

Effect of pH on 980 °C spinel phase-mullite formation of Al₂O₃-SiO₂ gels

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Different reaction paths of mullite formation via sol-gel processing techniques are reviewed. These variations are due to differences in hydrolysis/gelation behaviours of the silica and alumina components used. Variations of pH during processing without altering other variables follow three different routes of mullite formation. In the highly acidic region (pH ≤ 1), the gel does not exhibit a 980 °C exotherm but forms γ -Al₂O₃. Mullite forms at high temperature by diminution of α -Al₂O₃ and β -cristobalite, respectively. In the pH range of 3-4.5, gels exhibit a 980 °C exotherm and develop only mullite. In the highly alkaline region (pH ~ 14), the gel produces a Si-Al spinel phase at the 980 °C exotherm and mullite formation at the ~ 1330 °C exotherm takes place from the intermediate Si-Al spinel phase.

1. Introduction

Synthesis of mullite precursor has recently gained considerable importance to ceramic technologists, due to its wide application in structural, electronic and optical fields [1]. There are different techniques for producing homogeneous precursor powders for various ceramic materials [2-4]. The powder preparation techniques for mullite have been classified into three varieties by Sacks *et al.* [5], e.g. (i) the conventional mixing of SiO₂-Al₂O₃ powders, (ii) colloidal technique, and (iii) solution technique. It was shown that the latter technique is the best for achieving molecular-scale mixing of the two reactants, viz. Si and Al, such that the mullitization temperature can be brought down considerably in comparison with the other techniques. A number of solution-precipitation techniques and models for SiO₂-Al₂O₃ powder preparations, have been described [6, 7]. However, detailed reviews are scarce. Thus, in the present communication, detailed processing techniques and variations in 980 °C phase formation are reviewed; thereafter, different paths of mullite phase developments are discussed. The different techniques are as follows.

(i) Simultaneous precipitation or coprecipitation of two water-soluble components, e.g. SiCl₄, AlCl₃ etc., followed by hydrolysis by use of dilute ammonia solution (Table I).

(ii) Simultaneous hydrolysis or cohydrolysis and subsequent gelation of two organometallic compounds of Si and Al, e.g. tetra ethyl ortho silicate (TEOS), partially hydrolysed TEOS, tetra methyl ortho silicate (TMOS), Al-secbutoxide, Al-isopropoxide in the presence of a solvent such as water, methyl alcohol, ethyl alcohol, butyl alcohol, isopropyl alcohol or benzene, carried out in the presence of either a mineral acid or a base as hydrolysing agent (Table II).

(iii) Hydrolysis of one component in the presence of a salt. TEOS was hydrolysed slowly in the presence of a solvent such as ethyl alcohol containing dissolved

aluminium nitrate. In some cases, aqueous silica sol or sodium silicate was gelified in the presence of aluminium sulphate followed by washing or dialysis for Na⁺ removal and drying (Table III).

Monophasic gels prepared by different processing techniques (Tables I-III) showed two different paths of mullite developments. Some gels directly transformed to mullite at the 980 °C exotherm. Mullite obtained at this temperature was not well crystallized, there was no splitting of the 0.337 nm and 0.343 nm peaks; this non-splitting has led Okada [30], Shineider [31] and Li & Thompson [32] to suggest that this mullite is of a tetragonal form. Other gels formed Si-Al spinel phase at 980 °C exotherm, with a composition similar to that of orthorhombic mullite, thus it was designated as cubic mullite by Chakravorty & Ghosh [16]. In most cases, gels formed a mixture of Si-Al spinel and mullite at 980 °C, and thereafter complete mullitization took place at the 1250 °C exotherm, followed by transformation of the intermediate Si-Al spinel phase. Thus the formation and variation in the development of either mullite or Si-Al spinel or both at 980 °C exotherm, and the subsequent mullitization reaction path at the 1250 °C exotherm, were due to two major factors: (i) variations in the choice of starting components of SiO₂ and Al₂O₃ as used by different researchers, and (ii) variations in the rate of hydrolysis of the components used, and their subsequent gelification in different hydrolysing conditions. These depend on three major variables, (i) the medium of hydrolysis, i.e. aqueous or non-aqueous; (ii) hydrolysing agent, i.e. acidic or basic, which determines the velocity of hydration of the two components and their mechanisms (electrophilic or nucleophilic); and lastly (iii) the time/temperature required for completion of hydrolysis and gelation processes.

Out of all the parameters of hydrolysing conditions, the role of pH on phase development is the subject

TABLE I Cohydrolysis-coprecipitation

Reference	Components	Precipitation conditions	Thermal characteristics of gel as noted by DTA and XRD studies
(1) Inasley & Ewell [8]	Sodium silicate $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$	10% NaOH was added to neutrality; electro dialysed to remove Na^{+1}	Pronounced exotherm at 980 °C. Both spinel and mullite observed at the maximum of exothermic peak temperature. Ratio of the two crystalline phases formed depends on starting composition of gel
(2) Horte & Weigmann [9]	SiCl_4 and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	NH_4OH solution	980 °C exotherm. Exothermic peak area was found highest for gel of equimolecular $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio
(3) Demediwk & Cole [10]	As above	NH_4OH solution	Contrary to [9], the exothermic peak area was highest for gels of composition 3:2 mullite
(4) Croft & Marshall [11]	SiCl_4 and AlCl_3	Flash cohydrolysed by injecting ethereal mixture of components into a warm dilute NH_4OH solution in stirred condition	XRD of 800 °C-heated powder showed cubic spinel phase
(5) Mcgee & Wirkus [12]	AlCl_3 and SiCl_4	Appropriate quantities of methanolic solutions of components co-precipitated with NH_4OH solution	XRD analysis of 950–1000 °C-heated powder showed two broad, diffuse maxima which may be due to spinel phase
(6) Kaneko <i>et al.</i> [13]	AlCl_3 and sodium metasilicate	NaOH solution was added to pH 7	Observed 980 °C crystallization peak and formed both spinel and mullite
(7) Grofcsik & Vago [14]	Ethylorthosilicate (TEOS) and $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$	Mixed solution co-precipitated using NH_4OH	Observed very distinct exothermic peak at 950 °C. Gel of composition of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ showed only mullite at the temperature of exothermic effect
(8) Yamade and Kimura [15]	Silicon ethyl ester and aluminium ethyl ester	Urea used at 70 °C to evolve NH_3 gas to form homogeneous precipitation	Observed 980 °C exotherm and noted only spinel phase
(9) Chakravorty & Ghosh [16]	TEOS and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Dilute NH_4OH solution [14]	Observed small 980 °C exotherm with formation of both Si–Al spinel and mullite
(10) Hiraiwa <i>et al.</i> [17]	TEOS and AlCl_3	Mixed solution hydrolysed with ammonia	Observed spinel
(11) Rajendran <i>et al.</i> [18]	TEOS and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Stirred with NH_4OH solution	Observed spinel

