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The origins of mullite formation

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The evolution of mullite formation has been studied from Al_2O_3–SiO_2 gels. The studies have established (a) the identity of the controversial cubic phase, (b) the chemical, structural and compositional continuity in the evolution of mullite formation, (c) the existence of solid solutions between (3:2) and (2:1) mullites, (d) the origins of the exotherms, and (e) the origins of mullite formation. The Al–Si spinel has a composition and structure similar to that of the (2:1) mullite, i.e. $\square_x Al^{vi}_{16-x}[Al_x Si\square_{4-x}]^{iv}O_{32}$.

1. Introduction

The origins of mullite formation have been a subject of extensive but controversial investigation. Many studies have been concerned with the kaolinite–mullite reaction series and major problems have remained concerned with the nature of metakaolin, the manner in which it transforms into a spinel-type phase and mullite, as well as the relation of this spinel-type phase to mullite. These outstanding problems are not only exclusive to clay minerals but also to the SiO_2–Al_2O_3 system in general, irrespective of the nature and history of the starting raw materials or the techniques of preparation. The central controversy has always been focused on the exothermic reaction at around 930 to 1000° C. γ-alumina spinel or Al–Si spinel and mullite are thought to be associated with that exotherm, although the appearance of mullite may be delayed. Between 1200 to 1260° C, a second exothermic reaction occurs in which the spinel phase disappears and mullite becomes more developed. The intricacy of mullite formation is further complicated by the controversy over the composition of spinel phase and the relevance of the second exotherm.

Brindley and Nakahira [1] first set out to settle the controversy with considerable success, at least for the clay minerals. In their opinion, the dominant feature of the entire kaolinite–mullite series is the structural continuity and especially the maintenance of essentially close-packed oxygen layers at least as far as the spinel phase which they claimed to be spinel of gamma alumina with silica in solid solution and has the composition of $Si_3Al_4O_{12}$. However, recent attempts by various workers have rekindled the controversy. Percival and Duncan [2], Leonard [3] and Bullens *et al.* [4] have used infrared spectroscopy and X-ray fluorescence measurements, respectively, to investigate the kaolinite–mullite reaction sequence and they concluded that the formation of an Al–Si spinel was excluded while γ-alumina formed instead. The most convincing evidence for the formation of an Al–Si spinel came from the work of Chakraborty and Ghosh [5] who went on to suggest that the composition of the spinel is the same as that of (3:2) mullite.

Mazdiyasni and Brown [6] prepared an X-ray amorphous mullite composition powder, by hydrolysis of mixed alkoxides, in which mullite could only be detected after holding for 1 h at ~ 1200° C and no differential thermal analysis (DTA) exotherm was observed up to this temperature. Kanzaki and Tabata [7] investigated stoichiometric mullite powder prepared by spray pyrolysis of aluminium nitrate and ethyl silicate. Only one sharp exotherm at 970° C was obtained and X-ray diffraction (XRD) showed that direct transformation from amorphous to crystalline mullite occurred without the apparent formation of the spinel phase. This crystallization behaviour is similar to glasses of mullite composition prepared by the melt [8] or plasma synthesis [9] where tetragonal mullite is observed initially which slowly converts to the usual orthorhombic structure at ~ 1200° C. In their study of mono- and diphasic xerogels prepared from organic and inorganic precursors in the SiO_2–Al_2O_3 system, Hoffman *et al.* [10] observed substantial differences between these two xerogels of the same composition in relation to their crystallization characteristics. In the former, a sharp exotherm occurred at 960° C which gave rise to tetragonal mullite while no exotherm was observed in the latter with mullite formed only at temperatures above 1250° C.

Because of these complexities, the origins and structure of mullite remain enigmatic although the model proposed by Burham [11] has been generally accepted. In essence, the structure of mullite consists of chains of AlO_6 octahedra at the centre and corners of 1/4 of the unit cell bonded together by AlO_4 and SiO_4 tetrahedra and AlO_6 octahedra. The tetrahedral aluminium and silicon atoms are distributed randomly and some oxygen atoms shared by these cations are removed at random, giving rise to oxygen vacancies and new tetrahedral sites containing aluminium atoms which are being adopted adjacent to the position where each oxygen is lost [12]. The oxygen vacancies are in random distribution at high temperatures which rearrange themselves into ordered domains producing superlattice points in the reciprocal cell [13]. In terms of such a defect structure, Cameron [14] has expressed

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the solid solution of mullite by $Al_2^{vi}(Al_{2+2x}^{iv}Si_{2-2x}^{iv})O_{10-x}$ where x is the number of oxygen atoms missing per unit cell and (vi) and (iv) are the coordination states of the atoms.

On the basis of variation of the lattice parameter with composition, Cameron [15] proposed a continuous solid solution for mullite of $x = 0.17$ to 0.59, where a smooth variation was observed up to 84 wt % Al_2O_3, confirming previous studies of lattice parameter variations [16, 17].

The objective of this paper is to clarify the existing outstanding problems concerning (i) the nature of the exothermic reaction, (ii) the identity and composition of the spinel phase, (iii) the relation between mullite and the spinel phase, and (iv) the mechanisms of mullite formation.

TABLE I Petrographic phase analyses of mullites

Temperature (°C)	Time (h)	Mullite compositions (wt % Al_2O_3)			
		63%	72%	80%	100%
600	0	A	A	A	A
875	0	A	A	A	γ_s
950	0	A	A	A	γ_s
1000	0	A	A	A	γ_s
1100	0	A	A	A	γ_s, θ_w
1150	0	A	S_s	S_s	γ_s, θ_m
1200	0	A	M_m, S_s	M_w, S_s	γ_m, θ_m
1250	0	M_w, S_s	M_s, S_w	M_m, S_m	α_m, θ_w
1300	0	M_s	M_s	M_m, S_m	α_s
1300	2	M_s	M_s, θ_w	M_s, α_m	α_s
1300	10	M_s, C_t	M_s, θ_w	M_s, α_s	α_s
1400	0	M_s	M_s, θ_t, α_t	M_s, α_s	α_s
1500	0	M_s	M_s, θ_t, α_t	M_s, α_s	α_s

M, mullite; S, Al–Si spinel; γ, θ, α, γ, θ and α-alumina, respectively; C, cristobalite; s, strong; m, medium; w, weak; t, trace; A, amorphous.

2. Experimental methods

Alumino-silicate gels (containing 63 to 80 wt % Al_2O_3) obtained from hydrolysis of commercial purity silicon tetraethoxide and aluminium isopropoxide were heat treated in a Rigaku DTA furnace at a heating rate of 10° C min^{-1} and the crystalline phases formed were analysed with a Phillips X-ray Diffractometer (Model PW 1050/25). The mullite lattice parameters were computed by a method similar to that reported elsewhere [18]. The mullite composition was inferred from the unit cell edge or cell volume by the experimental relationships reported in the literature [15, 19]. The infrared spectra of the gel sample were recorded on a Pye-Unicam SP3-200 spectrometer. The specimen for the infrared analysis was prepared by the pellet method whereby the gel powder was mixed with KBr in a ratio of 1 : 250 and subsequently pressed into a thin disc. A reference pellet of KBr was also used. The chemical analysis of the sample involved leaching of amorphous phases from heat-treated mullite gels with 2% and 10% sodium hydroxide (NaOH) solutions. Hydrofluoric acid (HF) of similar concentrations were used to extract the silica phase. In the former method, 300 mg of the specimen was placed in a platinum crucible containing 100 ml NaOH solution which was allowed to boil in a water bath for various periods. After the solution has cooled down to room temperature, it was filtered and rinsed with distilled water several times before the residue was collected for further analysis. The same procedure was applicable to the second method except that the platinum crucible was replaced with a plastic container and the leaching process took place at the ambient temperature.

