

Crystallization of sol-gel-derived glass ceramic powders in the CaO–MgO–Al₂O₃–SiO₂ system

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Samples in the anorthite primary crystallization field were prepared in the CaO–MgO–Al₂O₃–SiO₂ quaternary system by sol-gel techniques. The homogeneous dried gels were characterized by infrared spectroscopy, thermal analysis and electron microscopy. The crystallization of gel-like glass as a function of temperature was followed by X-ray diffraction. Anorthite was detected as the only crystalline phase. Thermal analysis results indicated a mechanism of crystal growth dominated by surface nucleation. This fact could be related to the small size of the primary particles observed by electron microscopy.

1. Introduction

Although there has been much research on glass-ceramic materials in the quaternary system CaO–MgO–Al₂O₃–SiO₂ during previous years, it has focused on materials containing diopside as the main crystalline phase, the so-called Silceram [1–3]. Anorthite is a particularly desirable crystalline phase on account of its hardness, resistance to chemical attack and favourable, fine-grained microstructures. However, it is not a good subject for self nucleation and much residual glass is retained. Some authors have reported results on anorthite glass ceramics in the CaO–Al₂O₃–SiO₂ ternary system. Topping [4] investigated the composition (wt %) 38 CaO, 20 Al₂O₃, 42 SiO₂, which is the eutectic composition between anorthite, gehlenite and wollastonite primary crystallization fields, and found that in this composition it was extremely difficult to generate bulk nucleation. Of several nucleation agents studied, only TiO₂ was effective, and in amounts as large as 18 wt%. Further research by the same author [5] on compositions covering the useful glass-forming region of CaO:Al₂O₃ ratio ≥ 1 , whose liquidus temperature was $< 1600^\circ\text{C}$, has revealed that by using 18 wt% TiO₂ as a nucleating agent in the ternary system, the composition range in which good glass ceramic can be made is extended significantly from the SiO₂-rich corner. Glasser *et al.* [6], in a study of crystallization of glasses with liquidus temperatures $< 1500^\circ\text{C}$ in the ternary system, found that compositions with large amounts of network formers, Al₂O₃ and SiO₂, are difficult to crystallize, and if the amount of network former is reduced, self-nucleation of glasses is produced and crystallization occurs more readily, but the products of crystallization tend to react with water. Crystallized glasses with compositions in the range (wt %) 26–34 CaO, 23–21 Al₂O₃, 51–45 SiO₂ display an X-ray diffraction (XRD) pattern identical with that of a mixture of anorthite and 5CaO–3Al₂O₃. Recently, Leonelli *et al.* [7] have reported results for

compositions in the tie-line anorthite–diopside in the quaternary system. All the glasses investigated show complete crystallization starting from a simple surface nucleation process, without any addition of nucleating agents, any nucleating preheating treatment, or long intervals at the devitrification temperature.

The preparation of glasses and glass ceramics by the so called sol-gel techniques has been extensively applied. These alternative ways of preparing glasses have permitted the study of systems in which there have been difficulties in obtaining glasses, such as high melting temperatures and phase separation in the glassy state [8]. By sol-gel synthesis, glass network formation and chemical homogenization in a glass can be achieved in solutions near room temperature. Further heat treatment near the glass transition temperature is required to convert the extremely porous gel into dense glass [9]. The first purpose of the present work was to study the possibility of obtaining homogeneous gels in the CaO–MgO–Al₂O₃–SiO₂ quaternary system, with compositions in the anorthite crystallization primary field. In addition, the aim was to know the crystallization path and elucidate the mechanism of crystallization. Lastly, the effect of some thermal processing variables (temperature and soaking time) on the microstructure of developed materials was assessed.

2. Experimental procedure

2.1. Preparation of gel like glass

The composition studied was (wt %) 57 SiO₂, 20 Al₂O₃, 18 CaO, 5 MgO, which is localized in the anorthite primary crystallization field. The preparation of polymeric gels was carried out by addition of an alcoholic solution of aluminium alkoxide to a prehydrolysed solution of silicium alkoxide. An alcoholic solution containing CaCl₂·2H₂O (Merck, Darmstadt, Germany) MgCl₂·6H₂O (Aldrich, Milwaukee, USA) and TEOS (tetraethylorthosilicate, Merck, Darmstadt, Germany) was refluxed at 50°C for 20 h,

