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Crystallization of sol–gel derived glass ceramic powders in the CaO–MgO–Al_2O_3–SiO_2 system

Part II *Cordierite*

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Samples in the cordierite primary crystallization field were prepared in the CaO–MgO–Al_2O_3–SiO_2 quaternary system by sol–gel techniques, using both polymeric and colloidal gels. Dried gels were characterized by infrared spectroscopy, thermal analysis and electron microscopy. The crystallization of gel-like glass from both kinds of gels, as a function of temperature was followed by X-ray diffraction. Cordierite was detected as the only final crystalline phase, although some other crystalline phases, different for each kind of gel, were observed in the pathway reaction. The polymorphic modification of cordierite detected was pseudohexagonal, because no evidence of splitting was observed.

1. Introduction

As previously reported [1], there has been a great deal of research related to glass–ceramic materials in the quaternary system CaO–MgO–Al_2O_3–SiO_2 during recent years; although, this research has focused on materials containing diopside as the main crystalline phase, the so called Silceram, and not on other primary crystallization fields, such as cordierite [2, 3]. Cordierite is a well known crystalline phase, on account of its low thermal expansion properties and low dielectric constant, coupled with high chemical and mechanical stability. Several cordierite-based ceramic and glass compositions have been developed, and are being increasingly used in applications where thermal shock resistance and a low dielectric constant are critical. However, the polymorphism of cordierite can result in complicated microstructural evolution during processing of glass–ceramics.

Cordierite occurs in one metastable and two stable forms. The metastable phase (μ-cordierite) forms only from glasses and is a high-quartz solid solution, with hexagonal β-quartz crystal structure. The stable forms are the disordered hexagonal high temperature form (α-cordierite) and the ordered orthorhombic low temperature form (β-cordierite) [4].

A great amount of papers are concerned with synthesis of cordierite glasses, ceramics and glass ceramics in the MgO–Al_2O_3–SiO_2 ternary system. Gregory and Veasey [5–8] reported the crystallization of cordierite glass and the study of devitrification behaviour by differential thermal analysis (DTA) and infrared spectroscopy (i.r.), both of the base glass and the doped glass (with V_2O_5, WO_3 as dopants). Zdaniewski [9–11] studied the structure and changes occurring during the volume crystallization of a MgO–Al_2O_3–SiO_2 glass containing different nucleation agents (TiO_2, ZrO_2, CeO_2).

Further research was made by McCoy and coworkers [12, 13] about crystallization of glasses in the ternary system with different amounts of ZrO_2; the great interest of this research may be the use of transmission electron microscopy (TEM) as the main tool of work. Watanabe and Giess [14] studied coalescence and crystallization in powdered high-cordierite glass, with small amount of B_2O_3, with thermal analysis.

Most of the desirable properties of cordierite are very sensitive to the type of dopant and the processing method; so, the preparation of cordierite-based glasses and ceramics in the ternary system by so called sol–gel techniques has been extensively used during recent years [15–17]. These alternative ways of glass preparation have permitted study of systems in which there was some difficulty in obtaining glasses, such as high melting temperatures and phase separation in the glassy state [18]. By sol–gel synthesis, glass network formation and chemical homogenization in a glass can be achieved in solution near room temperature. In cordierite synthesis, the most used method is hydrolysis of alkoxides of aluminium and silicon, followed by addition of magnesium, either as an alkoxide or an acetate, to the resultant solution. The use of alkoxides as precursors, particularly the Mg and Al alkoxides, is fraught with difficulties, since the alkoxides are very water sensitive, and have different hydrolysis rates, which can lead to inhomogeneities both in the gel and in the final product. These drawbacks are especially important if one wishes to deviate significantly from

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the cordierite stoichiometry or to add other oxide precursors to make glass ceramics of more than four components.

The first purpose in the present work was to study the possibility of obtaining homogeneous gels in the CaO–MgO–Al_2O_3–SiO_2 quaternary system, with compositions in the cordierite primary crystallization field, both by a polymeric or metal–alkoxides route and by a colloidal or metal–inorganic salts route. On the other hand, it was intended that the crystallization path from either kind of precursors be known. Lastly, differences in the microstructures of the developed materials from both gels were assessed.

