JOURNAL OF MATERIALS SCIENCE 29 (1994) 6131–6138

Role of hydrolysis water–alcohol mixture on mullitization of Al_2O_3–SiO_2 monophasic gels

A. K. CHAKRABORTY
Central Glass and Ceramic Research Institute, Calcutta 700 032, India

Two kinds of monophasic gels were synthesized from silicon ethyl ester (TEOS) and aluminium nitrate mixture by varying the water–alcohol content of the system. The mullitization reaction paths of the two gels were studied by differential thermal analysis (DTA) and X-ray diffraction techniques. The first kind of monophasic gel exhibited cubic mullite (Si–Al spinel) on the 980 °C exotherm and a further two more broad exotherms at 1150 and 1243 °C. This phenomenon resembles the DTA thermogram of a kaolinitic clay. The later two exotherms have been explained as due to the formation of mullite by two different reaction paths from the two phases appearing in the 980 °C exotherm. Nucleation and crystallization of mullite from amorphous alumino silicate phase takes place at ~ 1150 °C, and transformation of cubic mullite to orthorhombic mullite takes place at ~ 1245 °C. The second kind of monophasic gel exhibited only one exotherm and produced exclusively tetragonal mullite at ~ 980 °C. The results suggest that pure mullite formation is possible when water induced hydrolysis of TEOS is avoided during the gelation process.

1. Introduction

Mullite precursors were synthesized from various sources of SiO_2 and Al_2O_3 components [1–3] by adapting different techniques, e.g. sol–gel, co-decomposition, co-precipitation, spray pyrolysis, chemical vapour deposition, freeze drying, etc. The dried gel powder transformed to the orthorhombic (o-) form of mullite by two different routes. By the first route, the precursor transformed first into an intermediate Si–Al spinel [4, 5] of a composition similar to 3:2 mullite at 980 °C. Thereafter, it transformed to o-mullite at 1250 °C.

$$\begin{array}{l}\text{Monophasic gel} \xrightarrow{980\,^{\circ}\text{C}} \\ \text{(first kind)} \\ \underset{\substack{\text{Si–Al spinel}\\ \text{(cubic mullite,}\\ \text{c-mullite)}}}{3\mathrm{Al_2O_3}\cdot 2\mathrm{SiO_2}} \xrightarrow{1250\,^{\circ}\text{C}} \underset{\text{o-mullite}}{3\mathrm{Al_2O_3}\cdot 2\mathrm{SiO_2}}\end{array} \tag{1}$$

Following the second route, the precursor powder transformed directly to tetragonal mullite [6, 7] at 980 °C, and later to o-mullite on further heating.

$$\begin{array}{l}\text{Monophasic gel} \xrightarrow{980\,^{\circ}\text{C}} \\ \text{(second kind)} \\ \underset{\substack{\text{(tetragonal}\\ \text{mullite}\\ \text{t-mullite)}\\ +\\ \mathrm{SiO_2}}}{2\mathrm{Al_2O_3}\cdot \mathrm{SiO_2}} \xrightarrow[\text{heating}]{\text{Continued}} \underset{\text{o-mullite}}{3\mathrm{Al_2O_3}\cdot 2\mathrm{SiO_2}}\end{array} \tag{2}$$

These two different types of transformation mechanism are responsible for the two major factors below.

(i) The source of Al_2O_3 and SiO_2 components. The phase development in Al_2O_3–SiO_2 gels leading ultimately to mullitization were shown to be a function of the choice of silica and alumina components [8], e.g. $SiCl_4$, Ludox, silica sol obtained by ion exchanging of sodium silicate solution, organic silicon compounds, such as silicon ethyl ester or TEOS, boehmite sol, aluminium salts such as $AlCl_3$, $Al(NO_3)_3 \cdot 9H_2O$, $Al_2(SO_4)_3 \cdot 16\,H_2O$, organic aluminium compounds such as aluminium ethyl ester, aluminium isopropoxide, aluminium sec butoxide, etc. As shown above, gels synthesized from these components showed either Si–Al spinel or a mixture of Si–Al spinel and mullite in the vicinity of the first exotherm.

(ii) Processing variables. The hydrolysis of the silicon and aluminium compounds mentioned above is very susceptible to the following variables, e.g. (a) the acidic or basic catalyst used [9–14]; (b) the temperature prevailing during hydrolysis [15]; (c) the time the period of hydrolysis was maintained [8, 16, 17]; and lastly (d) the medium of hydrolysis chosen [18, 19]. These four factors greatly influence the rate of hydrolysis–polycondensation, etc. Consequently, both the 980 °C exothermic reaction and the mullitization processes of the Al_2O_3–SiO_2 gels varied. The role of pH versus phase development was studied and discussed earlier [19]. The amount of hydrolysis agent used is an important factor in the present investigation. Hoffman *et al.* [18] first synthesized Al_2O_3–SiO_2 gels using 10.2 g $Al(NO_3)_3 \cdot 9H_2O$ and 2 ml TEOS with varying amounts of absolute alcohol. They showed that when "less ethanol" was used (10 ml), the