3. Results

3.1. Phase relations in the mullite solid solutions

Petrographic phase analysis of stoichiometric (72 wt % Al_2O_3) mullite is shown in Table I. The results revealed that prior to the formation of the mullite phase, an Al–Si spinel phase was always formed with particle size in the range of 1 to 5 nm which coarsen rapidly with increasing temperature. At about 1100° C, the spinel was observed to coexist with the mullite phase. At this temperature, the (1 2 0) and (2 1 0) lines of orthorhombic mullite were not distinctly split but a rather broad and diffuse maximum was obtained (Fig. 1) The same feature applied to (2 5 0) and (5 2 0) lines with the latter missing occasionally. It is interesting to note that the Al–Si spinel phase disappeared at or near the onset of the splitting of the (1 2 0) and (2 1 0) lines, which corresponded apparently to the formation of the well-crystallized orthorhombic mullite. There were no traces of theta or alpha alumina at 1300° C. These phases only appeared at higher temperatures or longer duration of heat treatment at 1300° C. Similar features were also noted for mullites containing 63 wt % and 80 wt % Al_2O_3 although the development of well-crystallized mullite was slightly delayed in the latter but enhanced in the former.

The thermo-chemical reactions taking place during the evolution of mullite gels with various alumina contents are depicted in Fig. 2. Mullite with the stoichiometric (3 : 2) composition gave a very sharp exothermic peak at about 970° C while mullite with 63 wt % alumina displayed a very broad exotherm extending from 900 to 1050° C. Only a relatively small and diluted exotherm, occurring at around 970° C, was obtained for mullite with 80 wt % alumina. This mullite was observed not to exhibit a second exotherm ranging from 1250 to 1300° C which was displayed by other mullites. This exotherm in (3 : 2) mullite which occurred at ~ 1250° C was broad and diffuse while it was sharp and distinct in the mullite with 63 wt % alumina where it centred at ~ 1280° C. Apparently, these two exotherms were associated with the crystallization of Al–Si spinel and orthorhombic mullite phases, respectively. Dehydration of the gel gave rise to the endotherm at ~ 120° C while the endotherm at 300–500° C was the consequence of dehydroxylation of residual alkoxides.

3.2. Cell dimensions of mullites

The unit cell edge, a, is shown plotted against composition of mullite (mol % Al_2O_3) in Fig. 3. The composition of mullites formed at various temperatures and from varying amounts of alumina seemed to lie on a straight line. The straight line relationship between cell parameter, a, and cell volume, C_v, depicted in

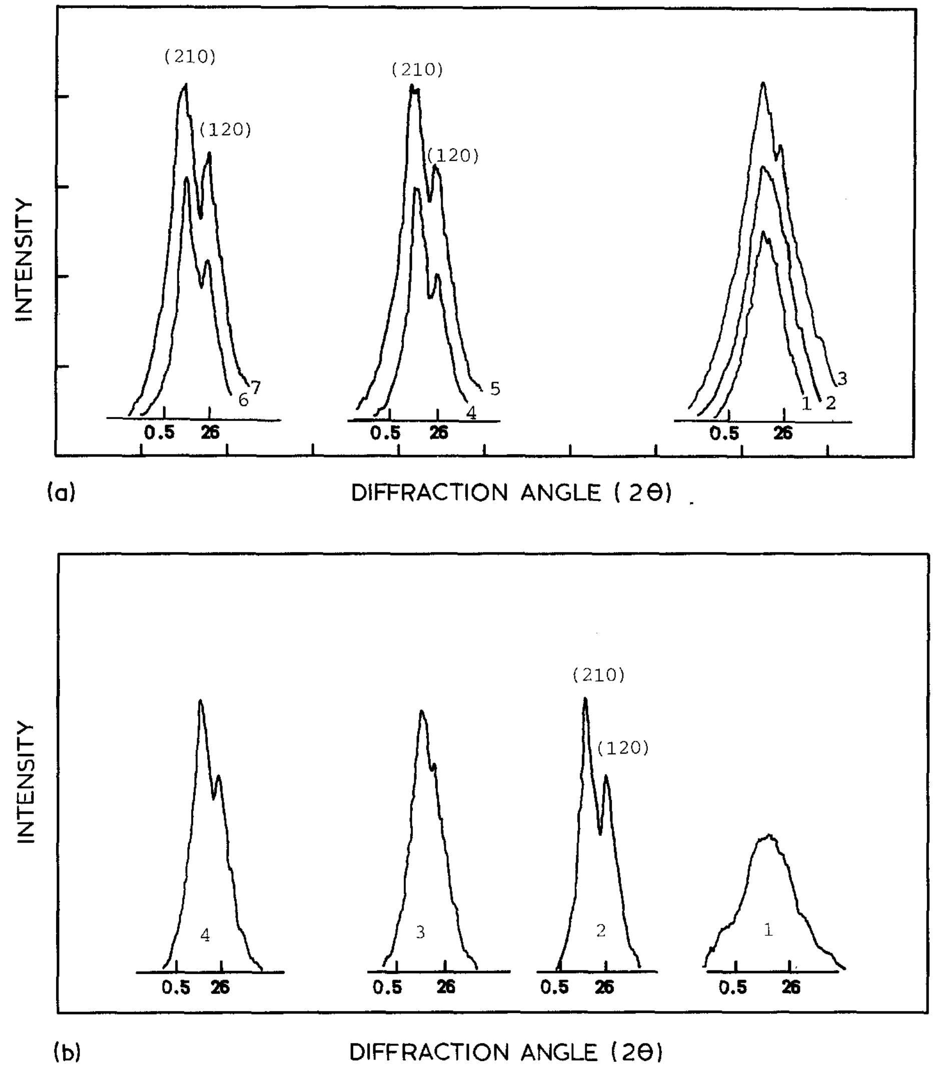

Figure 1 (a) (1 2 0) and (2 1 0) reflections of mullite gel composition heated at various temperatures; (1) 1200° C; (2) 1250° C; (3) 1300° C; (4) 1400° C; (5) 1500° C; (6) 1300° C (2 h); (7) 1300° C (10 h). (b) (1 2 0) and (2 1 0) reflections of mullites with 63 and 80 wt % Al_2O_3 heated at various temperatures: (1) 63 wt % Al_2O_3 at 1250° C; (2) 63 wt % Al_2O_3 at 1300° C; (3) 80 wt % Al_2O_3 at 1300° C; (4) 80 wt % Al_2O_3 at 1300° C for 2 h.

Fig. 4 lies between the lines of best fit obtained by Cameron [15] and Schneider and Wohlleben [19]. The composition of mullite (mol % Al_2O_3) as a function of temperature is displayed in Fig. 5. These results indicate that the well-crystallized mullite has a smaller alumina content than the poorly crystallized mullite and the mullite formed initially approximates to a (2 : 1) composition which gradually approaches a (3 : 2) composition with increasing temperatures and times. Apparently, most if not all of the mullites formed at low temperatures did not assume ideal tetragonal structures although their (1 2 0) and (2 1 0) lines were clearly indistinguishable. The linearity of the a against C_v plot (Fig. 4) suggests that there is some very simple relation between cell dimensions and either chemical composition or Al–Si order.