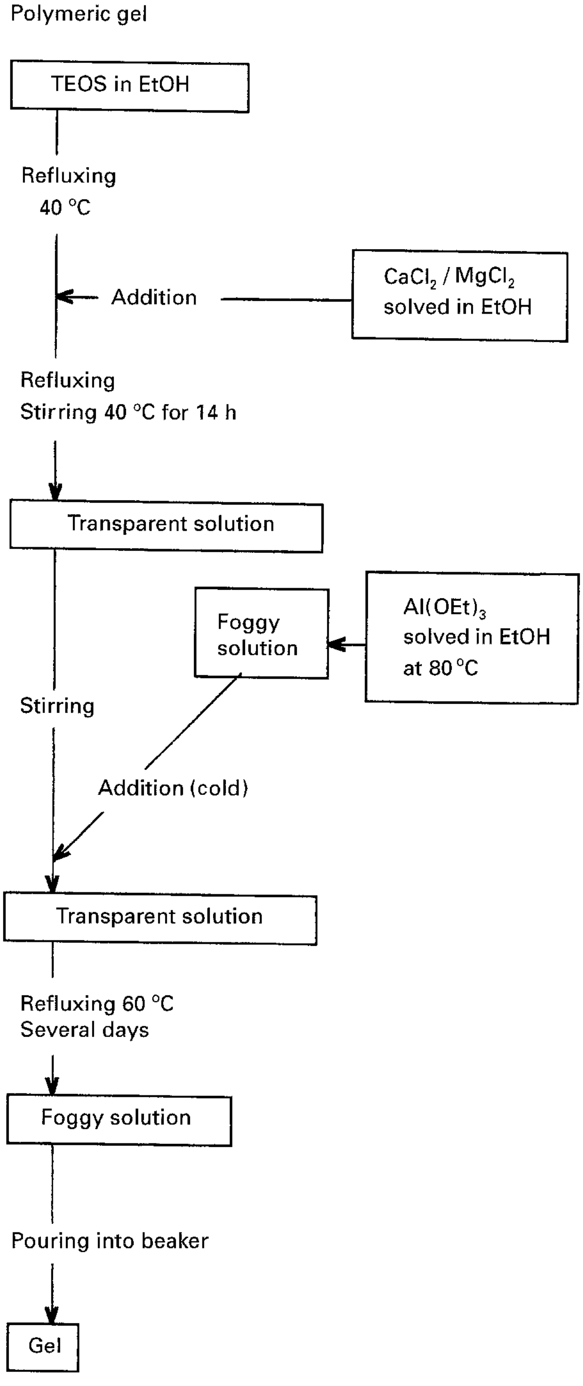

Figure 1 Schematic diagram of cordierite polymeric sol–gel synthesis.

2. Experimental procedure

2.1. Preparation of gel like glass

The composition studied was (wt %) 63% SiO_2, 22% Al_2O_3, 5% CaO and 10% MgO, which is localized in the cordierite crystallization field. Figs 1 and 2 show the flow chart followed to prepare multicomponent cordierite gel by polymeric and colloidal processes, respectively.

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 $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$ and tetraethylorthosilicate (TEOS) was refluxed at 40 °C for 14 h obtaining a transparent solution. The molar ratio TEOS: water:ethanol was 1:2:9. Aluminium triethylate [$Al(OEt)_3$] dissolved in ethanol by refluxing was added into the prehydrolysed TEOS solution. The resultant mixture, with a molar ratio of 1:0.4:2:21 for TEOS:$Al(OEt)_3$:water :ethanol, was held in a continuous stirring at 60 °C a gel appearing after several days.

In multicomponent systems in which the source of some components is not alkoxide, as in this case

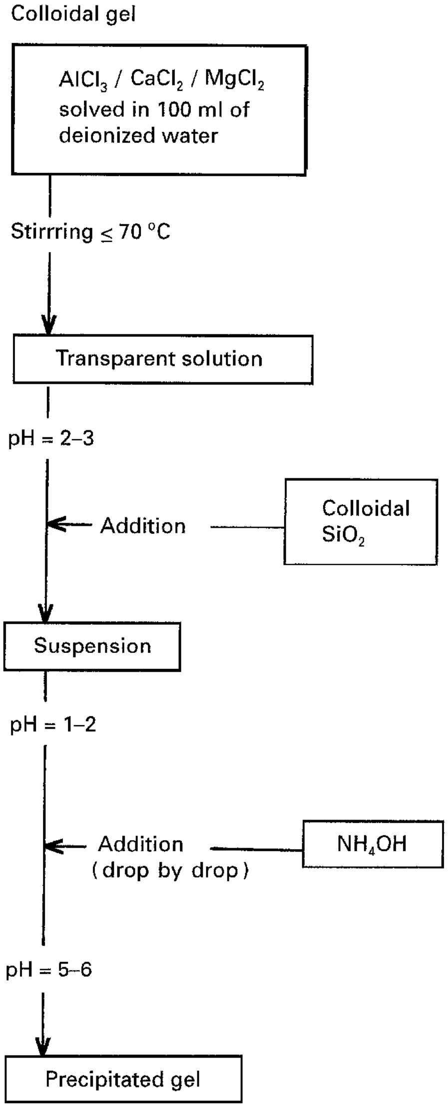

Figure 2 Schematic diagram of cordierite colloidal sol–gel synthesis.

calcium and magnesium, the use of acetates is often recommended. However, in this composition acetates cannot be used, because calcium acetate is practically insoluble in alcohol; another way may be the use of complexing agents or inorganic salts as precursors of calcium and magnesium oxides [17].

