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Sol–gel synthesis and crystallisation of $3CaO \cdot 2SiO_2$ glassy powders

G. Laudisio*, F. Branda

Department of Materials and Production Engineering, University of Naples, Federico II,
Piazzale Tecchio 80, 80125 Naples, Italy

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Abstract

A gel of composition $3CaO \cdot 2SiO_2$ was synthesised by means of sol–gel route involving hydrolysis of tetramethyl orthosilicate (TMOS) with calcium nitrate in alcoholic medium, and polycondensation reaction. The gel was submitted to DTA and TGA analysis and the resulted material was examined by FTIR spectroscopy and X-ray powder diffractometry. The thermal treatments required for the gel into glass conversion led to a partially devitrified product. The XRD analysis showed that the structure obtained is highly depolymerised. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Calcium silicate glass; Sol–gel synthesis

1. Introduction

The sol–gel process is a very powerful method for the production of glass and ceramics of technical importance [1]. The chemistry of sol–gel method involves hydrolysis and condensation of metal alkoxides, and is often not well characterised due to complexities of the reactions. By controlling some variables such as monomer precursor, reaction temperatures, water to alkoxide ratio, and catalyst, it is possible to vary the microscopic structure of the gel and, as a consequence, of the resulting ceramic. The important features, compared with solid state ceramics method, are high chemical homogeneity, lower processing temperature, control of size and morphology of the particles, the easy preparation of thin films and coatings and, in case of multicomponent systems, more uniform phase distribution and the possibility of preparing new crystalline or non-crystalline materials.

The main purpose of the use of the sol–gel method is to prepare glasses and ceramics at low temperatures, where the glass might not be produced in conventional melting technique, and the conventional powder compact consisting of oxide or carbonate crystalline raw materials might not be sintered well in the solid state reaction method.

The reported work is part of a more general study with the ultimate technological objective of determining the suitability and advantages of gels as starting materials for the preparation of bioactive glasses and glass ceramics. Bioactive are those materials that can bond to living tissue. As reported in literature [2] various kind of bioactive materials can be developed from $CaO–SiO_2$-based glasses. Since the dissolution

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* Corresponding author. Tel.: +39-81-768-2415; fax: +39-81-768-2595.
E-mail address: laudisio@unina.it (G. Laudisio).

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of the calcium ion from the glass and glass ceramics plays an important role in forming a biologically active bone like apatite layer on their surface in the body, it is expected that bioactivity increases with CaO amount in the glass composition.

As reported in literature [3] the range of glass formation in the CaO–SiO_2 system is limited for lower CaO content by the presence of a liquid–liquid immiscibility, and for higher CaO content by high liquids temperature. To overcome the impossibility of preparing these compositions by the conventional method, sol–gel processing can be successfully employed.

In a previous paper [4] glasses containing up to 20 mol% of CaO were prepared using TMOS and calcium acetate as precursor materials, and their properties were studied. These compositions lie in the liquid–liquid immiscibility dome of the phase diagram.

In previous papers [5–7] glasses for which the molar fraction of CaO is $0.30 \leq x_{CaO} \leq 0.55$ were also prepared by means of the sol–gel route starting from TMOS and calcium nitrate tetrahydrate. The glasses with $x_{CaO} = 0.40, 0.50, 0.55$ synthesised by this low-temperature technique were compared to the ones prepared by the melt-quenching technique from a mixture of oxides. Owing to its high liquidus temperature the glass with $x_{CaO} = 0.30$ is difficult to prepare by means of the traditional technique of quenching the melt so it is impossible to make a comparison.

The glass with $x_{CaO} = 0.30$ was proved to be bioactive. The glass of composition $2CaO{\cdot}3SiO_2$, prepared by sol–gel method, exhibited a different structure than the corresponding melt-quenched glass. The gel-derived glass was shown to be more active in attracting Ca and phosphate from SBF than the melt-quenched glass. In the case of $2.5CaO{\cdot}2SiO_2$ a completely amorphous sample was not obtained. Also in this case the experimental results suggested that the gel-derived material has a different structure than the corresponding melt-quenched glass.