matter of the present study, and accordingly the relevant works of earlier researchers are discussed below.

1. When acid was used externally as a hydrolysing catalyst, as in the case of coprecipitation or co-hydrolysis reactions of silica and alumina components, or when it was liberated by the hydrolysis of acidic salts such as aluminium nitrate, aluminium sulphate or aluminium chloride, the resultant gels exhibited a 980 °C exotherm and formed mullite, predominantly, along with a minor amount of Si–Al spinel (Tables I–III).

2. When NH_4OH was used as a hydrolysing catalyst, both silicon and aluminium components were uniformly precipitated by the OH^- concentration and the resultant gels sometimes exhibited a moderate [15] to weak [30] 980 °C exotherm and formed a Si–Al spinel phase (Tables I–III). Thus the present review shows that formation of the 980 °C phase is a function of the source of the starting components and of the pH of the gelation medium, respectively.

Furthermore, by using the same source of materials as in entries 4, 5, 6, 8 and 9 of Table II, but differing in the hydrolysis conditions, particularly the pH, the synthesized gels still showed variations in the intensity of the 980 °C DTA peak as well as the nature of the

phases e.g. the Si–Al spinel cubic form of mullite or the tetragonal form of mullite. Such variations in the development of 980 °C phases in acid against basic conditions have been demonstrated by Hirata *et al.* [24] and Hamano *et al.* [21] (Table II).

Paulick *et al.* [33] carried out hydrolysis and condensation reactions using TEOS and $\text{Al}(\text{OC}_3\text{H}_7)_3$ in the entire pH range from acidic to alkaline conditions. They obtained only mullite by heating gel powder prepared in neutral and basic conditions. Yamene *et al.* [34] suggest that hydrolysis and the subsequent polymeric reactions of TEOS were influenced by the pH of the solution, e.g. in the acid catalysed reaction, it was thought that a homogeneous precursor was probably formed and thus produced mullite directly at 1000 °C.

Chakravorty & Ghosh [16] also showed that monophasic gel prepared out of silica sol and aluminium sulphate formed only mullite at the 980 °C exotherm. The amount of mullite produced was dependent on the pH maintained during the gelation processes. It was further noted by XRD that the intensity of the 980 °C exotherm and the quantity of mullite formed were interrelated and these increased with an increase in pH of the mixed solution from 3 to 4.5.

TABLE II Solution-cohydrolysis-cogelation

Reference	Components	Gelation conditions	Thermal characteristics of gel as noted by DTA and XRD studies
(1) Mazdiyasi & Brown [19]	Silicon tetrakis-isopropoxide and aluminium isopropoxide	Mixed alkoxides refluxed with isopropyl alcohol and hydrolysed with ammoniated water	Gel heated to 600 °C showed needle-like acicular morphology of mullite, as seen by electron microscopy
(2) Prochazka & Klug [20]	Aluminium isopropoxide and ethyl silicate	Components dissolved in cyclohexane and then hydrolysed with NH ₄ OH solution and aged for 1 day, filtered, and dried at 120 °C	XRD analysis of 950 °C-heated gel showed formation of a spinel phase corresponding to 'd' spacing of 0.24, 0.195, 0.138 nm, etc. On further heating to 1200 °C, mullite formation was observed
(3) Hamano <i>et al.</i> [21]	Aluminium isopropoxide and methyl silicate in isopropanol	(i) Mixed solution added dropwise to a dilute NH ₄ OH solution at 60 °C (ii) Isopropoil-water solution added to mixed solution	DTA showed strong exotherm at 960 °C; XRD showed formation of Si-Al spinel DTA showed 980 °C exotherm and formed a mixture of Si-Al spinel and mullite
(4) Yoldas & Partlow [22]	Tetraethyl orthosilicate and aluminium sec butoxide	TEOS first hydrolysed partially with minimum quantity of water, and thereafter mixed with aluminium alkoxide and cohydrolysed	Strong 980 °C exotherm observed in DTA and showed mullite crystallization
(5) Pask <i>et al.</i> [23]	Tetraethyl orthosilicate and aluminium sec butoxide	As above. Gel designated as polymeric	Showed mullite formation at 980 °C exotherm with traces of spinel
(6) Hirata <i>et al.</i> [24]	Al(O-i-C ₃ H ₇) ₃ and Si (O-C ₂ H ₅) ₄	(i) Components dissolved in benzene and hydrolysed by adding a mixed solution of acidulated water and isopropyl at pH = 5.5 (ii) Hydrolysis with ammoniated water	XRD analysis showed formation of both mullite and Si-Al spinel in samples heated to 980 °C exotherm Gel showed weak 980 °C exotherm with formation of Si-Al spinel
(7) Mitachi <i>et al.</i> [25]	Al(O-i-C ₃ H ₇) ₃ Si (OCH ₃) ₄	Benzene solutions of the two components rapidly added by vigorous stirring into methyl alcohol-water mixture (pH 7)	Showed 980 °C exotherm and formed mullite with faint pattern of spinel phase
(8) Suzuki <i>et al.</i> [26]	As above	Partially hydrolysed TEOS was reacted with Al (O-C ₃ H ₇) ₃	Observed spinel at 980 °C
(9) Sanz <i>et al.</i> [27]	TEOS and aluminium sec butoxide	Hydrolysed with NH ₄ OH	Observed small exotherm at 985 °C with formation of spinel; thereafter formed mullite at 1250 °C exotherm