The preparation of colloidal gels, outlined in Fig. 2, began with dissolution of $AlCl_3 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$ and $MgCl_2 \cdot 6H_2O$ in deionized water (100 ml H_2O per 5 g end product). To this vigorously stirred solution at 70 °C was added colloidal SiO_2. After a few minutes a stable suspension (pH = 2) was obtained, to which a solution of ammonium hydroxide was added dropwise until gelation occurred (pH = 5–6).

Gels were slowly dried for several 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 ocher coloured gel samples were obtained by further drying at 40 °C for 60 h, and subsequently at 60 °C for 15 h only for colloidal gels.

Previously, in order to submit irregular fragments and powders of dried gels to thermal processing at different temperatures (between 900 and 1400 °C) and soaking times (3 and 9 h), gels were preheated at 750 °C, a slight lower temperature than the glass transition temperature. This step was necessary in order to obtain the so-called gel-like glass.

2.2. Characterization techniques

Dried gels were characterized by i.r. spectroscopy and thermal analysis. I.r. spectra were run with a Perkin Elmer infrared spectrophotometer, model 882, using the KBr pellet method in a range between 400 and 2000 cm^{-1}. Thermal analyses were recorded using a Perkin Elmer model 1700 thermal analyser and a Perkin Elmer model 7 thermogravimetric analyser, on 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 using graphite monochromated CuK_α radiation.

Microstructural characteristics of dried and heated gel samples were observed by SEM using a Hitachi model S-2500 scanning electron microscope. Some specimens were light etched with (5%) HF solution, washed with water, dried and coated with gold in an ion beam coater.

3. Results and discussion

3.1. Infrared spectroscopy

I.r. spectra of dried and thermally processed, at several temperatures, polymeric and colloidal gels are shown in Figs 3 and 4, respectively. As evidenced in similar samples with compositions belonging to the anorthite primary crystallization field, characteristic bands around 1200, 1100, 750 and 460 cm^{-1} are displayed in dried gels, which are indicating the formation of an Si–O anionic network in amorphous gels [1, 18, 19]. Broadly speaking, there are no striking differences between the features of the bands and their evolution with thermal treatment for both gels.

In polymeric dried gels, a strong band peaked at 1070 cm^{-1} and a shoulder around 1170 cm^{-1}, both are attributed to Si–O–Si asymmetric bond stretching vibration [20–22]. In samples submitted to temperatures at and above 900 °C that band became wider and the shoulder disappeared. A simultaneous shifting of the band to 1100 cm^{-1} was observed, which can be associated with the high strength of Si–O in the structure [20]. In colloidal dried gels this band is detected at 1120 cm^{-1}, and no shift with thermal treatment is observed. Moreover, the shoulder at 1170 cm^{-1} is observed only in polymeric gels and disappears with heat treatment, so it can have some contribution from vibrations in residual alkoxide, OR, groups [21].

Some additional vibration modes of Si–O and Si–O–Si are also observed in calcinated samples for both gels. Bands at 750 and 950 cm^{-1} are associated, the first one with the formation of a ring structure of SiO_4 tetrahedra [20, 21, 23], and the second with Si–O–M bond formation [16]. This band is especially significant during crystallization of the cordierite phase. Finally, other bands associated with Si–O and Al–O bonds peak in the 800–400 cm^{-1} range. At 460 cm^{-1}, the band generally associated to bond bending vibration of Si–O–Si [15, 20, 21], is observed in the full range of temperatures, although a shift toward

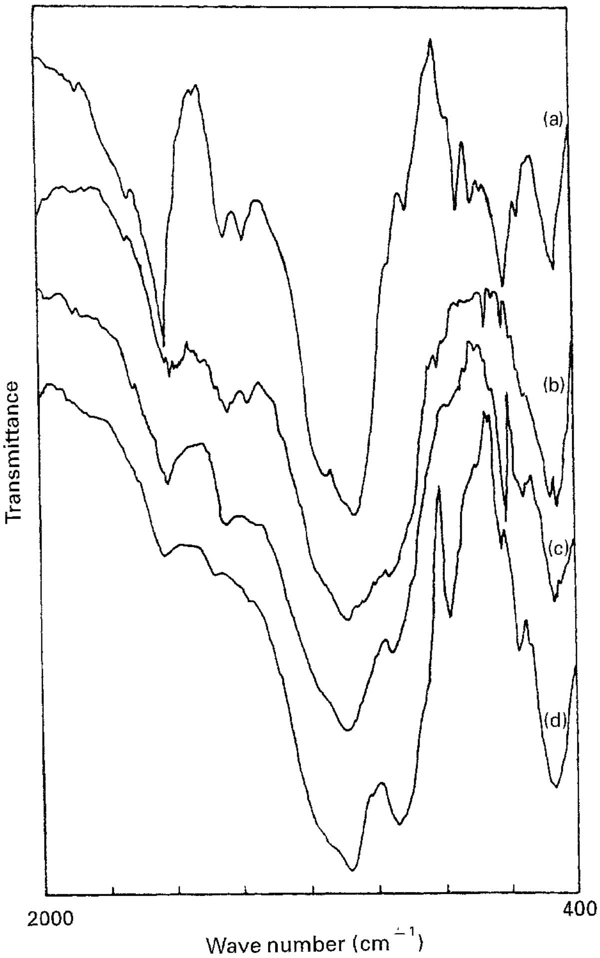

Figure 3 Infrared spectra of cordierite polymeric gel heated at several temperatures: (a) 40 °C for 60 h, (b) 900 °C for 9 h, (c) 1000 °C for 9 h, (d) 1100 °C for 9 h.