In the work reported in the present paper a glass of composition $3CaO{\cdot}2SiO_2$, difficult to prepare by conventional melting technique owing to high liquidus temperature, was synthesised by sol–gel method, following an experimental procedure closely related to the one used in the other cases [4–7], and its crystallisation behaviour was studied.

2. Experimental

A gel of composition $3CaO{\cdot}2SiO_2$ was prepared by means of the sol–gel method using TMOS and calcium nitrate tetrahydrate analytical grade reagents as starting materials. Fig. 1 shows the flow chart of gel synthesis by the sol–gel method. An alcoholic solution of TMOS was mixed under continuos stirring with $Ca(NO_3)_2$ diluted in C_2H_5OH at room temperature. Under this condition gelation occurred in 1 day. The gel obtained was clear and homogeneous. After gelation the gel was held for 10 days at room temperature before beginning the heat treatments.

The nature and the temperature ranges of the various reactions that occur during the heating of the dried gel were determined using thermogravimetric (TGA) and differential thermal analysis (DTA). Sample (20 mg) of the dried gel was subjected to a TGA run in N_2 at a heating rate of 10°C/min from room temperature to 950°C. A Netzsch TG 209 was used. DTA curves were recorded in N_2 for powdered specimens of ca. 50 mg. A Netzsch heat flux apparatus, model 404, was used with Al_2O_3 as reference material.

Fourier transform infrared (FTIR) transmittance spectra were recorded in the 400–2000 cm^{-1} region using Mattson 5020 system, equipped with a DTGS KBr (deuterated triglycine sulphate with potassium bromide windows) detector. A spectral resolution of 2 cm^{-1} was chosen. Each test samples was mixed with KBr (1 wt.% of gel) in an agate mortar, and then was pressed into 200 mg pellets of 13 mm diameter. The spectrum of each sample represents an average of 20 scans, which were normalised to the spectrum of the blank KBr pellet. The FTIR spectra have been elaborated by means of a Mattson software (FIRST Macros).

The amorphous nature of the gel and the devitrified samples were analysed by computer interfaced X-ray (Cu Kα) powder diffractometry (XRD) using a Philips diffractometer model PW 1710 with a scanning speed of 1° min^{-1} and a built-in computer search program. The X-ray diffraction (XRD) patterns were matched to JCPDS data and the phases identified.

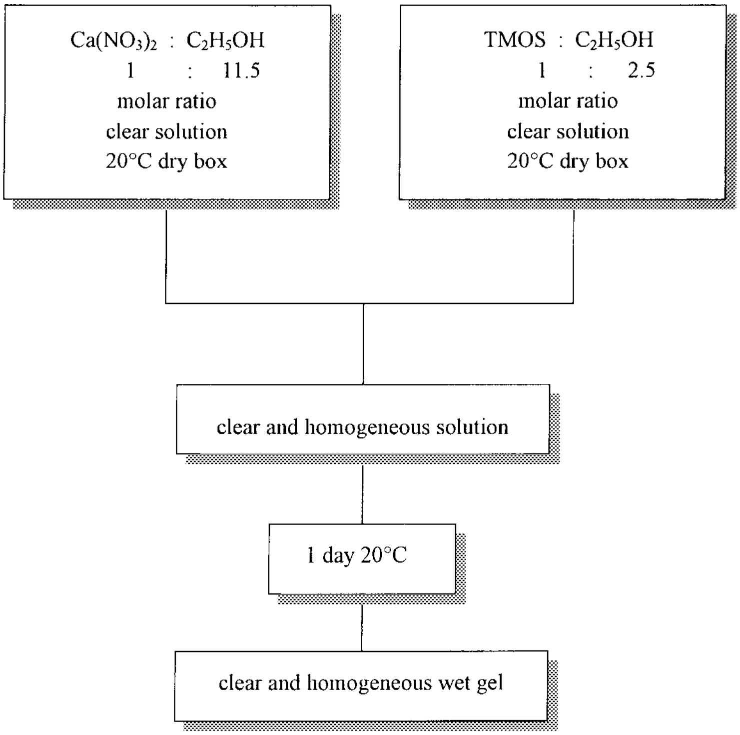

Fig. 1. Flow chart of gel synthesis.