0022–2461 © *1994 Chapman & Hall*

980 °C exothermic peak was sharp and intense. But a similarly sharp peak with a much less intense peak occurred when "more ethanol" was used (30 ml). Recently, Li and Thomson [16] repeated the synthesis of the above gels and denoted them 2D and 2W, respectively. Both these gels exhibited 980 °C exotherms analogous to those of Hoffman *et al.* [18] and formed spinel and mullite. At the first exothermic region, the high temperature dynamic X-ray diffraction (DXRD) intensity of the mullite peak in 2W was found to be more than in 2D. At the second exothermic peak, spinel phase disappeared and further mullitization occurred. With this evidence, Li and Thomson [16] suggested two-stage conversion in mullitization processes. However, the reasons behind the variation of the 980 °C phase formation using different components have not been fully explained. The extent of mullitization during the 980 °C exotherm has been assumed to be due to homogeneous mixing of the Al_2O_3 and SiO_2 components, i.e. the highest degree of Al–O–Si bonding in the precursor system [8, 10, 18, 20]. However, complete mullitization is a problem. Only Kanzaki *et al.* [21] succeeded by a spray pyrolysis method. Under almost all preparative conditions, e.g. monolithic gelation route [18], SH gel method [10], or polymeric method [9], or in the hybrid gel technique [22], a small amount of spinel was always formed together with regular formation of mullite. The causes of the formation of spinel have been explained as due to segregation in Al_2O_3–SiO_2 system arising out of the two dissimilar rates of hydrolysis of the components in water, and which actually aggravate the homogeneity in practice. Epitactic nucleation by γ-Al_2O_3 may be an additional cause for promoting spinel formation [22]. Other than the spray pyrolysis method, Chakravorty and Ghosh [8] suggested a process of synthesizing only pure mullite at 980 °C and further indicated that the use of varying amounts of water–alcohol was one of the main causes out of the four major factors behind the variation of 980 °C phase development. Using the same SiO_2 and Al_2O_3 components, such as TEOS and $Al(NO_3)_3 \cdot 9\ H_2O$, and by varying the water–alcohol content used during the gelation process, it was demonstrated that two types of monophasic alumino silicate gels had been formed. These two gels followed two separate mechanisms during the 980 °C reaction, e.g. (i) the gel marked G-31 formed t-mullite and exhibited a 980 °C exotherm, and (ii) the gel marked G-150 formed only Si–Al spinel during the 980 °C exotherm. The composition of the latter is analogous to 3:2 mullite. Suzuki *et al.* [5] showed the electron diffraction pattern of this Si–Al spinel phase and by EDS analysis they confirmed the composition as suggested by Chakravorty and Ghosh [8]. Si–Al spinel of a mullite-like composition was also shown in the K–M reaction series [23, 24] which was also substantiated by compositional analysis in an EDS study [25] in contrast to the composition $6Al_2O_3 \cdot SiO_2$ suggested elsewhere [26, 27] and $2Al_2O_3\ SiO_2$ proposed by Low and McPherson [28].

Thus, one of the main processing routes allowing direct control over the gel structure is influenced by varying the use of water or ordinary alcohol during gelation processes. In the present investigation, these two gels were again synthesized and the course of mullitization behaviour was compared with that of kaolinite. The results reveal that monophasic gel, which forms Si–Al spinel as intermediary, shows analogous mullitization behaviour to that of kaolinite. Secondly, the spinel phase formation was found to vary with variation of the amount of water used in the gelation processes. The interrelationship between the use of water–alcohol and the formation of Si–Al spinel has been substantiated.

2. Experimental procedure

2.1. Gel preparation

Monophasic Al_2O_3–SiO_2 gels were synthesized under three different set of conditions.

(a) G-150 (Al:Si = 3:1): 10 g $Al(NO_3)_3 \cdot 9\ H_2O$ was taken in a beaker, to which 60 ml ethyl alcohol was added and swirled gently to dissolve the salt. Then 2 ml TEOS was added. It was warmed in a hot-water bath at 60–65 °C until gelation was completed and then dried at 110 °C in an air oven.

(b) Gel-A (Al:Si = 3:1) was prepared using $Al(NO_3)_3 \cdot 9H_2O$ and TEOS in 10 ml absolute alcohol as in the earlier procedure of Hoffman *et al.* [18] or the "SH method" as adapted by Okada *et al.* [26].

(c) G-31 (Al:Si = 3:1): 10 g $Al(NO_3)_3 \cdot 9\ H_2O$ was taken in a beaker and heated gently just to dryness in order to remove its water of crystallization. The beaker was cooled, and 5 ml of absolute alcohol was added to dissolve the anhydrous white solid of $Al(NO_3)_3$. To this, 2 ml TEOS was added, swirled and gelled. Finally, the gel was dried at 110 °C and stored.

2.2. Characterization

All the dried gels were analysed by DTA (Shimadzu Thermal Analyser System) using approximately 80 mg ground gel and calcined alumina as reference material. Both samples and reference were heated dynamically at a rate of $10\,°C\,min^{-1}$. DTA tracings are shown in Figs 1–3, respectively.

A Philips X-ray diffractometer was used to analyse the crystalline phases formed on static heating of the gels, and the results are shown in Figs 4–6. Gels G-31 and G-150 were dynamically heated at $10\,°C\,min^{-1}$ in a DTA furnace to successively higher temperatures. After reaching the desired temperature the furnace was switched off. The heated samples contained in the DTA cell were allowed to cool down normally and finally analysed by XRD. The areas of the 0.53 nm peak (average of three XRD runs) of o-mullite formed from the above two gels were plotted against heat treatment temperature and are shown in Fig. 7.

3. Results and discussion

Attempts have been made to determine the underlying causes of the DTA exothermic phenomena of all three gels by identifying the crystalline phase(s) developed during heating using the usual XRD technique. These