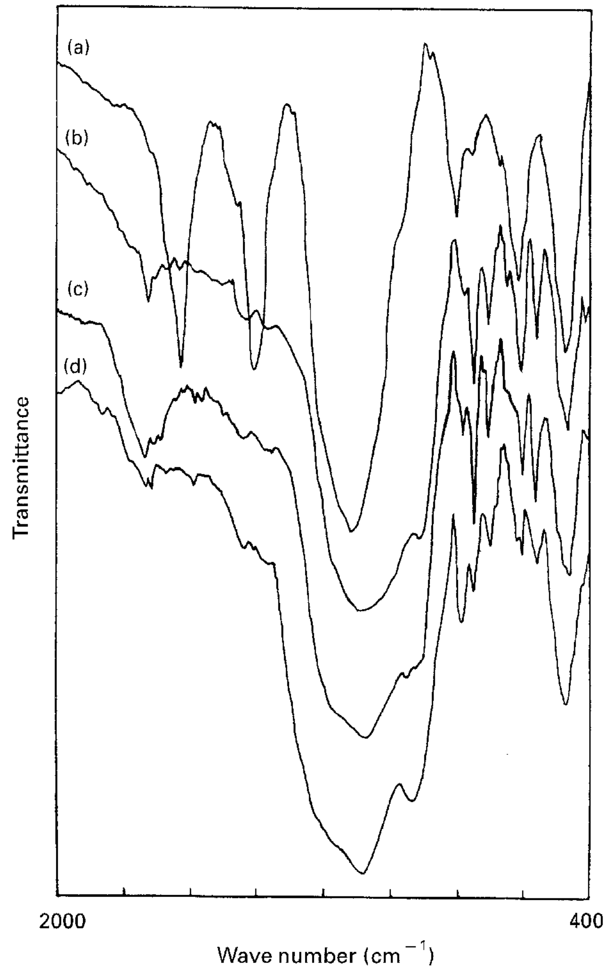

Figure 4 Infrared spectra of cordierite colloidal gel heated at several temperatures: (a) 40 °C for 60 h, (b) 900 °C for 9 h, (c) 1000 °C for 9 h, (d) 1100 °C for 9 h.

higher wave numbers (480 cm^{-1}) is observed with raising temperature as was already detected with bands placed at 1070 cm^{-1}. Likewise, bands between 720–680 and 620–597 cm^{-1} are associated with Al–O bonds, AlO_4 and AlO_6, respectively, [15]. Bands at 420 and 565 cm^{-1} are attributed to Si–O and Al–O bonds [20].

As inferred from above results, some minor differences may be detected between i.r. spectra of polymeric and colloidal gels, especially in bands centred at 1100 and 620 cm^{-1}.

3.2. Gel–glass characterization

The transformation from gels to glasses was studied as a general rule by differential thermal and thermogravimetric (DTA–TGA) analyses.

In polymeric dried gels the DTA curve displays an appearance similar to that previously reported for a sample in the anorthite primary crystallization field [1]. Thus, an endothermic peak is observed between 50 and 250 °C, centred at 170 °C, which is attributed to the evaporation of physically adsorbed water and alcohols. The broad exothermic peak starting from 400 °C is associated with 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. Those assignations are supported by TGA, in which a gradual weight loss is observed from 400 °C. Some further weight loss from 800 °C 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 cordierite crystallization is observed in DTA curves of dried gels.

