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Effect of ultrastructure on crystallization of mullite

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The effect of pre-mullite structure on crystallization of mullite from aluminosilicate gels was investigated. The aluminosilicate gels were prepared by hydrolytic poly condensation of silicon alkoxide aluminium with alkoxide, with colloidal alumina and with aluminium nitrate. The structural differences in these materials were characterized by ^{27}Al and ^{29}Si nuclear magnetic resonance and X-ray diffraction. Their thermal behaviour was monitored by differential thermal analysis. These investigations show that the crystallization process in this system is fundamentally affected by the nature of the ultrastructure. A spontaneous crystallization of mullite at ~ 980 °C is promoted by a high degree of homogeneity and the network connectivity between silicon and aluminium. A method that provides condensation of such an ultrastructure is also given.

1. Introduction

Owing to its technological significance, mullite formation by sol–gel methods has been investigated by a number of researchers [1–6]. A question of fundamental importance, and considerable debate, in these studies deals with the thermodynamic stability and crystallization processes leading to mullite formation. A number of investigators reported that crystallization of cubic spinel and α-Al_2O_3 precede mullite formation at 1200–1300 °C. Others reported that mullite may crystallize directly from amorphous gels at ~ 980 °C. In some studies, the differential thermal analysis (DTA) exotherm is related to spinel formation [7, 9], whereas in others, it is related to mullite [6–10].

Sol–gel methods involve the use of colloidal suspensions, soluble salts, and metal–organic compounds as starting materials. These materials produce different levels of homogoeneity and different types of ultrastructure in their pre-ceramic gels. When colloidal suspensions are used, the homogeneity is limited to the colloidal dimensions. When soluble salts such as nitrates are used, a high degree of homogeneity may be obtained without network connectivity. A room-temperature condensation of the oxide network with a high degree of homogeneity occurs only when alkoxides are used. Thus, these techniques produce different levels of homogeneity and different types of bonding in the pre-ceramic gels. Evidence indicates that the nature of the chemical bonding and the degree of homogeneity in these pre-ceramic gel structures, in turn, affect the crystallization, sintering and the microstructure [6, 11].

Because the hydrolytic polycondensation rates of aluminium alkoxides differ significantly from that of silicon alkoxides [12], a homogeneous oxide network cannot readily be condensed from the alkoxide mixtures in this system. Several techniques have been proposed to promote co-polymerization. It was found that the alkoxide mixtures condense to a more homogeneous oxide network when the overall condensation rate is significantly reduced [6]. For example, humidity hydrolysis of silicon and alumina alkoxide mixtures in a heavy alcohol, e.g. tertiary butanol, at low concentrations, 1%–3%, e.g. oxide, results in a homogeneous co-polymerization. Another method involves partial hydrolysis of $Si(OR)_4$ to a monomer state before the introduction of $Al(OR)_3$ [6]. In these methods the network homogeneity is extremely sensitive to the kinetics of the process. For this reason a less kinetically sensitive condensation method was devised which essentially eliminates the rate sensitivity of the process.

In the present work, different types of aluminosilicate ultrastructure were formed by different sol–gel methods, and their crystallization behaviour was investigated to elucidate the effect of pre-crystalline ultrastructure on mullite crystallization.

2. Experimental procedure

Samples were prepared by reacting $Si(OCH_3)_4$ with three different aluminium compounds. The first method involves the reaction of silicon methoxide, $Si(OR)_4$, with a colloidal alumina sol. This gel is referred to as a colloidal gel. The second method involves the condensation of an aluminosilicate network from aluminium and silicon alkoxides in a particular manner. This gel is referred to as a polymeric gel. The third method involves the use of a soluble aluminium salt, $Al(NO_3)_3 \cdot 9H_2O$, with $Si(OCH_3)_4$. This gel is referred to as nitride derived gel.