3.3. Infrared spectroscopy

To aid in interpreting the infrared spectra, bonding assignments for spectral bands of mullite obtained from an analysis of literature values [2, 20] are summarized in Table II.

Representative infrared spectra of mullites with various compositions and heat treatment histories are

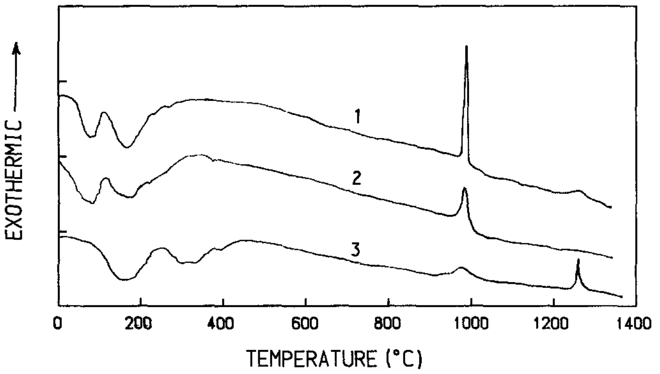

Figure 2 DTA curves of mullites with varying alumina contents. (1) 72 wt % Al_2O_3; (2) 80 wt % Al_2O_3; (3) 63 wt % Al_2O_3.

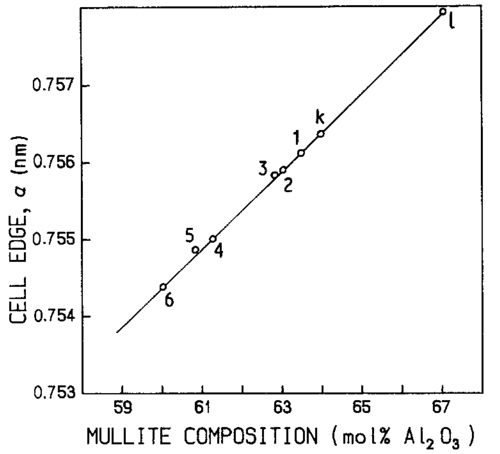

Figure 3 Variation of cell edge, *a*, with the alumina content of mullite. 72 wt % Al_2O_3: (1) 1200° C, (2) 1250° C, (3) 1300° C, (4) 1400° C, (5) 1500° C, (6) 1300° C (10 h). 1300° C: (k) 63 wt % Al_2O_3, (l) 80 wt % Al_2O_3.

shown in Fig. 6 while Fig. 7 depicts the infrared spectra of unleached and leached samples. The bands are given general assignments from Table II. Important features of Fig. 6 are the broad band which extends from 1200 to 1000 cm^{-1} and those at ~800 and 600 cm^{-1}. The first band was assigned to the stretching vibrations of Si–O bonds while the other two were the results of Al^{iv}–O and Al^{vi}–O vibrations, respectively. These results serve to indicate that aluminous mullites, formed at low temperatures, show prominent AlO_4 vibrations while mullites with alumina contents close to (3 : 2) composition (formed at high temperatures) display enhanced sharpness and intensity in the absorption band (~600 cm^{-1}) of AlO_6 octahedra. These observations are consistent with the theoretical and experimental contents of AlO_4 tetrahedra and AlO_6 octahedra in the crystal structure of mullites (Tables III and IV). Based on ^{27}Al magic-angle spinning nuclear magnetic resonance (MASNMR) studies on mullite gels heat treated at various temperatures, Komarneni and Roy [21] computed the ratio of tetragonal aluminium to octahedral aluminium and obtained values of 0.48 and 1.25 for mullite gels treated at about 1000 and 1380° C, respectively. The spectra of Fig. 7 show that leaching removes a considerable fraction of amorphous silica from the sample. The remaining absorption band of Si–O was probably due to the silica which was incorporated into the structure of the spinel phase in a form of solid solution. A comparison of the infrared spectrum of the spinel with that of pure γ-alumina (Fig. 6) serves to indicate that the spinel formed is not identical to γ-alumina as has been claimed by many workers.

TABLE II Assignment of mullite band wave numbers (cm^{-1})

SiO bond from SiO_4	Al^{iv}–O bond from AlO_4	Al^{vi}–O bond from AlO_6
1171 s	1165 s, br	850 m, br
1120 ms, sh	832 s, br	613 m, sh
960 ms, sh	740 m, sh	567 s
927 s, sh		
901 s, br		

s, strong; m, medium; ms, medium to strong; br, broad; sh, shoulder.

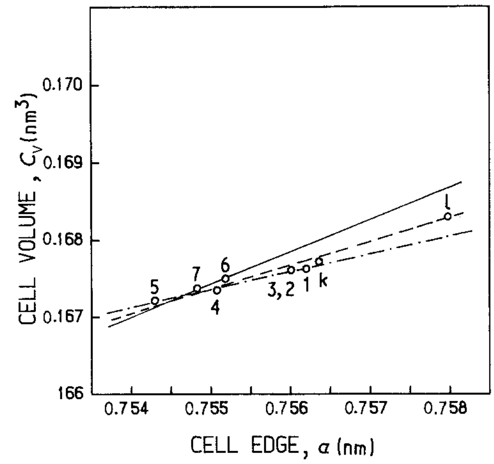

Figure 4 Variation of cell volume, C_v, with the cell edge, *a*, of mullite. 72 wt % Al_2O_3: (1) 1200° C, (2) 1250° C, (3) 1300° C, (4) 1300° C (2 h), (5) 1300° C (10 h), (6) 1400° C, (7) 1500° C. 1300° C: (k) 63 wt % Al_2O_3, (l) 80 wt % Al_2O_3. (——) [19], (- - -) present work, (-·-·-) [15].

4. Discussion

4.1. The origins and identity of the spinel phase

There is much controversy and uncertainty about the identity of the aluminium-containing cubic phase prior to the formation of mullite. The poor crystallinity of this spinel-type phase, either γ-alumina (γ-spinel) or γ-alumina containing silicon atoms (Al–Si spinel), limits the use of XRD techniques to reveal the structure. Infrared [2] and X-ray fluorescence [4] techniques have recently been employed to investigate the presence and changes of aluminium coordination in the kaolinite thermal sequence. Based on the fact that there were no aluminium atoms with four-fold coordination in the spinel phase, both techniques arrived at the same conclusion that the cubic phase was γ-alumina. Komarneni and Roy [21] studied both single phase and diphasic mullite gels by ^{27}Al and ^{29}Si by MASNMR. Based on the apparent absence of ^{29}Si MASNMR spectrum for the mullite gel heated treated at about 1000° C, they deduced that the cubic phase is essentially aluminium-rich (i.e. γ-alumina). A similar conclusion was derived by Brown *et al.* [22]. By accurate lattice parameter measurements and by careful leaching experiments, Brindley and Nakahira [1] and Chakraborty and Ghosh [5] have respectively

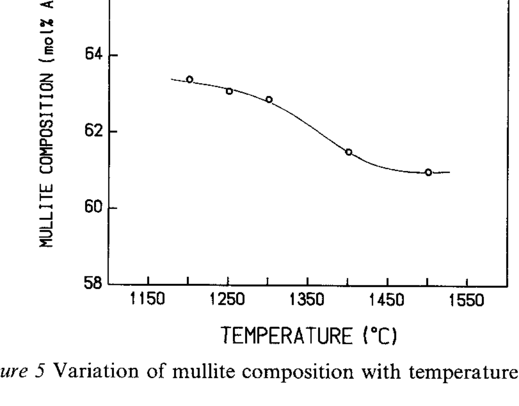

Figure 5 Variation of mullite composition with temperatures.

