

Gels, filaments and fibres from alkoxysilanes and aluminium chlorohydrate-polyol complexes

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Aluminosilicate gels, filaments and fibres may be formed using precursor solutions prepared from alkoxysilanes and aluminium chlorohydrate-polyol complexes. A precursor solution having the oxide stoichiometry of mullite has been prepared from the aluminium chlorohydrate-1,2-dihydroxypropane complex and either tetramethoxysilane, tetraethoxysilane or technical ethyl silicate (silica equivalent 40% wt/wt), the latter being preferred because it readily forms gels and filaments. Important practical advantages include the ability to draw filaments directly from the precursor solution prior to gelation thus eliminating both the need for a coagulating bath and the necessity of including an organic filament-forming polymer in the precursor solution. Viscosity measurements, chemical and magic angle spinning nuclear magnetic resonance investigations indicate that the alkoxysilane and the polyol complex undergo hydrolysis/condensation reactions giving intermediate $>Al-O-Si<$ groupings. The filaments and gels were converted to crystalline oxide ceramics on controlled firing. When the filament or gel has the oxide stoichiometry for mullite, the formation of mullite commences at a temperature below 1000°C and is complete at 1300°C. When compositions containing excess silica are fired to high temperature, mullite is formed and the excess silica appears as cristobalite. When compositions containing excess alumina are fired to high temperature, all the silica appears as mullite.

1. Introduction

Mullite, ideally of $3Al_2O_3 \cdot 2SiO_2$ stoichiometry, is a crystalline high-melting material which has long been used in heavy-duty refractories where mechanical strength and/or resistance to thermal shock are required. Mullite grain may be made [1] by sintering at high temperature a mixture of Bayer alumina and kaolinite, or by fusing a mixture of silica and alumina in an electric arc furnace, each mixture having the oxide stoichiometry required for mullite. Mullite precursor materials can be obtained by sol-gel procedures, for instance by a precipitation process in which hydrous alumina is precipitated on hydrous silica, or from gels having the oxide stoichiometry for mullite. Ethyl silicate and aluminium chlorides may be used [2] to prepare precursor solutions and gels whose oxide stoichiometry is in the mullite range. Suitable aluminium chlorides include the aluminium chlorohydrates $Al_2(OH)_nCl_{6-n}$, where n is 1 to 5, preferably 5. When the precursor solution and the resulting gel are formed from a technical ethyl silicate (silica equivalent ca. 40% wt/wt) [3] and an aluminium chlorohydrate $Al_2(OH)_5Cl$, which may be hydrated, homogeneous gels give the best yield of mullite and require the lowest conversion temperature.

Aluminosilicate ceramic fibres are widely used in thermal insulation for furnaces. A mullite ceramic

fibre would therefore be a material of considerable interest because of its refractoriness, strength, and thermal shock damage resistance. The present paper describes the preparation [4, 5] of aluminosilicate precursor solutions, some with the oxide stoichiometry in the mullite range, and the formation of clear rigid gels from these solutions, and in addition direct formation of filaments which convert to ceramic fibres on firing. These solutions are formed from alkoxysilanes and aluminium chlorohydrate-polyol complexes. The alkoxysilanes used were tetramethoxysilane, tetraethoxysilane and technical ethyl silicate [3], the latter being preferred because it has already been shown [6] to be superior to tetraethoxysilane in the formation of filaments. The aluminium chlorohydrate-polyol complexes used [5] are formed from aluminium chlorohydrates, preferably $Al_2(OH)_5Cl$ and polyols such as 1,2-dihydroxypropane, 1,3-dihydroxybutane, 1,2,3-trihydroxypropane and 1,1,1-trimethylolpropane, the 1,2-dihydroxypropane complex, which is commercially available being preferred. This complex is commonly referred to as "aluminium chlorohydrate" (C.A. Registry No. 53026-85-0) and has the nominal composition $Al_2(OH)_5Cl \cdot H_2O \cdot CH_3CH(OH)CH_2OH$. It is believed [7] to be a polynuclear coordination complex of aluminium chlorohydrate and 1,2-dihydroxypropane in which some of the water molecules

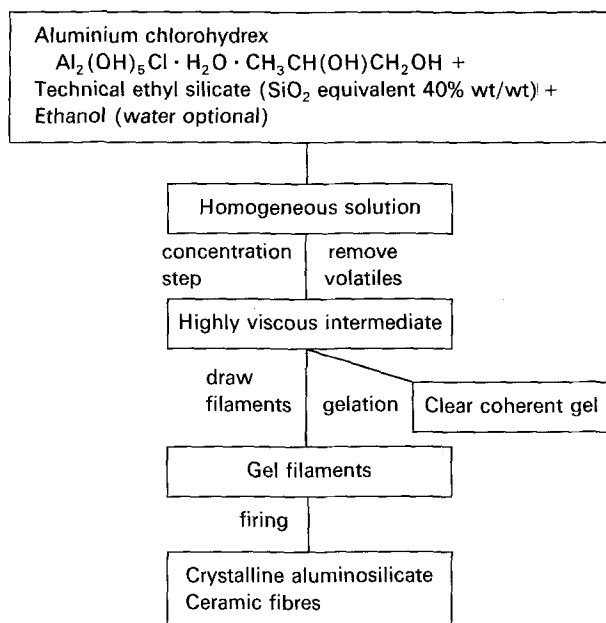


Figure 1 Preparation of clear coherent gels, filaments and ceramic fibres from aluminium chlorohydrate and technical ethyl silicate.

normally coordinated to aluminium in aluminium chlorohydrate have been displaced by the 1,2-dihydroxypropane resulting in a less polar complex of low water content, which is soluble in alcohols. Fig. 1 is a flow sheet illustrating the production of clear rigid gels, filaments and ceramic fibres from aluminium chlorohydrate and alkoxy silanes.

2. Experimental details

2.1. Materials

Tetramethoxysilane and tetraethoxysilane were supplied by BDH Chemicals Ltd, Poole and were used as-received. Technical ethyl silicate (silica equivalent in the range 40 to 42% wt/wt) was used as-received from WEX Chemicals Ltd, London. Analysis by gas-liquid chromatography (GLC) [8] showed the material to have a typical distribution of ethoxypolysiloxane oligomers. The aluminium chlorohydrate was supplied by Reheis Chemical Company, Berkeley Heights, New Jersey. Ethanol was the UK 74 over proof industrial methylated spirit. Distilled or deionized water was used throughout.

2.2. General procedures

The ability of a solution to form filaments was assessed by inserting into and pulling out of the solution a 10 mm diameter glass rod.

