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Sol−Gel Glasses as Precursors of Bioactive Glass Ceramics

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The aim of this work was to study the influence of the composition and thermal treatment on the in vitro bioactivity of glasses and glass ceramics obtained by the sol−gel method, to obtain bioactive glass ceramics in a simpler system than those at present. For this purpose, gels in the systems SiO_2−CaO (**70S**: 70/30) and SiO_2−CaO− P_2O_5 (**55S**: 55/41/4) were heated at temperatures ranging between 700 and 1400 °C. The samples were characterized by DTA/TG, XRD, FTIR, SEM, and EDS and an in vitro bioactivity study in SBF was carried out. The results showed that all materials obtained (glasses or glass ceramics) were bioactive. The bioactivity was influenced by the initial gel composition, by the thermal treatment, and by the different phases present in the glass ceramics. In glasses the bioactivity decreased with the stabilization temperature. In the glass ceramics the bioactivity was favored by the presence of pseudo-wollastonite (most soluble phase of $CaSiO_3$) and of tricalcium phosphate.

Introduction

So-called bioactive glasses promote bone-tissue formation at their surface and bond to surrounding living tissue when implanted in the living body.[1] A common characteristic of bioactive materials is the formation of an apatite-like layer on their surface when they are in contact with physiological fluids or solutions that mimic human plasma.[2,3] Hench et al. reported the first bioactive glass in the system CaO−SiO_2−P_2O_5−Na_2O, which was obtained by fusion.[4] Subsequent research has concluded that the limit of SiO_2 content for bioactivity in melt-derived glasses was about 60 mol %.[5] In the past decade, the sol−gel technique has been used to prepare glasses, which allowed the expansion of the bioactive compositional range up to 90 mol % SiO_2.[6] The sol−gel process allows one to obtain glasses of higher purity, surface area, and homogeneity than by the fusion method. In addition this method enables one to prepare glasses at low temperatures and does not need to include components with the aim of decreasing the melting temperature (i.e., Na_2O), which allows simplifying the composition.

The mechanical strength of these glasses is insufficient; hence, their applications have been limited to non-load-bearing implants. Kokubo et al.[7] developed the glass-ceramic A-W that bonds to living bone in a short period of time and maintains high mechanical strength for a long period in vivo.[8] Bioactive materials used today, such as Bioglass, Ceravital, and Cerabone A-W, typically contain CaO, P_2O_5, and SiO_2, but also contain other components (Na_2O, MgO, CaF_2, etc.) that are necessary for preparation.[9]

The aim of the present paper was to obtain bioactive sol−gel glass ceramics with the simplest composition and to study the influence of the initial gel composition and the crystalline phases, introduced by thermal treatment, on the bioactivity. Two bioactive sol−gel gels were selected among the different compositions previously studied by our research team.[6,10−19] Since most of the bioactive glass ceramics contain phosphorus, a sol−gel glass in the system CaO−SiO_2−P_2O_5 was selected.[13] The other one was chosen in the binary system CaO−SiO_2 to use the simplest composition.[6] The chosen glasses were the most bioactive of each system and in

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Table 1. Nominal Composition of Synthesized Glasses (mol %)

	SiO_2	CaO	P_2O_5		SiO_2	CaO	P_2O_5
70S	70	30		**55S**	55	41	4

turn they have a very different Si/Ca ratio to induce, by thermal treatment, the crystallization of different phases and therefore a different bioactive behavior.

Experimental Section

Samples Preparation and Characterization. Materials belonging to the systems SiO_2−CaO and SiO_2−P_2O_5−CaO were prepared by the sol−gel method (the nominal composition is shown in Table 1). The gels were synthesized by hydrolysis and condensation of stoichiometric amounts of tetraethyl orthosilicate (TEOS), calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$], and triethyl phosphate (TEP) (in the case of **55S**). The syntheses were carried out as described previously.[6,13]

The dried gels were milled and sieved and the fraction of particles with sizes ranging from 32 to 68 μm was selected. The pellets (13-mm diameter and 2-mm high) were obtained by compacting 0.5 g of the gels by uniaxial pressure at 55 MPa and isostatic pressure at 150 MPa. After that, the pellets were treated at different temperatures as shown in Figure 1 where X corresponds to 800, 900, 1000, 1100, 1200, 1300, and 1400 °C. Theses samples were compared with the glasses treated at 700 °C for 3 h, the stabilization temperature generally used for sol−gel glasses.[19] After stabilization at 700 °C these materials are still amorphous and the nitrates have been completely eliminated.

The particle size distribution of the dried gels was measured by sedimentation in a Micromeritics Sedigraph 5100 Size Analyzer. Differential thermal analysis of glasses treated at 700 °C was carried out using a Seiko TG/DTA 320 Thermo balance from 30 to 1300 °C at 5 °C/min under an air atmosphere.

The samples obtained after the thermal treatments were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS), and N_2 adsorption.

To obtain the XRD patterns of samples heated at different temperatures, the pellets were milled and the powder analyzed in a Philips X'Pert MPD diffractometer using Cu Kα radiation in the range of 5−120° 2θ with a step size of 0.02° and a time per step of 10 s. The phase quantification was made by the Rietveld method[20] using the program X'Pert Plus (Philips). FTIR analyses were made on a Nicolet Nexus spectrometer on pellets prepared mixing 1 mg of the samples and 250 mg of KBr (IR grade). For the study of the samples' surfaces, after in vitro tests, the materials surface was scraped and mixed with the KBr. The SEM study was made in a JEOL 6400 Microscope-Oxford Pentafet super ATW system. For the SEM study, the samples were gold-plated. For the EDS analysis the samples were coated with carbon to avoid the overlap of one peak of gold with the K line of phosphorus. The specific surface area was calculated from the N_2 adsorption isotherm by using the BET method in a Micromeritics ASAP2010 operating between 10 and 127 KPa.

