–Na_2O–CaO–P_2O_5 quaternary system obtained using the sol–gel method. After calcination below T_g, all of the samples presented a broad X-ray diffraction peak at approximately 32°, which could be attributed to a possible nanocrystalline apatite phase, except for a sample in which CaO was partially replaced by MgO. In this case, new diffraction peaks appeared in different regions, suggesting that MgO induced a phase transformation of this previously formed phase. It is known that Mg^{2+} ions can induce calcium apatites to transform into β-tricalcium phosphate at low temperatures [27]. Therefore, if a nanocrystalline apatite phase was in fact formed below T_g, one could expect that this phase was transformed to β-tricalcium phosphate induced by the presence of Mg^{2+} ions. Accordingly, we decided to use MgO as an additional tool for confirming the possible crystallization of nanoapatite domains during the formation of a bioactive glass below T_g.

2. Materials and methods

2.1. Bioactive glass syntheses

2.1.1. Materials

Tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$), nitric acid (HNO_3), TEP (triethyl phosphate, $OP(OC_2H_5)_3$), sodium nitrate ($NaNO_3$), calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) and magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) were used in the syntheses of the bioactive glasses.

2.1.2. Standard bioactive glass

A nominal glass composition of 64% SiO_2, 26% CaO, 5% P_2O_5 and 5% Na_2O (mol%) was initially proposed [26,28] (Table 1). The synthesis was performed at room temperature. TEOS was diluted with nitric acid and mixed until the solution became clear. Then, the other reagents were added in the respective proportions until the solution became clear again. Finally, the solution was stirred for an additional 1 h followed by storage in closed containers at room temperature for 10 days to allow for proper formation of the gel. The resulting gel was dried at 60 °C and 120 °C for 72 and 40 h, respectively. After drying, the material (xerogel) was ground, sieved and stored prior to heat treatment. The synthesis was performed in triplicate, and independent trials were employed to assess the reproducibility of the method.

2.1.3. MgO-containing bioactive glass

The synthesis of bioactive glass containing MgO was performed under the same conditions described above. However, the amount of calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) was reduced, while magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) was included at the same ratio. The nominal concentration of MgO was fixed at 1 and 3 mol%, which is inside the range that is typically acceptable in apatite structures [29] (Table 1).

2.2. Bioactive glass composition

The elemental composition of the bioactive glass was determined using wavelength-dispersive X-ray fluorescence (WDXRF). The analyses were performed with thermally treated samples at 700 °C using an X-ray fluorescence spectrometer (S8 Tiger, Bruker). The pellets were prepared for analysis with boric acid in a 9:1 ratio (bioactive glass).

2.3. Thermal behavior

The thermal behavior of the bioactive glasses was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA)

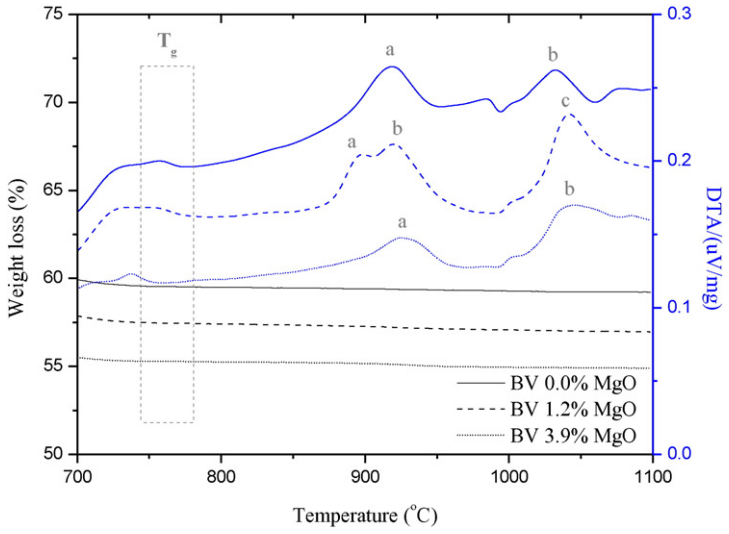

Fig. 1. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the bioactive glasses with different MgO concentrations. T_g: glass transition temperature; T_c: crystallization temperature; a: 1st crystallization event; b: 2nd crystallization event; c: 3rd crystallization event.