X-ray powder diffraction patterns were obtained from solid samples ground to a fine powder using an agate mortar and pestle. Diffraction patterns were obtained using a Philips PW1710 diffraction controller and diffractometer with a Philips PM8210 printer/recorder. A $\text{CuK}\alpha$ X-ray source, with a nickel filter, having a wavelength of 0.154 178 nm generated by a voltage of 40 kV and a current of 20 mA was used, and unless otherwise stated, samples were scanned over the range $2\theta = 10$ to 70° . Crystalline phases were identified from their X-ray diffraction patterns with the aid of the JCPDS International Centre for Diffraction Data, Inorganic Materials Alphabetical Index,

1984. Solvent distillates were analysed by gas-liquid chromatography using a Pye Unicam Model GCD chromatograph with air-hydrogen flame ionization detector, or for samples containing water, a thermal conductivity detector. The column, 1.5 m long, was packed with OV17 material and swept with nitrogen gas through a temperature programme of 70 to 250°C at 8°C min^{-1} . Water analysis was carried out by means of a Karl Fisher titration on a Baird and Tatlock AF3 automatic titrimeter. All viscosity measurements were carried out at ambient temperature using a Brookfield Synchroelectric Viscometer Model LVT. Thermogravimetric analysis (TGA) data were obtained using a DuPont 950 thermogravimetric analyser and differential thermal analysis (DTA) data were obtained using a DuPont 900 analyser. In each case a heating rate of $10^\circ\text{C min}^{-1}$ in an air atmosphere was used. Magic angle spinning nuclear magnetic resonance (MASNMR) spectra were recorded on a Varian VXR instrument at the University of Durham. ^{27}Al MASNMR spectra were recorded at 78.15 MHz and ^{29}Si MASNMR spectra were recorded at 59.58 MHz. The ^{27}Al and ^{29}Si spectra were referenced to $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and tetramethylsilane, respectively.

For scanning electron microscopy, samples were gold shadowed and examined on a Philips 505 instrument operated at 20 kV.

2.3. Preparation and treatment of gels and filaments

Clear transparent glass-like gels were prepared from technical ethyl silicate and aluminium chlorohydrate by Method A in Section 2.3.1. Filaments were obtained by Methods B to H in Sections 2.3.2 to 2.3.7. In most experiments, clear, transparent glass-like gels were also obtained. Unless otherwise stated, gels and filaments have an oxide stoichiometry in the mullite range. During such preparations, the volatiles were removed at a rate of about $5\text{ cm}^3\text{ min}^{-1}$ by distillation at 70°C on a rotary evaporator with vacuum assistance when necessary.

All firings were carried out in an air atmosphere. Firing up to 1000°C was carried out at an approximate heating rate of $10^\circ\text{C min}^{-1}$ to the required temperature. For higher temperatures, a heating schedule of 50°C h^{-1} from ambient temperature to 700°C was used followed by 200°C h^{-1} to the required temperature. All samples were held at the required temperature for a 2 h period.

2.3.1. Method A

Aluminium chlorohydrate (13.44 g) was dissolved in a solution of 27 cm^3 ethanol and 5.0 g technical ethyl silicate. Various amounts of water were added and the resulting solutions refluxed for different periods of time. Gelation occurred about 5 min after refluxing ceased. Table I summarizes the experimental conditions and gel characteristics. All gels were coherent. The molar ratio $\text{Al}_2\text{O}_3 : \text{SiO}_2$ was 2.88 : 2, which is in the mullite range of the alumina-silica system.

2.3.2. Method B

Aluminium chlorohydrate (13.44 g) was dissolved in a

TABLE I Gels formed from aluminium chlorohydrate and technical ethyl silicate

Volume of water added (cm ³)	Time to reach reflux (min)	Reflux time (min)	Gel characteristics
2.5	10	83	Slightly cloudy
3.5	12	89	Clear
4.5	5	67	Slightly cloudy
5.0	33	82	Very clear
5.5	8	83	Very clear
6.5	11	102	Slightly cloudy
7.5	13	52	Slightly cloudy

All gels were coherent gels. Molar ratio $Al_2O_3 \cdot SiO_2 = 2.88:2$, which is in the mullite range of the alumina-silica system.

solution of 5.0 g technical ethyl silicate and varying amounts of ethanol, then varying amounts of water were added to the resulting solution. These solutions were heated at or below the reflux temperature giving very viscous liquids. Table II summarizes the conditions under which filaments were formed together with the properties of the resulting filaments.

2.3.3. Method C

Aluminium chlorohydrate (13.44 g) was dissolved in a solution of 5.0 g technical ethyl silicate in varying amounts of ethanol. In some cases, varying amounts of water were added to the resulting solution. Varying amounts of solvent were removed by vacuum distillation, the residue being tested for filament formation and also for gelation. The results are given in Table III. All gels were coherent.

2.3.4. Method D

Aluminium chlorohydrate (13.44 g) was dissolved in a solution of 5.0 g technical ethyl silicate in varying amounts of ethanol. In some cases, varying amounts of water were also added. The resulting solutions were allowed to stand at ambient temperature or at 40°C and periodically tested for filament formation. The results are given in Table IV.

2.3.5. Method E

Filaments having the composition corresponding to the molar ratio $Al_2O_3 : SiO_2$ of 2.88 : 2, this ratio being in the mullite range of the alumina-silica system, were prepared by the following preferred procedures.

2.3.5.1. Procedure (i). Technical ethyl silicate (20 g) was added to 70 cm³ ethanol and vigorously stirred while 53.76 g aluminium chlorohydrate was slowly added. To the resulting stirred solution, 3.0 cm³ water was added, then the mixture was brought to reflux temperature and kept at this temperature for 1 to 1½ h. Filaments up to 22 cm in length could then be drawn for a period of 2 to 2½ h.

2.3.5.2. Procedure (ii). Aluminium chlorohydrate (80.64 g) was dissolved in a solution of 30 g technical ethyl silicate in 162 cm³ ethanol. The resulting solution was then evaporated using a rotary evaporator, 108 cm³ solvent being removed under reduced pressure at a temperature between 80 and 90°C during a period of about 20 min. Filaments could then be drawn from the viscous solution immediately up to ~90 cm in length and for a period of 24 h.

2.3.6. Method F

Aluminium chlorohydrate (100 g) was dissolved in a solution of 200 cm³ ethanol and 111.38 g technical ethyl silicate. This gave a solution in which the molar ratio of $Al_2O_3 \cdot SiO_2$ was 1 : 2. 135 cm³ solvent was removed at 70°C under reduced pressure, giving a solution from which filaments could be drawn and which ultimately formed a clear, transparent, glass-like gel.

2.3.7. Method G

Aluminium chlorohydrate (100 g) was dissolved in a solution of 200 cm³ ethanol and 53.04 g tetraethoxysilane. This gave a solution in which the molar ratio of $Al_2O_3 : SiO_2$ was 2.99 : 2. After removal of 118 cm³ solvent by distillation, filaments could be drawn and a clear, transparent, glass-like gel was formed on standing.