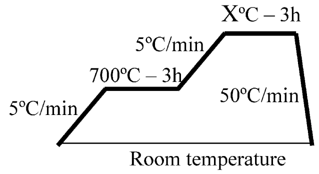

Figure 1. Scheme of the thermal treatment applied to the gels **70S** and **55S**.

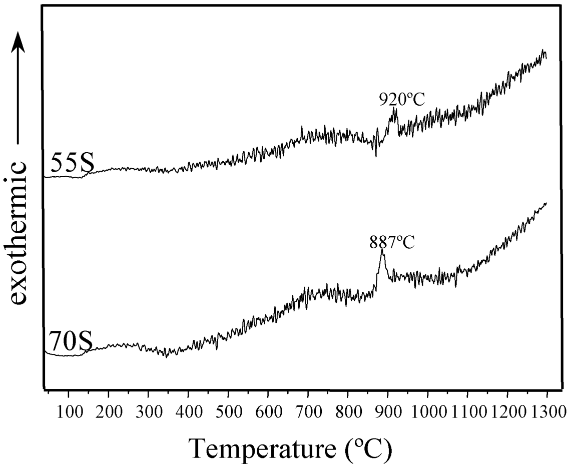

Figure 2. Differential thermal analysis (DTA) for **70S** and **55S** glasses after stabilization at 700 °C.

In Vitro Assays in SBF. In vitro assays were performed by soaking the disks, vertically supported in a platinum scaffold, in SBF[21] (pH = 7.30) at 37 °C. The geometric surface to solution volume ratio was 0.075 cm^{-1}. To avoid microorganisms contamination, the SBF was previously filtered using a 0.22-μm Millipore system and all operations were made in a laminar flux cabinet Telstar AV-100. The samples were soaked in SBF for 3 h, 1 day, 3 days, and 7 days. After soaking, specimens were removed from the fluid and gently rinsed with water and air-dried. Both the ionic concentration of the solution and the surfaces of the samples were studied.

The Ca^{2+} concentration and pH were measured in an Ilyte Na^+, K^+, Ca^{2+}, pH system. The formation of an apatite-like layer on the pellets surface was determined by glancing-angle incidence XRD, SEM-EDS, and FTIR analysis as described above.

Results

Starting Materials. The **70S** gel showed a wide particle size distribution with size ranging between 48 and 0.1 μm, the average equivalent diameter being equal to 9.3 μm. The **55S** gel showed a particle size ranging between 70 and 0.1 μm, but with a bimodal distribution centered at 30.2 and 1.1 μm and an average equivalent diameter of 2.0 μm.

The DTA thermograms of **70S** and **55S** previously stabilized at 700 °C are shown in Figure 2. The principal characteristic is the presence of an exothermic peak at 887 °C for the **70S** sample and 920 °C for **55S**. These

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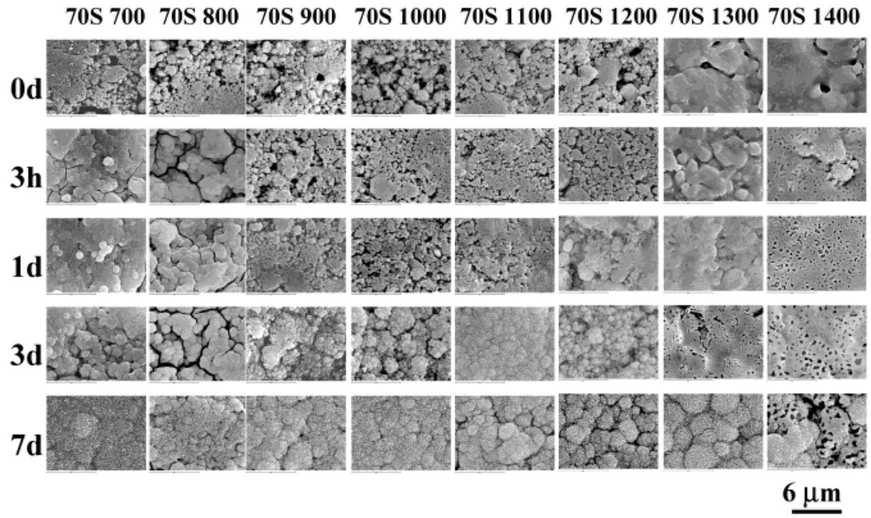

Figure 3. SEM micrographs of the **70S** sample heated at different temperatures (700−1400 °C) before (0d) and after soaking in SBF for 3 h (3h), 1 day (1d), 3 days (3d), and 7 days (7d).