3. Results and discussion

Gelation is the result of hydrolysis and condensation reaction according to the following equation:

$$\mathrm{Si(OCH_3)_4} + n\mathrm{H_2O} \Rightarrow \mathrm{Si(OCH_3)}_{4-n}\mathrm{(OH)}_n + n\mathrm{CH_3OH}, \quad n \leq 4$$

$$-\mathrm{SiOH} + \mathrm{CH_3O{-}Si}- \Rightarrow -\mathrm{Si{-}O{-}Si}- + \mathrm{CH_3OH} \qquad (2)$$

$$-\mathrm{Si{-}OH} + \mathrm{HO{-}Si}- \Rightarrow -\mathrm{Si{-}O{-}Si}- + \mathrm{H_2O} \qquad (3)$$

during drying at room temperature and firing at higher temperature reactions 2 and 3 go to completion and the gel shrinks to a densified product.

Fig. 2(a) shows the infrared transmittance spectra of the gel dried 3 h at 100°C. The infrared absorption peaks were assigned as follows: the sharp and weak peak at 823 $\mathrm{cm^{-1}}$ is attributed to the bending modes of $\mathrm{NO_3}^-$; the two bands at 965 and 1099 $\mathrm{cm^{-1}}$ were attributed, respectively, to stretching of $\mathrm{SiO_4}$ tetrahedra containing non-bridging oxygens and to the one with only bridging oxygens. The presence of nitrate groups is confirmed by the presence of a strong band at ca. 1400 $\mathrm{cm^{-1}}$ attributed to the stretching of $\mathrm{NO_3}^-$; finally the peak at 1645 $\mathrm{cm^{-1}}$ is due to stretching of $\mathrm{H_2O}$. The presence of traces of water, may be due to the reversibly absorption of water from the atmospheric moisture [8].

The dried sample was submitted to TG analysis in order to define the proper thermal treatments necessary for the gel into glass conversion. In Fig. 3(a) and (b) are reported the TGA curve and the corresponding derivative. As can be seen in Fig. 3(b) there is a small peak at about 100°C corresponding to loss of reversibly absorbed water. The weight loss of ca. 5% at 350°C is attributed to the reactions 2 and 3 with the consequent removal of the by-product. In the temperature range 500–600°C there is the largest weight loss, which may be attributed, as already proposed [9], to the decomposition of residual organic groups and nitrate.

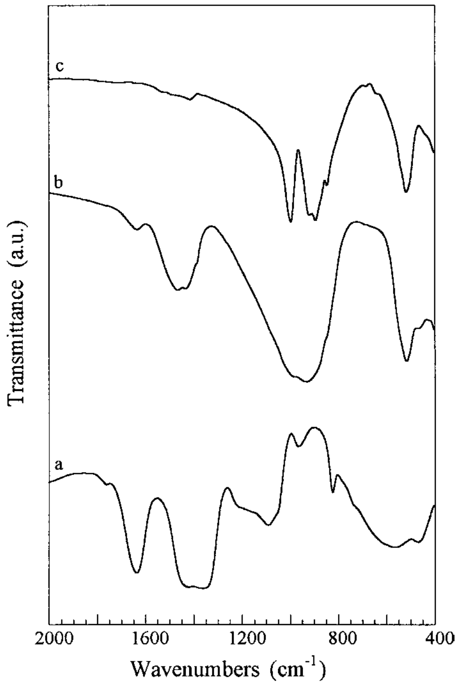

Fig. 2. FTIR spectra of: (a) gel dried 3 h at 100°C; (b) dried gel heated up to 600°C; (c) dried gel after a DTA run up to 1200°C.