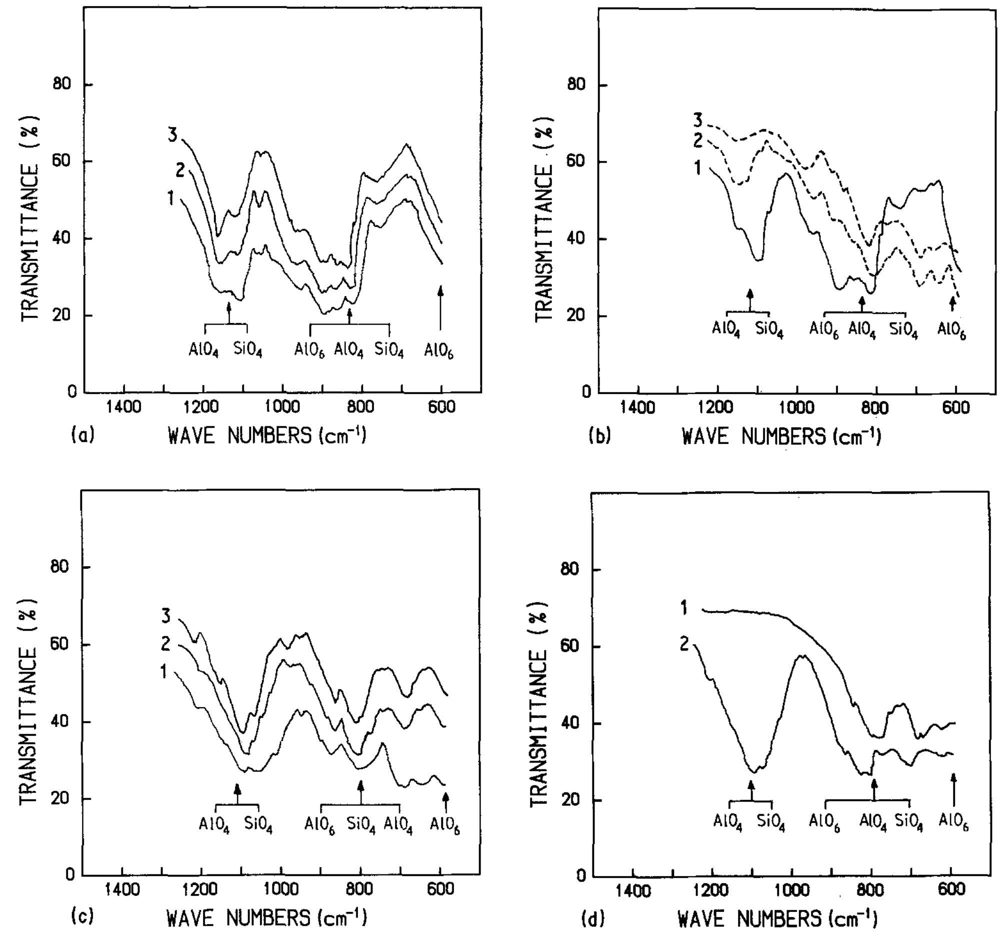

Figure 6 (a) Infrared spectra of mullite heated at 1300° C for various times. (1) 0 h; (2) 2 h; (3) 10 h. (b) Infrared spectra of mullites with various compositions heated at 1300° C. (1) 63 wt % Al_2O_3; (2) 80 wt % Al_2O_3 (2 h); (3) 80 wt % Al_2O_3. (c) Infrared spectra of mullite gel fired at various temperatures. (1) 1100° C; (2) 1200° C; (3) 1250° C. (d) Infrared spectra of (1) γ-alumina, and (2) Al–Si spinel.

established the cubic phase to be an Al–Si spinel, although with different compositions.

A perusal of the results obtained for the crystallization behaviour of stoichiometric mullite in this investigation serves to substantiate the evidence for the formation of an Al–Si spinel prior to the formation of mullite. The first evidence is clearly indicated by the vast difference in the crystallization temperatures of Al–Si spinel and γ-alumina (Table I). The latter crystallized at 870° C with no apparent exotherm while the former crystallized at $\sim 970°$ C with a sharp exotherm. At higher temperatures, γ-alumina transformed to corundum without passing through the intermediate phase of θ-alumina which can be readily stabilized by the presence of silica in the lattice structure of γ-alumina. Meanwhile, the Al–Si spinel gradually transformed to tetragonal-like mullite at $\sim 1150°$ C and orthorhombic mullite at $\sim 1250°$ C. The presence of θ-alumina indicates the composition of the cubic phase is aluminosilicate. In addition, accurate measurements of cell dimensions of these two cubic phases indicate that the Al–Si spinel has a unit cell size ($a = 0.7880$ nm) which is slightly smaller than that of γ-alumina ($a = 0.7900$ nm), confirming the existence of a solid solution of silica in the lattice of γ-alumina to form an Al–Si spinel. Unequivocally, the identity of the cubic phase is established to be that of an Al–Si spinel.

Indirect but powerful evidence for the Al–Si spinel is readily inferred from the leaching experiments on the mullite gel sample heated to $\sim 1000°$ C and heat treatments of the residue at 1300° C for 2 h. In contrast to the unleached sample, a considerable amount of corundum together with mullite were obtained, indicating that the residue (Fig. 7) has an aluminosilicate composition which formed a metastable mullite with composition close to (2 : 1) mullite upon further heating. In the absence of amorphous silica, the metastable mullite could not form an equilibrium (3 : 2) mullite as more silica would need to be incorporated into the tetragonal-like mullite. However, due to the metastability of this phase, the tetragonal-like

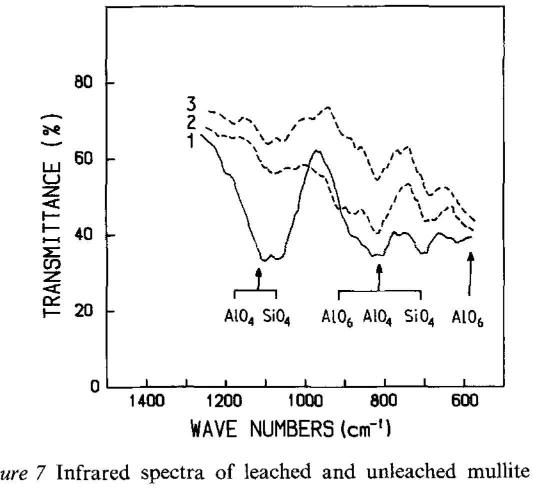

Figure 7 Infrared spectra of leached and unleached mullite gels which had been treated at 1150° C: (1) unleached; (2) leached with NaOH (10%) for 5 min; (3) leached with HF (10%) for 1 h.

mullite could not persist at temperatures greater than 1250° C and would achieve a more stable state by decomposing to form the equilibrium (3 : 2) mullite and corundum as follows

$$(2:1)\text{ mullite} \xrightarrow[2\text{ h}]{1300^\circ\text{C}} (3:2)\text{ mullite} + \text{corundum}$$

If the residue were γ-alumina, no mullite could be formed and only corundum would be obtained. No, or only a trace of corundum obtained in the unleached sample serves to indicate that the amorphous silica liberated during the formation of the Al–Si spinel is essential for the evolution of tetragonal-like mullite to equilibrium mullite probably by the substitution process of Si^{4+} for Al^{3+}. The absence of cristobalite formation suggests that the amorphous silica liberated was the equilibrium amount necessary for the substitution process to achieve (3 : 2) mullite.