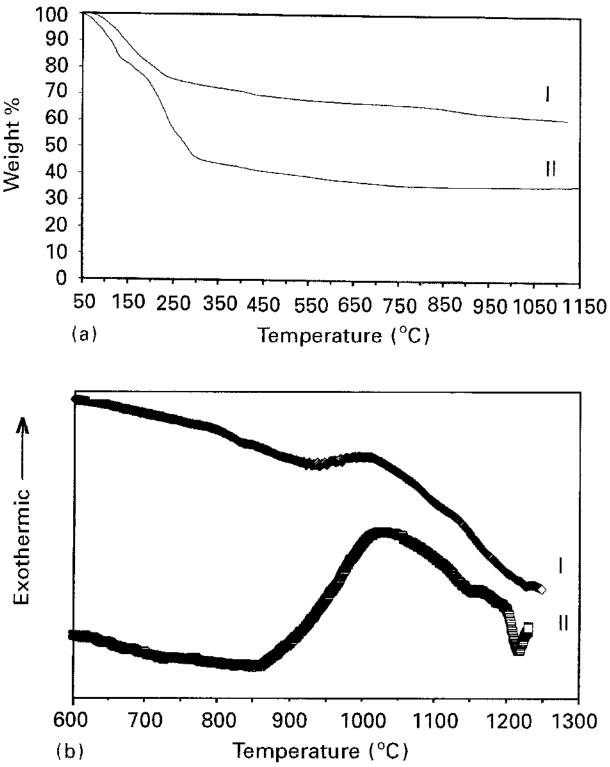

Figure 5 (a) TGA curves of dried gels and (b) DTA curves of gel derived glass powder samples: (I) polymeric, and (II) colloidal gel.

The TGA curve of the colloidal dried gel shows a double amount of weight loss compared with polymeric gel. The first important step, below 300 °C, is due to water and solvents evaporating, and may be caused by decomposition of inorganic salts too; from 300 to 750 °C a gradual weight loss associated to rejection of water hydrogen bonded to ≡Si–OH and =Al–OH [21]. Weight loss is constant from this temperature. Both TGA curves, for polymeric and colloidal dried gels, are displayed in Fig. 5a.

DTA curves of slowly calcined gels at 750 °C for 3 h display the thermal behaviour trends of gel derived glasses, as observed in Fig. 5b. From these results it can be inferred that the glass transition temperature for polymeric gel powders is about 810 °C; whereas no clear endothermic effect is observed in colloidal gels. This is in accordance with results previously reported on this type of transformation in cordierite gels and melt glasses [9–11, 24].

3.3. Crystallization of gel derived powders

The previous study of crystallization pathway, obtained from DTA, is furthered by XRD.

Due to retention of some carbon in gel derived glass structures, exothermic crystallization peaks are not easy to detect in DTA curves [25]. However, one maximum is observed at 1013 °C for polymeric powders with a shoulder at 1133 °C, and an endothermic melting peak at 1350 °C (Fig. 5b). This result could indicate the initial crystallization of β-quartz solid solution and its transformation to cordierite at higher temperature, as reported in the literature for the ternary system [10, 14, 17, 24]. XRD confirms that the first crystalline phase is μ-cordierite at 900 °C, but at 1000 °C the transformation to cordierite has begun, and at 1100 °C this is the major crystalline phase. However, it cannot be asserted whether this polymorph is orthorhombic or hexagonal, because no splitting of peaks, characteristic of the orthorhombic phase, is observed in the 28–30° (2θ) range. So, this phase is called pseudohexagonal.

In colloidal powders a broad exothermic peak centred at 1020 °C is observed; the melting point is at 1215 °C (Fig. 5b). X-ray diffractograms confirm that μ-cordierite is the first crystalline phase to appear following heat treatment at 900 °C, and only at 1100 °C is the transformation to pseudohexagonal cordierite important.

As a general rule, it was expected that the thermal evolution sequences of gel derived glasses were different for both preparation methods. This fact may be due to differences in homogeneity of gel and gel derived glasses and can be investigated by ^{27}Al and ^{29}Si magic angle spinning–nuclear magnetic resonance (MAS–NMR) [17].

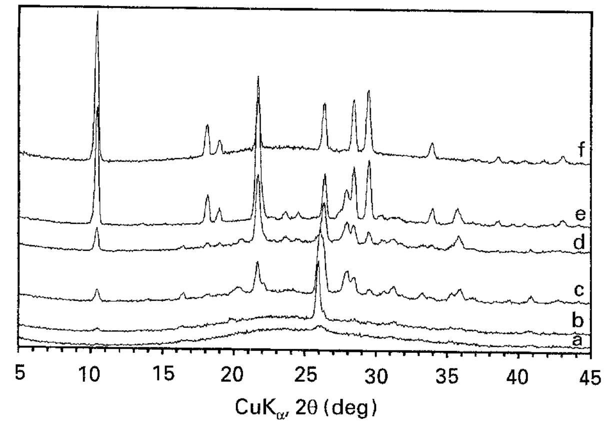

Figure 6 X-ray powder diffractogramms of polymeric gel derived powders heated at: (a) 750 °C for 3 h, (b) 900 °C for 9 h, (c) 1000 °C for 9 h, (d) 1100 °C for 9 h, (e) 1200 °C for 9 h, (f) 1250 °C for 9 h.

