

The Preparation and Thermal Evolution of Polymeric Gels with Garnet Stoichiometry in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{CaO-Cr}_2\text{O}_3\text{-SiO}_2$ Systems

J. Carda,^a M. I. Burguete,^b G. Monrós,^a P. Escribano^a & J. Alarcón^c

^a Department of Inorganic Chemistry, ^b Department of Organic Chemistry, University College of Castellón, University of Valencia, C/Borriol s.n., 12080 Castellón, Spain, ^c Department of Inorganic Chemistry, Faculty of Chemistry, University of Valencia, C/Dr Moliner 50, 46100 Burjassot, Valencia, Spain

(Received 21 September 1989; revised version received 15 February 1990; accepted 16 February 1990)

Abstract

The synthesis of gels with garnet stoichiometry in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{CaO-Cr}_2\text{O}_3\text{-SiO}_2$ systems and their evolution in thermal processing have been studied. Dried gels with the stoichiometry $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ show a homogeneous aspect without detectable crystalline phase. The thermal evolution of these gels indicates no formation of grossularite at temperatures up to 1000°C after 12 h. In the uvarovite garnet samples, $3\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3\text{SiO}_2$, a small amount of crystalline phase was detected in the dried gels. The homogeneity of the gels was checked by scanning electron microscopy. The infrared study of these polymeric gels confirmed the presence of Si-O-Me ($\text{Me} = \text{Cr}^{3+}$, Ca^{2+}) bonds. This may facilitate the formation of uvarovite at low temperatures.

Man untersuchte die Herstellung von Gelen mit Granatzusammensetzung in den Systemen $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ und $\text{CaO-Cr}_2\text{O}_3\text{-SiO}_2$ und deren thermisches Zersetzungsverhalten. Die getrockneten Gele der Stöchiometrie $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ sind homogen aufgebaut, ohne daß eine kristalline Phase festgestellt werden konnte. Die Untersuchung der thermischen Zersetzung dieser Gele zeigt, daß bis 1000°C innerhalb von 12 h kein Grossularit gebildet wird. In den Uvarovitgranatproben ($3\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3\text{SiO}_2$) wurden in den getrockneten Gelen kleine Gehalte einer kristallinen Phase nachgewiesen. Die Homogenität der Gele war mit dem REM überprüft worden. IR-Untersuchungen dieser polymeren Gele bestätigen die Anwesenheit von Si-O-Me -Bindungen ($\text{Me} = \text{Cr}^{3+}$, Ca^{2+}). Dies erleichtert möglicherweise die Bildung von Uvarovit bei niedrigen Temperaturen.

On a étudié la synthèse de gels possédant la stoechiométrie du grenat dans les systèmes $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ et $\text{CaO-Cr}_2\text{O}_3\text{-SiO}_2$ et leur évolution lors d'un traitement thermique. Les gels séchés de stoechiométrie $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ ont un aspect homogène et ne présentent aucune phase cristalline détectable. L'évolution de ces gels ne conduit pas à la formation de grossularite après 12 h à des températures allant jusqu'à 1000°C .

Pour les échantillons de structure grenat uvarovite $3\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3\text{SiO}_2$, on a détecté des traces de phase cristalline dans les gels séchés. L'homogénéité de ceux-ci a été contrôlée par MEB. L'analyse IR de ces gels polymériques confirme la présence de liaisons Si-O-Me ($\text{Me} = \text{Cr}^{3+}$, Ca^{2+}). Ceci pourrait faciliter la formation de l'uarovite à basses températures.

1 Introduction

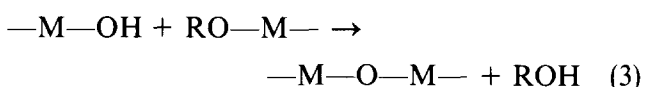
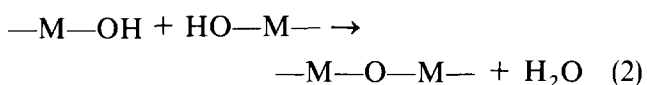
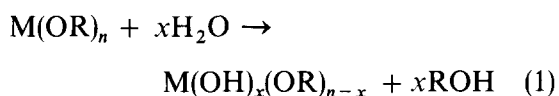
Garnets, which have a general formula $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$, incorporate cations with dodecahedral, octahedral and tetrahedral coordination, and are suitable models for the study of the influence of ionic substitution and for crystal chemical investigations. The IR characterization of garnet group minerals has been studied in detail by Wickersheim *et al.*¹ and Tarte.²

The so-called 'sol-gel' process has been widely used in recent years for the preparation of glasses, fibers, abrasives, thin films, etc. Gelation produces colloidal or polymeric gels, characteristics of which are controlled by a number of factors such as solvent type, concentration, pH, catalyst and temperature. These techniques seem to be particularly appropriate for the preparation of ceramics containing more than one oxide, because of the high level of homogeneity that can be achieved.

Use of the sol-gel process has led to some important technological opportunities, especially in the preparation of new glasses and fully dense materials which cannot be prepared by conventional methods.³ However, application to the synthesis of crystalline structures has been much less explored.

In earlier studies,^{4,5} we have described how the transformation of garnets phases from gels takes place at lower temperatures than when the ceramic method is used. Evidence was obtained for the formation of a silica gel network at molecular level which is able to interact with the various cations. This would increase the homogeneity of the system and facilitate the synthesis.

Polymeric oxide gels are usually prepared from metal alkoxides, $M(OR)_n$, where M is a metal ion and R is an alkyl group. These compounds readily hydrolyze upon addition of water, and polymerized oxide networks can be formed with appropriate control of conditions. In general, metal alkoxides are dissolved in anhydrous organic media and then partially hydrolyzed by the addition of an amount of water which is below the stoichiometric quantity. Hydrolysis of groups $-M-O-R$ takes place and is followed by dehydration of hydroxy groups or dealcoholation, according to eqns (1)–(3):



The formation of linear polymers or weakly crosslinked polymer clusters can be regulated by adjustment of the reaction parameters.