The infrared results of cubic phases obtained from mullite and alumina gels treated at 1000 and 900° C (Fig. 6d) provide substantial evidence for the dissimilarity of Al–Si spinel from γ-alumina in relation to their compositions and bond strengths. Clearly, the spectra are not identical even if the absorption band of Si–O bonds were ignored. Apparently, the formation of a solid solution between γ-alumina and silica has profound influence on the bond strengths and vibrations of the γ-alumina lattice. Interestingly, absorption bands due to AlO_4 tetrahedra are observed to exist in both the cubic phases although with different concentrations. This observation confirms the results reported by Chakraborty and Chosh [5] and others [23, 24] that aluminium ions do exhibit both four- and six-fold coordination. In addition, these results reported by Chakraborty and Ghosh [5] and composition of mullite where both coordination states of aluminium prevail. This proposition agrees with the composition of Al–Si spinel obtained by Chakraborty and Ghosh [5] but is in contradiction with the model of Brindley and Nakahira [1] where only six-fold coordination aluminium was assumed to exist in the Al–Si spinel, which incidentally has led Percival and Duncan [2] and Bullens *et al.* [4] to draw the wrong conclusions regarding the identity of the cubic phase. According to Brindley and Nakahira [1], the Al–Si spinel has a composition of $Si_3Al_4O_{12}$ while Chakraborty and Ghosh [5] proposed a composition of $Si_2Al_6O_{13}$ which is equivalent to that of a (3 : 2) mullite.

It is beyond any doubt that, in view of the massive evidence in the literature and the convincing results obtained in this investigation, the identity of the Al–Si spinel is established. However, the controversy now centres on the composition of the Al–Si spinel. The composition proposed by Brindley and Nakahira is clearly incorrect because of the presence of aluminium with both four and six-fold coordination in the spinel while that suggested by Chakraborty and Ghosh is most convincing. Unfortunately, the composition of the spinel proposed by the latter is not consistent with the results obtained in this study on the gel-derived mullite and also in other studies. The inconsistency lies in the fact that an aluminous mullite, close to (2 : 1) composition, is always formed prior to the formation of the equilibrium (3 : 2) mullite. This observation has been reported in mullites derived or prepared from clay minerals [12, 16]; gels [6, 10, 25], alumino-silicate melts [8, 26, 27] and plasma synthesis [9]. If the spinel had a composition of $Si_2Al_6O_{13}$ as proposed by Chakraborty and Ghosh [5], the formation of the tetragonal-like mullite would be inconceivable. The Al–Si spinel would have to decompose to (2 : 1) mullite with the liberation of silica. Ironically, Chakraborty and Ghosh observed no further liberation of silica after the first stage of silica liberation following the formation of the spinel! Hence, the above decomposition could not have taken place and the composition of the spinel is unlikely to be similar to that of (3 : 2) mullite. It follows therefore that the composition of the Al–Si spinel is most likely similar, if not, the same as the (2 : 1) mullite, i.e. $SiAl_4O_8$ or more specifically, $\square_4Al^{vi}_{12}[Al_4Si_4]^{iv}O_{32}$, where □ represents a vacancy and (iv) and (vi) are the coordination states of aluminium ions.

The proposed structure and composition of the Al–Si spinel is derived from the normal spinel AB_2O_4 or $B(AB)O_4$ with layer structures shown in Fig. 8. Brindley and Nakahira [1] adopted the same approach to derive their ill-fated spinel. The structure as a whole tolerates a number of statistically distributed cation vacancies. To satisfy the valency requirements of the mixed A–B layer, it is postulated that in the Al–Si spinel, 4 Si^{4+} and 4 Al^{3+} occupy the available 8 tetrahedral sites with $1\frac{1}{3}$ Al^{3+} in the octahedral sites leaving 4 octahedral sites being left vacant, as shown in Fig. 8. The layers purely in octahedral sites are occupied by $10\frac{2}{3}$ aluminium ions. On this basis, the composition of the unit cell is $\square_4Al^{vi}_{12}[Al_4Si_4]^{iv}O_{32}$. The alternative but similar model for the spinel would be $\square_4Al^{vi}_{16-x}[Al_xSi_4\square_{4-x}]^{vi}O_{32}$ where the possibility of only $x(<4)$ aluminium ions actually occupying the tetrahedral sites is taken into consideration. The former model is most suitable for the ideal or hypothetical ordered spinel only while the latter is more appropriate for the complex, highly unstable and less ordered spinel which may be conceived as the precursor of the ordered Al–Si spinel.

The above model has elegantly shown the presence of aluminium ions with both coordination numbers in the spinel. This proposition is consistent with the results reported by various workers mentioned earlier. Table III summarizes the Al(iv) and Al(vi) content of some compounds calculated theoretically. The average content of Al(iv) in both pure kaolinite and (3 : 2) mullite, as obtained by Bullens *et al.* [4], is given in Table IV. A perusal of these results suggests an initial increase in the content of Al(iv) when the (2 : 1) mullite is formed. This value then decreases gradually with increasing equilibrium heat-treatment temperature until the (3 : 2) mullite is formed. This phenomenon is consistent with the infrared results obtained in this investigation (Fig. 6) where a rather strong AlO_4 tetrahedral absorption band was observed for both the spinel and the tetragonal-like mullite phases. This band diminished in intensity while the intensity of AlO_6 octahedra absorption bands ($\sim 600\,\text{cm}^{-1}$) became more prominent when the orthorhombic mullite formed. Apparently, aluminium

TABLE III Theoretical Al(iv) and Al(vi) content of some compounds

Compound	Formula	% Al(iv)/Total	% Al(vi)/Total	Reference
Al spinel	$Al_8^{iv}(Al_{13\,1/3}\square_{2\,2/3})^{vi}O_{32}$	37.5	62.5	[1]
Al spinel	$(Al_{7.1}\square_{0.9})^{iv}(Al_{14.2}\square_{1.8})^{vi}O_{32}$	33.3	66.6	[41]
Al-Si spinel	$Si_8^{iv}(Al_{10\,2/3}\square_{5\,1/3})^{vi}O_{32}$	0	100.0	[1]
Al-Si spinel	$(Si_{4.9}Al_{3.1})^{iv}(Al_{11.7}\square_{4.3})^{vi}O_{32}$	20.9	79.1	[5]
Al-Si spinel	$(Si_4Al_4)^{iv}(Al_{12}\square_4)^{vi}O_{32}$	25	75	This study
Al-Si spinel	$(Si_4Al_x\square_{4-x})^{iv}(Al_{16-x}\square_x)^{vi}O_{32}$	0–25	75–100	
(3 : 2) Mullite	$3Al_2O_3 \cdot 2SiO_2$	55.5	44.5	[4]
(2 : 1) Mullite	$2Al_2O_3 \cdot SiO_2$	58.3	41.7	[4]

ions prefer to be in octahedral coordination because of minimal electrostatic energy or excess free energy (ΔG), a condition which is most favourable for the formation of stable or equilibrium phases.

So far, the identity and composition of the cubic phase have been unequivocally established. However, the relation of this phase to the sharp exotherm at ~ 970° C is yet to be clarified. The origin of this exotherm in kaolinite has been a matter of controversy for an extensive period of time. It has been attributed to several single effects: (a) crystallization of γ-alumina [2, 4, 28, 29]; (b) crystallization of quartz [30]; (c) crystallization of cristobalite [31]; (d) the formation of a double cation Al–Si defect spinel [1]; (e) nucleation of mullite [32, 33].