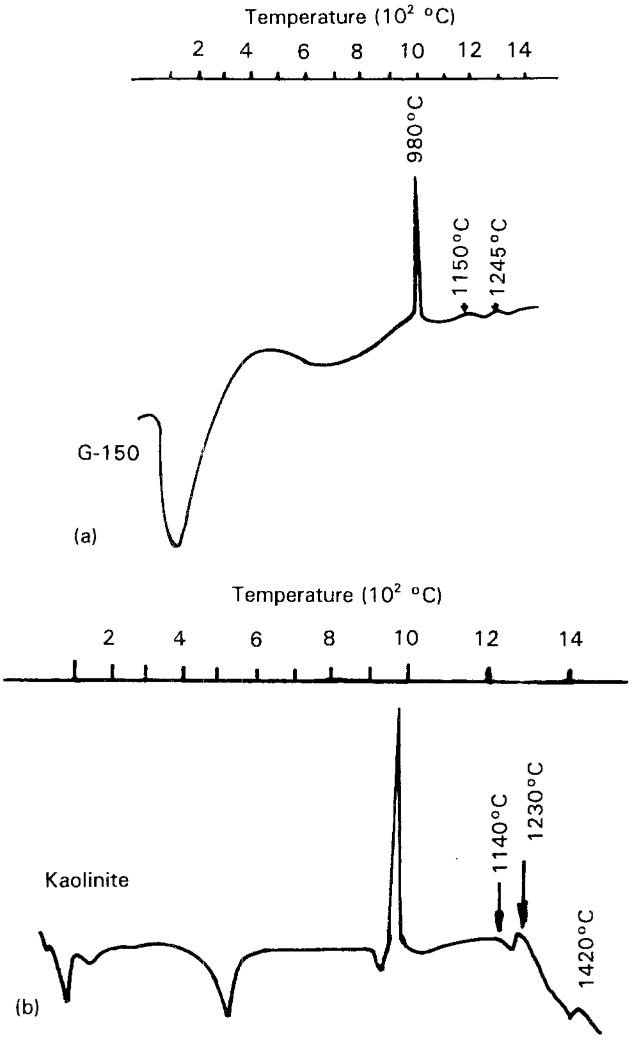


Figure 1 DTA curve of (a) Gel G-150, compared with (b) kaolinitic clay.

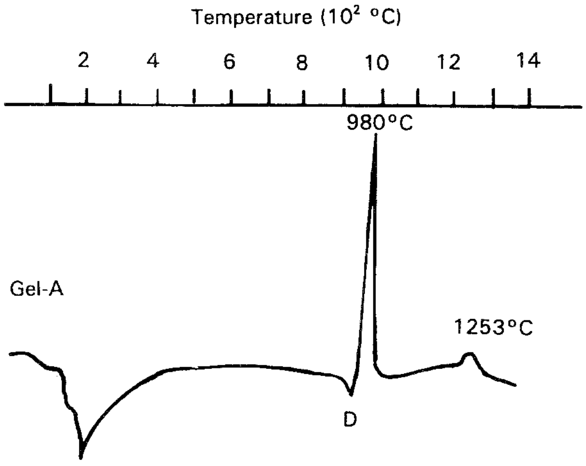


Figure 2 DTA curve of gel-A.

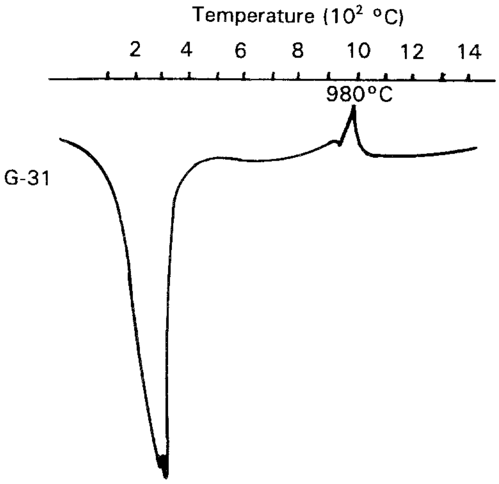


Figure 3 DTA curve of gel G-31.

results were then compared with the transformation sequences of kaolinite, and are shown in Table I.

3.1. Mullitization in G-150

The thermogram of the gel G-150 (Fig. 1a) shows the first exotherm at 980 °C as noted by several researchers of the mullite community. It exhibits two more exotherms; one, a broad exotherm with $T_m \simeq 1150$ °C and the other ~ 1245 °C. These three exothermic events, 980, 1150 and 1245 °C, tally with

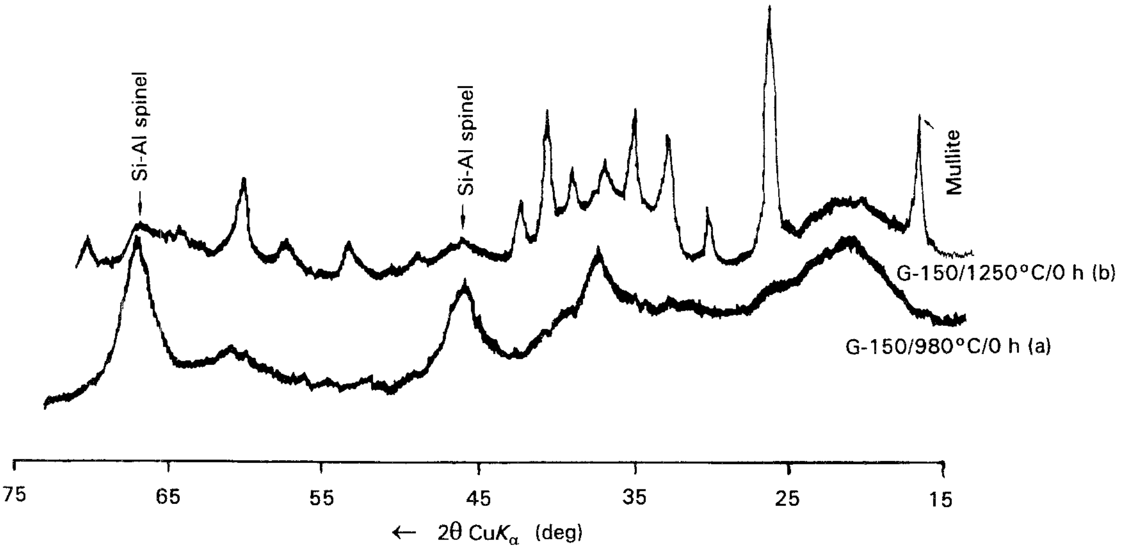


Figure 4 (a) G-150 heated to 980 °C exotherm as above, showing cubic mullite; (b) G-150 heated to 1250 °C exotherm showing a major amount of mullite and traces of unconverted cubic mullite.