Colloidal alumina sol is prepared by hydrolysing 1 mol aluminium secondary butoxide, $Al(OC_4H_9)_3$, in 100 mol water at 70 °C and peptizing it with 0.07 mol HNO_3 acid to a clear state. This sol contains

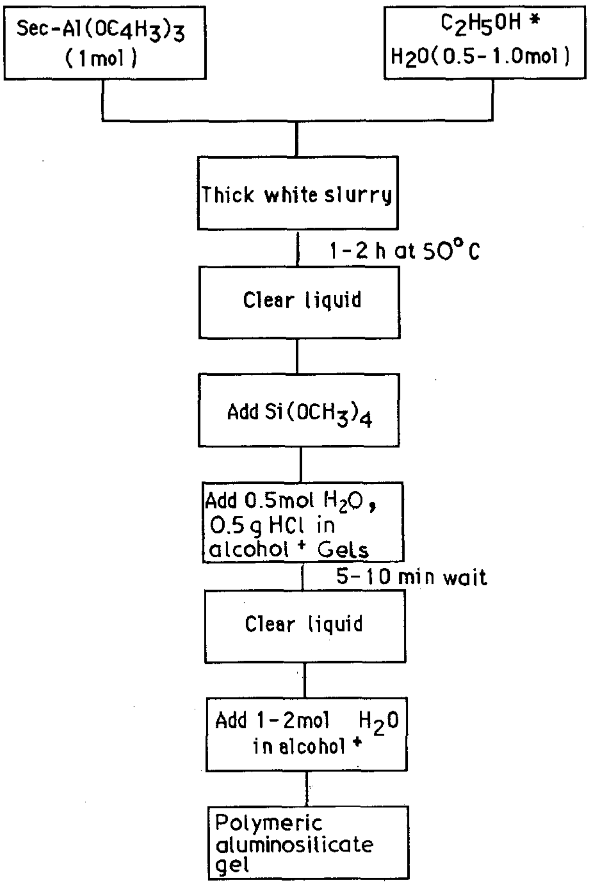
10–30 nm size AlO(OH) colloids whose detailed preparation is given elsewhere [13]. The sol was concentrated to a 10 wt % eq. Al_2O_3 level by evaporation of H_2O and diluted back to a 5 wt % level by methanol to facilitate the miscibility of $Si(OR)_4$. The stoichiometric amount of $Si(OCH_3)_4$ was added while stirring to produce the mullite composition. Mixing of these two components leads to gelling within a short period of time. Drying and heat treating the gel yields large transparent granules having mullite composition, $3Al_2O_3 \cdot 2SiO_2$. This results in the formation of a chemically bonded silica shell around and between the AlO(OH) colloids. Although chemical bond formation occurs between aluminium and silicon by the reaction

$$\equiv \text{Si–OR} + \text{HO–[AlO(OH)}_{(n-1)/n}]_n \rightarrow \equiv \text{Si–O–[AlO(OH)}_{n-1/n}]_n + \text{ROH} \quad (1)$$

the ultrastructure is a nanocomposite, whose homogeneity is limited to dimensions of AlO(OH) colloids.

The polymeric gel preparation method involves an initial formation of a clear, stable polyorganoaluminium solution by hydrolysis of $Al(OR)_3$ with 0.5–1.0 mol water in dry ethanol [14]. The experimental solution used for this investigation was prepared by adding 6 g water to 375 g dry ethyl alcohol in a glass jar. To this, 123 g $Al(OC_4H_9)_3$ (1/2 mol) was added and vigorously shaken. A thick white slurry resulted which turned into a water-clear liquid within an hour when kept at ~ 50 °C. This happens only when the total water presence is between 0.5 and 1.0 mol per mol alkoxide. After clarity was obtained, 25.4 g $Si(OCH_3)_4$ was added to this solution to correspond to stoichiometric mullite composition, i.e. Al/Si = 3. 9 g water mixed with 0.5 g HCl and 100 g methanol were added at once to this solution and vigorously shaken. Immediate gelling occurred creating aluminium silicon linkage. This gel returned to a clear liquid state within 5–10 min. To complete the hydrolytic condensation, another 13 g water were mixed with 100 g methanol and added to this clear liquid. The liquid gelled for the second time within 5–10 min, this time irreversibly. The gel was dried and heated to 500 °C to form the polymeric mullite precursor. A schematic representation of this process is shown in Fig. 1.