Lemaitre and Delmon [34] have recently proposed that the exothermic effect of metakaolinite could have a two-fold origin: (i) nucleation of mullite, and (ii) formation of γ-alumina. A three-fold origin was demonstrated by Chakraborty and Ghosh [5] in which liberation of amorphous silica was believed to occur in concert with the formation of Al–Si spinel and mullite. Thus, the sharp exotherm has been attributed to various causes, probably because of the extensive variation in the techniques of sample preparation and thermal treatments adopted by previous investigators.

The XRD results obtained for the heat-treated stoichiometric (3 : 2) mullite gel (Table I) serve to suggest that following the exothermic reaction at ~ 970° C, liberation of amorphous silica and crystallization of the Al–Si spinel occurred concurrently. The existence of these two phases was verified by the infrared results (Figs 6 and 7). The above sequence of reaction may also be perceived from the theoretical consideration of the chemical reactions which are thermodynamically possible following the thermal treatment of a mullite gel (Fig. 9).

According to the chemical reaction in Fig. 9, both Al–Si spinel and amorphous silica are formed following the thermal treatment of the mullite gel at ~ 1000° C. The enthalpy released gives rise to the elusive and controversial exotherm. Hence, the origin of the sharp exotherm is thus elegantly demonstrated. The equation in Fig. 9 also reveals that the formation of the spinel and the (2 : 1) mullite proceeds gradually with compositional and structural continuity. The structure and composition of the spinel formed in this reaction sequence is consistent with those rigorously formulated earlier.

TABLE IV Average Al(iv) content of fired samples [4]

Compound	Temperature (° C)	Time (h)	Al(iv) (%)
Pure kaolinite	800	24	69.7
Pure kaolinite	900	124	47.4
(3 : 2) mullite	1450	7	32.6

The enthalpy released determines the intensity of the exotherm which correlates with the extent of spinel formation and the liberation of amorphous silica. Gradual liberation of amorphous silica and gradual formation of spinel may occur if the mullite gel is given an equilibrium thermal treatment for an extensive period of time at a temperature below the 970° C exotherm. Subsequent heat treatment at a temperature well above the exotherm would only display a much diluted exotherm because much of the spinel formation and liberation of amorphous silica had already taken place, leaving the remnant to proceed gradually with the reaction. Complete disappearance of the exotherm may even occur if the equilibrium thermal treatment below 970° C is allowed to proceed for very long durations such that complete formation of Al–Si spinel and liberation of amorphous silica take place. Under favourable conditions, some (2 : 1) mullite may even form. This may offer an explanation as to why Roy *et al.* [32] observed the cubic phase at 850 and 650° C, respectively, in kaolinite and halloysite heated for long periods. The same argument applies to the result reported by Comer [35] who obtained mullite when his kaolinite was heated at 850° C for 20 h.

The gradual transformation of the spinel to (2 : 1) mullite following an equilibrium treatment at ~ 1000° C is readily viable according to the above reaction. This viability may serve to explain why previous investigators wrongly ascribed the formation of mullite as a possible cause for the exothermic reaction. The rate of spinel to (2 : 1) mullite transformation is controlled by many factors [36] and it is the interplay and complexity of these factors which has given rise to much uncertainty and confusion among previous workers.

The second exotherm of the reaction sequence in kaolinite has also attracted much controversy. Chakraborty and Ghosh [5] convincingly demonstrated that the second exotherm is the conversion of the spinel to (3 : 2) mullite rather than due to the crystallization of cristobalite. The absence of cristobalite in the mullite gel treated at 1300° C for 10 h (Table I) serves to verify the results obtained by the above workers. Similar observations were also reported by Wahl and Grim [37] and Slaughter and Keller [38].

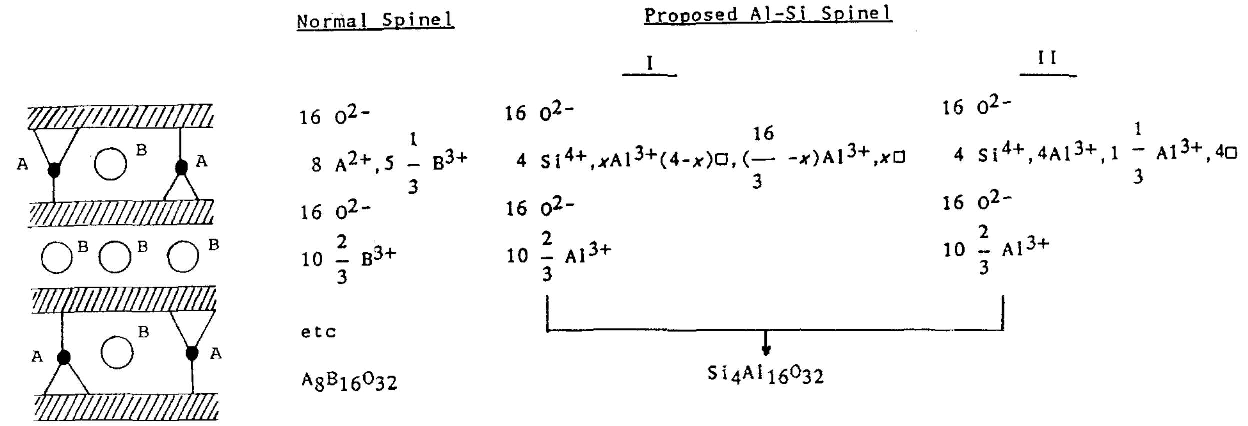

Figure 8 Schematic representation of layer succession in a normal spinel structure. Shaded bonds represent layers of oxygen atoms. (○) Atoms in octahedral coordination, (●) atoms in tetrahedral coordination.

4.2. The mechanisms of mullite formation

As has been shown by the reaction sequence in Fig. 9, the transformation of the spinel to (2:1) mullite is a gradual and continuous process because of the remarkable resemblance in the composition and structure between these two phases. According to the proposed model for the composition of the cubic Al–Si spinel, i.e. $\square_x \mathrm{Al}^{\mathrm{vi}}_{16-x}[\mathrm{Al}_x\mathrm{Si}_4\square_{4-x}]^{\mathrm{iv}}\mathrm{O}^{32}$ and the contents of tetrahedral aluminium ions in the spinel ($<25\%$), (2:1) mullite (58.3%) and (3:2) mullite (55.5%), the formation of (2:1) mullite from the spinel would inevitably involve a redistribution of aluminium ions, probably via lattice diffusion, whereby some octahedral aluminium ions migrate to tetrahedral sites, causing the content of aluminium ions with tetrahedral coordination to increase. The presence of a large number of vacancies and their ordering mechanism may serve to enhance this process, giving rise to a gradual improvement in crystallinity and ionic bond strengths. Formation of (3:2) mullite from (2:1) mullite is far more complicated than the reduction of aluminium ions with four-fold coordination because they have rather different compositions, unit cell volumes and crystal defect concentrations or morphology. The ordering of vacancies and the concomitant formation of large vacancy domains are believed to be responsible for the superlattice reflections observed by Cameron [15], Sadanaga *et al.* [12] and Tokonami *et al.* [13] in their aluminous or (2:1) mullites. Apparently, the (2:1) mullite has a high degree of order, with respect to its high concentration of vacancies, in comparison with the equilibrium (3:2) mullite. This observation is consistent with results obtained by ^{27}Al MASNMR on mullite gels heat treated at high temperatures [21]. Heat treatment of gels at 500° C caused partial conversion of octahedral aluminium to tetrahedral aluminium. The aluminium in highly crystalline mullite of gels treated at 1380° C is much more disordered compared to poorly crystalline mullite or gels treated at low temperatures. It follows, therefore, that the transformation of the (3:2) mullite from the (2:1) mullite would inevitably involve the random substitution of silicon for aluminium ions in the ordered (2:1) mullite. As more silicon is substituted, there are fewer vacancies left so that a correlation between them becomes more difficult and as a result, the superstructure reflections become more diffuse and domains widths smaller [15]. In summary, siliceous mullites have very diffuse superstructure reflections and a short domain repeat but with increasing Al_2O_3 content, the spots become sharper and domains grow larger. In short, as mullite becomes more aluminous, its degree of order increases.