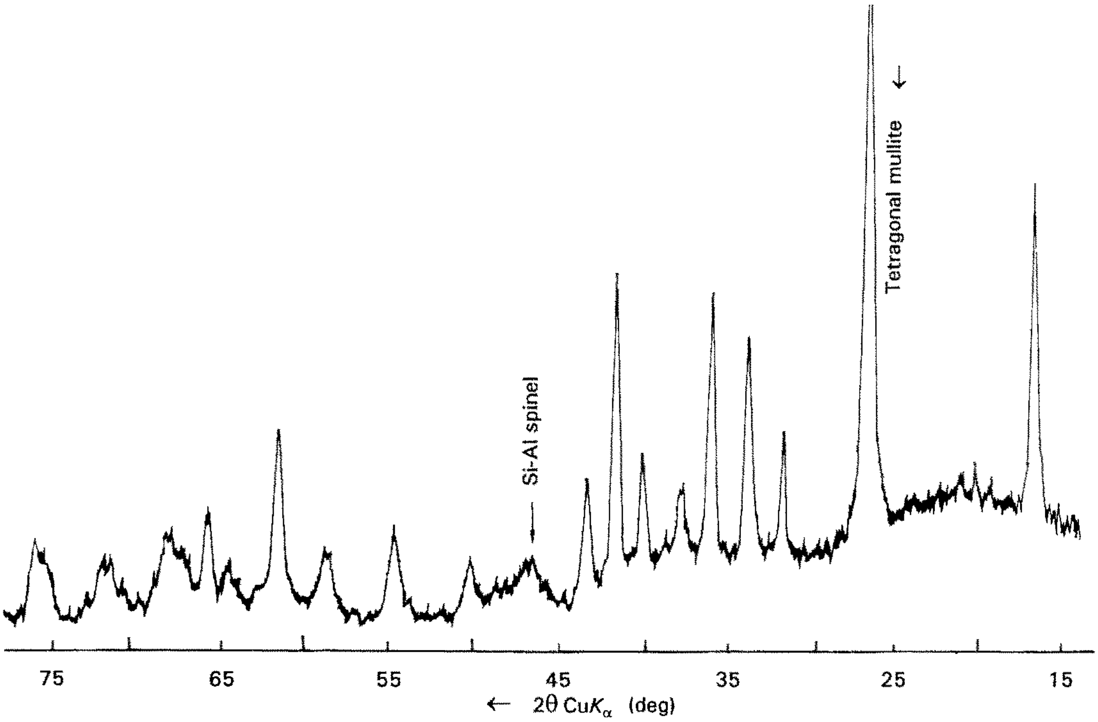


Figure 5 X-ray diffraction pattern of Gel-A at the 980 °C exotherm showing both tetragonal and cubic mullite.

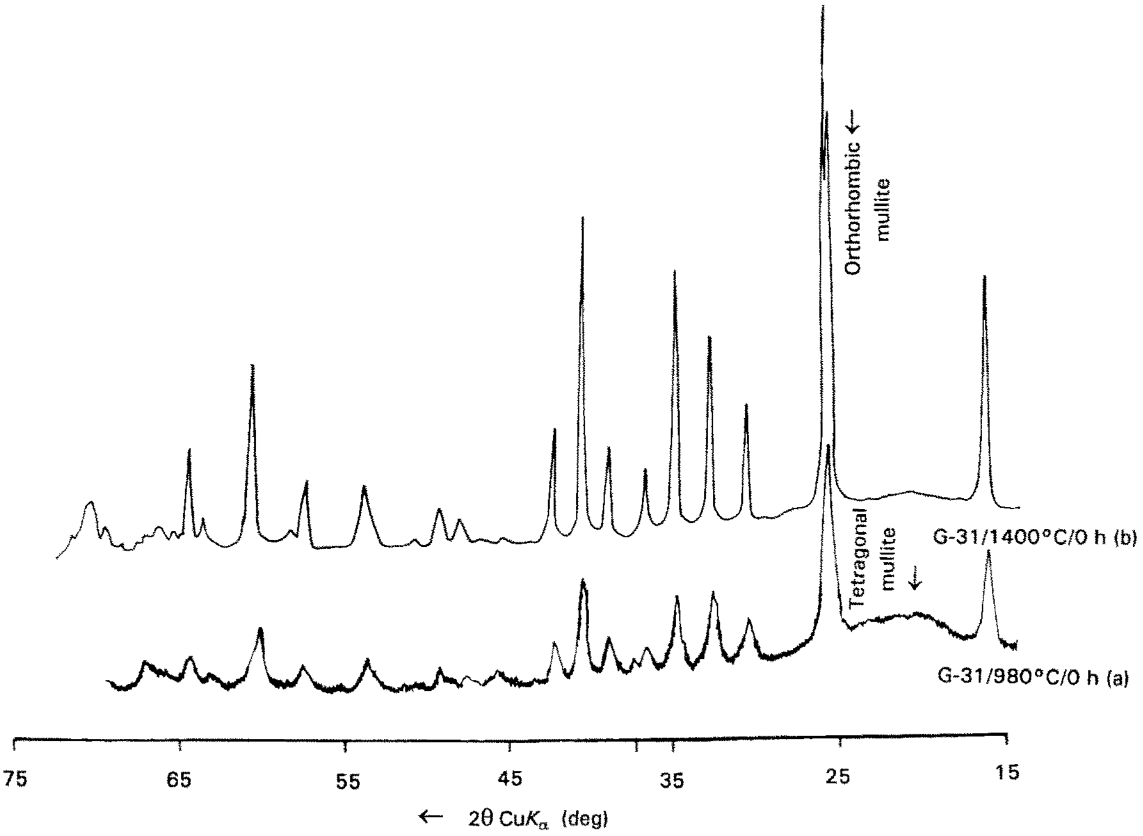


Figure 6 X-ray diffraction pattern of the heat treated gels: (a) G-31 heated to the 980 °C exotherm with no soaking time and cooled in a desiccator, showing tetragonal mullite; (b) G-31 heated to 1400 °C with no soaking time and cooled in a desiccator, showing orthorhombic mullite.

those occurring in the DTA trace of a kaolinitic clay (Fig. 1b) but differing only in their temperature of occurrence. Therefore, it would not be erroneous to conclude that the thermal transformation phenomenon of G-150 bears a similarity to the high-temperature reaction sequence of kaolinite. Chakravorty and Ghosh [23] showed that kaolinite at the 980 °C exotherm formed 20–25 wt % cubic mullite (Si–Al spinel)