2.3.8. Method H

Aluminium chlorohydrate (100 g) was dissolved in a solution of 38.76 g tetramethoxysilane in 200 cm³ ethanol. This gave a solution in which the molar ratio of $Al_2O_3 : SiO_2$ was 2.99 : 2. After removal of 110 cm³ solvent by distillation, filaments could be drawn and a clear, transparent, glass-like gel was formed on standing.

TABLE II Filament formation from aluminium chlorohydrate and technical ethyl silicate under reflux conditions

Volume of ethanol added (cm ³)	Volume of water added (cm ³)	Time to reach reflux (min)	Reflux time (min)	Filament lengths prepared (cm)
15.0	2.5	8	31	5
20.0	2.5	10	63	1
15.0	2.5	6	33	1
17.5	2.5	7	43	1
17.5	1.5	9	75	1.5
22.0	5.5	2	30	1.5
17.5	5.5	5	30	1.5
17.5	1.7	70-79°C for 70 min		7
17.5	1.2	70-79°C for 55 min		7.5
17.5	0.7	70-79°C for 77 min		10
17.5	0.5	70-79°C for 112 min		15
17.5	0	4	90	Solution left to stand for 4 days - gave filaments of 7.5 cm

TABLE III Filament formation from aluminium chlorohydrate and technical ethyl silicate by removing solvent

Volume of ethanol initially (cm ³)	Volume of water initially (cm ³)	Boiling point of solution (°C)	Time to reach boiling point (min)	Time at boiling point (min)	Volume of solvent removed (cm ³)	Comments
27.0	-	68	28	22	13.0	2 cm filament formation immediately. After 24 h filaments up to 50 cm could be formed. The solution gelled after another 4.5 h
27.0	-	59	15	16	15.5	8 cm filament formation immediately. After 1 h 15 cm filaments formed. After another 1.75 h filaments up to 50 cm formed. After a further period of 21.5 h filaments up to 10 cm formed. Solution gelled overnight
27.0	-	63	20	15	18.0	50 cm filaments immediately; 24 h later - 30 cm filaments. The solution gelled after another period of 3.5 h
27.0	-	63	12	42	20.5	Filaments up to 50 cm formed immediately; 6.5 h later - 15 cm filaments. The solution gelled after another 14.5 h
17.5	-	63	20	17	8.0	6 cm filaments immediately. After 0.75 h - 15 cm filaments. After further period of 21 h - 35 cm filaments. After further period of 22.5 h - 15 cm filaments. Gelled after a further period of 6 h
27.0	0.8	39	6	17	16.0	10 cm filaments immediately. After 1 h - 25 cm filaments. Gelled overnight
27.0	3.3	62	5	18	20.0	5 cm filaments immediately. After 0.5 h - 30 cm filaments. Gelled overnight
27.0	5.5	46	2	20	20.0	5 cm filaments immediately. After 2 h - 20 cm filaments. Gelled overnight

TABLE IV Filament formation from aluminium chlorohydrate and technical ethyl silicate at ambient temperature (AT) and 40°C

Volume of ethanol (cm ³)	Volume of water (cm ³)	Temperature (°C)	Results
27.0	–	AT	Gelation time = 11 days. Filaments could be formed after 7 days, filaments up to 50 cm could be formed after 8 days
22.5	–	AT	Gelation time = 9 days. Filaments could be formed after 2 days, filaments up to 38 cm could be formed after 4 days
17.5	–	AT	Gelation time = 7 days. Filaments could be formed after 2 days, filaments up to 45 cm in length could be formed after 4 days
27.0	–	40	Gelation time = 6 days. Filaments could be formed after 2 days, filaments up to 22 cm could be formed after 3 days
22.5	–	40	Gelation time = 3 days. Filaments could be formed after 22 h, filaments up to 15 cm in length could be formed after 3 days
17.5	–	40	Gelation time = 3 days. Filaments up to 12 cm in length could be formed after 22 h
17.5	0.8	AT	Gelation time = 8 days. Filaments could be formed after 2 days, filaments up to 22 cm could be formed after 3 days
17.5	3.3	AT	Gelation time = 8 days. Filaments could be formed after 6 days (10 cm in length)
17.5	5.5	AT	Gelation time = 6 days. No filaments could be prepared from this composition
17.5	0.8	40	Gelation time = 3 days. Filaments could be formed after 20 h, these were 10 cm in length
17.5	3.3	40	Gelation time = 3 days. Filaments could be formed after 2 days, these were 5 cm in length
17.5	5.5	40	Gelation time = 3 days. Filaments could be formed after 2 days, these were 4 cm in length

2.3.9. Method I

To investigate the hydrolysis and gelation mechanisms, 50.0 g aluminium chlorohydrate was dissolved in 100 cm³ ethanol and varying amounts of technical ethyl silicate added to prepare solutions with the oxide stoichiometry given in Table V. The solutions were gelled by removal of volatiles, which were retained for analysis, then the gels were dried to constant weight.

2.3.10. Method J

For viscosity investigations, 100 g aluminium chlorohydrate was dissolved in 200 cm³ ethanol and the required amount of alkoxysilane added. Solvent was removed by distillation as required, and the viscosity of the resulting solutions determined at various con-

centrations up to the point of gelation. All the solutions were stored in sealed containers between viscosity measurements in order to eliminate any discrepancy due to inadvertent solvent loss on standing.

3. Results and discussion

The results given in Tables I to IV show that for technical ethyl silicate the gelation time decreases with increasing volumes of water added. Clear, homogeneous gels were obtained unless otherwise stated. The results also show that the presence of excess water adversely affects filament formation and that filament formation is improved by removal of excess volatiles. Filament formation is optimum when no additional water is added and the ethanol added initially is the

TABLE V Effect of technical ethyl silicate concentration on the composition of distillates

SiO ₂ equivalent (wt/wt %)	Gel oxide stoichiometry	Technical ethyl silicate (g)	Ethanol (g)	Distillate (g)	Weight loss of sample on drying (g)	Mass balance (%)	(Weight loss – weight of ethanol, (g))	Water content of distillates (mg H ₂ O/250 μl)
0	Al ₂ O ₃	–	78.45	80.33	81.22	98.9	2.77	9.4
9.09	11.79Al ₂ O ₃ · 2SiO ₂	4.72	78.54	83.02	84.76	97.2	6.22	6.8
19.09	5Al ₂ O ₃ · 2SiO ₂	11.14	78.47	85.88	87.72	97.9	9.25	5.5
28.57	3Al ₂ O ₃ · 2SiO ₂	18.56	79.04	89.66	91.49	98.0	12.45	3.6
54.10	Al ₂ O ₃ · SiO ₂	27.84	79.04	93.44	94.48	98.9	15.44	3.7
46.92	2Al ₂ O ₃ · 3SiO ₂	41.77	78.92	97.11	98.49	98.6	19.57	2.8
54.10	Al ₂ O ₃ · 2SiO ₂	55.69	78.53	101.71	103.31	98.4	24.78	1.8