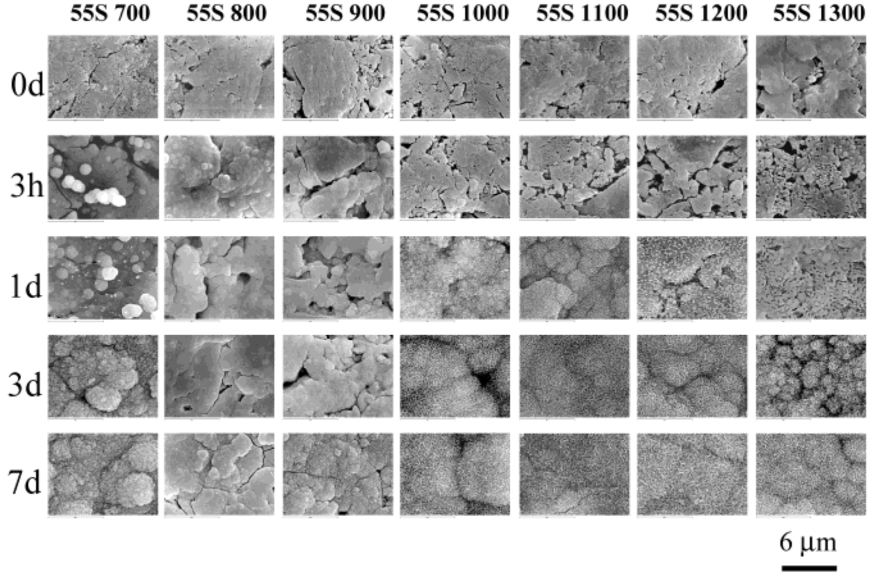

Figure 4. SEM micrographs of the **55S** sample heated at different temperatures (700−1300 °C) before (0d) and after soaking in SBF for 3 h (3h), 1 day (1d), 3 days (3d), and 7 days (7d).

peaks correspond to the crystallization temperatures of the samples. Endothermic processes at lower temperature were not observed, indicating that the previous thermal treatment (700 °C, 3 h) was enough for complete elimination of the nitrates.[22]

Samples Characterization. Although the same preparation conditions were used for both kinds of samples, the height of the **55S** gel pellets were lower than the that of the **70S** gel pellets, indicating better packing. Also, a higher contraction of the **55S** pellets was observed when the samples were heated. In addition, in the case of sample **55S** heated at 1400 °C, a fusion process took place and therefore this sample could not be studied.

In Figures 3 (0d) and 4 (0d) the morphology of the samples heated at different temperatures before soaking in SBF can be observed. The samples of **70S** (Figure 3, 0d) and **55S** (Figure 4, 0d) were constituted by irregular particles of small size and some agglomerates of them, being better compacted in the sample **55S**. The sintering process was not appreciable until 1300 °C in both samples.

The evolution of surface area (BET) of the samples vs temperature is shown in Figure 5 (maximum $\Delta x = 0.3$). As can be observed, the surface area greatly decreased in both compositions between 700 and 900 °C (from 78 to 10 and 88 to 7 m^2/g in **70S** and **55S**, respectively) and at higher temperatures the reduction was less pronounced (to <2.0 m^2/g).

Figure 6 shows the XRD patterns of **70S** and **55S** samples treated at different temperatures. The results of the phase quantification in both samples are shown in Table 2. The patterns of samples **70S-700** and **70S-800** are characteristic of the amorphous materials and no crystalline phases were detected. The samples heated between 900 and 1200 °C show maxima that correspond to pseudo-wollastonite (PsW, α-$CaSiO_3$)[23] and wollastonite (W, β-$CaSiO_3$)[24] with PsW being the majority phase. The PsW/W rate remains almost constant along

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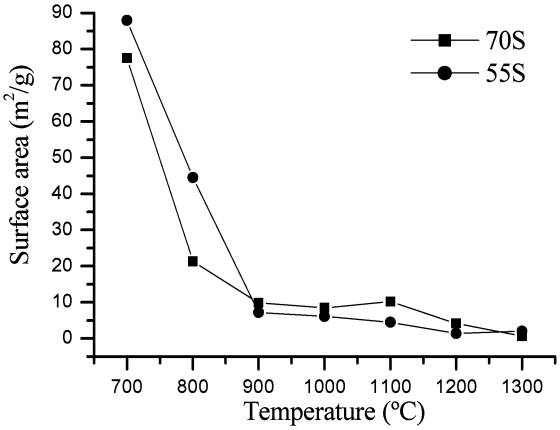

Figure 5. Surface area versus temperature for samples **70S** and **55S**.

this temperature range. However, in the sample heated at 1300 °C the W phase was not detected and a small maximum appeared at 21.5° 2θ that could be attributed to Cristobalite (Ct, SiO_2).[25] At higher temperature (1400 °C) the intensity of this maximum (21.5° 2θ) increased significantly and other maxima corresponding to Ct appeared, the Ct and PsW being the only phases present.

XRD patterns of samples **55S-700/800** correspond to amorphous materials, but a diffuse diffraction maximum at 32° 2θ was observed. This maximum was assigned to the (211) reflection of an apatite-like phase. When the sample was heated at 900 °C, the presence of crystalline phases could be detected by XRD but this phase/s could not be indexed. In samples heated at temperatures between 1000 and 1200 °C maxima corresponding to PsW and W phases were observed. In addition, another maximum at 30.7° 2θ, which is assigned to tricalcium phosphate (TCP, $Ca_3(PO_4)_2$),[26] was detected. In this temperature range the W was the majority phase. At 1300 °C, besides W, PsW, and TCP phases, a new maximum (21.5° 2θ) corresponding to Ct was detected and a great increase of the PsW phase took place.

Figure 7 shows the FTIR spectra of glasses treated at different temperatures. The FTIR spectra of samples **70S** and **55S** at 700 and 800 °C showed the characteristic bands for sol−gel glasses with these compositions. The band at 1090 cm^{-1} corresponds to the Si−O−Si stretching mode, whereas the one at 792 cm^{-1} is associated with a Si−O symmetric stretch. The band at 476 cm^{-1} is assigned at the Si−O−Si bending mode and the shoulder at 950 cm^{-1} is related to the Si−O−Ca vibration mode.[27] The FTIR spectra of samples of **55S** (containing P) showed in addition a doublet at 569, 603 cm^{-1}, which is associated with the stretching vibrations of phosphate groups[28] related to the presence of crystalline phosphates in the glasses. Besides, in these samples of **55S**, the band at 1090 appears at 1046 cm^{-1}.