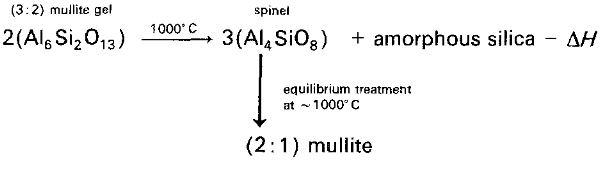

Figure 9 Schematic route for the crystallization of a mullite gel.

The results of cell dimension measurements (Figs 3 and 4) indicate that (3:2) mullite has a smaller cell volume but a higher content of silica than the (2:1) mullite which may serve to suggest that some form of substitution between aluminium and silicon cations has taken place. Because the ionic bond lengths of Al(iv)–O, Al(vi)–O and Si–O are 0.1971, 0.1852 and 0.1740 nm, respectively, substitution of silicon for Al(iv) would inevitably shorten the cell dimensions of (3:2) mullite and reduce the content of aluminium ions with tetrahedral coordination. The latter may offer a satisfactory explanation for the reduction of the content of tetrahedral aluminium ions from 58.3% in the (2:1) mullite to 55.5% in the (3:2) mullite (Table IV). High heat-treatment temperatures and long equilibrium heating were most effective in enhancing the substitution process ($2\mathrm{Si} + \mathrm{O} \leftrightarrows 2\mathrm{Al} + \square$), with the latter being the most pronounced (Fig. 5). A high degree of crystallinity with stronger ionic bonds may also contribute to reduce the cell dimensions or cell volume further in the well-crystallized (3:2) mullite. The readily available silicon and oxygen ions are believed to come from the amorphous silica which is released during the 970° C exothermic reaction. According to the above substitution process, a vacancy is eliminated for every two aluminium ions being replaced by silicon ions. Oxygen atoms play an essential role during the (2:1) to (3:2) mullite evolution. These observations are consistent with the fact that fewer vacancies are present in the orthorhombic mullite and the superlattice reflections are more diffuse.

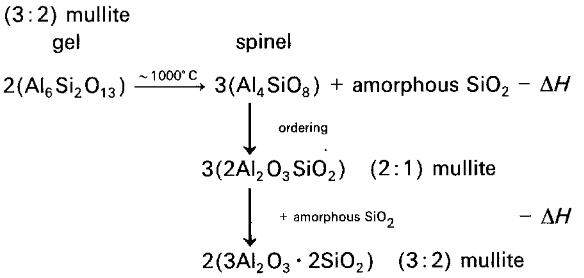

Figure 10 Schematic route of mullite evolution.

Two probable chemical reactions may be proposed for the transformation of (2:1) to (3:2) mullites

$$3(2Al_2O_3SiO_2) + \text{amorphous } SiO_2 \xrightarrow{\sim 1250°C} 2(3Al_2O_32SiO_2) \quad (1)$$

$$5(2Al_2O_3SiO_2) + \text{amorphous } SiO_2 \xrightarrow{\sim 1250°C} 3(3Al_2O_32SiO_2) + Al_2O_3 \quad (2)$$

According to the above reactions, no cristobalite is expected from Reaction 1 while some corundum (7.4%) forms in Reaction 2. A perusal of the results in Table I apparently favours the second reaction. However, only traces of corundum were obtained in the (3:2) mullite composition, which could be the result of unavoidable minor inhomogeneity in the gel rather than due to the chemical Reaction 2. Therefore, the complete details of mullite gel to crystalline phase evolution may be written as shown in Fig. 10.

According to the schematic route in Fig. 10, the equilibrium amount of amorphous silica released is being utilized for the substitution process of 2Si + O $\rightleftharpoons$ 2Al + □ in order to achieve the formation of equilibrium (3:2) mullite. It follows that if the silica is leached out partially or completely, then, there is insufficient silica left for the completion of the substitution process to form the (3:2) mullite and the (2:1) mullite formed should in theory persist indefinitely irrespective of post-treatment temperatures and duration. In practice, the (2:1) mullite formed would decompose into the stable phases of (3:2) mullite and corundum (~ 19%) as follows

$$\underset{(2:1)\text{ mullite}}{2(2Al_2O_3SiO_2)} \xrightarrow{1300°C} \underset{(3:2)\text{ mullite}}{3Al_2O_32SiO_2} + \underset{\text{corundum}}{Al_2O_3}$$

Therefore, the corundum obtained in the leaching experiments is a result of the decomposition of (2:1) mullite rather than derived from the γ-alumina liberated following the leaching of the cubic phase as claimed by previous investigators [2, 5]. As a matter of fact, the leached samples of these investigators were Al–Si spinels which, in the absence or presence of insufficient silica, formed metastable (2:1) mullites which subsequently decomposed to (3:2) mullites and corundum. These observations are consistent with the structure and composition of the Al–Si spinel and serve to provide further evidence for the identity of the controversial cubic phase. This decomposition of (2:1) mullite is also believed to be responsible for the formation of corundum in the mullite with 80 wt % Al_2O_3 [36]. Because this mullite is outside the range of the solid solution of mullite which extends from 72 to 78 wt % Al_2O_3, the amount of amorphous silica liberated is insufficient for complete substitution reaction, leaving the excess (2:1) mullite formed to decompose to stable phases of mullite and corundum. A similar argument applies to metakaolinite (46 wt % Al_2O_3). In this case, the amorphous silica liberated would be more than sufficient for the equilibrium process of silicon for aluminium substitution and the excess silica is crystallized as cristobalite. This model is consistent with the decomposition of mullite by silica volatilization as reported by Iwai and Watanabe [39]. They also observed that when mullite decomposed into corundum, their oxygen close-packed planes were almost preserved. Clearly, volatilization of silica deprives the mullite of the equilibrium amount of silica, resulting in the formation of a metastable aluminous mullite which subsequently decomposes to the stable form of mullite with corundum being released. A similar observation was also reported by Davis *et al.* [40].

Perhaps the most convincing evidence and verification of the model proposed above comes from the work of Brown *et al.* [22]. Interpretation of XRD results and solid state ^{29}Si and ^{27}Al nuclear magnetic resonance spectra of kaolinite fired at 800 to 1450° C led these workers to arrive at the following conclusions about the high-temperature transformations in the kaolinite–mullite reaction sequence. (a) Removal of the final residual hydroxyl radicals of metakaolinite at around 970° C triggers the separation of a considerable amount of amorphous silica and the formation of poorly crystalline mullite and a spinel phase; (b) mullite and spinel form in tandem, the former originating in the vicinity of Al–O units of regular octahedral and tetrahedral symmetry randomly distributed throughout the metakaolinite structure; (c) the mullite initially formed is alumina-rich but at higher temperatures it progressively gains silica, approaching the conventional $3Al_2O_3 \cdot 2SiO_2$ composition; (d) the spinel phase contains insufficient silicon to be detected by ^{29}Si NMR but has a ^{27}Al NMR spectrum consistent with γ-alumina. On further heating, the spinel is converted to mullite by reaction with some of the amorphous silica, the balance of which eventually becomes cristobalite.