obtaining a transparent solution. The molar ratio TEOS:water:ethanol was 1:2:9. $\text{Al}(\text{OEt})_3$ (aluminium triethylate, Merck, Darmstadt, Germany) dissolved in ethanol by re-fluxing was added into the prehydrolysed TEOS solution. The resultant mixture with a molar ratio of 1:0.4:2:20 for TEOS: $\text{Al}(\text{OEt})_3$:water:ethanol was held in continuous stirring at 50 °C, a gel appearing after several days. In multicomponent systems in which the source of some components is not alkoxide (in this case, calcium and magnesium) it is often recommended to use acetates. However, acetates could not be used because calcium acetate is practically insoluble in alcohol.

The gel was slowly dried for 9 days by covering the beaker containing the gel with a plastic film to slow down solvent loss by evaporation. To control the speed of evaporation, the film was drilled with a needle. The final ochre-coloured gel samples were obtained by further drying at 120 °C for 24 h. Before submitting irregular fragments and powders of dried gels to thermal processing at different temperatures (between 900 and 1300 °C) and soaking times (3 and 9 h), gels were preheated at 750 °C, a slightly higher temperature than the glass transition temperature. This step was necessary to obtain the so-called gel-like glass.

2.2. Techniques of characterization

Dried gels were characterized by infrared (IR) spectroscopy and thermal analysis. IR spectra were run with a Perkin Elmer Infrared Spectrophotometer Model 882 (Beacons Field, Bucks, UK), using the method of KBr pellet in the range between 400 and 2000 cm^{-1} . Thermal analyses were recorded using a Perkin Elmer Model 1700 Thermal Analyser (Norwalk, Connecticut, USA) with different particle sizes on bulk and particulate samples, with alumina as the reference material at a heating rate of 10 °C min^{-1} . Crystallization of the heat-treated gel-like glasses was investigated by X-ray powder diffraction patterns, obtained on a Siemens Model D-500 X-ray powder diffractometer (Karlshruhe, Germany).

Microstructural characteristics of dried and heated gel samples were observed by scanning electron microscopy (SEM) using a Hitachi Model S-2500 SEM (Tokyo, Japan). Some specimens were light etched with (5%) HF solution, washed with water, dried and coated with gold in an ion-beam coater. The shapes and particle structures were also examined by transmission electron microscopy (TEM) using a Hitachi Model H-800 TEM (Tokyo, Japan). These samples were also coated with graphite by the same procedure.

3. Results and discussion

3.1. Infrared spectroscopy

IR spectra of dried and thermally processed gels are shown in Fig. 1. The characteristic bands around 1200, 1100, 750 and 460 cm^{-1} associated with Si–O bonds are observed in dried gels. These indicate the formation of a Si–O anionic network in amorphous gels [10, 11]. The features and evolution of these bands with thermal treatment give a great deal of information on the structural evolution of gels. In dried gels, a