TABLE III Gelation of one component in presence of a salt

Reference	Components	Gelation conditions	Thermal characteristics of gel as noted by DTA and XRD studies
(1) Chakravorty [28]	Aqueous silica sol and aluminium sulphate	Reacted in very dilute conditions, then gelled by evaporation of moisture in an air oven	980 °C exotherm shown to be highest in gel of mullite composition, as in Demediuk & Cole [10]. XRD of 980 °C, heated gel showed only Si-Al spinel phase
(2) Hoffman <i>et al.</i> [29]	TEOS and Al(NO ₃) ₃ 9H ₂ O	Gelation carried out by heating alcoholic solution of components at 60 °C in water bath	DTA showed 980 °C exotherm; its intensity depended on the amount of absolute alcohol used during gelation. XRD of 1015 °C-heated gel showed a mixture of Si-Al spinel and mullite
(3) Okada & Otsuka [30]	As above	(i) Slow hydrolysis method: components dissolved in absolute alcohol and gelled slowly in air gelled slowly in air oven at 60 °C for 1-2 weeks (ii) Rapid hydrolysis method: mixed solution rapidly gelled by use of NH ₄ OH solution	980 °C exothermic peak sharpest and highest in the gel of mullite composition. XRD of gel fired at the temperature of exotherm showed mullite. In some cases a trace of spinel was noted in association to mullite Weak 980 °C exotherm and formed spinel phase

In alkaline conditions, e.g. pH = 8.3–10, Hsi *et al.* [35] prepared a number of $\text{Al}_2\text{O}_3\text{-SiO}_2$ gels and observed that the gels were either predominantly monophasic, a mixture of monophasic and diphasic, or purely diphasic depending upon the amount of bayerite formed. It has been shown by the present author [36] that at pH = 10–14, the resultant gel behaved as diphasic in character and formed Si–Al spinel prior to mullitization at $\sim 1300^\circ\text{C}$ exotherm. A review of the literature reveals that little work has been done so far on the 980°C phase development for gels prepared at pH = 1. In the present communication, it has been shown that gels prepared at pH ≤ 1 behave differently from monophasic gels (synthesized at pH = 3–4.5) in its phase transformation behaviour. Secondly, comprehensive data on the effects of pH in the entire range (i.e. from 1–14) on the thermal transformations of different $\text{Al}_2\text{O}_3\text{-SiO}_2$ gels have been presented.

2. Experimental procedure

2.1. Gel preparation

Aqueous silica sol as synthesized previously [16] was mixed with aluminium sulphate (A. R. grade) of Sarabhi Merck, Bombay, India, in the stoichiometry of 3 : 2 mullite. The pH of the 250-ml mixed solution was measured and found to be ~ 1.0 . The solution gelified within 5 to 10 min after mixing. It was dried and marked 7030 (N). A set of gels were prepared by using a different alumina source, e.g. aluminium sulphate (A.R.) from British Drug House, Bombay, in addition

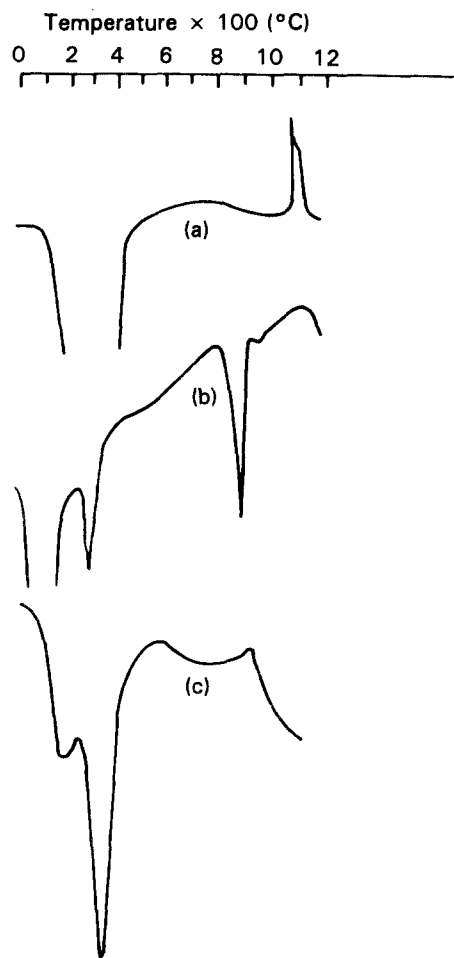


Figure 1 DTA traces of SiO_2 and Al_2O_3 components. (a) Silica gel; (b) $\text{Al}_2(\text{SO}_4)_3 \cdot 16 \text{H}_2\text{O}$; (c) amorphous Al_2O_3 .