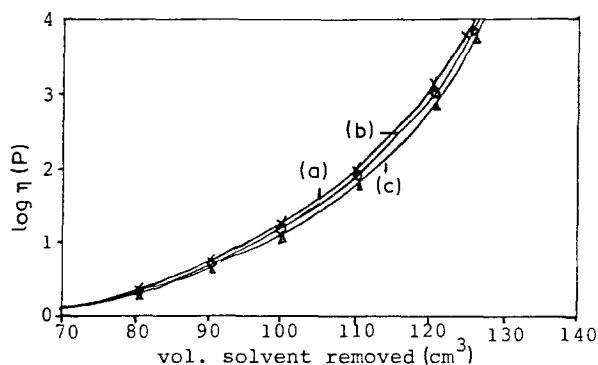


Figure 2 Dependence of viscosity on concentration for ethanolic solutions of aluminium chlorohydrate and various alkoxy silanes. (a) Technical ethyl alcohol, (b) $\text{Si}(\text{OMe})_4$, (c) $\text{Si}(\text{OEt})_4$. All starting solutions: 100 g aluminium chlorohydrate, 200 cm^3 EtOH and corresponding amount of alkoxy silane.

minimum volume required to give a homogeneous solution. Drawing a filament produces a dramatic increase in the surface area: volume ratio, resulting in rapid volatilization of any remaining solvent, and gelation so that the filament is coherent. Thus the stability of the drawn filament is delicately balanced on the sol:gel transition point, and the success of filament formation being dependent on the homogeneous nature of the precursor composition.

Similar filament lengths could also be obtained from ethanolic solutions of aluminium chlorohydrate and either tetramethoxysilane, tetraethoxysilane, or technical ethyl silicate. Fig. 2 gives a plot of viscosity against volume of solvent removed by distillation for solutions prepared as described in Method J, Section 2.3.10. Viscosity is developed in the order

technical ethyl silicate > $\text{Si}(\text{OMe})_4$ > $\text{Si}(\text{OEt})_4$

which is the order of the silica equivalents of the alkoxides. The difference in viscosity development is related to the formation of alcohol during concentration, arising from various hydrolysis/condensation reactions. Fig. 3 shows the change in viscosity with time for solutions prepared as described in Method J, Section 2.3.10 and concentrated by distillation of solvent. At very high concentration, the gelation time is short, typically of the order of minutes. At lower concentrations, the gelation time is much longer, generally of the order of days. Solutions showed filament-forming ability when the viscosity ranged from ~ 10 P to the gel point, although at very high viscosities (7500 to 10 000 P), the filaments obtained were of poor quality. The preparation of filaments suitable for conversion to ceramic fibres usually requires [9] the presence of a filament-forming organic polymer to be dissolved in the solution. For example, solutions giving filaments which may be converted to alumina ceramic fibres may be prepared [10] from an aluminium salt such as aluminium chlorohydrate, a filament-forming organic polymer (for instance polyethylene oxide) and a mutual solvent for the aluminium salt and the polymer. Filaments which form alumina ceramic fibres can also be obtained [11] by extruding an aqueous solution of aluminium chlorohydrate into a coagulating bath comprising an alcohol

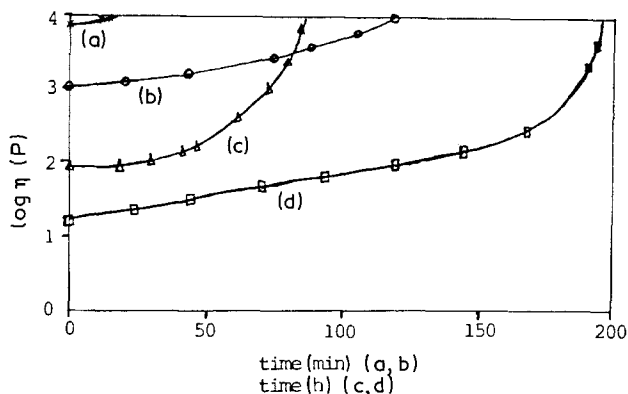


Figure 3 Increase in viscosity with time, for concentrated ethanolic solutions of aluminium chlorohydrate and technical ethyl silicate. Volume of solvent removed from starting solution: (a) 125 cm^3 , (b) 120 cm^3 , (c) 115 cm^3 , (d) 110 cm^3 .

(such as ethanol, iso-propanol, or tert-butanol) with or without acetone. Thus two important advantages [4, 5] of the use of pre-formed aluminium chlorohydrate-polyol complexes to form filaments follow directly. Eliminating the organic polymer reduces the amount of organic material to be burned away to form the ceramic fibre. Eliminating the need for a coagulating bath simplifies filament formation. Depending on the reaction temperature and the reaction time, filaments may be obtained continually up to the point of gel formation. During removal of the solvent, hydrolysis and condensation-polymerization reactions cause a steady increase in the viscosity and at a particular point, it becomes possible for filaments to be formed from the solution and ultimately a clear, coherent and rigid gel is obtained. To obtain a gel of maximum clarity, the reaction temperature should be at least 60°C.

By careful adjustment of the conditions, an acid hydrolysate of technical ethyl silicate and aluminium chlorohydrate, with oxide stoichiometry in the mullite range, can be gelled by a base to give a homogeneous gel suitable for binding refractory grains [2, 12]. Other hydrolysates of ethoxysilanes and aluminium salts may also be treated with a base to give gels suitable for binding refractory grains [13]. A base gelation accelerator is not necessary to obtain the clear, transparent glass-like gels whose preparation is described in the present paper. It is important to note that coherency does not equate with homogeneity and hence transparency.