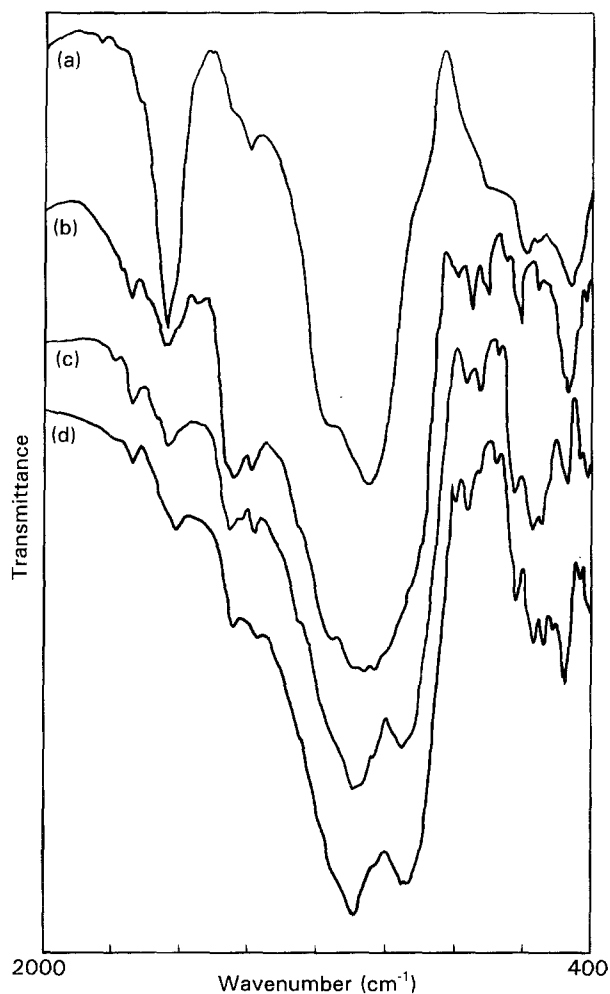


Figure 1 Infrared spectra of anorthite polymeric gel heated at several temperatures: (a) 120 °C/24 h; (b) 750 °C/3 h; (c) 1000 °C/3 h; (d) 1200 °C/3 h.

strong band peaked at 1051 cm^{-1} and a shoulder around 1180 cm^{-1} ; both are attributed to Si–O–Si asymmetric bond stretching vibration [8, 12, 13]. In samples submitted to temperatures above 1000 °C, that band became wider and the shoulder disappeared. A simultaneous shifting of the band peak to 1100 cm^{-1} was observed: the shifting of bands towards higher wavenumber values is associated with a high strength of Si–O in the structure [8]. Some additional vibration modes of Si–O and Si–O–Si were observed in samples heated at 750 °C.

Bands at 750 cm^{-1} were observed in samples calcinated above 1000 °C, in accordance with the literature, which are associated with the formation of a ring structure of SiO_4 tetrahedra [8, 12, 14]. Finally, the band peak at 460 cm^{-1} , generally associated with bond bending vibration of Si–O–Si [8, 12, 15], was observed in the full range of temperatures. This band is shifted toward higher wavenumbers (480 cm^{-1}) with increasing temperature. This effect was already detected for bands placed at 1051 cm^{-1} .

In addition to those mentioned above, other bands were observed. Thus, at temperatures above 1000 °C a band peak around 930 cm^{-1} appeared, which is associated with Si–O–M bond formation [16]. This band is especially significant during crystallization of the anorthite phase. Likewise, bands in ranges between 720–680 and 620–597 cm^{-1} are displayed. These are

associated with Al–O bonds, AlO_4 and AlO_6 , respectively [15]. On the other hand, the band at 1620 cm^{-1} , assigned to rotation–vibration of OH radicals, remained unaltered in position at high temperatures, but decrease in intensity. Similar trends are observed for bands at 1450 and 1380 cm^{-1} associated to OR groups remaining in the structure. Finally, bands at 420 and 565 cm^{-1} are attributed to Si–O and Al–O bonds [8]. Specimens in which the crystalline phase was sufficiently developed displayed IR spectra characteristic of the anorthite crystalline phase.

3.2. Gel-to-glass characterization

A differential thermal analysis (DTA) curve of the dried gels shows an endothermic peak between 70 and 250°C , centred at 160°C , which is attributed to the evaporation of physically adsorbed water and alcohols. The broad exothermic peak starting from 400°C is associated to the oxidation of organics. The maximum observed in that broad exothermic effect can be associated with the pyrolysis of residual organic groups in the gel. These assignments are both supported by thermogravimetric analysis (TGA) in which a gradual weight loss is observed from 400°C . Some further weight loss is attributed to network condensation, which had not reacted by the end of the drying step and consequently did not evaporate from the gel prior to calcining.

No exothermic peak associated to anorthite crystallization was observed in DTA curves of dried gels. However, DTA curves of slowly calcined gels at 750°C over 3 h display the trends of thermal behaviour of gel-derived glasses. From these results, it can be inferred that the glass transition temperature for gel powders is about 720°C , irrespective of particle size.