According to this TG analysis a first thermal treatment consisting in a slow heating at 5°C/min till 600°C was chosen, closely analogous to the heat treatment chosen in the case of the glasses having a CaO molar fraction $0.30 \leq x_{\mathrm{CaO}} \leq 0.55$ [5–7].

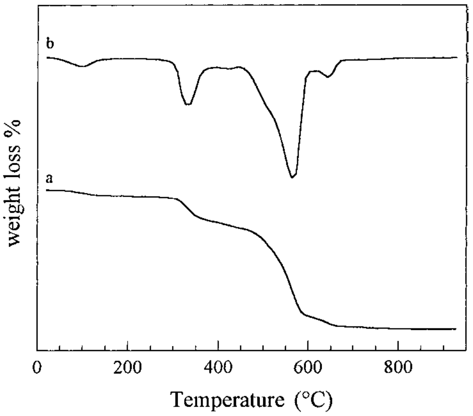

Fig. 3. (a) TGA of the gel dried 3 h at 100°C; (b) DTG.

The gel-derived material obtained by this thermal treatment was submitted to FTIR, DTA and XRD analyses.

Comparing the spectrum of Fig. 2(a) with that obtained for the heat treated gel Fig. 2(b) it is possible to display some clear differences. First, the relative intensities of the peaks change from one to another spectrum. The two peaks related to water and nitrate at, respectively, 1645 and about 1400 cm^{-1} are reduced, as expected after the thermal treatment. The peak at 1099 cm^{-1}, attributed to the stretching of SiO_4 tetrahedra with only bridging oxygens, shifts towards lower wavenumbers and covers a broader wavenumbers range. This behaviour can be explained considering that during the thermal treatments, as above stated, the nitrate decomposes and the calcium ion can be included in the silica network. It is well known [10,11], in fact, that when a modifier oxide is added to silica, the 1100 cm^{-1} band shifts to lower wavenumbers and covers a broader wavenumbers range the greater the amount of modifier oxide. This has been attributed to the presence of SiO_4 tetrahedra bearing different number of non-bridging oxygens [10,11].

In Fig. 4(a) the XRD pattern of the gel-derived material obtained after heat treatment at 600°C, required to remove nitrate and residual organic groups, is reported. In this pattern the presence of some broad peaks is attributed to the formation of Ca_2SiO_4 microcrystals during the heat treatment. The successful formation of glass is, in general, the result of a competition between those phenomena which lead to densification and those which promote crystallisation. In the preparation of $2CaO{\cdot}3SiO_2$ [6] and $2.5CaO{\cdot}2SiO_2$ [7] the same heating schedule, for the removal of nitrate and residual organic groups, led to completely amorphous materials. Owing to the higher CaO content in the $3CaO{\cdot}2SiO_2$ gel, the resulting network is highly depolymerised and the nucleation is kinetically favoured.

In Fig. 5 is reported the DTA curve recorded at 10°C/min in N_2 atmosphere. This curve exhibits a slope change in the 800–900°C temperature range followed by an exothermic peak. The slope change can be attributed to the glass transformation temperature, while the exothermic effect is due to the formation and growth of crystalline phases.