The preparation of multicomponent gels represents a much more complicated situation.³ An ideal approach to these systems would be to start from several metal alkoxides ($M(OR)_x$, $M'(OR)_y$, ...) which hydrolyze at similar rates, so that a homogeneous polymeric network, with a regular distribution of $-M-O-M'$ bonds could be formed. However, metal alkoxides usually hydrolyze at very different rates, and such compounds are not always suitable for the preparation of multicomponent gels; also, some of the metal cations have to be introduced as organometallic compounds, either as their salts (chlorides or nitrates) or as their complexes.

The aim of the present work is to study the advantages and characteristics of the sol-gel processes in the preparation of crystalline structures of

garnet type. For this study we have selected two garnet structures: uvarovite ($Ca_3Cr_2Si_3O_{12}$) and grossularite ($Ca_3Al_2Si_3O_{12}$).

Uvarovite has been obtained at atmospheric pressure, and is stable up to 1370°C;⁶ however, grossularite has never been obtained by firing at ambient pressure.

Gels with the stoichiometry of both systems have been prepared from a silicon alkoxide and different precursors for the rest of cations. We have studied the influence of precursors, catalysts and solvents in the formation of a tridimensional network in gels as well as their evolution under firing.

2 Experimental

Anhydrous alcoholic solvents were chosen for our work, and experiments were carried out with ethanol, iso-propanol and *n*-butanol. As the precursor for silicon, tetraethoxysilane (TEOS; Merck) was always used. $CaCl_2$ (95%, Panreac), $Ca(NO_3)_2 \cdot 4H_2O$ (98.5%, Panreac), CaH_2 (90%, Merck) and $Ca(O_2CCH_3)_2 \cdot H_2O$ (AR, Panreac), were tested as precursors of calcium. For aluminium, $AlCl_3 \cdot 6H_2O$ (95%, Panreac), $Al(NO_3)_3 \cdot 9H_2O$ (AR, Panreac) and aluminium triethylate (97%, Panreac) were selected. As precursors for chromium, $CrCl_3 \cdot 6H_2O$ (>93%, Merck), $Cr(NO_3)_3 \cdot 9H_2O$ (AR, Panreac) and Cr(III) acetyl acetonate (100%, Aldrich) were used. Finally, three different catalysts were assayed: HCl, HNO_3 and CH_3CO_2H .

In general, gels were prepared by dissolving the precursor(s) in the anhydrous solvent in a flask under a positive pressure of argon, and heating the mixture at $\sim 70^\circ C$. The catalyst was added either with the precursor(s) or after a period of time. After being heated and stirred at the required temperature for 3 h, under argon, the samples were kept at room temperature open to the air for various periods of time and were oven dried at $60^\circ C$.

After drying, ternary compositions were fired in an electrical furnace up to $1000^\circ C$ in various steps, with soaking times of 2–12 h.

Infrared spectroscopy (KBr pellets) was used to study the structural evolution of gels; NaCl crystal windows were used for liquid samples or solutions. The IR spectra were taken with a Perkin-Elmer 1330 spectrophotometer with a 3600 data station, using the standard program CDS-13 for data handling.

Crystalline phases were detected, after firing the ternary samples, by X-ray diffraction (XRD), using a Philips PW-1729 diffractometer.

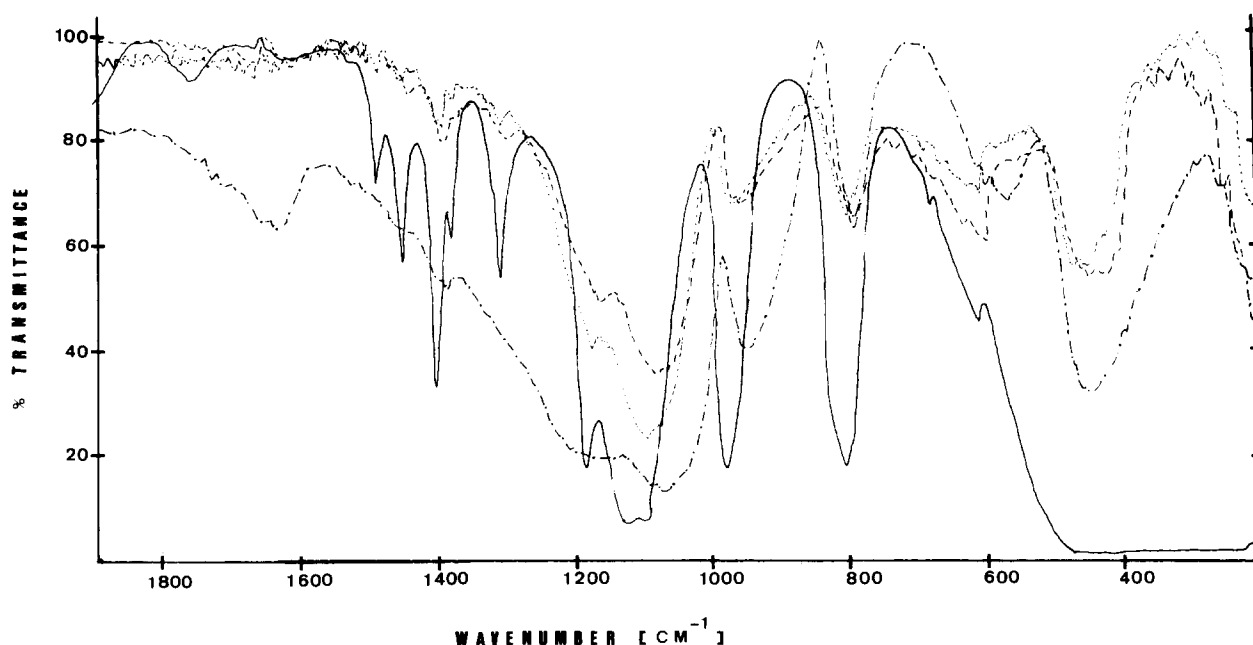


Fig. 1. Infrared spectra of gels prepared with TEOS and ethanol. —, Sample A; ···, sample B; ---, sample C; - · - ·, sample D.