Several reactions or types of reaction may occur during the gelation of aluminium chlorohydrate-alkoxy silane solutions. In these systems, the co-ordinated water present in the initial aluminium chlorohydrate reagent is both sufficient in quantity and lability to initiate alkoxy silane hydrolysis as well as the subsequent condensation reactions necessary to cause gelation. It should also be born in mind that no additional catalysts need to be added to ensure that such reactions proceed at a reasonable rate. Thus although one possibility is that no interaction occurs between the silicon and aluminium species present, this would mean that the alkoxy silanes would undergo hydrolysis and condensation independently giving

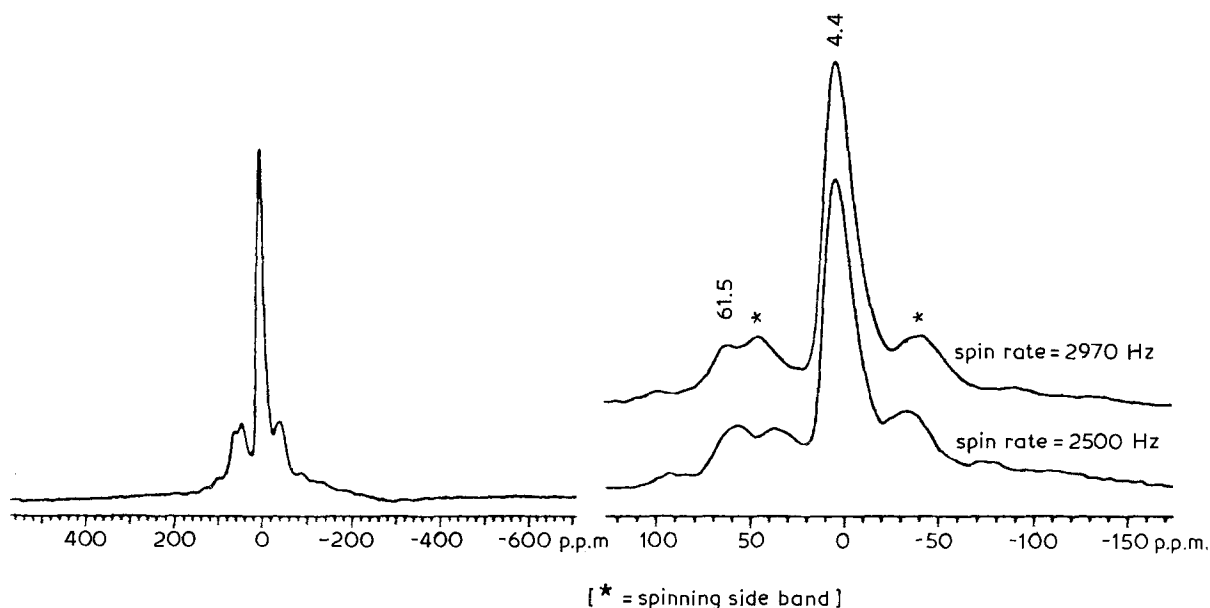
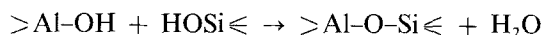
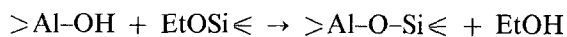


Figure 4 ^{27}Al MASNMR spectra of a mullite stoichiometry gel.

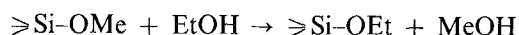
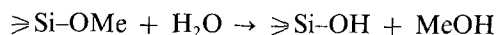
$\geq\text{Si-O-Si}\leq$ oligomers and polymers. Such reactions normally require catalysis but would also result in predominantly a diphasic gel structure. Alternatively, significant interaction between the various species present in the reacting mixture could occur to form $>\text{Al-O-Si}\leq$ structures by condensation reactions such as



Reactions of this type will result in a homogeneous single-phase gel structure. Furthermore, if both reaction sequences occur, it is possible that a gel with a structure intermediate between the single and diphasic state will form.

Table V presents the analyses of distillates collected when various amounts of technical ethyl silicate were added to an ethanolic solution of aluminium chlorohydrate, which was gelled by removal of solvent under reduced pressure as in Method I, Section 2.3.9. The resultant gels were further dried to constant weight, also as in Table V. The distillates contained only water and ethanol; no 1,2-dihydroxypropane or alkoxy silanes

were detected. No chloroethane was observed. The highest concentration of technical ethyl silicate gave a minimum water content in the distillate and a maximum weight loss. The fact that the minimum water content is not simply a concentration effect follows from a comparison between the pure aluminium chlorohydrate system and the system containing the highest amount of technical ethyl silicate in which the water content of the distillate decreases by $\sim 80\%$ whereas the increased weight loss is only 28%. Therefore at gelation, substantial hydrolysis of the technical ethyl silicate has occurred. When technical ethyl silicate was replaced by tetramethoxysilane, the distillate also contained methanol as well as ethanol and water. The methanol could have formed either by hydrolysis or ethanolysis of tetramethoxysilane:



A solid state magic angle spinning nuclear magnetic resonance (MASNMR) spectroscopic study of the dried gel, having the mullite oxide stoichiometry, prepared from aluminium chlorohydrate and

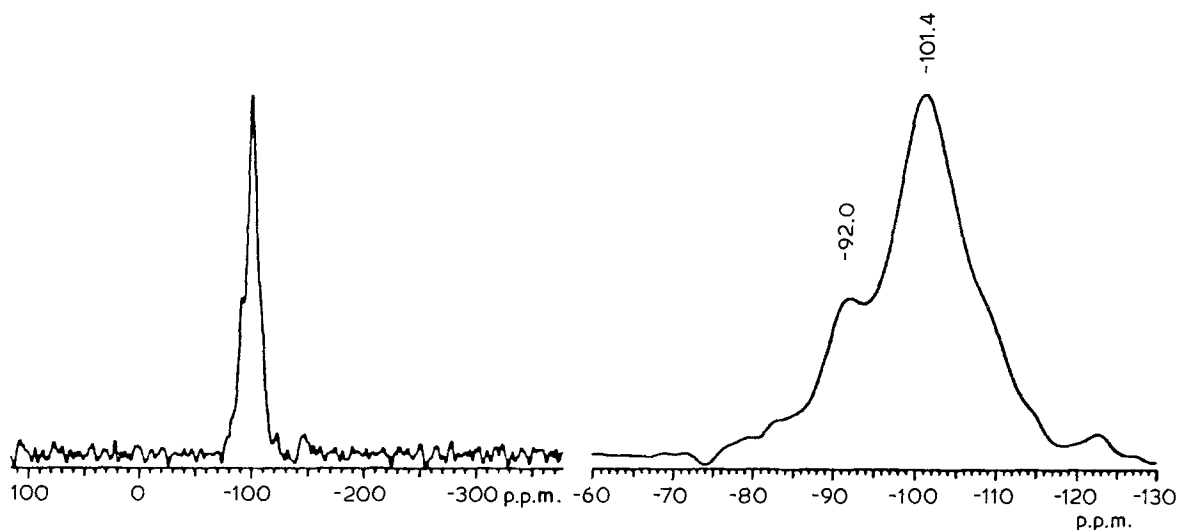


Figure 5 ^{29}Si MASNMR spectrum of a mullite stoichiometry gel.