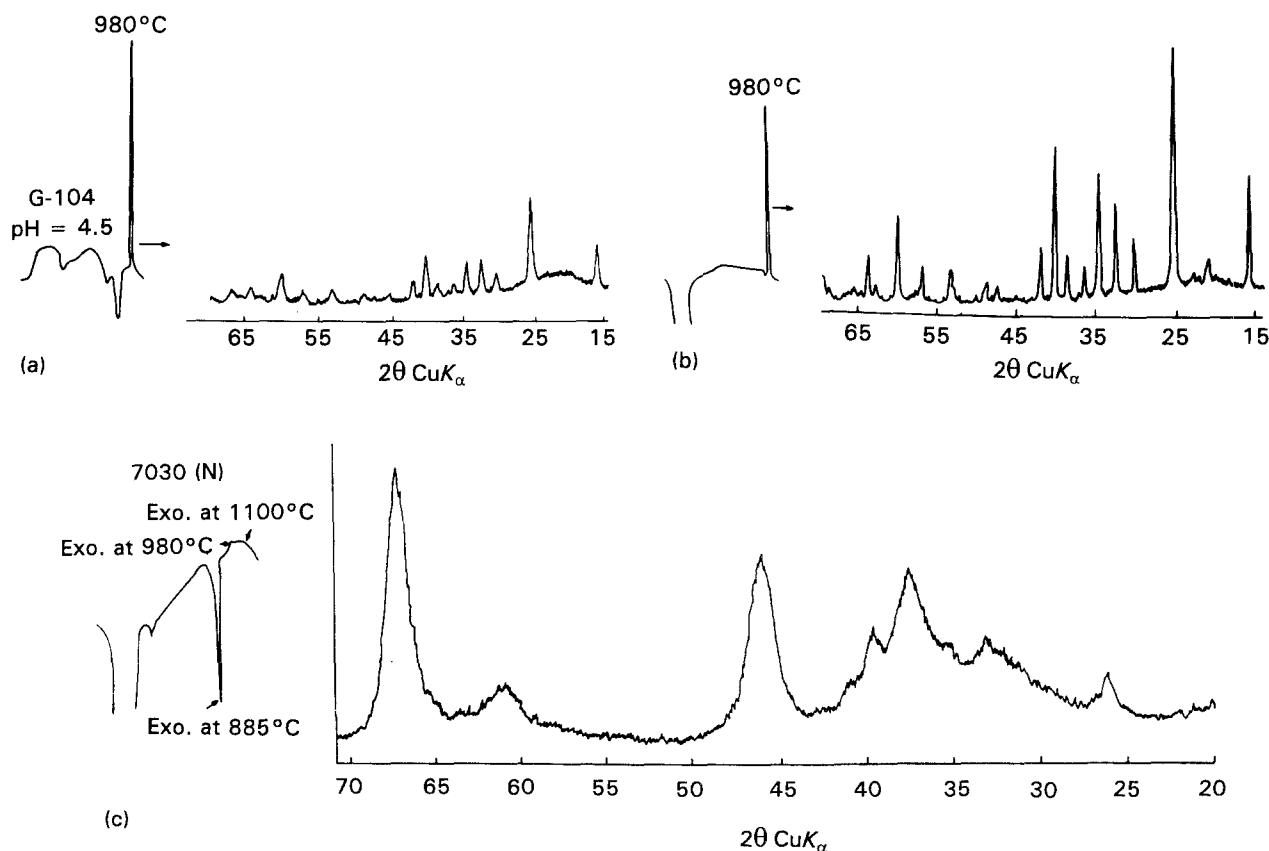


Figure 2 Characterization of $\text{Al}_2\text{O}_3\text{-SiO}_2$ gels by DTA and XRD. (a) Left, DTA trace of G-104; right, XRD recording of G-104 heated to $1000^\circ\text{C}/\text{oh}$ soaking. (b) Left, DTA trace of G-162; right, XRD recording of G-162 heated to $1000^\circ\text{C}/\text{oh}$ soaking. (c) Left, DTA trace of 7030(N); right, XRD recording of 7030(N) heated to $1000^\circ\text{C}/\text{oh}$ soaking.

to the same aqueous silica sol (containing 5 wt% SiO₂) aged for different durations. The mixed solution was shown to gelify between 24 and 48 h.

2.2. Characterization by differential thermal analysis and X-ray diffraction

The dried gels were analysed for differential thermal analysis (DTA) in a Shimadzu dilatometric system: sample weight, 80 mg; rate of heating, 20 °C min⁻¹; reference material, α-Al₂O₃. DTA traces of gels and their respective components are shown in Figs 1 and 2 for comparison and to ascertain the course of phase transformation behaviour. Each of the dried gels was heat treated at different temperatures for 2 h in an electric muffle furnace at the rate of 100 °C h⁻¹ and then cooled, ground and the phases developed were identified by X-ray diffraction (XRD) (see Figs 2–4).

3. Results

3.1. Spinel formation

Pure silica sol obtained from commercial sodium silicate by the ion-exchange technique shows an exotherm at ~ 1060 °C (Fig. 1a) due to the formation of β-cristobalite, as revealed by XRD. Pure aluminium sulphate hydrate (BDH) shows a large endothermic peak at 150 °C due to the liberation of water of crystallization. Thereafter, it shows an endothermic peak at ~ 850 °C, indicating its decomposition with loss of SO₂ and formation of γ-Al₂O₃, as observed by XRD analysis of aluminium sulphate hydrate heated at 900 °C. With a further rise in temperature, it shows a broad exotherm at ~ 1130 °C due to crystallization of α-Al₂O₃ (Fig. 1b). The Al₂O₃-SiO₂ gel (G-104) prepared using the above-mentioned components exhibits exotherm at neither 1060 nor 1130 °C (Fig. 2a) due to independent crystallization peaks of β-cristobalite and α-Al₂O₃, respectively. On the contrary, a new exotherm is seen at ~ 980 °C which occurs at a lower temperature than the crystallization temperatures of both components used. XRD analysis of this DTA run sample shows abundant crystallization of mullite (Fig. 2a). Al₂O₃-SiO₂ gel G-162, prepared using aluminium nitrate instead of aluminium sulphate as previously, also shows similar results. The gel does not exhibit crystallization peaks at 885 and 1060 °C due to corundum and cristobalite formations, as in the pure system, but forms mullite at temperatures a little higher than 885 °C, with the exotherm at ~ 980 °C (Fig. 2b). These two monophasic gels show that in the presence of SiO₂, neither the alumina component nor the silica component follows its own crystallization path.

In contrast to the above-mentioned gels, the gel marked 7030(N) behaves differently. Instead of exhibiting a very sharp 980 °C exothermic peak, its thermogram shows a very small peak (Fig. 2c). XRD of the 980 °C-heated gel shows only the formation of traces of mullite along with a large concentration of spinel phase (Fig. 2c). Results of DTA and XRD of different gels prepared in the acidic range of varying pH and heated to 980 °C are shown in Table IV.

