

LOW TEMPERATURE SYNTHESIS, STRUCTURE AND BIOACTIVITY OF $x\text{CaO}\cdot(1-x)\text{SiO}_2$ GLASSES

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Abstract

Glasses of composition expressed by the following general formula $x\text{CaO}\cdot(1-x)\text{SiO}_2$ ($0.30 \leq x \leq 0.50$) can be prepared by means of the sol-gel route starting from tetramethylorthosilicate and calcium nitrate tetrahydrate. They are all difficult to prepare by means of the traditional technique of quenching the melt, because of the high liquidus temperature, T_l , that in the case of $x=0.3$ glass is $T_l=1650^\circ\text{C}$. The DTA apparatus appears a valuable tool for defining the procedure necessary to obtain the glass through the sol-gel route. The glass $x=0.3$ is bioactive. The experimental results suggest that the gel structures, such as obtained at room temperature, are very similar; only at high temperature do the reactions of hydrolysis and polycondensation go to completion and the structural units characteristic of each glass are obtained.

Keywords: bioactivity, calcium silicate, glass, sol-gel method, structure

Introduction

It's known that glasses of the system $\text{CaO}-\text{SiO}_2$ for which the molar fraction of CaO is $0.30 \leq x_{\text{CaO}} \leq 0.55$ are bioactive [1]. However they are difficult to prepare owing to the high liquidus temperature, T_l , that for the $x=0.3$ glass is $T_l \approx 1650^\circ\text{C}$ [2]. Therefore the possibility of preparing them at low temperature by means of the sol-gel method is attractive. In this paper a manner to prepare them by means of this low temperature synthesis is described. Bioactivity tests were also performed on the $x=0.3$ glass.

Experimental

Glasses of the following general formula $x\text{CaO}\cdot(1-x)\text{SiO}_2$ $0.30 \leq x \leq 0.50$ were prepared, as indicated in the following section, by means of the sol-gel method by using analytical reagent grade tetramethyl-orthosilicate (TMOS) and calcium nitrate tetrahydrate. The $x=0.4$ and $x=0.5$ glasses were also prepared by melting analytical grade reagents CaCO_3 and SiO_2 in a platinum crucible in an electric oven.

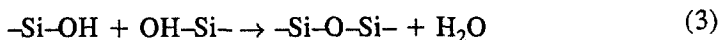
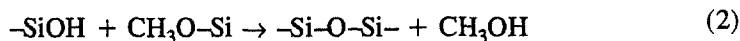
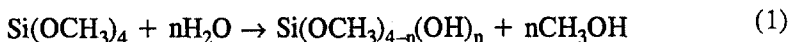
Differential thermal analysis (DTA) was carried out by means of a Netzsch Differential Scanning Calorimeter model 404M on about 50 mg powdered samples ($63-90 \mu\text{m}$) at heating rates $\beta = 10^\circ\text{C min}^{-1}$. Powdered Al_2O_3 was used as reference material.

In order to study their bioactivity, as made by other researchers [3], samples of the studied glasses were soaked in a simulated body fluid (SBF) with ion concentrations, as reported elsewhere [3], nearly equal to those of the human blood plasma. During soaking the temperature was kept fixed at 37°C. The ability to form an apatite layer was studied by submitting reacted samples to IR spectroscopy. Powders (-170+230 mesh) were soaked in SBF and analysed in IR spectroscopy. Taking into account that [4, 5, 7] the ratio of the exposed surface to the volume of the solution influences the reaction, a constant ratio was respected of 50 mm² ml⁻¹ of solution, as in [3]. Fourier transform infrared (FTIR) transmittance spectra were recorded in the 400–1200 cm⁻¹ region using a Mattson 5020 system, equipped with a DTGS KBr (Deuterated Triglycine Sulphate with potassium bromide windows) detector, with a resolution of 2 cm⁻¹ (20 scans). KBr pelletised disks containing 20 mg of sample and 200 mg KBr were made. The FTIR spectra have been elaborated by means of a Mattson software (FIRST Macros).