At temperatures higher than 800 °C, in both samples, new bands were observed. In samples of **70S** these bands appear at 988, 938, 920, 809−800, 718, 644, 563, 472, and 432 cm^{-1}, whereas in samples of **55S** the principal bands were registered at 940, 903, 807, 719, 682, 644, 605, 565, 470, and 418 cm^{-1}. Another difference between samples **70S** and **55S** was that the band corresponding to the Si−O−Si stretching mode was observed at 1096 in **70S** samples whereas in **55S** samples this band appears at 1078 cm^{-1}.

The IR spectra of samples of **70S** heated between 900 and 1200 °C were similar and showed the bands previously mentioned, which are characteristic of PsW except the band at 644 cm^{-1}, which corresponds to W.[29] However, at higher temperatures (1300 and 1400 °C) the band assigned to W (644 cm^{-1}) was not present and in the sample **70S-1400** a new band at 620 cm^{-1} (corresponding to Ct[29]) appeared.

In the samples of **55S** the observed bands are characteristics of W and only one band (719 cm^{-1}) of PsW was observed up to 1200 °C. At 1300 °C other bands assigned to PsW were observed, but the band of Ct was not detected. In samples of **55S** two bands at 603 and 569 cm^{-1} corresponding to crystalline phosphates were observed.

In Vitro Assays in SBF. Figure 8 shows the cumulative variation of calcium concentration and pH of the samples of **70S** and **55S** heated at different temperatures for the soaking times in SBF used in this study. The general behavior of both compositions was a fast calcium release to the solution and increase of pH during the first day; such variations become lower between 1 and 3 days and very small changes of these values were observed between 3 and 7 days. In all samples studied the values of calcium concentration and pH were higher than those in the starting SBF solution (dashed line in Figure 8).

In samples of **70S**, at a soaking time of 3 h, the calcium concentration and the pH became lower as the samples were heated at higher temperature. At higher soaking times (1 and 3 days) the variations observed were quite different. For samples heated at 700 °C and between 900 and 1200 °C a great increase of calcium and pH values were observed whereas for samples heated at 800/1300/1400 °C the variations of these values were lower.

In samples of **55S** at a soaking time of 3 h a behavior similar to that mentioned above for the **70S** samples was observed. However, for higher soaking times the behavior was almost contrary to that previously described for samples of **70S**. In this case the calcium concentration and pH values for **55S** samples heated between 800 and 1200 °C were much lower than those observed for samples **55S-700** and **55S-1300**.

Figure 3 shows the SEM micrographs of samples of **70S** at different soaking times in SBF. The samples of **70S** heated at 700 and 800 °C showed similar behaviors.

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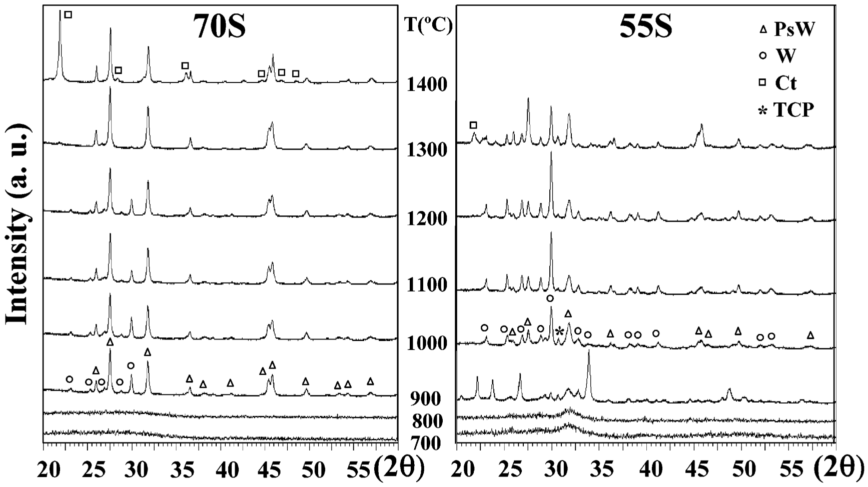

Figure 6. XRD patterns of samples **70S** and **55S** heated at different temperatures.

Table 2. Phase Composition of the Glass Ceramics Obtained (wt %)

		PsW	W	Ct	TCP
70S	**900**	77.2 ± 0.7	22.8 ± 0.2		
	1000	78.7 ± 0.1	21.3 ± 0.8		
	1100	80.3 ± 0.1	19.7 ± 0.8		
	1200	76.2 ± 0.8	23.8 ± 0.9		
	1300	98.0 ± 0.3		2.0 ± 0.8	
	1400	58.7 ± 0.8		41.3 ± 0.7	
55S	**1000**	31.8 ± 0.8	62.5 ± 0.5		5.7 ± 0.6
	1100	24.7 ± 0.3	72.3 ± 0.4		3.0 ± 0.6
	1200	25.2 ± 0.1	71.9 ± 0.4		2.9 ± 0.7
	1300	54.5 ± 0.3	37.6 ± 0.5	4.0 ± 0.5	3.9 ± 0.4

At a soaking time of 3 h, the surface was fully covered by a new layer formed of spherical particles. No appreciable differences were observed until 7 days of immersion where the SEM micrographs showed that the spherical particles were constituted by numerous small needlelike aggregates of higher size for the sample **70S-700**. In the samples treated between 900 and 1200 °C the new layer was not observed until 3 days of soaking. At this time, the layer was constituted by needlelike crystalline aggregates and an increase in the size of these needlelike crystals could be appreciated at 7 days of immersion. In the samples **70S-1300** and **70S-1400** the layer only could be observed after 7 days of soaking. This layer fully covered the surface in the sample **70S-1300** but in the **70S-1400** the surface was only partially covered, and in the zones where the layer was not present, small crystals on the material surface were observed. On the surface of both samples numerous pores were observed after soaking in SBF, and the size of these pores increased with the immersion time in SBF. This indicates the presence of a soluble phase in glass ceramics.