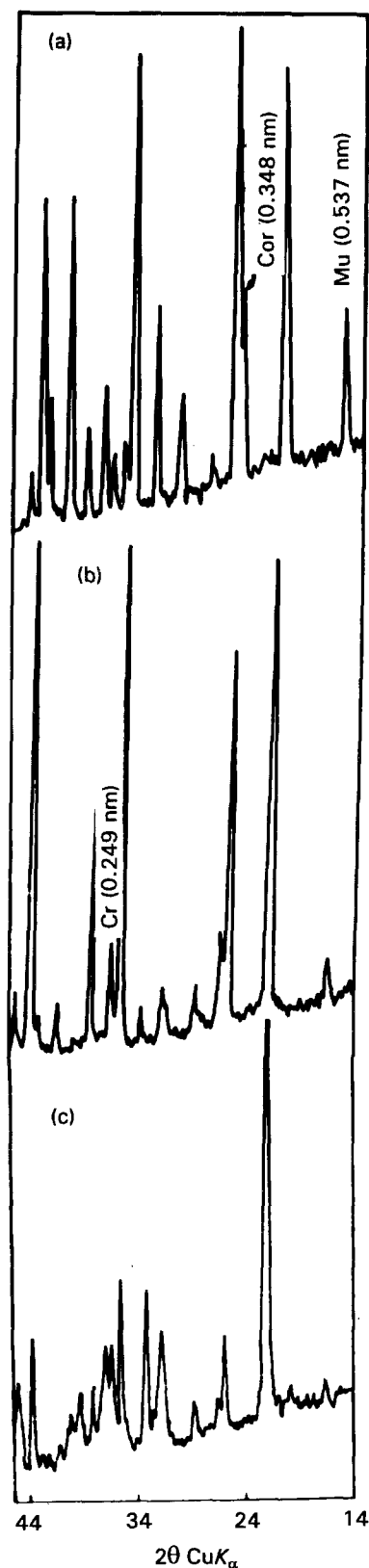


Figure 3 Portion of XRD recording of gel 7030(N) heated to different temperatures. 7030(N) heated to (a) 1200 °C/2h; (b) 1300 °C/2h; (c) 1400 °C/2h.

3.2. Mullite formation

Monophasic gels namely G-104, G-162 etc. do not develop corundum and cristobalite, but form only mullite even on further heat treatment. However, gel 7030(N) on heating at ~ 1200 °C develops a mixture of corundum and β-cristobalite. The intensities of these two phases increase with rise of temperature at

TABLE IV DTA and XRD analysis of monophasic gels up to 980 °C

Gel mark	Starting material	pH of the salt-sol mixture	DTA analysis	XRD analysis (980 °C-heated gel sample)
G-104 [16]	Silica sol made by ion exchange of sodium silicate and aluminium sulphate hydrate	~ 4.5	Very strong 980 °C exotherm	Mullite
G-96	As above	4.0 (adjusted by use of NH ₄ OH solution)	Strong 980 °C exotherm	Mullite
G-107	As above	3.8	Medium-strong 980 °C exotherm	Mullite
7030 (N)	Same silica sol as above and aluminium sulphate hydrate of (S, M)	~ 1.0	Very insignificant 980 °C exotherm	γ -Al ₂ O ₃

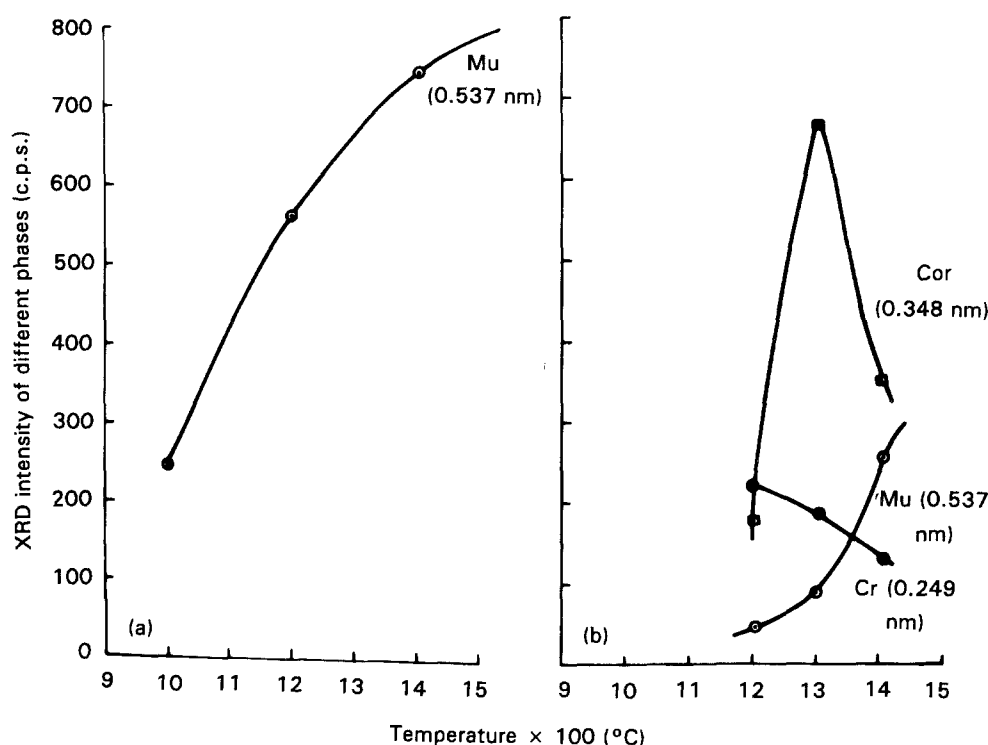


Figure 4 XRD intensities of phases formed against firing temperature of gels. (a) G-104; (b) 7030(N).

1300 °C (Fig. 3) At ~ 1400 °C, mullite forms with marked diminution in the intensities of both α -Al₂O₃ (0.348 nm peak) and β -cristobalite (0.249 nm peak) phases (Fig. 3c). The crystallization behaviours of these three phases are shown in Fig. 4, and the mullitization behaviour of G-104 is compared with 7030(N).