Results and discussion

Glasses of the system CaO–SiO₂ containing up to 19% of CaO have been, recently, prepared by means of the sol–gel route starting from tetraethylorthosilicate (TEOS) and calcium nitrate tetrahydrate [6] in ethyl alcohol solution. The studied glasses were prepared in a similar manner by using molar ratios of 22:1 and 5:1 of the alcohol with respect to the nitrate and TMOS respectively. The water was added, partly, altogether with the calcium nitrate; the water compressively added and the TMOS were in a molar ratio of 4:1. The clear and homogeneous solutions gave, in about 14 h, clear and homogeneous wet gels. After 10 days a 10% shrinkage was observed.

In Fig. 1 several DTA curves recorded at 10°C min⁻¹ are reported. The curve 1a is representative of the behaviour of all the gel samples. The endo peaks at 120 and 215°C may be assigned to evaporation of absorbed water and alcohol. The endo peak at 520°C may be attributed, as already proposed, to the decomposition of the residual organic groups and nitrate [6]. A broad exo-effect is observed in the temperature range 840–950°C, that should be due to formation of crystalline phases. It's interesting to compare Fig. 1a to 1b and 1c, in which the DTA curve are reported of the $x=0.4, 0.5$ glasses prepared by melting and quenching oxides mixtures. In these cases a slope change is clearly observed in the glass transformation range, in the temperature range 760–800°C, that is absent in the gel curve. The difference is due to the fact that glass formation, through the sol–gel route, occurs only at high temperature. In fact the following reactions are responsible of the gel formation [6]:



as the effect of the reported reactions, a gel forms at room temperature possessing a greater specific volume with respect to the glass. During drying at room tempera-

ture and firing at high temperature, reactions (2) and (3) go to completion and gel shrinks to glass. However the thermal treatment must be well selected in order to avoid the gel shrinking directly to the glass-ceramic product. This is supposed to occur in the case of Fig. 2a, thus justifying the absence of the T_g effect. In order to obtain a glassy product, the following procedure was followed: at first the gel was slowly heated at 5°C min^{-1} till 600°C , in order to eliminate the volatile species and the residual organic and inorganic products; afterwards it was rapidly heated at 765°C and left at this temperature for two hours. This temperature was chosen taking into account the DTA curves of Fig. 1a and 1b. In fact Fig. 1a indicates that the temperature $T=765^\circ\text{C}$ is sufficiently far off the temperature range in which the devitrified product is directly formed. Otherwise, from Fig. 1b, it can be estimated that the temperature $T=765^\circ\text{C}$ (which is 15°C lower than T_g) could be suited for the annealing of the 'quenched glass'; therefore at $T=765^\circ\text{C}$ the gel is expected to be

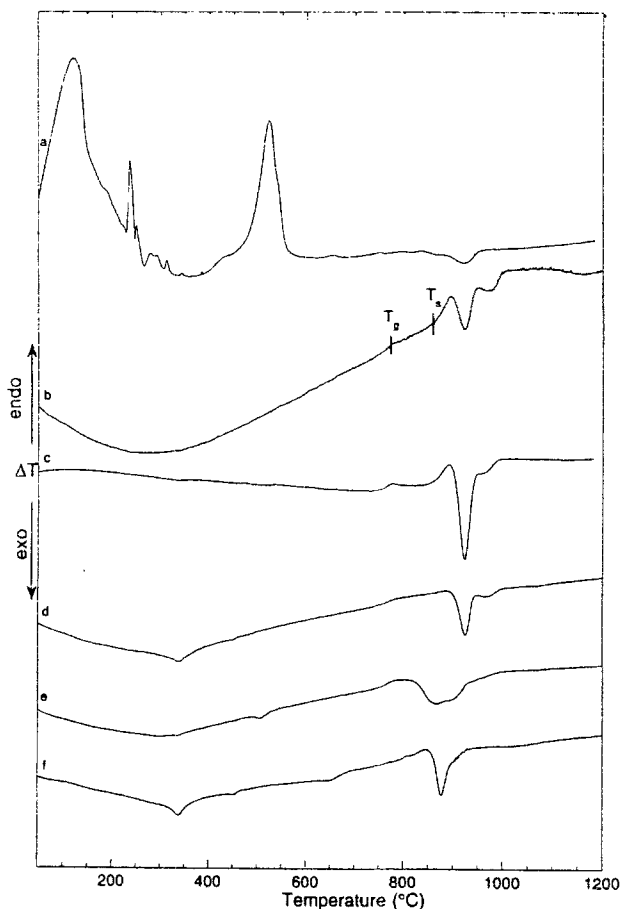


Fig. 1 DTA curves recorded at $10^\circ\text{C min}^{-1}$ of: a) gel $x=0.4$; b) 'quenched glass' $x=0.4$; c) 'quenched glass' $x=0.5$, d) 'gel glass' $x=0.3$, e) 'gel glass' $x=0.4$, f) 'gel glass' $x=0.5$; T_g =glass transformation temperature; T_s =softening temperature