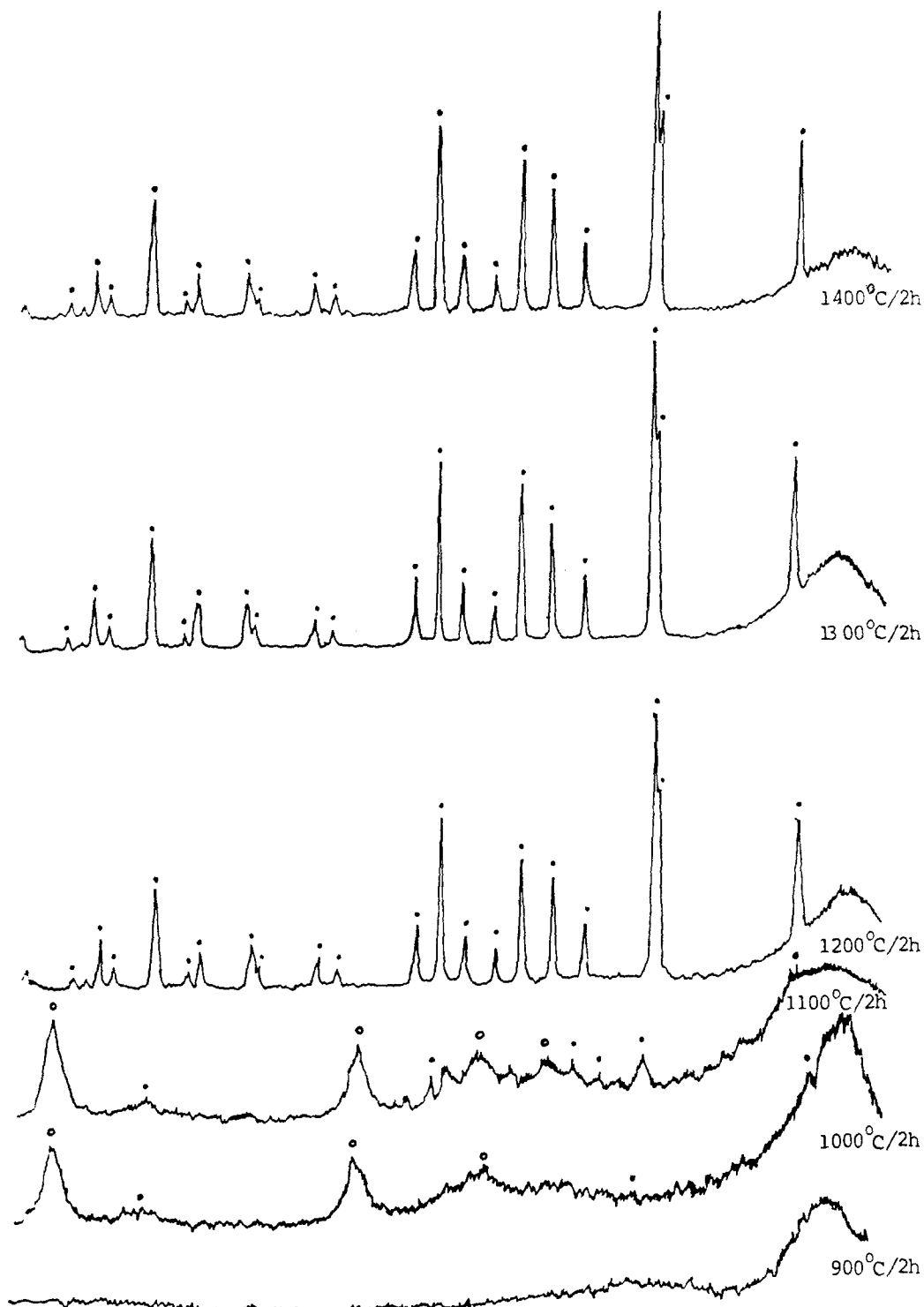


Figure 6 X-ray data for mullite stoichiometry gel filaments prepared from $\text{Si}(\text{OMe})_4$ ($2\theta = 10$ to 70°). (○) $\gamma\text{-Al}_2\text{O}_3/\text{AC-Si}$ spinel, (●) mullite.

tetraethoxysilane gave good evidence for considerable interaction between the aluminium and silicon species to produce a single-phase homogeneous gel structure. Tetraethoxysilane was used in preference to technical ethyl silicate to avoid introducing condensed silicon species. The ^{27}Al MASNMR spectrum given in Fig. 4 shows resonances due to both tetrahedral and octahedral coordination of aluminium, at 4.4 and 61.5 p.p.m., respectively, the octahedral resonance being much stronger. This assignment is based on the observation [14] that aluminium atoms when octahedrally coordinated by oxygen or hydroxyl resonate at ~ 0 p.p.m. and at ~ 50 p.p.m. when tetrahedrally

coordinated. The ^{29}Si MASNMR spectrum shown in Fig. 5 is broad, indicating a variety of distorted silicon environments. Two resonances are observed, a principal one at -104.4 p.p.m. with a less intense resonance at -92.0 p.p.m. Compared with pure silica gel which resonates [15] at -109.3 p.p.m., these low-field shifts are consistent with the presence of aluminium in the next-nearest-neighbour environment. The resonance at -101.4 p.p.m. indicates [16] an Si(1Al) environment, and the resonance at -92 p.p.m. indicates an Si(2Al) environment. For comparison, a single-phase gel of mullite oxide stoichiometry prepared [17] from tetraethoxysilane and alumin-