The morphology of the raw and fired gels was followed by scanning electron microscopy–energy-dispersive X-ray (SEM–EDX), using an electron microscopy with a TRACOR detector, provided by Zeiss.

3 Results and Discussion

3.1 Formation of gels from TEOS

Gels of TEOS in ethanol were prepared and treated in various conditions as shown in Table 1. Ethanol was added in an ethanol/TEOS ratio of 4/1 (v/v). The catalyst in Sample D was 3M HNO₃ added in a ratio of 3×10^{-3} mol of acid per mol of TEOS. The H₂O/alkoxide molar ratio was 1/1. The water was introduced as a 3M HNO₃ solution. After treatment as described in Table 1, samples B, C, and D were kept open to the air at room temperature, to obtain complete hydrolysis of TEOS. The gels formed were

analyzed by IR spectroscopy and the spectra were compared with that for pure TEOS (sample A) (Fig. 1). Table 2 summarizes the most significant bands.

Clearly, IR spectra of sample A (pure TEOS) show bands at 1478, 1439, 1392 and 1295 cm⁻¹, corresponding to organic fragments present in the molecule. These bands disappear almost completely in samples B, C and D after hydrolysis and smooth drying. Bands for Si–O stretching (1162, 1108, 1080, 790, 450 cm⁻¹) are very similar for samples B–D, but the bands due to Si–OH and Si–OM bonds are different for sample D (960 cm⁻¹) compared with those present in the samples not treated with an acid catalyst (B and C, 950 cm⁻¹). The acid treatment clearly affects the nature and number of –Si–O–M (M = H, metal) groups present in the network. A band at 570 cm⁻¹ is also observed in sample D, and is indicative of a partially

Table 1. Gels prepared from TEOS in ethanol

Sample	Composition	Conditions
A	TEOS	—
B	TEOS–ethanol	Reflux (3 h) in Ar atmosphere
C	TEOS–ethanol	Reflux (3 h), after cooling at room temperature (24 h), both in Ar atmosphere
D	TEOS–ethanol–HNO ₃	Reflux (3 h) in Ar atmosphere

Table 2. Most significant bands in the IR spectra of TEOS and gels obtained from it

Wavenumber (cm ⁻¹)	Band	Reference
1620	H–O–H bending	7
1480–1370	C–H bands NO ₃ ⁻ group	8
1200		
1100		
1080	Si–O stretching	7–12
790		
420		
960	Si–OH stretching Si–O–M stretching	8–12

different arrangement around the Si atom in the catalyzed system. Bands in this region have been assigned by Suwa and Naka¹³ and Nogami⁷ to different SiO₄ vibrations.

No significant differences were observed when the solvent was changed from ethanol to iso-propanol or *n*-butanol.

3.2 Study of the formation of gels from precursors for Ca, Al and Cr

In an attempt to select the most suitable conditions for the preparation of gels from ternary mixtures, we studied the behaviour of the various precursors for Ca, Al and Cr in the solvents and conditions suitable for our work. Table 3 shows the results obtained when the precursor was heated at 70°C (in an argon atmosphere) in the solvent (the ratio of solvent/precursor was 4–8/1, v/v). For compounds where low solubility is indicated, it was checked that solubility was not greatly affected by either the addition of catalyst or by increasing the contact time.

From the data in Table 3 it can be seen that all three aluminium precursors are adequate; however, according to the general sol-gel process, Al triethylate seemed to be a more appropriate precursor, as it does not involve the introduction of additional anions in the system. For Ca and Cr, the only appropriate precursors seemed to be their chlorides or nitrates.

3.3 Study of the 3CaO · Al₂O₃ · 3SiO₂ system

The stoichiometry of the system 3CaO · Al₂O₃ · 3SiO₂ corresponds to grossularite garnet. As mentioned before, this garnet can be obtained only at high pressures. The reason for this behaviour is considered to be the Ca—O distance in the structure, which is shorter than the mean value for dodecahedral coordination of Ca²⁺ in oxides and which cannot be increased because Al—O and Si—O

distances are at their maxima for silicates with an aluminium in octahedral coordination.^{14,15} A proposed method to synthesize such silicate garnets, in which the high strength of the Si—O bonds prevents formation of the lattice from deformed polyhedra, involved the presence of water in the reacting mixture. The bond strength in the tetrahedra is weakened as part of the SiO₄ could be replaced by (OH)₄ and the required distortion of the polyhedra could be achieved.

Pancrazi¹⁰ has described the preparation of gels from metal alkoxides in the CaO · Al₂O₃ · SiO₂ system to give fully dense glasses, and reported that no bands characteristic of Si—O—Al bonds could be observed in the IR spectra. Bands for these bonds usually appear in the 800–400 cm⁻¹ region in crystalline aluminosilicates; the exact position depends on the coordination of aluminium ions. Increase in the aluminium content is always reflected in an increase of the absorption in that region.

In accordance with earlier studies, the precursors selected for our work were TEOS, aluminium triethylate and calcium nitrate, with ethanol as solvent and no catalyst. The experimental sequence is outlined in the scheme given in Fig. 2.