It is believed that the equilibrium and reversible reaction of 2Si + O $\leftrightharpoons$ 2Al + □ is responsible for the existence of a solid solution between (3:2) and (2:1) mullites. This evidence is indicated by the linear plots of cell parameter, *a*, and cell volume, C_v, against composition (Figs 3 and 4). The results suggest that chemical composition rather than Al–Si order is the underlying cause of this simple relation. Differing states of order are highly unlikely to give rise to such a simple relation, even though mullites were treated in diverse thermal histories. These varying degrees of order are exhibited as superlattice reflections with varying intensities or sharpness.

As mentioned earlier, Chakraborty and Ghosh [5] proposed that the second exotherm in the DTA curve corresponded to the disappearance of the Al–Si spinel and the subsequent formation of the (3:2) mullite. However, they did not explain why the cristobalite

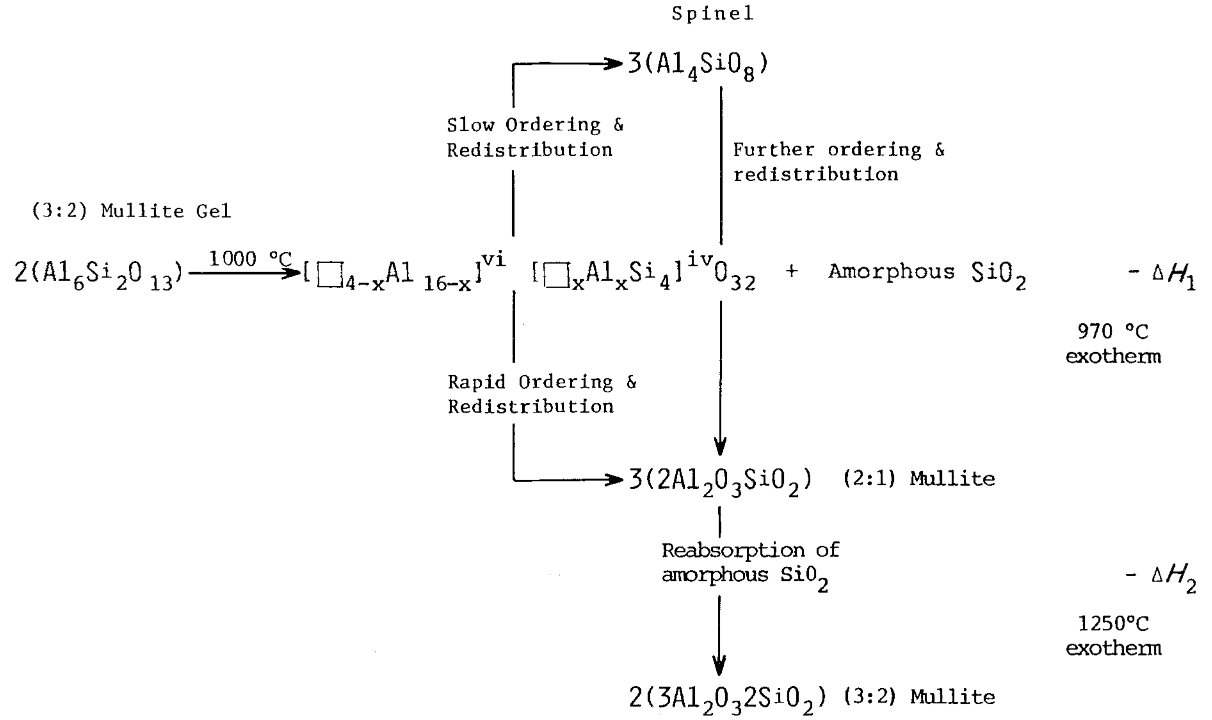

Figure 11 Schematic routes for the phase transformations in the evolution of mullite formation.

phase crystallized without any exothermic reaction. It follows, therefore, that the second exotherm could be due to the crystallization of cristobalite in kaolinite. This hypothesis may also be applicable to gels. A perusal of the results in Table I indicates a persistent absence of cristobalite even if the mullite gel was treated for 10 h, thus excluding the crystallization of cristobalite as the cause of the second exotherm. Because (3 : 2) mullite forms only at a temperature after the second exotherm, a direct correlation between them exists.

It is believed that the intensity of the second exotherm depicts the rate at which (2 : 1) mullite transforms to (3 : 2) mullite and this rate is controlled by a number of factors. Similarly, the intensity of the first exotherm is thought to be governed by the rate at which the spinel precursor converts to the transitional phase (either spinel or (2 : 1) mullite) prior to the formation of the equilibrium (3 : 2) mullite. As reported elsewhere [36] the author has attributed the elusive behaviour of crystallization and phase transformations in alumino-silicate systems to the excess free energy present which in turn is a complex function of many variables, with parent materials and preparation process being most crucial. The origins and phase transitions during mullite formation in an alumino-silicate system irrespective of parent materials and preparation process are summarized in Fig. 11.

5. Conclusions

The crystallization behaviour of gels with mullite compositions has been studied in detail by XRD, DTA, infrared and chemical analysis. The results of this investigation have established: (i) the identity of the controversial cubic phase; (ii) the chemical, structural and compositional continuity in the evolution and transformation of mullite gel to crystalline phases; (iii) the existence of a solid solution between (3 : 2) and (2 : 1) mullites; (iv) the origins of the exotherms, and (v) the origins of mullite formation.

The results obtained indicate that an Al–Si spinel precursor ($\Box_x Al^{vi}_{16-x}[Al_x Si_4 \Box_{4-x}]^{iv} O_{32}$) with a composition similar to that of the (2 : 1) mullite is always formed which may either reorder gradually or instantaneously to (2 : 1) mullite. This ordering process is believed to be very sensitive to the parent materials used and the preparation process adopted in which they serve to introduce many variations in the excess free energy of these mullite systems which ultimately dictate the rate of ordering in the spinel precursor and the behaviour of crystallization in alumino-silicate systems.

The first exotherm during the thermo-chemical reaction of a mullite has been attributed to the formation of the spinel in concert with the liberation of amorphous silica and heat. The same applies to the single exotherm which is displayed in alumino-silicates where direct mullite formation occurs. The amorphous silica is very essential for the transformation of the metastable (2 : 1) mullite to the equilibrium one via a substitution process of silicon for aluminium. Excess silica may crystallize as cristobalite as in kaolinites. Insufficient or lack of amorphous silica can cause the metastable mullite to decompose to (3 : 2) mullite and corundum as in mullites with more than 78 wt % Al_2O_3 or in chemically (NaOH or HF) leached mullite samples. The transformation of (2 : 1) mullite to (3 : 2) mullite gives rise to the formation of the second exotherm in kaolinites and some gels. The absence of this exotherm in mullites derived from melts, plasma and some gels may be due to structural variations inherent in them as a result of the parent materials used and preparation process adopted.

The cell dimension measurements suggest that mullite, irrespective of its starting composition and its method of preparation, always displays a simple solid solution between the extremes of $3Al_2O_32SiO_2$ and $2Al_2O_3SiO_2$ where the cell parameters vary smoothly with alumina content.

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