The SEM micrographs of samples of **55S** at different soaking times in SBF are shown in Figure 4. The behavior of **55S-700** was similar to that previously mentioned for **70S-700** but the needlelike crystalline aggregates were observed at 3 days of soaking. However, for samples of **55S** heated at 800 and 900 °C a change on the surface took place after 3 h of soaking, but the spherical particles were not observed and only after 7 days of soaking small crystallites could be observed in the sample **55S-900**. However, in the samples **55S-1000/1100/1200**, the layer constituted by crystalline aggregates was formed after 1 day, increasing the size of the needlelike crystals with the soaking time. In the sample **55S-1300** after 1 day of soaking, small pores on the surface were observed and after 3 days a new layer fully covered the entire surface.

Results obtained by EDS for samples before soaking agree with the nominal composition of the starting glasses. After 7 days of immersion the silicon content decreased whereas calcium and phosphorus increased in all samples. That indicates the formation of a layer rich in calcium and phosphorus on the sample's surface.

Figure 9 shows the glancing-angle diffraction patterns of samples **70S** and **55S** after 7 days of soaking in SBF. The X-ray diffraction pattern of the sample **70S-700** showed two wide diffraction maxima at 26 and 32° 2θ, corresponding to (002) and (211) reflections of an apatite-like phase. The XRD pattern of **70S-800** did not show maxima corresponding to any crystalline phase, suggesting that it was amorphous or the size of crystallites was too small to be detected by XRD. At higher temperatures (900−1200 °C) the samples of **70S** showed the two diffraction maxima mentioned above and, in addition, another diffraction maximum corresponds to the W, present in the initial sample. In the sample **70S-1300** the XRD pattern showed some maxima that could be attributed to PsW and Ct, besides those corresponding to an apatite phase. On the other hand, no apatite maxima were detected in sample **70S-1400**, and only maxima corresponding to PsW and Ct were observed.

The XRD pattern of sample **55S-700** showed the maxima corresponding to an apatite-like phase. However, the XRD patterns of samples **55S-800** and **55S-900** did not show the presence of an apatite-like phase. In **55S-1000/1100/1200** apatite maxima were observed and in addition maxima corresponding to W appeared. In the sample heated at 1300 °C, besides apatite maxima, other maxima assigned to Ct were observed. It is worth noting that in samples of **55S** the apatite maxima were sharper and more intense than those in samples of **70S**. That means that the layer formed was more crystalline in **55S** than in samples of **70S**.

The FTIR spectra of samples **70S** and **55S** before and after soaking in SBF for 7 days are shown in Figure 10. In the samples of **70S**, the main observations were the appearance of a doublet at 608−568 cm^{-1} (except