When the solution of Ca(NO₃)₂ · 4H₂O was added, an instant partial gelification was observed. This gelification is fast either by addition of water or by the action of ambient moisture. In the first case, the gel is formed in the first 2 h, and in the second case, it takes 3–4 h. White gels were formed and after drying were fired at 500°C for 2 h, 700°C for 12 h and 1000°C for 12 h.

Figure 3a, shows absorption IR spectra for the gel obtained by addition of water and for the same sample after firing at 500 and 1000°C. Similar

Table 3. Results obtained with the precursors in different solvents

Precursor	Solubility in ethanol, iso-propanol, n-butanol
CaH ₂	Low solubility
Ca(O ₂ CCH ₃) ₂ · H ₂ O	Low solubility
Ca(NO ₃) ₂ · 4H ₂ O	Clear and homogeneous solution
CaCl ₂	Clear and homogeneous solution
AlCl ₃ · 6H ₂ O	Clear and homogeneous solution
Al(NO ₃) ₃ · 9H ₂ O	Clear and homogeneous solution
Al(OEt) ₃	Clear and homogeneous solution
CrCl ₃ · 6H ₂ O	Green homogeneous solution
Cr(NO ₃) ₃ · 9H ₂ O	Dark green homogeneous solution
Cr(C ₅ H ₇ O ₂) ₃	Low solubility

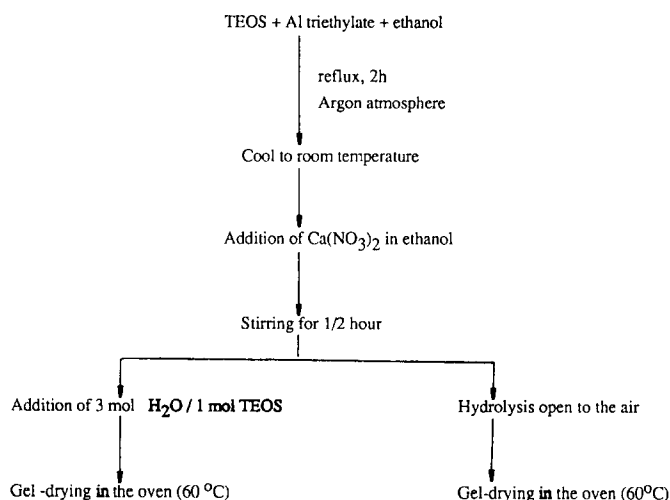


Fig. 2. Scheme of the experimental procedure followed for the preparation of gels in the 3CaO · 3Al₂O₃ · 3SiO₂ system.

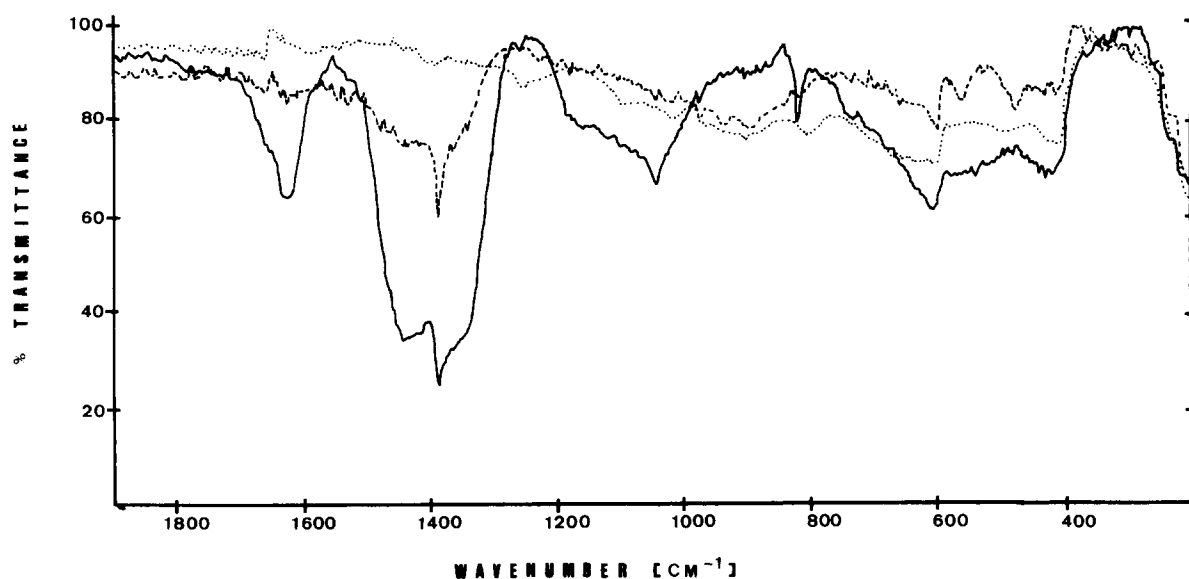


Fig. 3a. Infrared spectra for the sample obtained by addition of water in the system $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ (dried gel and sample after firing). —, Dry gel; ---, 500°C , 2 h; ···, 1000°C , 12 h.

bands and evolution were observed for the sample hydrolyzed with ambient moisture. The band at 1620 cm^{-1} in the spectrum of the gel is assigned to water, and disappeared with heating. The band at 1400 cm^{-1} is characteristic of the nitrate group, and disappeared at 700°C . A small band at 1050 cm^{-1} is also present in the gel (Si—O stretching); its intensity decreased with heating and it was shifted to lower frequencies. This behaviour has been described for gels with a low silica content.^{10,16} A broad band between 800 and 400 cm^{-1} is also present in the gel, and would include any Si—O—Al absorption, but bands in this region also are weakened on heating. At higher resolution (Fig. 3b) a

region is obtained. Bands at $\sim 500\text{ cm}^{-1}$, characteristic of the formation of —O—Si—O— bonds, can be observed only after heating above 500°C .