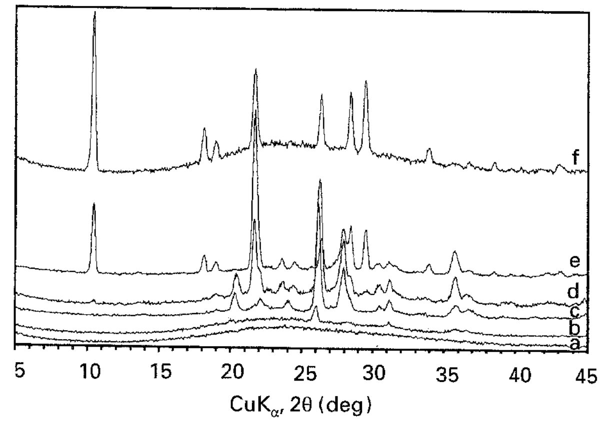

Figure 7 X-ray powder diffractogramms of colloidal gel derived powders heated at: (a) 750 °C for 3 h, (b) 900 °C for 9 h, (c) 1000 °C for 9 h, (d) 1100 °C for 9 h, (e) 1200 °C for 3 h, (f) 1250 °C for 9 h.

Previous to thermal processing of samples, dried gels were calcined at 750 °C for 3 h with the aim of obtaining a gel-like glass, yielding an amorphous material as checked by XRD.

The evolution of polymeric cordierite gel with thermal processing as a function of temperature is displayed in Fig. 6.

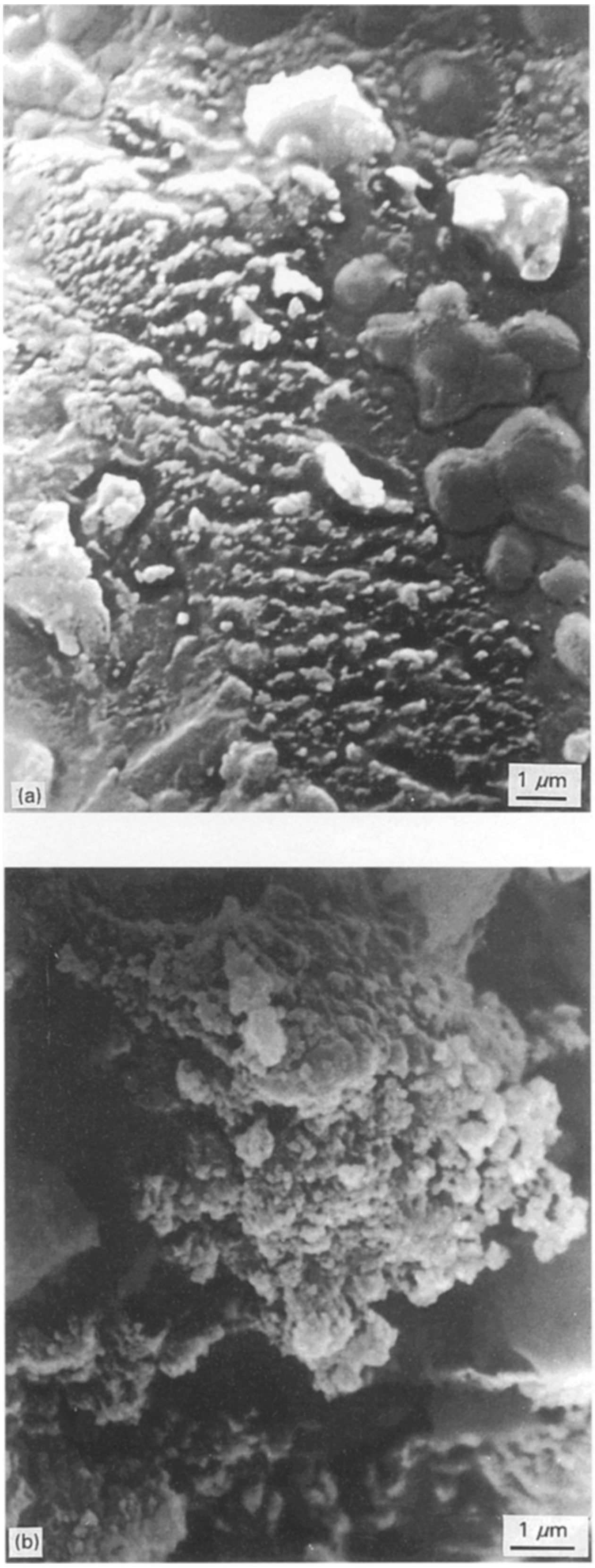

Figure 8 SEM micrographs of (a) polymeric dried gels, and (b) colloidal dried gels (bar = 2 μm).