TABLE I Phase transformation of different types of gel compared with kaolinite

Sample	Water/ TEOS ratio	Transformation temperature		
		980 °C	1100–1300 °C	1250 °C
Kaolinite	–	Exhibits a sharp exotherm and forms cubic mullite and aluminosilicate phase	Exhibits a broad exotherm. Aluminosilicate phase crystallizes to mullite	Exhibits a less-sharp exotherm. Cubic mullite polymorphically transforms into orthorhombic mullite
G-150	4:1	As above	Exhibits a broad exotherm at ~ 1150 °C owing to crystallization of mullite from aluminosilicate phase	As above
Gel-A	External water addition was not used, water of crystallization of $Al(NO_3)_3$ is the source of water	Exhibits a sharp exotherm and forms a major amount of tetragonal mullite and a minor amount of cubic mullite	No exotherm	As above
G-31	Nil	Exhibits a sharp exotherm and transforms into tetragonal mullite	No exotherm	–

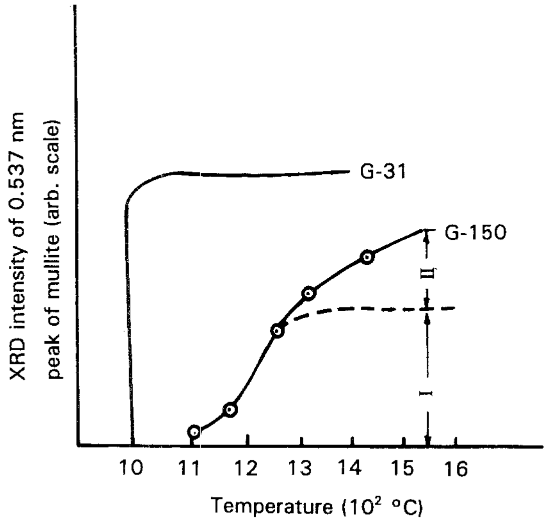


Figure 7 XRD intensity of orthorhombic mullite versus firing temperature of different gels.

and left a 40 wt % amorphous aluminosilicate phase as residue. Subsequently, Chakravorty [24] showed that cubic mullite and the amorphous aluminosilicate phase exhibited two exotherms with abundant crystallization of the orthorhombic form of mullite. The present study shows that G-150 first forms cubic mullite at the 980 °C exotherm (Fig. 4a) like kaolinite, and then transforms to orthorhombic mullite at 1250 °C (Fig. 4b). Secondly, the growth of mullite in G-150 consists of two stages (Fig. 7a). In the first stage, mullite formation occurs rapidly at 1200–1250 °C and thereafter in the second stage it increases gradually with rise of temperature. Thus, the occurrence of the DTA exotherm at 1245 °C coincides with the formation of the orthorhombic form of mullite from the complete elimination of cubic mullite (Fig. 4a) as shown by X-ray analysis. Thus, mullitization in the case of G-150 is analogous to kaolinite and it follows two reaction paths;

(i) cubic mullite formed (on heating from G-150 during) at 980 °C transforms polymorphically to orthorhombic mullite at 1245 °C, constituting path I; and

(ii) the exhibition of the exotherm at 1150 °C could be explained as being due to mullitization in the amorphous aluminosilicate phase as in path II, similar to kaolinite as has been reported earlier. The latter process proceeds at a comparatively slower rate than path I. The initial step portion accounts for mullite formation by path I and the subsequent gradual rise is due to mullitization from the amorphous aluminosilicate phase by nucleation and subsequent crystallization by path II. Therefore, the mullitization behaviour of cubic mullite gel is derived as follows

$$\begin{array}{lll} Al_2O_3\text{–}SiO_2 \text{ gel} \xrightarrow[\text{Exotherm}]{980\,^\circ\text{C}} & & \\ \text{G-150} & & \\ \text{(i) } 3Al_2O_3\cdot 2SiO_2 & \xrightarrow[\text{Exotherm}]{1245\,^\circ\text{C}} & 3Al_2O_3\cdot 2SiO_2 \\ \text{Cubic mullite} & \text{path I} & \text{Orthorhombic mullite} \\ \text{(ii) Aluminosilicate phase (Amorphous)} & \xrightarrow[\text{Exotherm}]{1150\,^\circ\text{C}} & 3Al_2O_3\cdot SiO_2 \\ & \text{path II} & \text{Orthorhombic mullite} \end{array} \qquad (3)$$

3.2. Mullitization of Gel-A

The dried Gel-A decomposed below 980 °C with the elimination of residual –OH groups at the temperature marked "D" in the DTA trace, and then exhibited a very strong 980 °C exotherm (Fig. 2) with the formation of both forms of Si–Al spinel and t-mullite

(Fig. 5). The former phase on further heating exhibits a broad peak of lower magnitude at ~ 1253 °C with the formation of o-mullite. These results confirm the mullitization behaviour of SH gel [10, 26] and DXRD data for 2H, ID and 2D gels [16].

3.3. Mullitization of gel G-31

The thermogram of gel G-31 shows a broad 980 °C exotherm preceeded by a very small endothermic dip. The present study shows that the growth of mullite is found to be very sudden (Fig. 7b) and the transformation is found to be completed in one step, as the growth curve does not increase with increasing temperature. The most significant fact is that, except for the 980 °C exotherm, G-31 does not exhibit any other high-temperature peak between 1200 and 1300 °C, such as is shown in Gel-A and gel G-150. Heat treatment of gel G-31 at higher temperature causes a sharpening of the Bragg diffraction peaks and splitting of the 0.33 and 0.34 nm peaks of mullite (Fig. 6a and b). Therefore, the transformation of gel G-31 follows Equation 2. The composition of t-mullite was suggested to contain 66 mol % Al_2O_3 by TEM study [29]. As the firing temperature was increased to 1400 °C, the chemical composition of mullite gradually approached $3Al_2O_3 \cdot 2SiO_2$. The variations in the 980 °C phase development in the two types of monophasic gel, G-31 and G-150, and the variations in their mullitization mechanism as outlined above, are, in reality due to two different types of aluminosilicate gels forming during gelling by the varying water contents, even though both gels were synthesized from the same source materials of $Al(NO_3)_3 \cdot 9H_2O$ and TEOS.