The XRD spectra showed the presence of an amorphous phase up to 700°C (Table 4). There was no sign of the crystalline phase identified by XRD in the dried gel. It is known that the formation pH is the most important factor controlling the precipitate and crystalline phase in the xero-gel in the $\text{Al}_2\text{O}_3\text{—SiO}_2\text{—H}_2\text{O}$ system.¹⁷ By SEM of dried gel samples, the presence of small particles located on large blocks of amorphous phase can be observed (Fig. 5). Semi-quantitative analysis (EDXA) shows a higher amount of silicon in the large blocks than in the small particles. The silicon content in the small

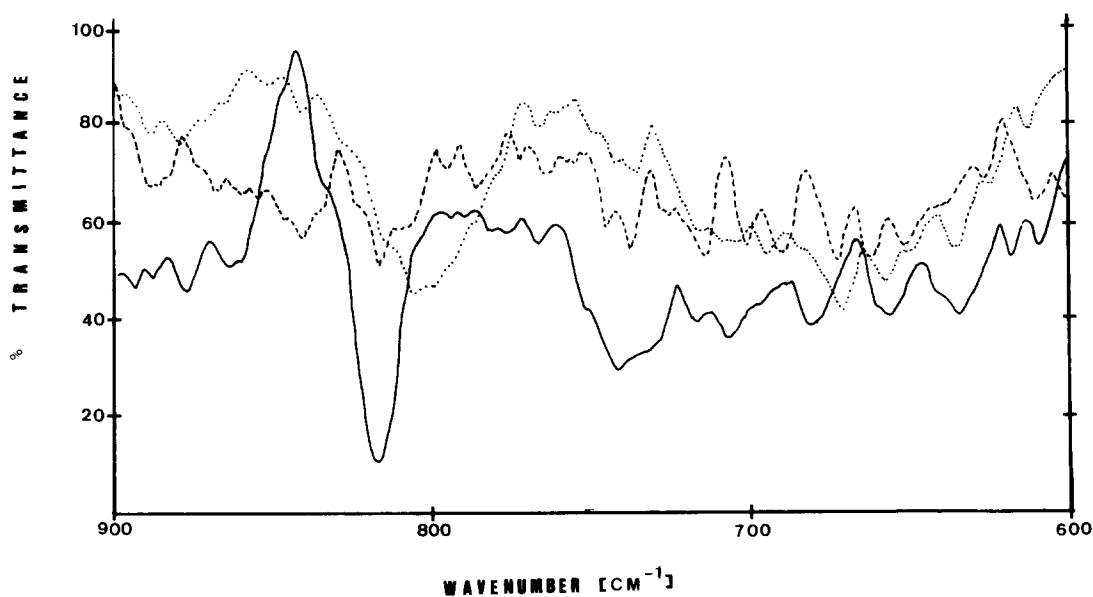


Fig. 3b. High-resolution IR spectra in the region $900\text{--}600\text{ cm}^{-1}$. —, Dry gel; ---, 500°C , 2 h; ···, 1000°C , 12 h.

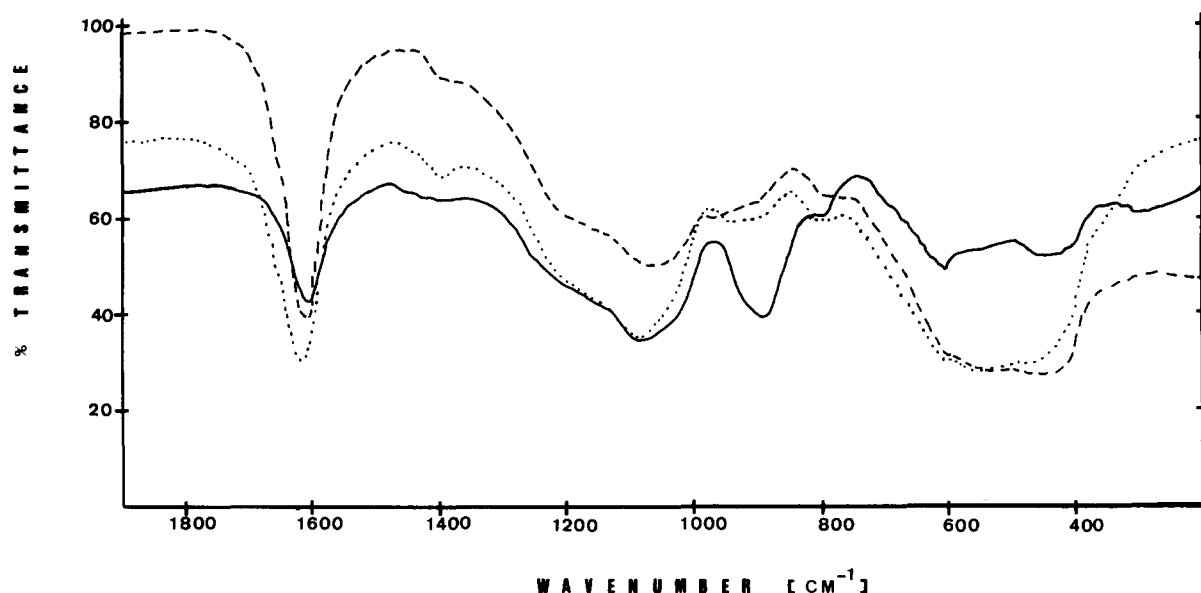


Fig. 4a. Infrared spectra for sample A in the system $3\text{CaO} \cdot 3\text{Cr}_2\text{O}_3 \cdot 3\text{SiO}_2$ (dried gel and sample after firing). —, A; ---, B; ···, C.

particles is similar to the average value in the sample. In Table 4 the evolution of the observed phases with thermal processing is summarised. At 1000°C , peaks assigned to wollastonite and gehlenite,¹⁸ can be observed but not those corresponding to grossularite. It should be noted that Hummel,¹⁹ using the ceramic method, described the production of anortite and pseudowollastonite by firing pure metal oxides with the same stoichiometry.