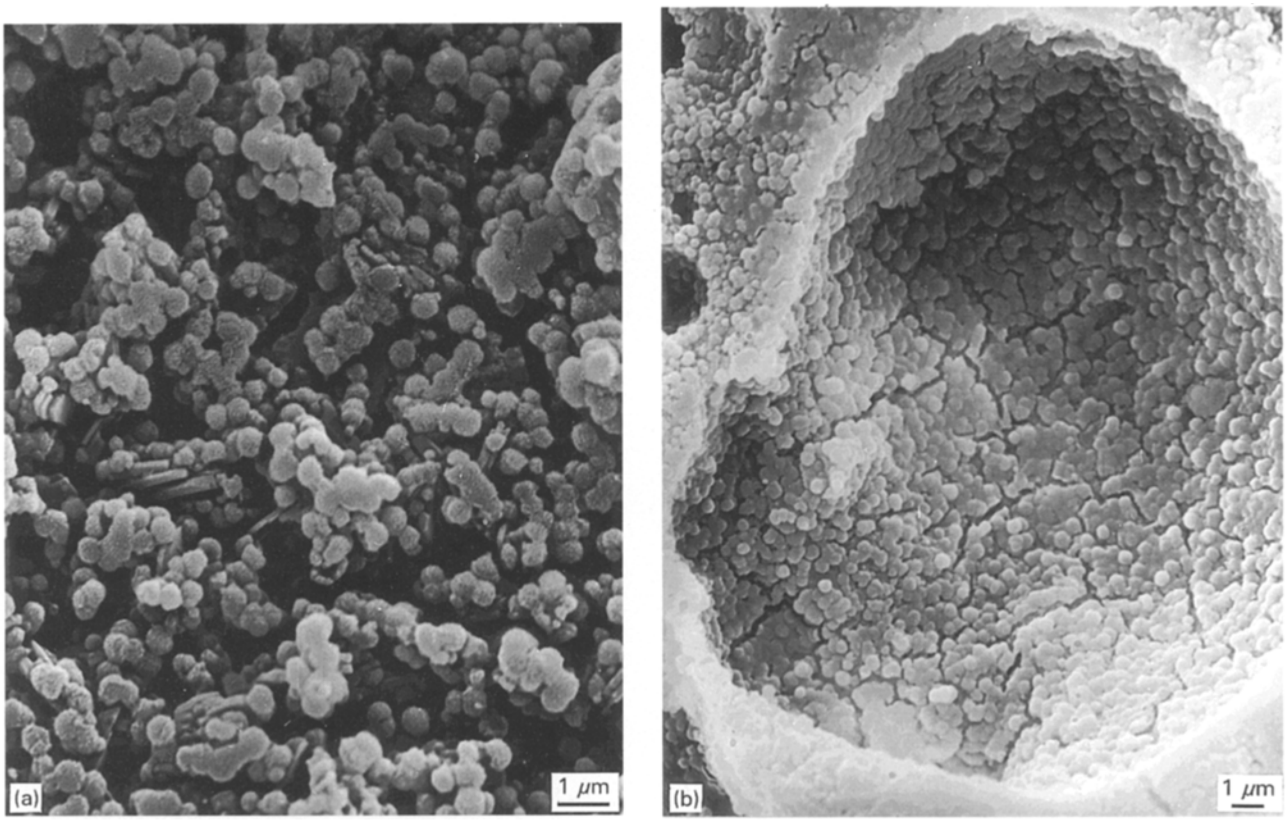

Figure 9 SEM micrographs of polymeric powders (etched) fired at (a) 1000 °C for 3 h (bar = 1 µm), and (b) 1100 °C for 9 h (bar = 2 µm).