4. Discussion

The comparative crystallization curves as shown in Fig. 4 indicate that the spinel phase formed on heating gel 7030(N) before the formation of corundum is γ -Al₂O₃, and as a result there is no exhibition of an exothermic peak in the vicinity of 980 °C in the DTA analysis. Mackenzie [37] did not observe any exothermic peak due to γ -Al₂O₃ formation in his DTA study

of Al(OH)₃ gel. Yoldas & Partlow [22] observed a high-temperature exotherm at 1230 °C due to α -Al₂O₃ formation, and no exotherm due to intermediate γ -Al₂O₃ formation. Thus both DTA analysis of the dried gel, and XRD analysis of heat-treated gel 7030(N), are distinctly different from that of the monophasic gel G-104. These variations are found to be due to variations in the pH of the mixed solution produced by the use of two different sources of aluminium sulphate hydrate (Table IV).

Therefore, pH plays a vital role in the development of gels of different characters, which in turn determines the differences during subsequent thermal sequences. In the pH range of 3–4.5, Al₂O₃-SiO₂ gels transform directly to mullite at the 980 °C exotherm, whereas in the gel prepared at pH ≤ 1, mullite forms via intermediate γ -Al₂O₃ formation.

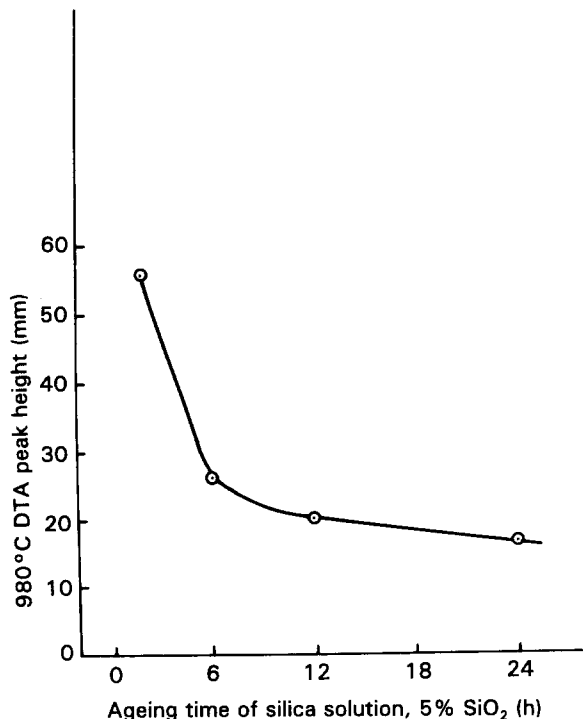


Figure 5 980°C peak height against ageing time of silica sol used for synthesizing different Al₂O₃-SiO₂ gels.

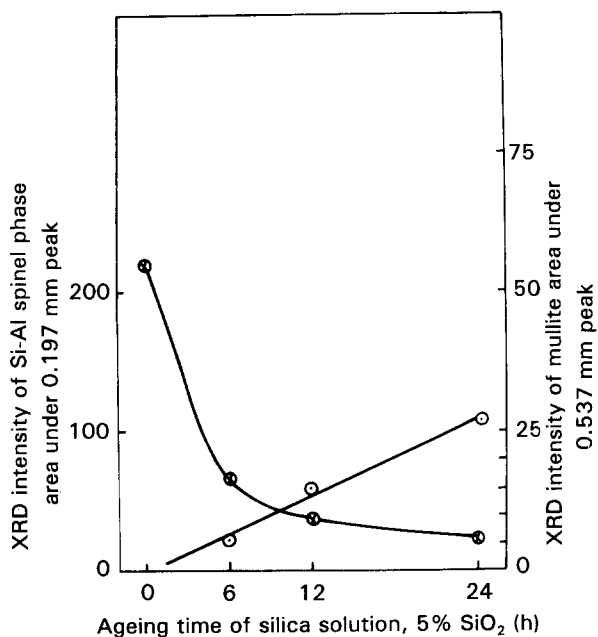


Figure 6 Intensity of ⊗ mullite and ⊙ Si-Al spinel formed on heating at 1000°C/oh against ageing time of silica sol used for synthesizing different Al₂O₃-SiO₂ gels.

Accordingly there are two different mechanisms of gelation reaction.

4.1. Gelation mechanism in the pH range 3-4.5

The monosilicic acid molecule "Si(OH)₄" is very unstable due to incomplete co-ordination of silicon (in hydrated form it is 6) with respect to OH⁻, and thus

condensation of two silanol ($-\overset{|}{\text{Si}}-\text{OH}$) groups takes place leading to the formation of siloxane ($-\overset{|}{\text{Si}}-\text{O}-\overset{|}{\text{Si}}-$) bonds with elimination of the water molecules. As a result, silica sol does not remain in true equilibrium. There is room for irreversible interaction of hydroxyl groups with other Si(OH)₄ molecules forming more and more siloxane linkages. Consequently on standing the sol becomes colloidal with a continued rise in viscosity [38] as well as molecular weight. Therefore, on mixing aluminium salt with silicic acid sol, two reactions take place simultaneously: polymerization of silicic acid itself, and aluminosilicate hydrate formation. The polymerized silica sol units will react with the Al⁺³ ion later. The effect of polymerized silica sol on 980°C reaction of different Al₂O₃-SiO₂ gel has been reported. As shown in Fig. 5, the intensity of the 980°C DTA peak (height) and quantity of mullite formed (XRD intensity of 0.537-nm peak) at the same temperature (Fig. 6) are both significant in the case of gel prepared from aluminium sulphate (BDH) and freshly prepared silica sol, (i.e. with no ageing time). Gels prepared with silica sol with increased ageing times show (i) the intensity of the 980°C exotherm decreases rapidly from the highest value and then proceeds very slowly; (ii) the amount of mullite also decreases very rapidly and thereafter the formation of Si-Al spinel commences and then increases gradually. Thus, the existence of an interrelationship between 980°C exothermic peak in DTA and the nature/amount of 980°C phase development of silica sols aged for increasing durations has been shown for the synthesis of mullite gels. This suggests that the essential condition for obtaining pure mullite is that the silica component will either be monomeric or will contain small aggregated colloidal particles.