3.3. Crystallization of gel-derived powders

The evolution of samples with thermal processing as a function of temperature is shown in Fig. 2. The previous calcination of dried gels at 750°C for 3 h with the aim of obtaining a glass-like gel yields an amorphous material, as revealed by XRD. With increasing the

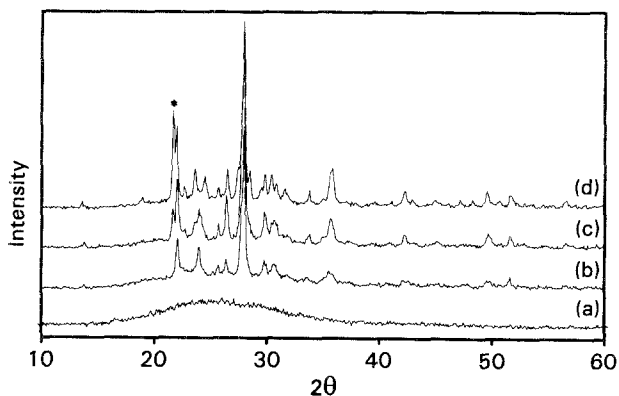


Figure 2 X-ray powder diffractograms of gel-derived powders heated at: (a) $750^\circ\text{C}/3\text{ h}$; (b) $900^\circ\text{C}/3\text{ h}$; (c) $1100^\circ\text{C}/3\text{ h}$; (d) $1200^\circ\text{C}/3\text{ h}$. *, Cordierite.

temperature to 800°C and the soaking time to 9 h , anorthite begins to be detected as the crystalline phase. At 900°C , significant crystallization of anorthite is observed. Some unindexed diffraction peaks can be associated to cordierite. With increasing either the temperature or the soaking time at higher temperatures, the amount of glassy phase is lowered. Thus the anorthite is fully developed at 1200°C , with some cordierite as a minor phase and a small amount of glassy phase. The sample calcinated at 1300°C melts partially, and after a soaking time of 9 h a translucent glass is observed.

These results are not totally comparable with the findings of other authors, because the methods of glass preparation used are different. Leonelli *et al.* [7], in a sample with composition (wt %) 49.4 SiO_2 , $18.3\text{ Al}_2\text{O}_3$, 21.6 CaO , 9.24 MgO localized in the anorthite primary crystallization field of the quaternary system, obtained a complete crystallization at 1100°C . The main crystalline phase was diopside, although the starting glass sample was prepared by the conventional method. Glasser *et al.* [6], for ternary compositions also prepared by melting in the anorthite primary crystallization field, ranging from (wt %) $51\text{--}45\text{ SiO}_2$, $21\text{--}28\text{ Al}_2\text{O}_3$, $34\text{--}26\text{ CaO}$, reported crystallizations of anorthite and orthorhombic phase $5\text{CaO}\text{--}3\text{Al}_2\text{O}_3$.

Time–Temperature–Transformation (T–T–T) curves of the gel-like glass samples submitted to thermal treatments are shown in Fig. 3. The diagram represents a range of conditions for different amounts of crystalline phase. In order to be able to compare the crystallization of sol–gel-derived glasses and melt glasses, the different thermal histories of gel-derived and melt glasses must be considered. Thus in cases when gel powders were heated to obtain dense glass, independently of whether or not monolithic formation takes place, this could result in a lower crystallization temperature and faster nucleation and crystallization rates relative to melted glasses [17]. These differences have been attributed to the lower viscosity of the gel powder caused by the higher hydroxyl content [18] and to the excess free energy due to the larger interior surface and structural differences [19].

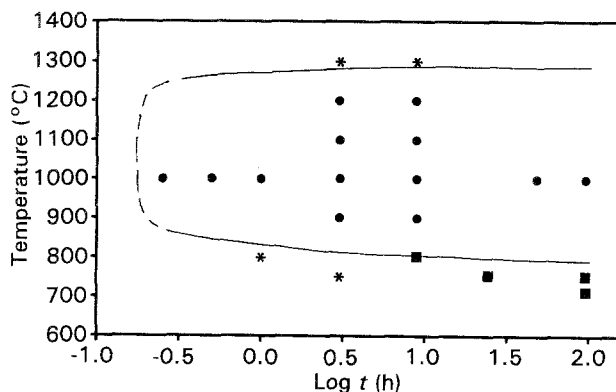


Figure 3 Time–temperature–transformation (T–T–T) for the 750°C calcined anorthite gel-derived glass powder: *, amorphous; ■, low crystallization; ●, high crystallization.