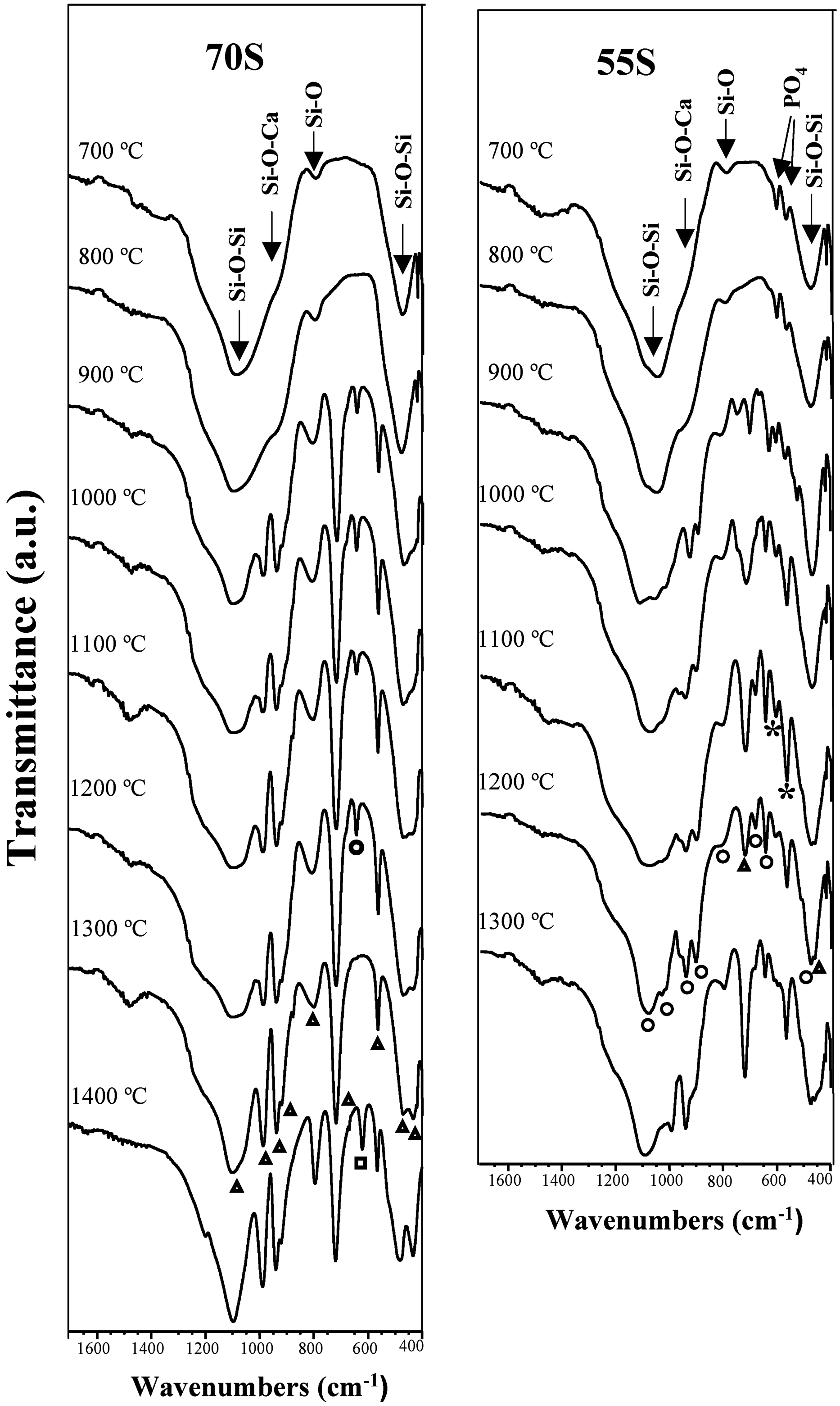

Figure 7. FTIR spectra of samples **70S** and **55S** heated at different temperatures. Symbols correspond to vibration modes characteristics of △ = pseudowollastonite, ○ = wollastonite, □ = cristobalite, and * = tricalcium phosphate.

in the samples **70S-800** and **70S-1400**) and a great decrease in the intensity of the bands of PsW.

The FTIR spectra of the samples of **55S** after 7 days of soaking in SBF were similar to the ones registered before soaking but some differences could be observed. In all samples, except **55S-900**, the intensity of the doublet at 608−568 cm^{-1} increased and, on the other hand, a decrease in the intensity of the bands corresponding to PsW were observed in the samples heated at temperatures between 1000 and 1300 °C.

Discussion

Samples Characterization. The XRD and FTIR analysis of samples of **70S**, heated at different temperatures (Figures 6 and 7), showed that at 700−800 °C amorphous materials were obtained, whereas when the

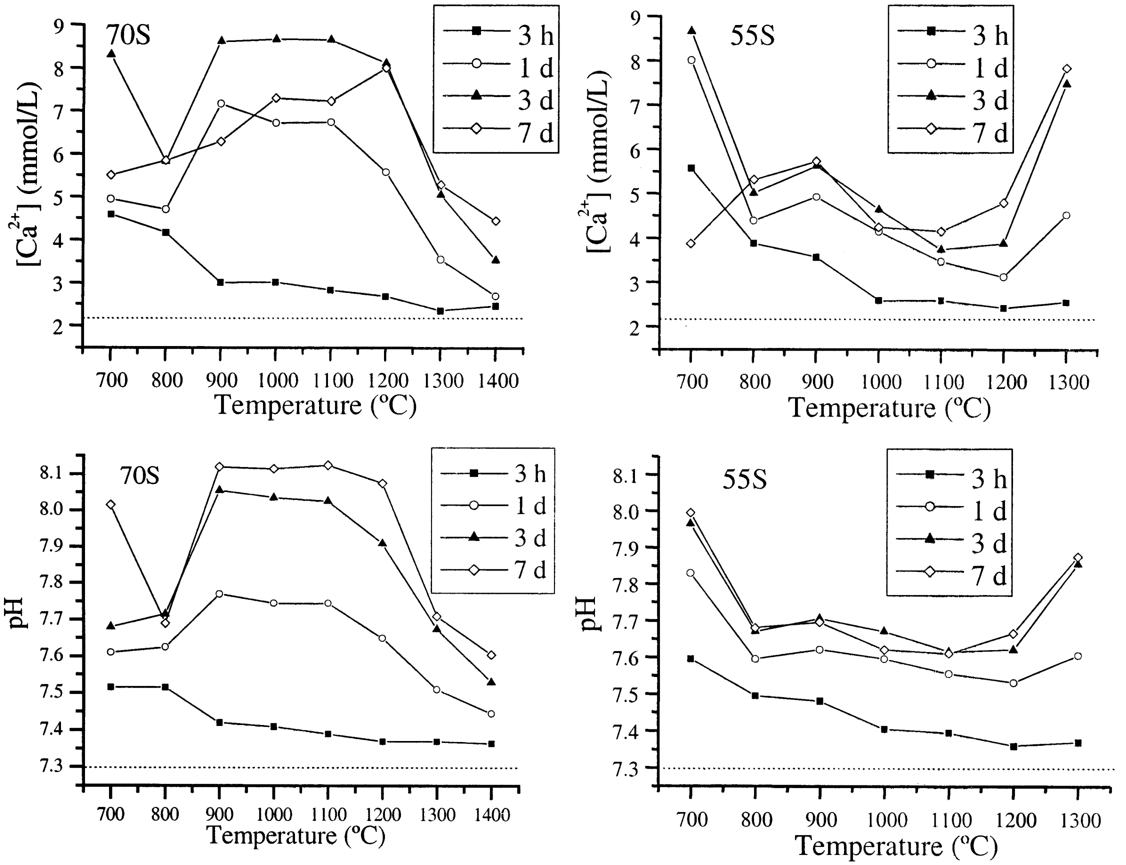

Figure 8. Changes in Ca^{2+} concentration and pH of samples **70S** and **55S**, heated at different temperatures, when soaked in SBF for 3 h, 1 day, 3 days, and 7 days.