The mechanism of the reaction between silicic acid sol and Al⁺³ for the formation of simple units of

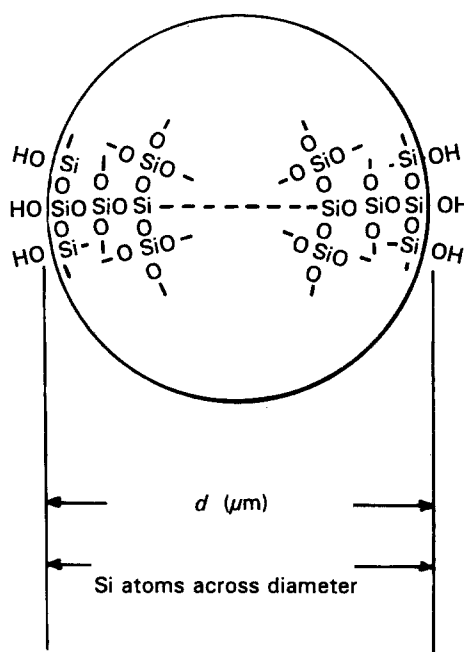


Figure 7 Particle size of colloidal silica according to Carman [41].

differently sized colloidal particles. A model for such particles is presented by Carman [41] (Fig. 7). The interior structure of the particle shows that each Si is surrounded on all sides by oxygen atoms in an orderly three-dimensional state. Surface silicons complete its tetrahedral co-ordination by adsorption of water/hydroxyl groups. It is obvious that interactions of such variously sized, charged silica particles with aluminium sulphate may produce gel particles of different Al:Si ratio, and may lead to gross inhomogeneities. For example, gels prepared by using aluminium sulphate and silica sol aged for a few hours form Si-Al spinel on heating at 980 °C, rather than pure mullite, and gels prepared using the same source of aluminium sulphate but with silica sol aged for 24 h form a mixture of both mullite and Si-Al spinel. This may explain the findings of many earlier researchers (Tables I-III) that pure mullite was not forming at 980 °C exotherm, and was an admixture of Si-Al spinel. In this connection, it is recalled that kaolinite/metakaolinite contains tetrahedral silica sheet in *a-b* directions. It also forms Si-Al spinel analogous to some Al₂O₃-SiO₂ gels; as shown above from our preliminary observations, the silica components in the form of a cluster or polymeric chain of silica may be responsible for Si-Al spinel formation at the 980 °C exotherm.

4.2. Gelation mechanism at pH = 1

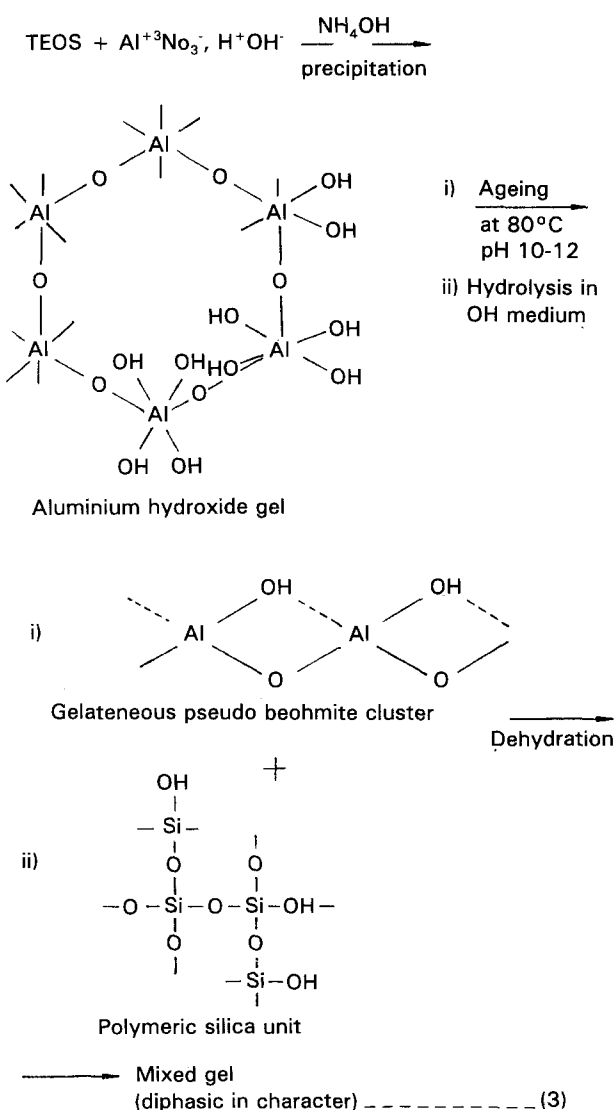
In contrast to the formation of a chemical bond between two components during gelation in the pH range 3-4.5, silica sol does not interact on mixing with aluminium salt solution at pH ≤ 1. On the other hand, it rapidly gelified by losing its stability due to diminution of the negative charge of the sol by Al³⁺ counterions. On heating such a gel mixture, the components initially follow their own independent crystallization paths, as shown by XRD analysis (Fig. 3). DTA analysis also corroborates the same view. The aluminium sulphate content of gel 7020 (N) first dehydrates, then decomposes, and finally transforms to corundum with an exotherm at ~ 1130 °C (Fig. 2c). The silica gel component of the gel forms β-cristobalite, although it does not exhibit the exotherm at 1060 °C as seen in the case of the pure system. This may be due to diffusion of a minor amount of aluminium in the silica gel network [42]. At high temperature (~ 1400 °C), as shown in Fig. 3, there is a solid-state reaction between α-Al₂O₃ and β-cristobalite, forming a viscous aluminosilicate phase [43]. Thereafter, nucleation of mullite occurs and finally crystallizes slowly in contrast to the rapid mullitization taking place in the case of G-104 (Fig. 4).

The sequential crystallization behaviours of the two components of gel 7030(N) and its subsequent mullitization indicate that this gel behaves in a truly diphasic manner, as previously thought by Hoffmann *et al.*, [29] and are identical to those observed by Wheat *et al.* [44] and Kumazawa *et al.* [45] in the thermal transformation of Ha powder.