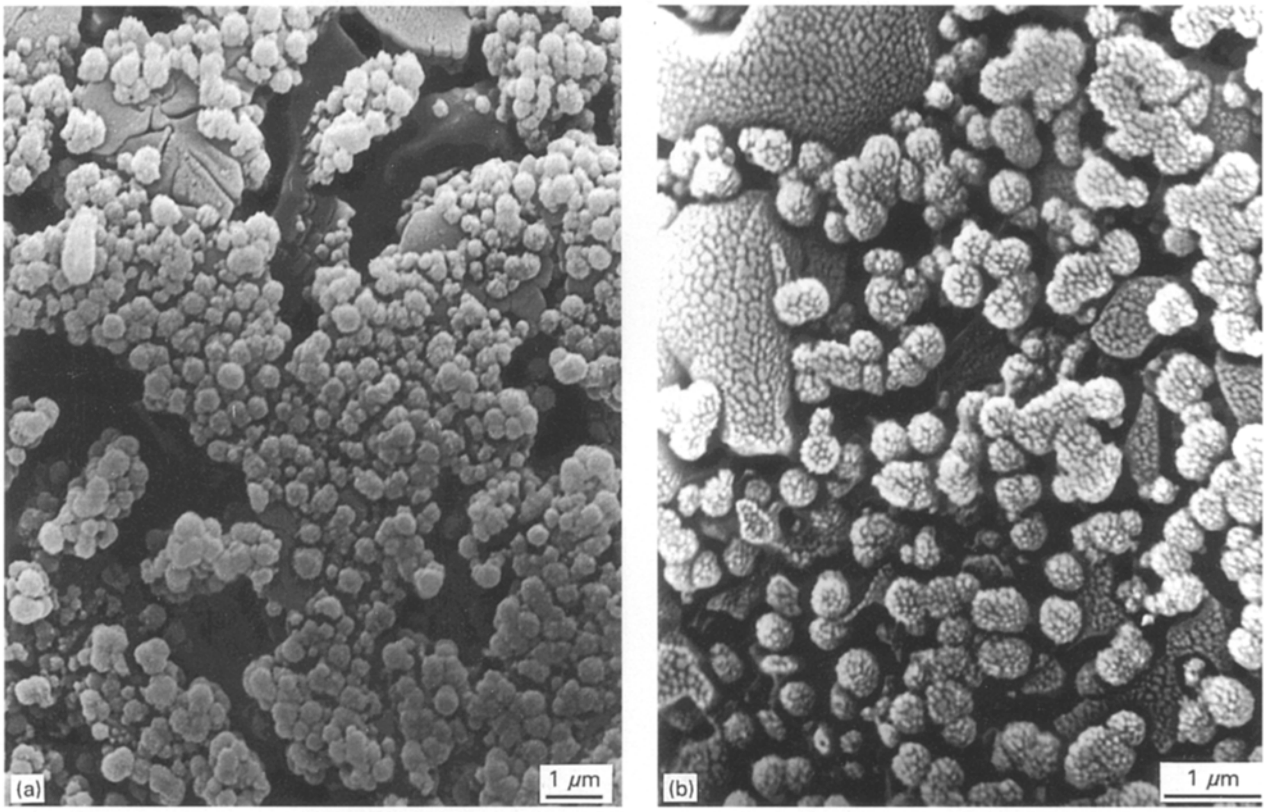

Figure 10 SEM micrographs of colloidal powders (etched) fired at (a) 1000 °C for 3 h (bar = 1 µm), (b) 1200 °C for 9 h (bar = 1 µm).

At 900 °C initial crystallization of β-quartz solid solution is observed. Some secondary diffraction peaks can be associated with cordierite and mullite. At 1000 °C the crystallization of cordierite is significant, and at 1100 °C the transformation is nearly complete. Thus, cordierite is developed fully at 1200 °C, some anorthite appearing as a minor phase, and with a small amount of glassy phase. At 1250 °C only pseudohexagonal cordierite is observed. The sample calcined at 1300 °C melts partially and after 1400 °C heat treatment a translucent glass is observed.

Fig. 7 shows the XRD patterns of heat treated cordierite prepared by the colloidal method. In this case β-quartz solid solution and spinel ($MgAl_2O_4$) are the major crystalline phases, at 900 and 1000 °C. From 1100 °C pseudohexagonal cordierite crystallizes, although some β-quartz is present. The thermal evolution at higher temperatures is similar to polymeric powders, but at 1300 °C a translucent melt is observed.

Remarkably, in order to be able to compare crystallization of sol–gel derived glasses and melt glasses some considerations have to be made, because of the different thermal histories of gel derived and melt glasses [1, 26–28].

3.4. Microstructure

Microstructural evolution of gel and gel derived glass is monitored by SEM techniques.

Polymeric dried gel powders (Fig. 8) show irregular shape and large agglomerates, whose surfaces are formed of small spherical particles less than 0.1 μm in diameter. Similar trends are observed in colloidal dried gels, although in these powders less agglomeration and particles of less than 50 nm in diameter are detected. The presence and the size of very fine primary particles is not detected by this technique.

Gel derived glasses were studied by SEM too, but no significant differences showed with respect to the microstructure of dried gels. So, agglomeration of particles were observed too, although the surface of these agglomerates were more continuous.

SEM characterizations of fired colloidal and polymeric samples (etched) display the presence of spherical agglomerate dispersions formed by small crystalline particles (about 150 nm mean diameter) in the glassy matrix (Figs 9 and 10).

As can be seen in micrographs of samples fired at 1000 °C, in which the main crystalline phase is a β-quartz solid solution, the amount of glassy phase is still high, and crystalline particles are almost monosized and of spherical shape. On increasing temperature, with crystallization of pseudohexagonal cordierite, the size of the particles does not show large variation, although the amount of crystallization is high.

4. Conclusions

Cordierite based glass ceramic materials have been prepared by crystallization of quaternary gel derived glasses. Samples were prepared as polymeric and colloidal gels from mixtures of alkoxides (silicium and aluminium ethylates) and salts (magnesium and calcium chlorides), and colloidal SiO_2 and salts (aluminium, magnesium and calcium chlorides), respectively. Absorption bands in the i.r. spectra for dried gels indicated formation of an Si–O three-dimensional network.

Crystallization of gel derived glass in polymeric samples was characterized by the primary appearance of a metastable β-quartz solid solution that transformed to a pseudohexagonal cordierite by increasing the temperature. This is the only crystalline phase at 1250 °C, although some anorthite is detected at intermediate temperatures. In colloidal gels, Mg–Al spinel was present beside β-quartz solid solution in the first steps of crystallization, indicating differences in homogeneity of colloidal and polymeric derived precursors.

In the microstructural study (SEM) of gel derived glasses, very small size primary particles were observed. This fact could determine that the mechanism of crystal growth could be dominated by surface nucleation, as occurred previously in the anorthrite crystallization field in this system [1].

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