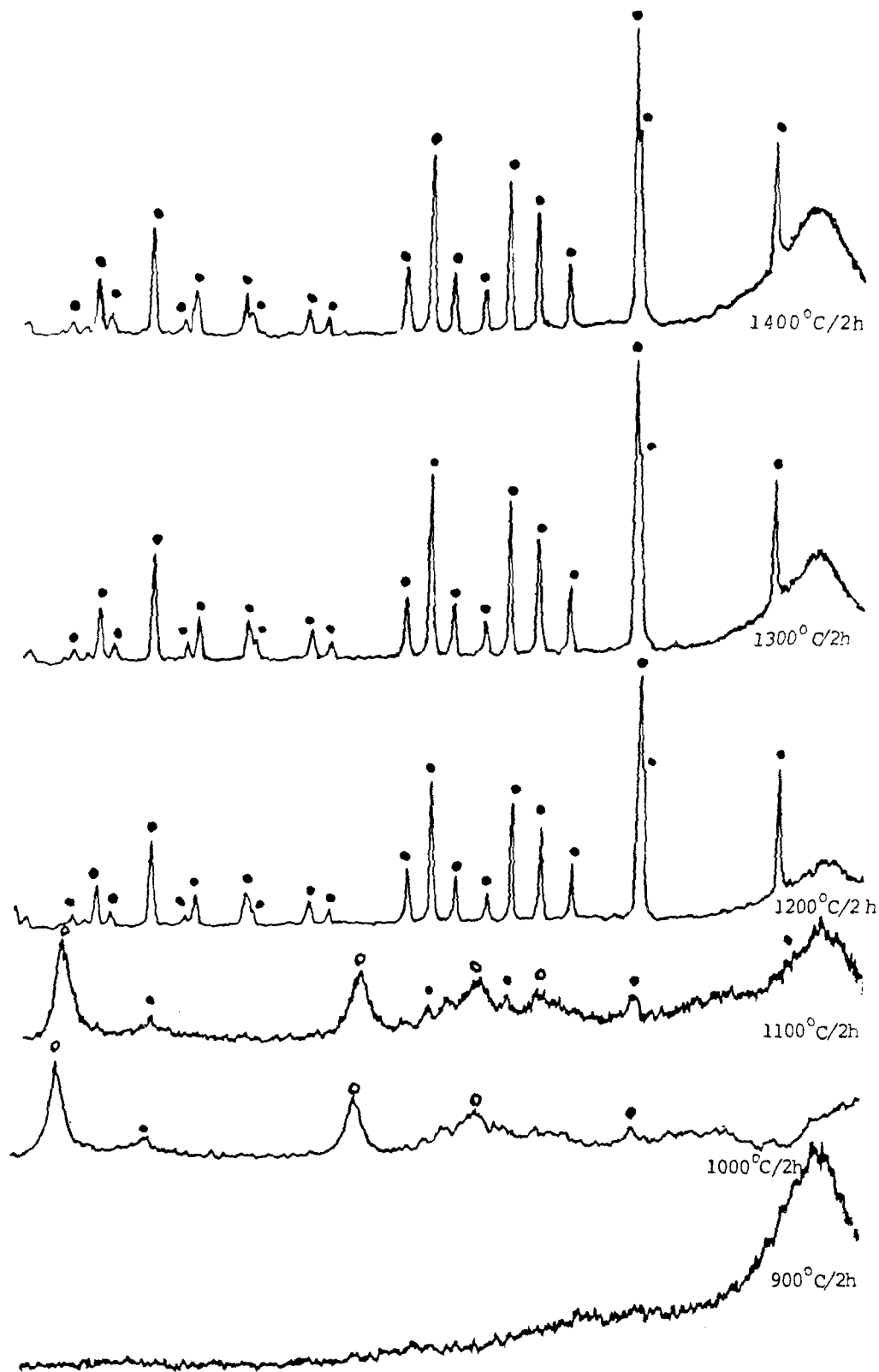


Figure 7 X-ray data for mullite stoichiometry gel filaments prepared from $\text{Si}(\text{OEt})_4$ ($2\theta = 10$ to 70°). (○) $\gamma\text{-Al}_2\text{O}_3/\text{Al-Si}$ spinel, (●) mullite.

ium(III) nitrate gave a broad ^{29}Si MASNMR resonance at -103.3 p.p.m. which was assigned to an $\text{Si}(1\text{Al})$ environment. This is similar to our observation and is supporting evidence for interaction between silicon and aluminium species giving a single-phase homogeneous gel structure.

Clear coherent gels and gel filaments prepared from aluminium chlorohydrate and either tetramethoxysilane, tetraethoxysilane or technical ethyl silicate, having the oxide stoichiometry required for mullite

were amorphous to X-rays at ambient temperature. In each case, substantially complete crystallization to mullite occurred at high temperature, being preceded by the formation of an intermediate cubic phase. The gels and gel filaments prepared from different silicon alkoxides showed similar behaviour on firing. DTA and TG results, summarized in Table VI, showed an initial endotherm, followed by a broad exotherm and later by a sharp exotherm due to crystallization. The initial endotherm is due to loss of residual solvent and

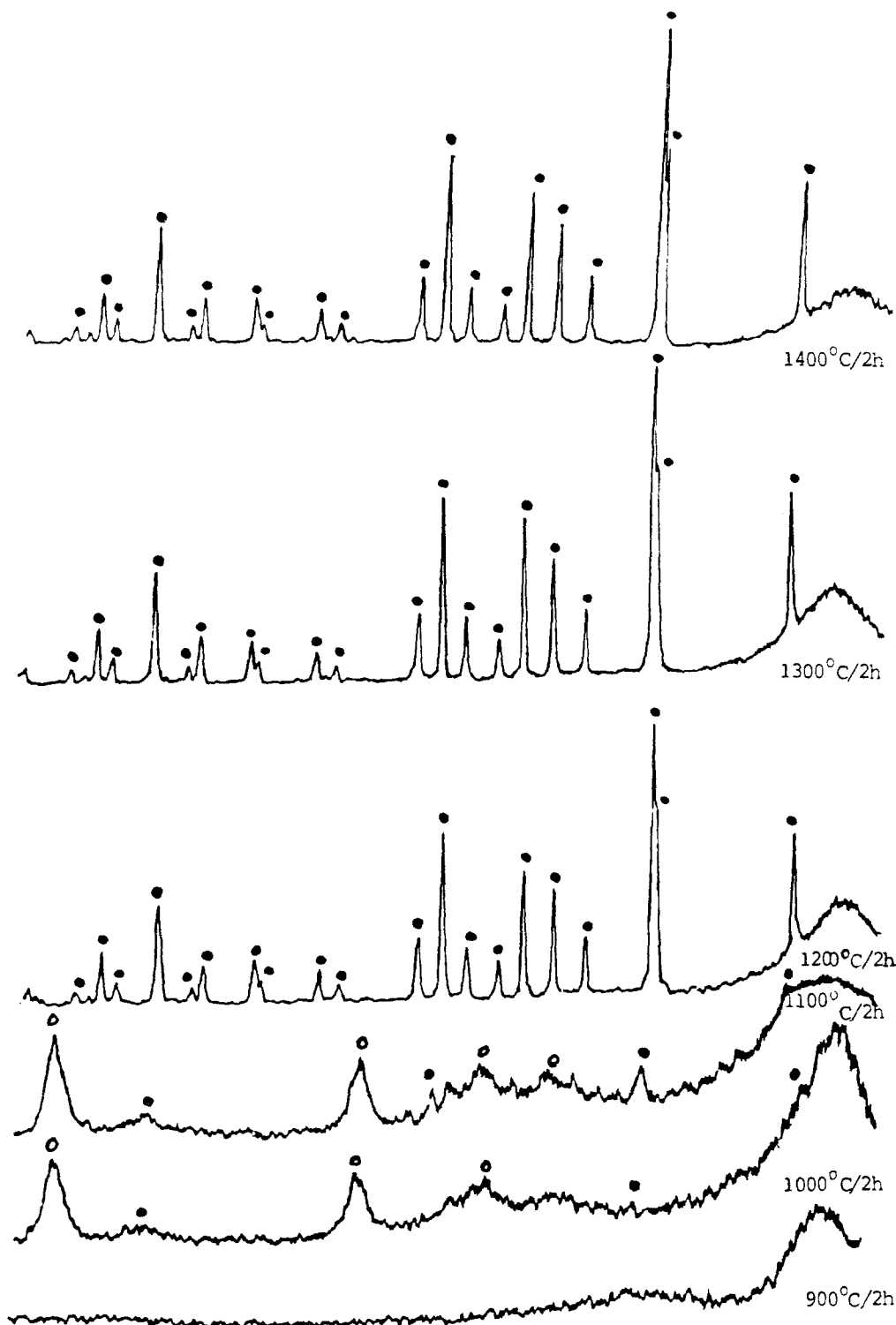


Figure 8 X-ray data for mullite stoichiometry gel filaments prepared from technical ethyl silicate ($2\theta = 10$ to 70°). (○) γ - Al_2O_3 /Al-Si spinel, (●) mullite.