fluid enough so that the excess volume can be eliminated and reactions (2) and (3) go to completion. Figures 1b and c show that the T_g changes slowly with the composition, in the studied composition range; therefore the same temperature was chosen for the final isothermal treatment of all the gels. When the products of this thermal treatments, that will be indicated as 'gel glasses', are submitted to DTA, the curves reported in Fig. 1d,e,f were obtained. In these curves a slope change in the glass transformation temperature range is clearly observed, preceding the devitrification exopeak.

In Fig. 2 the infrared absorption spectra of the gels are reported. The bands at 3400 and 1600 cm^{-1} are to be attributed to water [3, 7]. The 1400 cm^{-1} bands is, otherwise, due to NO_3^- stretching modes [6]. The bands at 1080 and 470 cm^{-1} are due to the stretching and bending modes of SiO_4 tetrahedra [8, 9]. As can be seen only slight differences appear between the spectra, although the CaO content is increased as much as 70%. In Fig. 3 the IR spectra of the 'gel glasses' are reported. As can be seen the described heat treatment is effective in promoting decomposition of nitrate. The water bands are not eliminated; otherwise it is known that water is rapidly and reversibly absorbed at room temperature [7]. The spectra of the 'gel glasses' are different in the wavenumber region $500\text{--}1200\text{ cm}^{-1}$. As can be seen the IR absorption band relative to the SiO_4 stretching model extends over a wider wavenumber range, the greater is the CaO content. It's worth remembering that the IR absorption band of SiO_4 , in the case of silica, is relatively sharp and occurs at 1100 cm^{-1} . When a modifier oxide is added, it shifts towards lower wavenumbers and covers a broader wavenumber range when greater amounts of the modifier are added [8, 10]. This has been attributed to the presence of SiO_4 tetrahedra bearing different number of nonbridging oxygens [8, 10]. Therefore of the modification of the IR

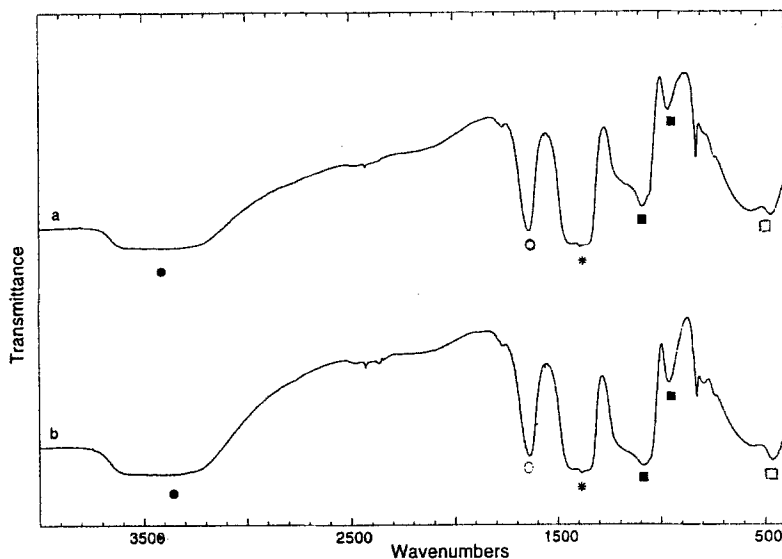


Fig. 2 FTIR spectra of a) gel $x=0.3$, b) gel $x=0.5$; • - H_2O stretching, o - H_2O scissoring, * - NO_3^- vibration, ■ - SiO_4 stretching; □ - SiO_4 bending