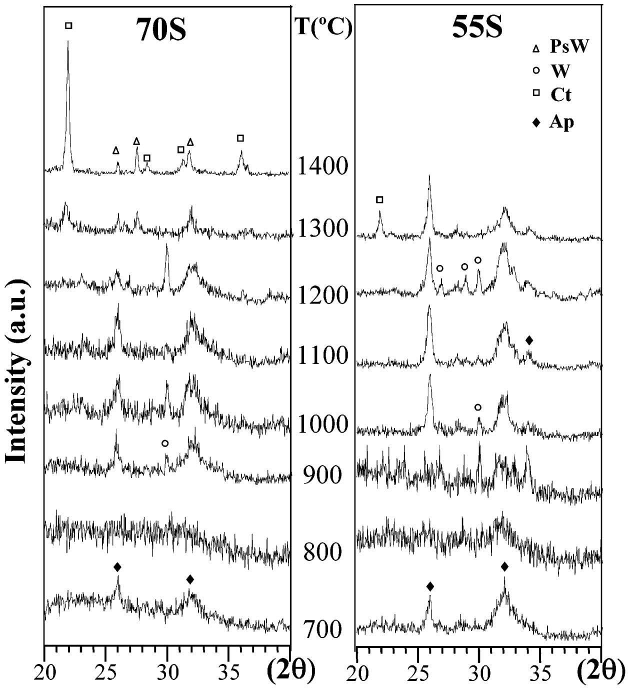

Figure 9. Glancing-angle incidence XRD patterns of samples **70S** and **55S** heated at different temperatures, after 7 days of soaking in SBF (Ap = apatite).

samples were heated at temperatures between 900 and 1200 °C a glass ceramic, with PsW and W crystalline phases, was obtained with PsW being the majority phase. At 1300 °C only PsW and a small amount of Ct were present, due to the transformation of the W phase in PsW, which is the stable phase at high temperature.[30] At 1400 °C a great increase of Ct phase was observed.

The XRD patterns and FTIR spectra of samples **55S-700/800** were characteristics of glasses with phosphorus in their compositions (Figures 6 and 7). In samples of **55S** heated between 1000 and 1200 °C, crystalline silicates were detected but in these samples the presence of TCP was also observed. Another difference when compared to **70S** samples is that in samples of **55S** the majority phase was the W. In samples heated at 1300 °C the presence of Ct was also detected. In the case of sample **55S-900** the crystalline phases could not be indexed. The DTA thermogram indicated that at 900 °C the crystallization process was not finished and for this reason the XRD pattern showed the presence of intermediate phases that could not be indexed. At higher temperature the crystallization was complete and therefore the stable crystalline phases were identified.

The results obtained indicate that the differences in the initial composition give rise to differences in the crystalline phases of the glass ceramics obtained, mainly in the ratio of $CaSiO_3$ (PsW/W) phases. In this sense, PsW was the majority phase in samples of **70S** whereas in samples of **55S** the majority phase was W. In addition, in samples of **55S** the presence of TCP was observed. On the basis of these results, the presence of phosphorus induces the crystallization of TCP and seems to stabilize the W phase, even at high temperatures where the PsW is the most stable phase.

It is worth noting that in both samples (**70S** and **55S**) glass ceramics were obtained and the crystallization of

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[30] Philips, B.; Muan, A. *J. Am. Ceram. Soc.* **1959**, *42*, 414.

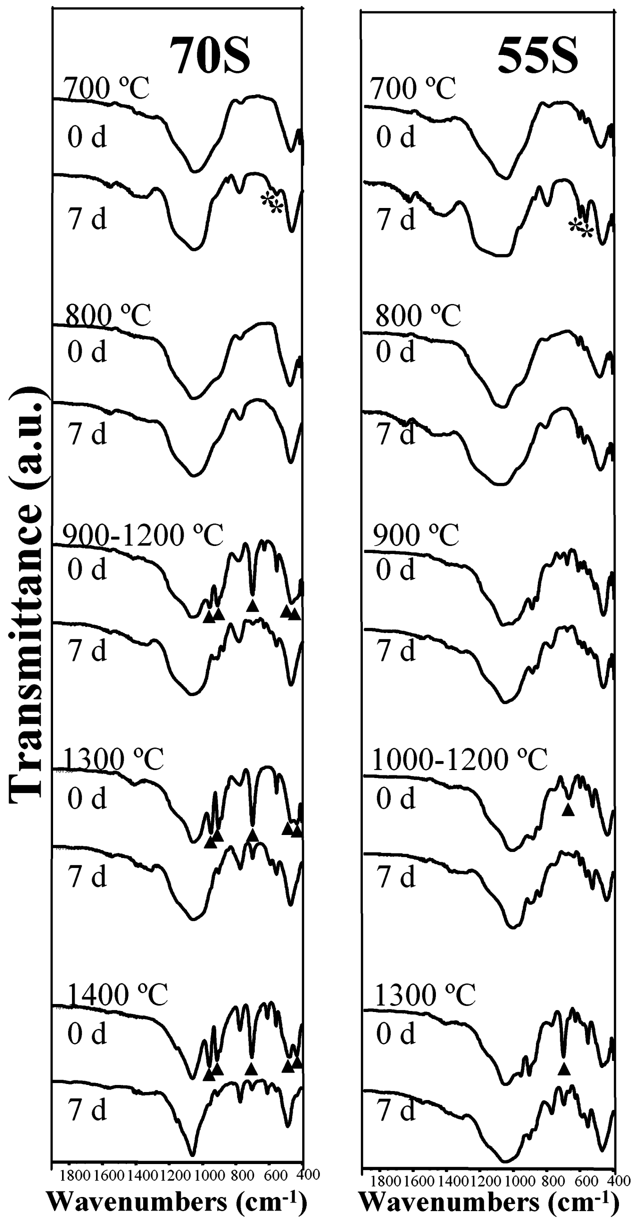

Figure 10. FTIR spectra of samples **70S** and **55S**, heated at different temperatures, before and after 7 days of soaking in SBF. Highlighted bands with higher variations (▲ = pseudowollastonite; * = tricalcium phosphate).