Therefore, essentially, when a large amount of water is used during hydrolysis of TEOS, the resultant gel G-150 will no doubt form orthorhombic mullite on heating but it will invariably be associated with an appreciable amount of non-crystalline aluminosilicate phase. The formation of this phase is unwanted in the present-day requirements for achieving mullite ceramics in so far as improved hot modulus of rupture and high creep resistance properties are concerned. Even gel prepared by eliminating the major water of crystallization e.g. Gel-A, does not fulfil the objective. Besides the formation of a major amount of tetragonal mullite, a minor amount of cubic mullite is also formed. The question is: what type of methodology is to be adapted for obtaining absolutely pure tetragonal/orthorhombic mullite and free from any liquid phase, as thought of by Pask *et al.* [20]? The present study highlights this from a comparison of the phase transformation behaviours of G-150, Gel-A and G-31 (Table I) and it is suggested that water used for hydration and hydrolysis of the components, e.g. TEOS, should be drastically minimized so that extensive polymerization would be minimized, e.g. Gel G-31, which transforms to t-mullite without any intermediary undesirable phase formation.

3.4. Role of water on mullite development

The present study shows that the amount of water used during gelation influences the development of monophasic gels of purely two characters, e.g. G-31 and G-150, and those gels, in turn, determine whether the mullitization reaction will take place according to path I or path II. But how does the water act during gelation? Hydrolysis of TEOS by the use of a stoichiometric amount of water in the presence of either acid or ammonia as a catalyst in the temperature range 60–70 °C had been reported [30–34].

In the present work, the nature of the acid catalytic reaction has been discussed. The first step of the reaction is the union between one ethoxy group of TEOS with one molecule of water to form a monomeric species with the elimination of one molecule of ethyl alcohol. In this way, other ethoxy groups of the TEOS molecule hydrolyse one after another in the presence of a large amount of water. The mechanism of this type of hydrolysis has been described as electrophyllic. The overall reaction consists of two separate equilibria. The first one is hydrolysis of TEOS to ethoxysilane or silanol groups, and the second is the polymerization and condensation of silanol groups to form primary particles by Oswald ripening. Different possible reactions are given below and there may be different intermediates as reported by Schmidt *et al.* [35].

$$Si(OR)_4 + H_2O \rightarrow HOSi(OR)_3 + ROH \quad (4)$$

$$HOSi(OR)_3 + H_2O \rightarrow (HO)_2Si(OR)_2 + ROH \quad (5)$$

$$(HO)_2Si(OR)_2H_2 \rightarrow (HO)_3Si(OR) + ROH \quad (6)$$

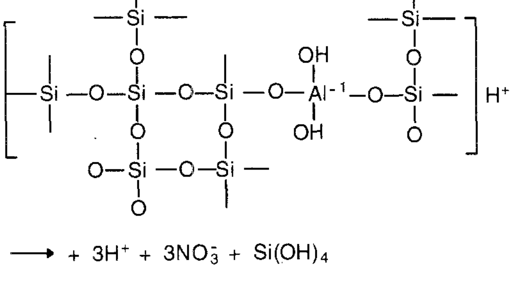
$$(HO)_3Si(OR) + H_2O \rightarrow Si(OH)_4 + ROH \quad (7)$$

$$\equiv Si{-}OR + HO{-}Si\equiv \; \rightarrow \; \equiv Si{-}O{-}Si\equiv \; + ROH \quad (8)$$

$$\equiv Si{-}OH + HO{-}Si\equiv \; \rightarrow \; \equiv Si{-}O{-}Si\equiv \; + HOH \quad (9)$$

Now, what will happen when a system containing $Al(NO_3)_3 \cdot 9H_2O$, TEOS, a small amount of water and a little mineral acid is heated in a boiling water bath? The work of Hazel *et al.* as reported by Iller [36] shows the possibility of the formation of alumino–silicic acid hydrate by the interaction of silicic acid sol and Al^{3+} solution. However, the condensation reaction was shown to be a function of the quantity of water, i.e. the ratio of H_2O:TEOS used, and the time permitted [37, 38]. The rate of hydrolysis increases with the concentration of HCl [39]. The condensation rate is similarly influenced by pH [40]. The maximum gelling rate is found at pH 5–6, whereas silica sol is stable at pH = 2. In practice it is difficult to separate hydrolysis equilibrium from polymerization reactions. Later reactions would invariably start immediately after hydrolysis occurs. Thus monosilicic acid will soon polymerize to polysilicic acid. Aggregation will take place thereafter to form sols and subsequently large particles of silicic acid [40, 41]. Yoldas [34] pointed out the possibility of the formation of polymeric clusters, either as a two-dimensional chain which may be linear and planar, or three-dimensional micelles by chemical polymerization and cross-linkages. Sakka and Kamiya [42] noted that the molar ratio of water to metal alcoholate is the most important factor affecting the type of molecules formed. For example, when the molar ratio of water to TEOS was less than 4, the hydrolysed product showed spinability which indicates that a chain-like polymer has actually formed during hydrolysis. On the other hand, when the molar ratio of water to alcoholate was larger than 4, the hydrolysed mass had a three-dimensional network structure.