No clear improvements to our results were obtained by the addition of a catalyst or by the introduction of aluminium alkoxide after partial hydrolysis of the silicon alkoxide.

3.4 Study of the $3\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3\text{SiO}_2$ system

The phase diagram for this system indicates the formation of uvarovite garnet at ambient pressure from CaSiO_3 and Cr_2O_3 ; this garnet is stable up to 1320°C .²⁰

According to earlier studies, gels were formed from TEOS, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and CaCl_2 using the stoichiometry ratio $3\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3\text{SiO}_2$. Three different samples were prepared using a different TEOS/water molar ratio in each case (Table 5). The amount of ethanol used was 4–8 times in excess of the TEOS (v/v).

In sample B, 2×10^{-4} mol HCl/mol TEOS was

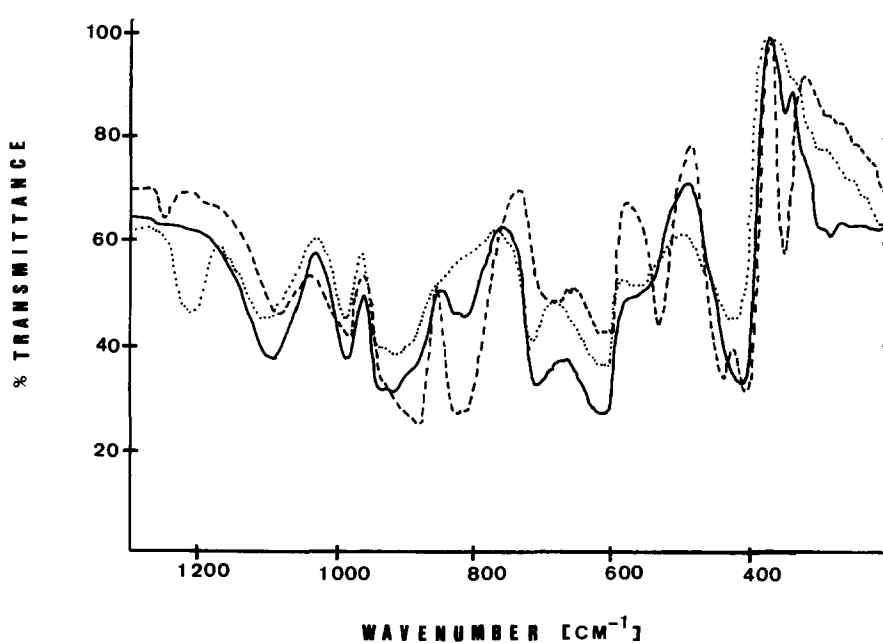


Fig. 4b. High-resolution IR spectra in the region $1300\text{--}200\text{ cm}^{-1}$. ···, 700°C , 12 h; —, 800°C , 12 h; ---, 1000°C , 12 h.

Table 4. Evolution of the observed phases in the gel formed with no water addition

<i>T</i> (°C)	<i>Physical aspects</i>	<i>Phases detected</i>
500°C/2 h	Not concretion	Amorphous
700°C/12 h	Not concretion	Amorphous
1 000°C/12 h	Slight concretion	G(s), B(w)

G = Gehlenite syn., $\text{Ca}_2\text{Al}_2\text{SiO}_7$.

B = Wollastonite, $\beta\text{-CaSiO}_3$.

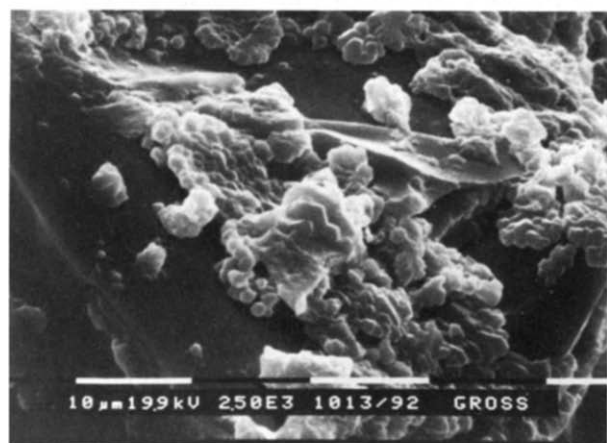
s = Strong, w = weak.

added as catalyst. The gels were prepared by mixing the starting materials in ethanol in an argon atmosphere, and refluxing the mixture for 24 h. The samples were then left open to the air for 3 days.

A polymeric gel is formed in sample B after the refluxing period. Gelification is observed in sample C after 36 h, but in sample A a viscous liquid is formed which gelifies only after complete drying. The colours of the three dried gels are different: grey-green for sample A, green for sample B and grey-violet in sample C.



(a)



(b)

Fig. 5. Micrographs of the Ca–Al–Si dried gel.**Table 5.** Samples prepared with different TEOS/water molar ratio

<i>Sample</i>	<i>Molar ratio TEOS/water</i>	<i>Catalyst</i>
A	1:2	—
B	1:8	HCl
C	1:20	—

Low-intensity peaks of the crystalline phase $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ were detected in dried gels by XRD. It was observed that the amount of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was smaller with an increasing TEOS/water molar ratio.

The evolution of crystalline phases with firing was determined by XRD and is given in Table 6. No important differences are observed for the three samples. An amorphous phase is present up to 500°C. At 700°C, low-intensity peaks assignable to uvarovite are observed, and the reaction is complete at 1000°C. No evolution of the system was detected after higher soaking times or at higher temperatures.