PsW and Ct was reached at temperatures lower than that proposed for Philips et al.[30] This could be attributed to the higher reactivity of the starting materials obtained by the sol−gel method.

In Vitro Assays in SBF. The study of the surface modifications of the glasses **70S-700** and **55S-700**, after soaking in SBF, revealed that a new layer assuming typically spherical particles was formed after 3 h soaked and that it was constituted by calcium phosphate.

When glasses were heated at temperatures lower than that necessary for the crystallization of stable phases (800 °C for the **70S** sample and 800−900 °C for the **55S** sample), the behavior was quite different from the one mentioned above. In these samples the release of calcium ions to the solution after soaking in SBF was lower than the one observed for the samples heated at 700 °C. The SEM study showed the formation of a new layer on the surface and the EDS results indicated that calcium content was lower and silicon content was higher with respect to those observed in samples heated at 700 °C. However, the results obtained by XRD and FTIR did not allow confirmation of the formation of an apatite-like layer. This means that the layer formed was more amorphous and less thick than the one formed on samples treated at 700 °C. A great decrease in the surface area was observed when glasses were heated from 700 to 900 °C. These results agree with those previously observed by Arcos et al.[17] They stated that the stabilization temperature has a great influence on the structural and textural features of sol−gel glasses and therefore the bioactive behavior of these glasses decreases as the stabilization temperature increases.

On the other hand, when the samples were heated at higher temperatures, the crystallization of stable phases took place and glass ceramics were obtained. The samples **70S-900/1000/1100/1200** showed a similar behavior and the apatite-like layer was observed by SEM (Figure 3) after 3 days of soaking in SBF whereas for samples **55S-1000/1100/1200** the new layer was observed after 1 day of soaking (Figure 4). In these samples the layer was constituted by needlelike crystalline aggregates whereas in the corresponding glasses these crystalline formations were observed at higher immersion times, although the layer was formed previously. The formation of an apatite-like layer after 7 days of soaking in SBF was confirmed from the XRD, EDS, and FTIR data. At this immersion time, besides the maxima corresponding to apatite, diffraction maxima corresponding to W were observed by XRD and the maxima corresponding to PsW were not observed even in the samples where it was the majority phase. In addition, by FTIR was observed that after SBF soaking the intensity of the bands corresponding to PsW decreased more than the ones corresponding to W. These results indicate a higher solubility of the PsW phase, which agrees with the behavior previously reported.[31] Therefore, the different behavior in Ca release and pH variations observed in the **70S** and **55S** glass ceramics must be related to the PsW content.

However, in sample **70S-1300**, with the highest PsW content, the calcium concentration and pH were lower than those in glass-ceramics **70S** obtained at lower temperatures. This indicates that although the PsW content plays an important role, it is not the only factor to be taken into account. In this sense, the great sintering process observed by SEM in this sample obstructs the process of dissolution of the PsW mainly from the bulk and therefore delays the formation of the apatite-like layer, which could only be observed at 7 days of soaking in SBF. In the sample **70S-1400**, in which the sintering process was higher, the apatite-like layer did not fully cover the surface, being observed only in some areas of the surface material, which indicates that although the sample was bioactive, the rate of formation of the layer was lower.

The nucleation and growth mechanism of an apatite-like layer on bioactive materials containing $CaO-SiO_2$, as first proposed by Kokubo et al.[32] in such materials, propose that an interchange between the Ca^{2+} ions of the material and the solution H_3O^+ takes place, giving

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(31) Lide D. R. *Handbook of Chemistry and Physics,* 73rd ed.; CRC Press: London, 1992; pp 4−94.

rise to the formation of Si−OH groups on the material surface that induce the apatite nucleation. The nuclei thus-formed later grow at the expense of the ions in the solution that has been saturated with respect to apatite.

On the basis of the proposed mechanism, it could be expected that the higher the Ca release is, the faster the new layer is formed. In this paper we have observed that the Ca release is related to the PsW content. However, in the samples **55S-1000**/**1100**/**1200** the new apatite-like layer was observed after 1 day of soaking (Figure 4) whereas in the corresponding samples of **70S** it was observed after 3 days, although in the latter samples the PsW content was higher. This could be attributed to the presence of TCP in the composition, which acts as a nuclei agent and catalyzes the formation of the new layer, in a way similar to those observed in bioactive glasses that contain phosphorus.[12,18] Therefore, in samples of **55S** heated at temperatures higher than 900 °C, the presence of crystalline TCP favors the crystallization of the apatite-like layer, although the calcium release and the pH variations were lower than those of **70S**.

Conclusions

Glasses and glass ceramics have been obtained as a result of heat treatments of gels prepared by the sol−gel method in the systems $CaO-SiO_2$ (**70S**) and $CaO-SiO_2-P_2O_5$ (**55S**). All samples were bioactive, even in the binary system.

In glass ceramics the bioactivity depends on phase composition determined by the initial composition and by the thermal treatment. In glass ceramics in the system $CaO-SiO_2$, the bioactivity was governed by the PsW content as well as by the degree of sintering. However, in the system $CaO-SiO_2-P_2O_5$ the existence of TCP as the crystalline phase favors the bioactivity more than the PsW content.

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(32) Kokubo, T. *Anales de Quimica: International Edition* **1997**, *93*, S49.