In Fig. 2(c) is reported the FTIR spectrum of the devitrified product after a DTA run up to 1200°C. As

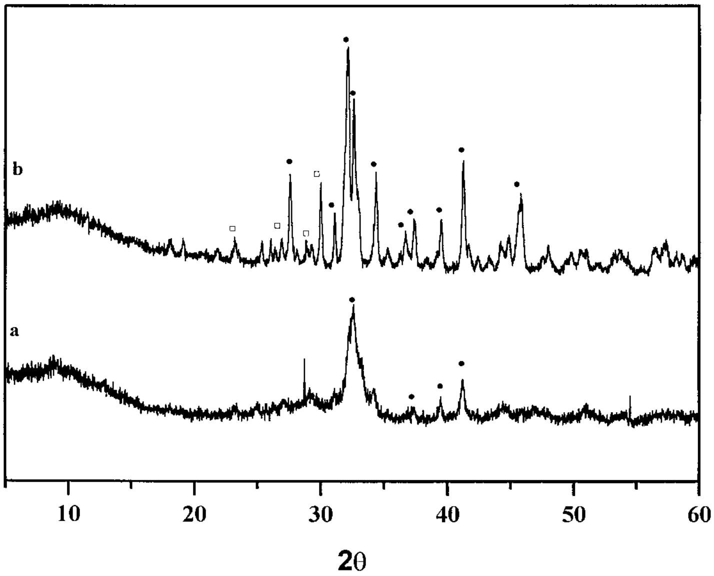

Fig. 4. XRD patterns of: (a) dried gel heated up to 600°C; (b) dried gel after a DTA run up to 1200°C; (●) Ca_2SiO_4 (JCPDS card 29/369); (□) wollastonite (JCPDS card 27/88).

can be seen this spectrum is very similar to that of Fig. 2(b) except for the absence of the band at about 1400 cm^{-1}, due to nitrate, which is completely removed after the heat treatment, and for a better resolution of the silicate absorption bands due to formation of crystalline phases.

To identify the phases crystallising during the DTA run, XRD measurement was carried out on gel sample heated in DTA furnace up to 1200°C. The XRD pattern of this sample, reported in Fig. 4(b), exhibits several sharp peaks that were attributed to Ca_2SiO_4 crystals. In addition to these peaks, the strongest reflection of wollastonite crystal was found. The formation of a small quantity of wollastonite crystals is most likely due to the rearrangement of the amorphous gel phase when the dehydroxylation occurs. It must be concluded that the non-crystalline gel phase is chemically inhomogeneous on an extremely fine scale with segregation of SiO_2 rich phase.

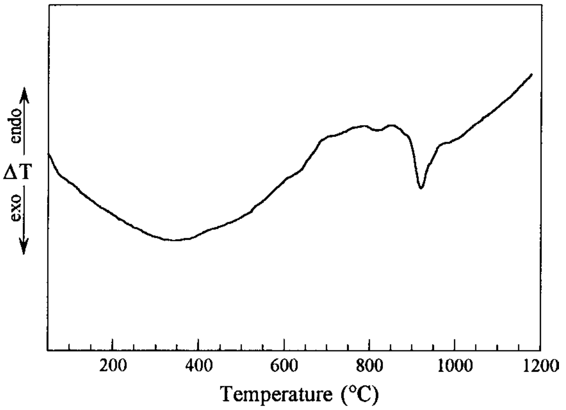

Fig. 5. DTA curve recorded at 10°C/min in N_2 atmosphere of the dried gel heated up to 600°C.

4. Conclusion

The gel preparation involves hydrolysis and polycondensation reaction of TMOS and calcium nitrate tetrahydrate in alcoholic solution. The gel thus prepared is an amorphous solid containing water and organic residues that are lost on heating. In order to obtain the glass, a thermal treatment, very similar to the one successfully used in the case of the glasses with a CaO molar fraction $0.30 \leq x_{CaO} \leq 0.55$ was chosen. In the present work the heat treatment, at lower temperature, necessary for eliminating nitrate and organic groups led to the precipitation of a small quantity of Ca_2SiO_4 microcrystals in an amorphous matrix. This behaviour is due to the high content of CaO that makes the gel network highly depolymerised and kinetically favoured to devitrification. The presence of small traces of wollastonite in the devitrified material, after a DTA run up to 1200°C, suggests a phase separation in the amorphous gel.

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