The textures of dried gel samples with various TEOS/water molar ratios are shown in Figs 6–8. It can be seen that, with increasing molar ratio, larger compacted amorphous blocks were formed. This fact could be explained by the higher degree of hydrolysis and polymerization of the starting materials.

Figure 4 shows the evolution of IR absorption spectra for sample A on heating. Samples B and C gave very similar results. In the dried gel, bands associated with the silica-gel network are observed at 1210, 1080 and 795 cm^{-1} . The band at 950 cm^{-1} is assigned to Si—O—M (M = H or metal) groups.^{8,12} This band disappears on firing at 500°C, as expected from condensation reactions of these groups. However, a band in this region (980 cm^{-1}) is again observed after heating at 700°C. In studies of $\text{ZrO}_2\text{—SiO}_2$ ²¹ and $\text{SiO}_2\text{—Y}_2\text{O}_3$ ¹¹ systems, this band has been assigned to Si—O—Zr and Si—O—Y bonds. The bond appears at the temperature at

Table 6. Evolution of the observed phases in sample A

<i>T</i> (°C)	<i>Physical aspects</i>	<i>Phases detected</i>
500°C/12 h	Not concretion Dark green	Amorphous
700°C/12 h	Not concretion Dark green	U(vw), A(w), C(m)
800°C/12 h	Not concretion Light green	U(s), A(vw), C(vw)
1 000°C/12 h	Not concretion Light green	U(s), A(vw), C(vw)

U = Uvarovite, $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$; A = pseudowollastonite, $\alpha\text{-CaSiO}_3$; C = Cr_2O_3 .

s = Strong; m = medium; vw = very weak.

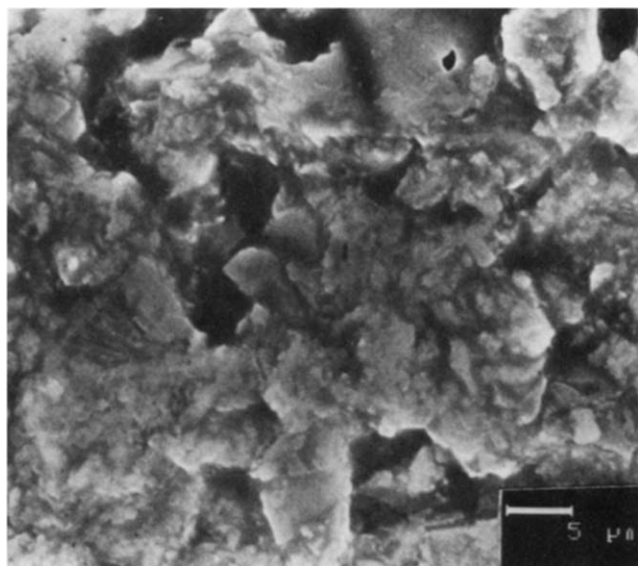


Fig. 6. Micrograph of the sample A dried gel (Table 5).

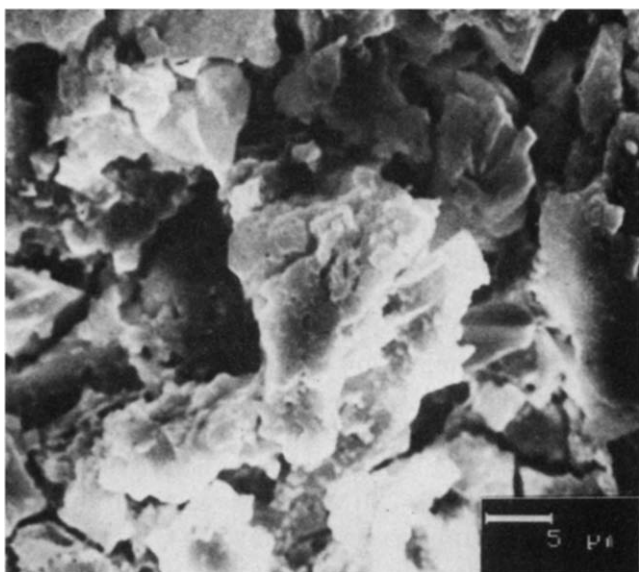


Fig. 7. Micrograph of the sample B dried gel (Table 5).

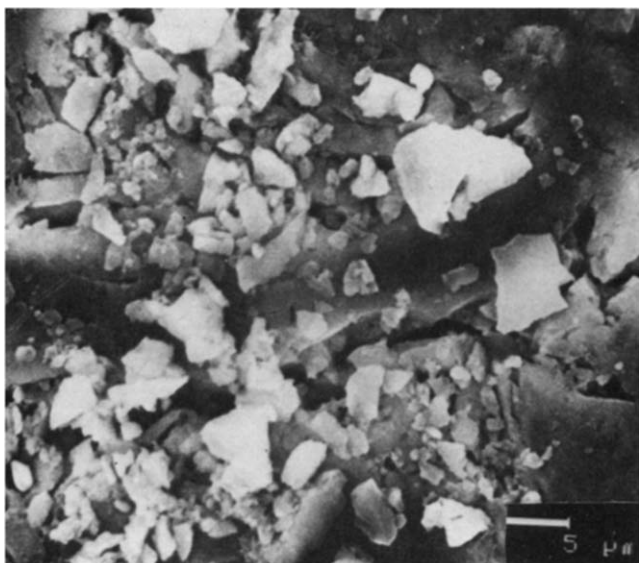


Fig. 8. Micrograph of the sample C dried gel (Table 5).

which formation of the garnet structure is observed by XRD, so that it can probably be assigned to the formation of Si—O—Me bonds (Me = Cr³⁺ or Ca²⁺). Bands in the region 950–350 cm⁻¹ are assigned to vibration of tetrahedral SiO₄; the frequencies of these bands decreases with increase in the radii of dodecahedral and octahedral cations. The resolution of these bands clearly increases as the formation of uvarovite garnet takes place. Bands at 440 and 410 cm⁻¹ are assignable to octahedral vibrations.¹³

4 Conclusions

(1) The acid catalyzer plays an important role in determining the nature of the bonds present in the network formed from TEOS.