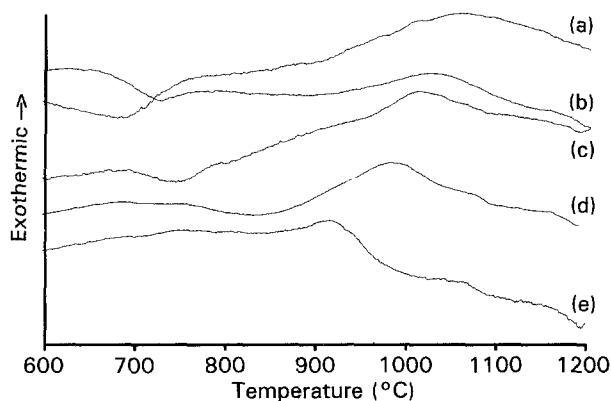


Figure 4 DTA curves of gel-derived glass powder samples as a function of particle size at $10^{\circ}\text{C min}^{-1}$ heating rate: (a) > 200 ; (b) $200\text{--}100$; (c) $100\text{--}50$; (d) $50\text{--}25$; (e) < 25 μm .

3.4. Nucleation

From the above results, it was demonstrated that the quaternary gel-derived glasses can be crystallized into anorthite-based glass ceramics. However, to control glass ceramic microstructures is necessary to understand how the particle characteristics affect nucleation and growth. In order to investigate the nucleation behaviour of the calcined gel powders, it was necessary to measure the effects of particle size on the crystallization temperature.

DTA curves of gel-like glass as a function of particle size are presented in Fig. 4. As can be observed, the crystallization of gel-like glass powders was associated with a single exothermic peak at temperatures ranging from 915 to 1060°C , depending on the particle size. The finer the powder, the lower the temperature of the peak. That result in which the temperature of the exothermic crystallization peak is strongly dependent on the surface area of the powder and the absence of the splitting of the exothermic peak is indicative of domination of surface nucleation in the mechanism of crystal growth [7]. The effect of the heating rate on the exothermic peak has been studied. Irrespective of the gel-like glass powder particle size, the exothermic peaks shifted to higher temperatures with increasing heating rate.

The microstructural evolution of gel and gel-derived glass was monitored with SEM and TEM techniques. The SEM study of dried gel powders (Fig. 5a) shows agglomerates of large particles, whose surfaces are formed of small spherical particles $\sim 60\text{--}90$ nm diameter. In gels calcined at 750°C (Fig. 5b), near to the T_g (glass transition temperature), agglomerates of smoother surface and less porosity are observed. Those agglomerates are also formed by small particles but present more compacity than in uncalcined gels. At 1200°C , gel-derived powders (Fig. 5c) show no significant differences in the external microstructure of agglomerates. However, when powders heated at 1200°C are pressed into pellets and etched, a homogeneous distribution of spherical particles, mean diameter ~ 150 nm, are distinguished. The above evolution of microstructural characteristics, obtained by SEM, is supported by TEM of the gel and gel-derived powders.

4. Conclusions

Anorthite-based glass ceramic materials were prepared by crystallization of quaternary gel-derived glasses. Gels were prepared by hydrolysis of alkoxides (silicium and aluminium ethylates) and salts (magnesium and calcium chlorides). Absorption bands in the IR spectra for dried gels indicated formation of a Si-O