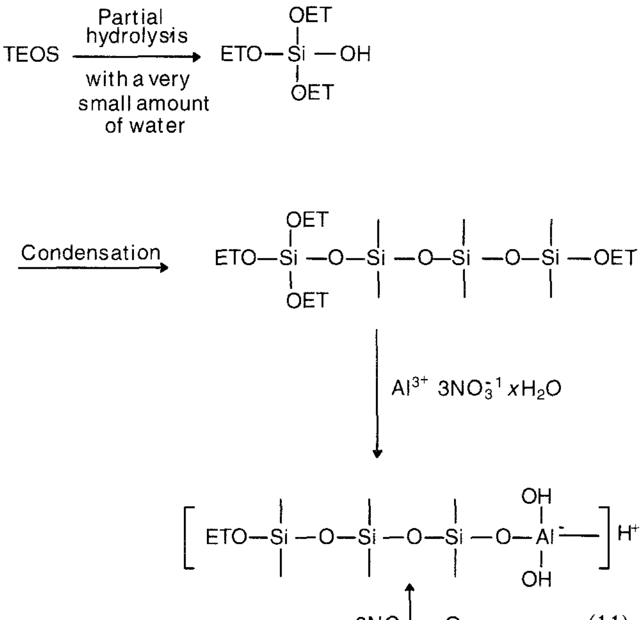
Therefore, in case of gelation of G-150 when excess water was used, the circumstances of hydrolysis and the simultaneous polymerization reaction would be more complex. The resultant $Si(OH)_4$ aggregate would be a three-dimensional one, as discussed already. The chemical bond formation between silicon and aluminium by the mutual reaction of $Si(OH)_4$ and its polymerized aggregate with soluble Al^{3+} salt may be very slow. This reaction was found to be predominent when a freshly prepared very dilute silica sol reacts with Al^{3+} ion at pH 3–4.5 as is the case in G-153 synthesis [8]. Thus, when TEOS is used as the SiO_2 source, there is every possibility that hydrolysis reactions (Equations 4–7) and self-polymerization reactions (Equations 8 and 9) will be more rapid as the concentration of water increases. As reactions 8 and 9 predominate, the aluminosilicate formation will surely decline, which will cause inhomogeneity in the gelation process. The suggested Al_2O_3–SiO_2 gels, on heating to 980 °C, form both cubic mullite (Si–Al spinel) and aluminosilicate glassy phase (Table I). The formation of the latter phase is undesirable. The tentative nature of this reaction may be visualized by assuming that colloidal polymeric molecules of $Si(OH)_4$ absorb Al^{3+} ions from the solution. In this case, a partial substitution absorbing Al^{3+} ions from the solution of aluminium in the silioxane chain, may occur, which will cause the formation of aluminosilicate hydrate and possibly form a more complex aluminosilicate hydroxy polymeric gel particle. The model of this particle could be contemplated as a three-dimensional chain of the type shown by Equation 10 below.



(10)

During heating, this gel transforms into an unstable anhydrous aluminosilicate intermediate phase at the endothermic dip just before the 980 °C exotherm.

In the case of gelation of Gel-A, where the water of hydrolysis was present as water of crystallization associated with the $Al(NO_3)_3 \cdot 9H_2O$ crystal and no free amount of water has been used, two types of mullite are formed at the 980 °C exotherm (which is still undesirable). Therefore, Gel-A is similar to the polymeric gel synthesized by Pask *et al.* [20]. They observed two exotherms at 980 and 1250 °C, similar to what has been reported in the present study (Table I). Unlike their explanation, it can be argued that the appearance of the 1250 °C exotherm is surely indicative of the formation of Si–Al spinel in addition to the usual tetragonal mullite formation at the 980 °C exotherm. It is presumed that a small amount of water available during the gelling of Gel-A and in the preparation of the polymeric gel of Pask *et al.* [20] was responsible for spinel phase formation. So, segregation eventually occurred during heating, and mullitization took place from the two-phase system by a two-stage conversion process as shown by Li and Thomson [16] in their DXRD diagram. Thus, when a small amount of water is present, the gel powder has the equivalent oxide composition of mullite and is not essentially rearranged into a mullite lattice. There may be some possibility of interdifusion into phase separation prior to mullitization. Thus, the resultant hydrolysed product of TEOS, in this case where the availability of moisture content is low, will form a chain-like polymer instead of a giant three-dimensional network of $Si(OH)_4$. The interacted product of thin polymeric chain with Al^{3+} may be as follows (Equation 11).



(11)

The schematic model of Gel-A shows that only a few aluminium atoms are tetra-coordinated, which is supported by the data of Co-no of aluminium measured by Leonard *et al.* [43] in their X-ray fluorescence spectroscopy (XRF) and radial electron density distribution (RED) studies of amorphous silico-aluminas. In the case of G-31, gelation was performed almost in the absence of water. It is expected that owing to this restricted rate of hydrolysis of TEOS, no large clusters of $Si(OH)_4$ are formed by extensive polymerization nor chain-like polymeric species. Instead, simple molecules of ethoxy silicate–aluminium nitrate hydrate complex may form which on further heating, completely transformed into tetragonal mullite at the 980 °C exotherm.

4. Conclusion

Using the same source of alumina and silica components, different monophasic Al_2O_3–SiO_2 gels have been synthesized by varying the use of water–alcohol content as a hydrolysing agent. These gels show different behaviour in the appearance of the 980 °C peak and in mullitization paths, as noted below.

(a) Monophase gel, synthesized in the presence of a large quantity of ordinary alcohol, not only exhibits the usual 980 °C exotherm due to c-mullite formation, but also shows two more exotherms at ~ 1150 and 1245 °C. The exhibition of the 980 °C peak is due exclusively to the usual c-mullite formation explained earlier [8]. The formation of the latter two exotherms in the DTA trace are explained as being due to mullitization by two possible reaction paths. For example, the occurrence of the third exothermic peak, 1245 °C, is due to the usual c-mullite to o-mullite formation. The phenomenon of the second exotherm at ~ 1150 °C, which really occurs and is distinctly observed in the present investigation, may be explained as being due to the formation of an additional quantity of mullite formation by nucleation in the amorphous aluminosilicate phase, generated during the 980 °C exothermic reaction of gel G-150. Thus, the mullitization behaviour is analogous to that of kaolinite.

(b) Monophasic gel prepared in a minimum amount of water, e.g. water of crystallization of aluminium nitrate as the only source, exhibits a sharp exotherm at 980 °C with the formation of both c-mullite and o-mullite. The former phase subsequently transforms to o-mullite with the appearance of another exotherm at ~ 1250 °C.

(c) Monophasic gel prepared with almost negligible water content, exhibits only one broad exotherm at ~ 980 °C with the formation of t-mullite by a similar route to the spray pyrolysis method.

Finally, the role of water during hydrolysis and the condensation behaviour of TEOS in the mixture of $Al(NO_3)_3$ has been discussed in detail. The formation of hydrated aluminosilicate with different network formations has been suggested.

Acknowledgement

The author thanks the Director, Dr B. K. Sarkar, for permission to publish this paper, and acknowledges the assistance of Mr D. K. Ghosh, Mr M. Datta and Mr S. Chakraborty in the preparation of the manuscript.