4.3. Gelation reaction in alkaline conditions

It is evident that Si-Al spinel phase is an inevitable

intermediary phase in the thermal transformation of gels processed under alkaline conditions. The role of OH⁻ during gelification of a mixture of silica and alumina components can be explained in the following way. On the addition of NH₄OH, both components will be hydrated and precipitated in the colloidal state. For example, Al(OH)₃ colloids increase in size with increasing time, and there is a good possibility of its agglomeration into varying sizes, as noted in TEM studies [46]. The formation of cluster and nucleation of different crystalline modifications, e.g. boehmite, bayerite etc., are generally dependent on processing variables (pH and temperature) [47]. Side by side, Si(OH)₄ micelles also polymerize when co-precipitated. The colloidal interactions of two oppositely charged Al(OH)₃ and Si(OH)₄ macromolecules of different sizes may also lead to heterogeneity. The possible reaction will be as follows.



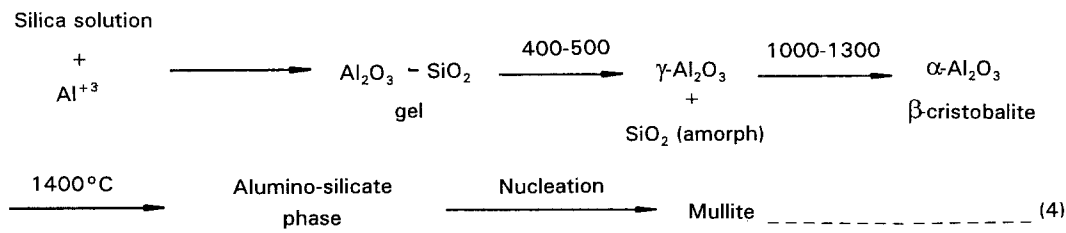
Thus formation of large colloidal units of both silicic acid and Al(OH)₃ in an alkaline medium is responsible for the development of the Si-Al spinel phase.

5. Conclusions

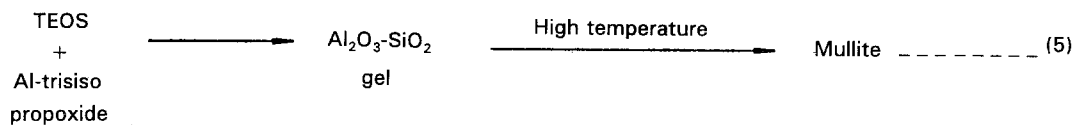
The phase transformation of Al₂O₃-SiO₂ gels pre-

pared in the entire pH range of $\leq 1-7-14$, as carried out by several researchers, are summarized below.

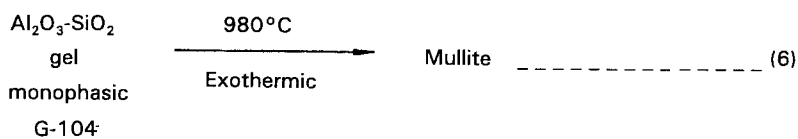
1. At pH ≤ 1 , the present study shows that $\text{Al}_2\text{O}_3\text{-SiO}_2$ gel behaves as purely diphasic in character.



2. At pH 2, Paulick *et al.* [33] observed the formation of mullite as in the following reaction.



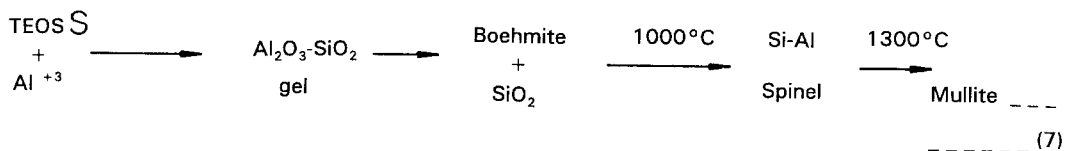
3. At pH 3-4.5, the present study and the work of Yamane *et al.* [34] show the formation of mullite as follows.



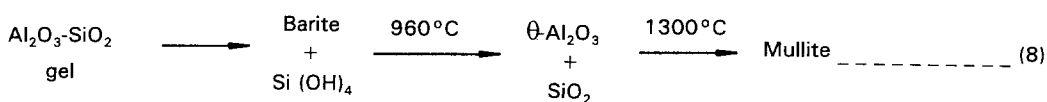
The present data also show that during heating of the gel at 980°C, mullite so formed is mixed with an amount of Si-Al spinel and is dependent on the ageing period of silica sol.

4. At pH 7, Paulick *et al.* [33] observed the formation of an amount of corundum along with mullite development.

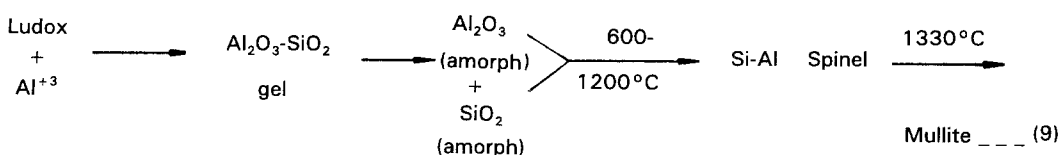
5. At pH 8.3, Hsi *et al.* [35] observed the formation of mullite as follows.



6. At pH 9.5-10.4, the above authors reported mullite formation according to the following equation.



7. At pH 10, Chakravorty [36] observed that the gel was purely diphasic and was a mixture of boehmite and amorphous silica, and transformed in the following way.



Thus, in sol-gel processing techniques, the question of pH in the preparation of $\text{Al}_2\text{O}_3\text{-SiO}_2$ gels play an important role, and is in turn responsible for variations in the path of mullitization. Different mechanisms of mullite formation are due to variations in the reactions between the components used in the gelation processes. The results also predict that the method of synthesis of G-104 is the best approach to the development of pure mullite, as no segregation takes place during its thermal transformation.

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