(2) In the system Ca–Al–Si, there is no indication of the formation of gels with a regular structure or of the formation of Si—O—Al bonds.

(3) In the thermal treatment of gels in this system, β-CaSiO₃ and Ca₂Al₂SiO₇, mineralogically known as gehlenite, are formed as the only crystalline phases. Hummel¹⁹ has described the formation of pseudowollastonite and anortite in the firing of pure metal oxides with the stoichiometric ratio of grossularite at 1240°C for 150 h.

(4) The much faster hydrolysis rate of Al(OEt)₃ as compared with TEOS, produces the complete gelification or precipitation of aluminium species before the formation, to an appreciable extent, of a polymeric silica-gel network. Thus, the construction of a regular homogeneous system with the existence of Si—O—Al bonds cannot take place. In agreement with the absence of such a regular network, grossularite garnet is not formed after firing.

(5) Infrared analysis of the gels in the Ca–Cr–Si system suggests the existence of homogeneous polymeric network. The presence of a band at 950 cm⁻¹ in these gels, attributed to Si—O—Me (Me = Cr³⁺ or Ca²⁺), could be the reason for uvarovite being obtained at such low temperatures.

Acknowledgement

The authors are grateful to the CICYT for the financial support (project MAT88-0429) which made this paper possible. The authors also thank Dr Jesús M. Rincón López, Instituto Cerámica y Vidrio (CSIC) for his assistance in the SEM–EDX analysis.

References

- Wickersheim, K. A., Lefever, R. A. & Hanking, B. M., Infrared absorption spectrum of the silicate ion in the garnet structure. *J. Chem. Phys.*, **32** (1960) 271–6.
- Tarte, P., Etude expérimentale et interprétation du spectre infrarouge des silicates et des germanates. Application à des problèmes structuraux relatifs à l'Etat Solide. Acad. Roy. Belg. Cl. Sci. Mem., **35** (1965) 103–19.
- Zelinski, B. J. J. & Ullmann, D. R., Gel technology in ceramics. *J. Phys. Chem. Solids*, **45** (1984) 1069–90.
- Carda, J., Monros, G., Escribano, P. & Alarcon, J., Synthesis of uvarovite garnet. *J. Am. Ceram. Soc.*, **72** (1989) 160–2.
- Carda, J., Monros, G., Escribano, P. & Alarcon, J., Síntesis de la uvarovita. Estudio comparativo entre el método cerámico y el de formación de geles. *Bol. Soc. Esp. Ceram. Vidr.*, **28** (1989) 15–21.
- Glasser, F. P. & Osborn, E. F., Phase equilibrium studies in the system CaO–Cr₂O₃–SiO₂. *J. Am. Ceram. Soc.*, **41** (1958) 358–67.
- Nogami, M., Glass preparation of the ZrO₂–SiO₂ system by the sol–gel process from metal alkoxides. *J. Non-Cryst. Solids*, **69** (1985) 415–23.
- Villegas, M. A. & Fernandez Navarro, J. M., Vidrios del sistema Li₂O–SiO₂ preparados por la técnica sol–gel. *Bol. Soc. Esp. Ceram. Vidr.*, **28** (1989) 169–78.
- Bellamy, L. J., *The Infrared Spectra of Complex Molecules*. Chapman and Hall, London, 1975, pp. 385–93.
- Pancrazi, F., Phalippon, J., Sorrentino, F. & Zarzycki, J., Preparation of gels in the CaO–Al₂O₃–SiO₂ system from metal alkoxides. *J. Non-Cryst. Solids*, **63** (1984) 81–93.
- Edney, C. V., Condrate, R. A., Crandall, W. B. & Washburn, M. E., Infrared and Raman spectra of Y₂O₃–SiO₂ glasses prepared by sol–gel process. *J. Mater. Sci. Lett.*, **6** (1987) 308–12.
- Tohje, N., Matsuda, A. & Minami, T., Coating films of 20B₂O₃·80SiO₂ by the sol–gel method. *J. Am. Ceram. Soc.*, **70** (1987) C13–15.
- Suwa, Y. & Naka, S., Infrared spectra of the solid solution between uvarovite and spessartine. *Am. Mineral.*, **60** (1975) 1125–6.
- Mill, B. V., Crystal chemistry of garnet formation. *Neorg. Mater.*, **5** (1969) 1604–9.
- Geller, S., Crystal chemistry of the garnets. *Z. Kristallogr.*, **123** (1967) 1–47.
- Yoldas, B. E., Preparation of glasses and ceramics from metal–organic compounds. *J. Mater. Sci.*, **12** (1977) 1203.
- Hsi, C. H., Yen, F. S. & Chang, Y. H., Characterization of co-precipitated Al₂O₃–SiO₂ gels. *J. Mater. Sci.*, **24** (1989) 2041–6.
- Anon., X-ray powder diffraction data file. *ASTM Card 20-199*. American Society for Testing and Materials, Philadelphia, PA.
- Hummel, F. A., Synthesis of uvarovite. *Am. Mineral.*, **35** (1950) 324–5.
- Glasser, F. P. & Osborn, E. F., On the stability and synthesis of uvarovite Ca₃Cr₂Si₃O₁₂. *Amer. Min.*, **44** (1959) 1301–3.
- Lazarev, A. N., *Vibrational Spectra and Structure of Silicates*, translated by G. D. Archard, ed. V. C. Farmer. Consultants Bureau, New York, 1972.