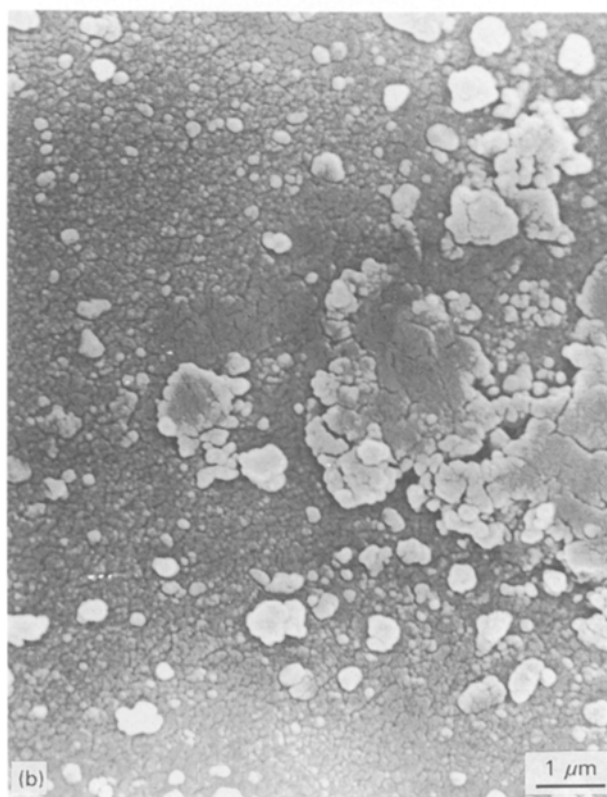
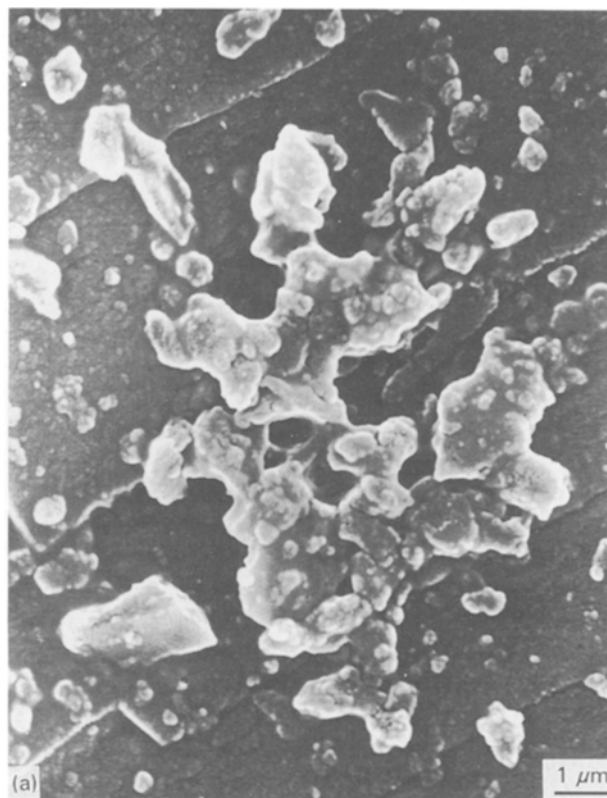


Figure 5 SEM micrographs of: (a) dried gels at $120^{\circ}\text{C}/24$ h; (b) calcined gels at $750^{\circ}\text{C}/3$ h; (c) calcined gels (etched) at $1200^{\circ}\text{C}/3$ h.

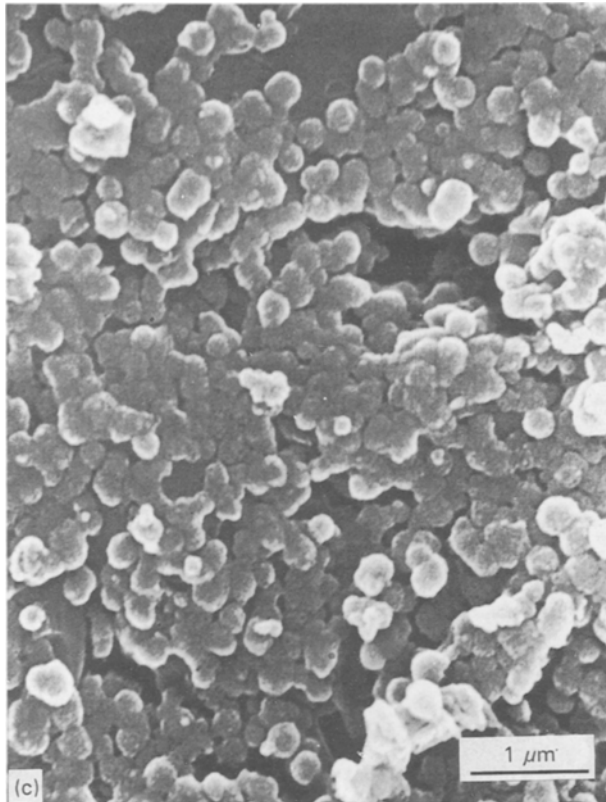


Figure 5 continued

three-dimensional network. Crystallization of gel-derived glass was characterized by the appearance of anorthite phase at 800 °C. Crystallization was enhanced by increasing the temperature up to 1200 °C, but cordierite was observed as minor phase at this temperature. The mechanism of crystal growth was dominated by surface nucleation, as shown by DTA experiments in which the effect of particle size on the crystallization temperature was measured. This result is consistent with microstructural studies (SEM) of gel-derived glasses, in which a very small size was observed in the primary particles.

Acknowledgements

Financial support for the present work was provided by CICYT (Project MAT92-0423).

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Received 28 January
and accepted 8 October 1993