References

1. K. OKAKA, N. OTSUKA and S. SOMIYA, *J. Am. Ceram. Soc.* **70** (1991) 1633.
2. A. AKSAY, D. M. DABBS and M. SARIKAYA, *ibid.* **74** (1991) 2343.
3. M. D. SACKS, H. W. LEE and J. A. PASK, in "Ceramic Transactions", Vol. 6, "Mullite and Mullite Matrix Composites", edited by S. Somiya, R. E. Davis and J. A. Pask (1990) p. 167.
4. A. K. CHAKRABORTY, *J. Am. Ceram. Soc.* **62** (1979) 120.
5. H. SUZUKI, H. SAITO, Y. TOMOKIYO and Y. SUYAME, in "Ceramic Transactions", Vol. 6, edited by S. Somiya, R. E. Davis and J. A. Pask (1990) p. 263.
6. H. SCHNEIDER and T. R. LIPINSKI, *J. Am. Ceram. Soc.* **71** (1988) C-162.
7. D. X. LI and W. J. THOMSON, *J. Mater. Res.* **6** (1991) 819.
8. A. K. CHAKRAVORTY and D. K. GHOSH, *J. Am. Ceram. Soc.* **71** (1988) 978.
9. B. E. YOLDAS and D. P. PARTLOW, *J. Mater. Sci.* **23** (1988) 1895.
10. K. OKADA and N. OTSUKA, *ibid.* **5** (1986) 1315.
11. Y. HIRATA, K. SAKEDA, Y. MATSUSHITA and K. SHEVNADA, *Yogo-Kyokai-Shi*, **93** (1985) 101.
12. K. HAMANO, Z. NAKAGAWA, G. GUN-JI and T. SATO, in "Mullite", edited by S. Somiya, (Uchida Rokakoho, Tokyo, Japan, 1985) pp. 37–49.
13. L. A. PAULICK, Y. F. YU and T. I. MAH, in "Ceramic Powder Science, Advances in Ceramics", Vol. 21, edited by G. L. Messing, K. S. Mazdiyasni, J. W. McCauley and R. A. Haber (American Ceramic Society, Westerville, OH, 1987) pp. 121–9.
14. CHI. S. HSI, H. Y. LU and F. S. YEN, *J. Am. Ceram. Soc.* **72** (1989) 2208.
15. A. K. CHAKRAVORTY, unpublished work (1985).
16. D. X. LI and W. J. THOMSON, *J. Am. Ceram. Soc.* **74** (1991) 574.
17. K. OKADA and N. OTSUKA, in "Ceramic Transactions", Vol. 6, edited by S. Somiya, R. E. Davis and J. A. Pask (1990) p. 425.
18. D. W. HOFFMAN, R. ROY and S. KERNARNENI, *J. Am. Ceram. Soc.* **67** (1984) 468.
19. A. K. CHAKRAVORTY, *J. Mater. Sci.* (1994) in press.
20. J. A. PASK, X. W. ZHANG, A. P. TOMSIA and B. E. YOLDAS, *J. Am. Ceram. Soc.* **70** (1987) 700.
21. S. KANZAKI, H. TABATA, T. KUMAZAWA and S. OHTA, *ibid.* **68** (1985) C-6.
22. J. C. HULING and G. L. MESSING, *ibid.* **74** (1991) 2374.
23. A. K. CHAKRAVORTY and D. K. GHOSH, *ibid.* **74** (1991) 1401.
24. A. K. CHAKRAVORTY, *ibid.* **75** (1992) 2043.
25. K. SRIKRISHNA, G. THOMAS, R. MARTINEZ, M. P. CORRAL, S. DE. AZA and J. S. MOYA, *J. Mater. Sci.* **25** (1990) 607.
26. K. OKADA and N. OTSUKA, *J. Am. Ceram. Soc.* **69** (1986) 652.
27. B. SONUPARLOK, M. SARIKAYA and I. A. AKSAY, *ibid.* **70** (1987) 837.
28. I. M. LOW and R. MCPHERSON, *J. Mater. Sci.* **24** (1989) 926.
29. K. OKADA and N. OTSUKA, *J. Am. Ceram. Soc.* **70** (1987) C-245.
30. C. J. BRINKER, K. D. KEEFER, D. W. SCHAEFER and C. S. ASHBY, *J. Non-Cryst. Solids* **48** (1982) 47.
31. J. ZARZYEKI, M. PRASSAS and J. PHALIPPOU, *J. Mater. Sci.* **17** (1982) 3371.
32. S. P. MUKHERJEE, *J. Non-Cryst. Solids* **42** (1980) 477.
33. K. C. CHEN, T. TSUCHIYA and J. D. MACKENZIE, *ibid.* **81** (1986) 227.
34. B. E. YOLDAS, *ibid.* **83** (1986) 375.
35. H. SCHMIDT, H. SCHOLZ and A. KAISER, *ibid.* **63** (1984) 1.
36. R. K. ILLER, "The Colloid Chemistry of Silica and Silicates" (Cornell University Press, New York, 1955) p. 68.
37. R. AELION, A. LOEBEL and F. ERICH, *J. Am. Chem. Soc.* **72** (1950) 5706.
38. M. F. BECHTOLD, R. D. VEST and L. P. PLAMBECK Jr, *ibid.* **90** (1968) 4590.
39. YU. PAOTING, LIU, HSIAOMING and W. YUGUANG, *J. Non-Cryst. Solids* **52** (1982) 511.
40. R. K. ILLER, "The Colloid Chemistry of Silica and Silicates" (Cornell University Press, New York, 1955) pp. 40–45.
41. B. E. YOLDAS, *J. Am. Ceram. Soc.* **66** (1982) 387.
42. S. SAKA and K. KAMIYA, *J. Non-Cryst. Solids* **42** (1980) 403.
43. A. J. LEONARD, P. RATNASAMY, E. D. DE. CLERCK and J. J. FRIPIAT, *Disc. Farad. Soc.* **52** (1971) 98.

Received 3 December 1993
and accepted 16 May 1994