decomposition of species derived from aluminium chlorohydrate. The broad exotherm is due to combustion of organic material, overshadowing an endotherm due to removal of chloride. The sharp exotherm observed at 984°C indicates the commencement of crystallization (or the growth of nuclei formed at the broad exotherm) and the conversion of the amorphous filaments into crystalline oxide fibres. After firing at 1000°C for 2 h, the X-ray diffraction patterns (Figs 6 to 8) showed broad diffuse reflections attributable to a cubic phase which is either γ -alumina [18] and/or an Al-Si spinel [19]. In all cases, weak mullite reflections were also visible. The amount of mullite increased on

firing to 1100°C , but the same cubic phase was still present. At 1200°C only mullite was detected and by estimating the conversion from peak heights, mullite

TABLE VI Thermal analysis of filaments having mullite oxide stoichiometry

Alkoxysilane	$\text{Si}(\text{OMe})_4$	$\text{Si}(\text{OEt})_4$	Technical ethyl silicate
Endotherm temp. ($^\circ\text{C}$)	21–380	21–320	21–340
Weight loss (%)	37.0	33.0	34.0
First exotherm temp. ($^\circ\text{C}$)	380–615	320–660	340–700
Weight loss (%)	12.5	16.5	15.0
Second exotherm	984	984	984

TABLE VII Thermal analysis of filaments and gels having oxide stoichiometry other than that required for mullite

Composition		Weight loss at 1000°C (%)	Endotherm peak (°C)	1st exotherm peak (°C)	2nd exotherm peak (°C)
SiO ₂ equivalent (% wt/wt)	Molar ratio Al ₂ O ₃ · SiO ₂				
4.76	23.57:2	57.39	296	514	910
9.09	11.79:2	54.43	264	528	945
19.09	5:2	51.06	271	521	976
37.02	1:1	44.75	261	555	985
46.92	2:3	42.92	259	624	986
54.10	1:2	54.10	269	628	988

crystallization was complete at 1300°C. Fibre lengths up to 10 cm were obtainable when gel filaments were fired at 1400°C for 2 h. As would be expected from the method of preparation, fibre diameters varied widely. Scanning electron microscopy revealed fine-grain structures without major flaws.

Clear coherent gels and filaments having oxide stoichiometry other than that required for mullite were also prepared from technical ethyl silicate and aluminium chlorohydrate and were also amorphous to X-rays at ambient temperature. DTA and TG results given in Table VII were broadly similar to the results obtained for gels and filaments with the oxide stoichiometry required for mullite. Again the initial endotherm is due to loss of residual solvent and decomposition of species derived from aluminium chlorohydrate; the broad exotherm is due to the combustion of organic material and again overshadows an endotherm due to loss of chloride; the crystallization exotherm often being much less sharp. The temperature at which the endotherm and the two exotherms are observed depends on the oxide stoichiometry, which also determines the sharpness of the crystallization exotherm. The crystal phases present at high temperature are given in Table VIII and depend on the oxide stoichiometry. Formation of mullite is rapid above 1000°C. When silica-rich compositions are fired to high temperature, mullite is formed and the excess silica appears as cristobalite, the crystallization of mullite being preceded by the formation of an intermediate cubic phase. These compositions when fired to 1000°C contain the intermediate cubic phase with poorly crystallized mullite. Formation of mullite

TABLE VIII Crystalline phases formed when gels and filaments having oxide stoichiometry other than that required for mullite are fired to 1400°C for 2 h

Composition		Phases present	
SiO ₂ equivalent (% wt/wt)	Molar ratio Al ₂ O ₃ · SiO ₂	Major	Minor
4.76	23.57:2	α-alumina	mullite, also other aluminas
9.09	11.79:2	α-alumina	mullite
19.09	5:2	θ-alumina	mullite
37.05	1:1	mullite	cristobalite (trace)
46.92	2:3	mullite	cristobalite
56.10	1:2	mullite	cristobalite

The material having molar ratio Al₂O₃:SiO₂ = 1:2 contained about 1.5 times more cristobalite than the material of molar ratio Al₂O₃:SiO₂ = 2:3.

is rapid on firing above 1000°C. When compositions high in alumina are fired to high temperature (1400°C), the silica always appears as mullite, the form of the residual alumina depending on the alumina content. Thus the formation of mullite from all of the aluminosilicate gels occurs irrespective of their oxide stoichiometry. All these gels are homogeneous gels. Their ready conversion to mullite on firing agrees with the main conclusions drawn from the results of our previous studies [2] on the formation of mullite from gels prepared from technical ethyl silicate and other aluminium chloride species.

4. Conclusions

1. Alkoxysilanes and aluminium chlorohydrate-polyol complexes, for instance the 1,2-dihydroxypropane complex, aluminium chlorohydrate, may be used to prepare precursor solutions from which clear, coherent, glass-like gels and/or filaments which convert to ceramics or ceramic fibres on firing can be obtained.

2. The alkoxysilane undergoes hydrolysis and coagulation reactions with the complex. Reactions are best performed at a temperature above 60°C.

3. Optimum conditions for filament formation require the minimum amount of water and solvent ethanol, filament formation being possible in the viscosity range from ~10 P to the gel point.

4. Important practical advantages of the use of an aluminium chlorohydrate-polyol complex in preparing filaments are (a) it is not necessary to include a filament-forming organic polymer in the precursor solution, and (b) a coagulating bath is not needed.

5. Filaments and gels convert to crystalline oxide ceramic materials on firing. Mullite formation commences at a temperature under 1000°C and is complete at 1300°C when the filament or gel has the oxide stoichiometry for mullite.

6. When compositions containing excess silica are fired to high temperature, mullite is formed and the excess silica appears as cristobalite. When compositions containing excess alumina are fired to high temperature, all the silica appears as mullite.

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