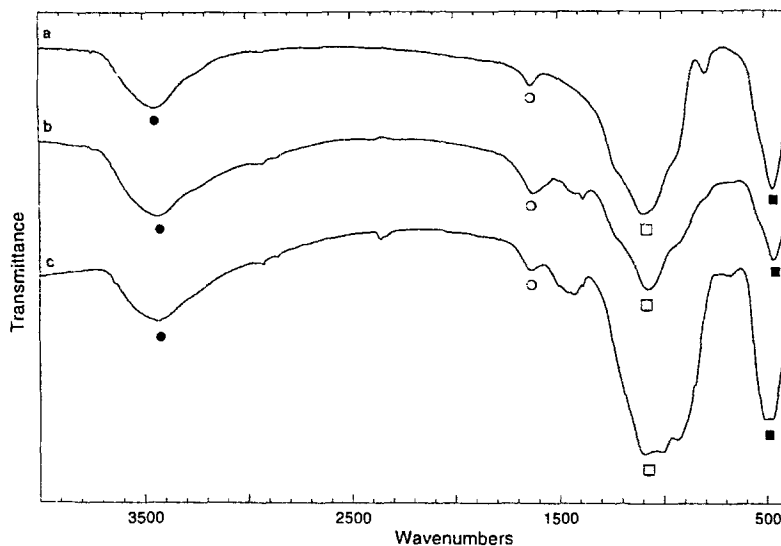


Fig. 3 FTIR spectra of a) 'gel glass' $x=0.3$, b) 'gel glass' $x=0.4$, c) 'gel glass' $x=0.5$. Symbols as in Fig. 2

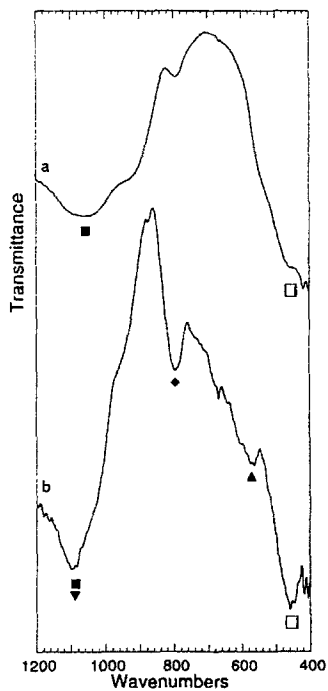


Fig. 4 FTIR spectra of the 'gel glass' $x=0.3$ before (a) and after (b) 7 days of exposure; ■ - SiO_4 stretching, □ - SiO_4 bending, ◆ - Si-O-Si vibration between two adjacent tetrahedra, ▽ - P-O stretching, Δ - P-O bending

spectra of 'gel glasses' in the Fig. 3 are consistent with the change of the glasses composition; the ratio of the number of oxygen for Si atom, in the case of the studied series, in fact, changes from $O/Si=2.43$, very close to the value $O/Si=2.5$ characteristic of phyllosilicates, (one non bridging oxygen per SiO_4 tetrahedron) to $O/Si=3$ characteristic of inosilicates (2 non-bridging oxygens per SiO_4 tetrahedron).

Therefore the results of Figs 2 and 3 indicate that the gel structure obtained at room temperature are very similar and that, with the preceding discussion about DTA curves, only at high temperature do reactions (1–3) go to completion and the structural units, characteristics of each glass, are obtained.

In Fig. 4 the results of bioactivity tests are reported for the 'gel glass' in which the content of calcium oxygen is the lowest ($x=0.3$). The IR spectra after 7 days exposure to SBF shows evidence of formation of a hydroxyapatite layer: the 1116 and 1035 cm^{-1} bands, usually assigned to P–O stretching [9], and the 580 cm^{-1} one usually assigned to the P–O bending mode [9] appear. Also the band at 800 cm^{-1} that can be assigned to the Si–O–Si band vibration between two adjacent tetrahedra characteristic of silica gel [12], appears thus supporting the hypothesis that a surface layer of silica gel forms as supposed in the mechanism proposed in the literature for hydroxyapatite deposition [1, 11].

Conclusions

Glasses whose composition is expressed by the general formula $xCaO(1-x)SiO_2$ ($0.30 \leq x \leq 0.50$) can be prepared through the sol–gel route, while being difficult to be produced by quenching the melts, owing to the high liquidus temperature. The $x=0.3$ glass has proved to be bioactive. The gel structures, such as obtained at room temperature, are very similar; only at higher temperature reactions (1–3) go to completion and the structural units, characteristics of each glass, develop.

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