Mullite precursor providing molecular level homogeneity without network connectivity was prepared from $Al(NO_3)_3 \cdot 9H_2O$ and $Si(OCH_3)_4$ in an alcohol



* Dry ethanol used to assure 0.5-1.0 mol total water present, for best results use at least 10 mol ethanol/mole alkoxide.

\+ Water should be diluted in alcohol, 1/10 ratio to prevent inhomogeneous gelling

Figure 1 The polymeric aluminosilicate condensation method.

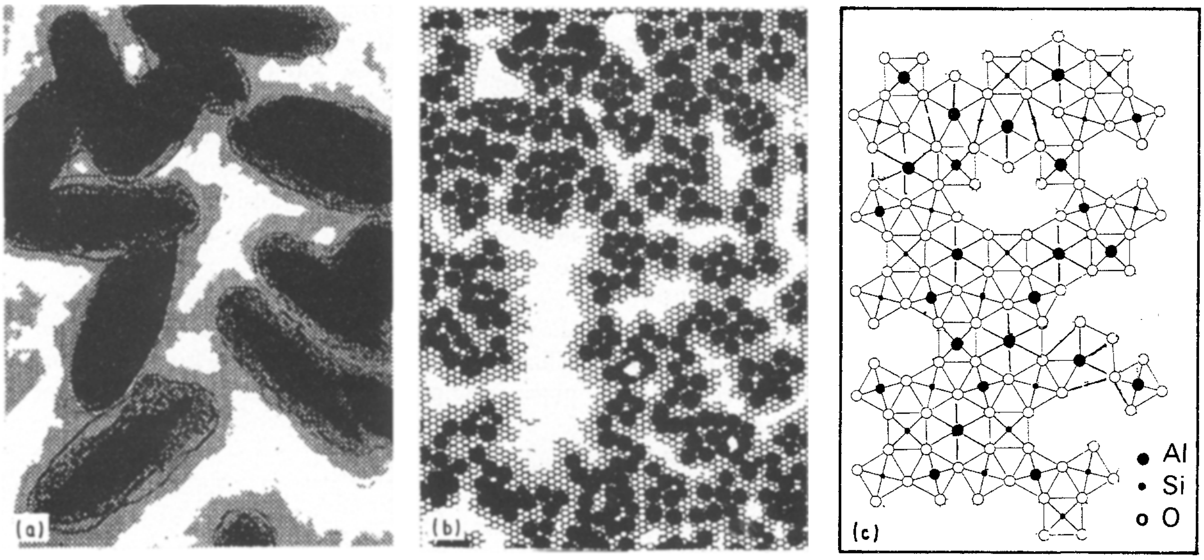


Figure 2 Schematic representation of aluminosilicate ultrastructure formed by reaction of $Si(OCH_3)_4$ with (a) colloidal alumina, (b) aluminium nitrate, and (c) aluminium alkoxide by copolymerization method.

solution. This was done to delineate the effects of these two parameters. A schematic representation of the ultrastructures expected from these preparations is shown in Fig. 2.

3. Results and discussion

^{27}Al magic angle spinning (MAS) NMR spectra were obtained using a spectrometer (Model 360-1, Spectral Data Services, Inc. Champaign, IL) operating at 94.7 MHz. The samples were spun at 8–10 kHz with a 2.1 μs pulse. At least 5000 scans were accumulated for the Fourier transformation. Structural studies of mullite precursor gels by ^{27}Al MAS NMR have been conducted by other investigators [15–19].

Fig. 3 shows the ^{27}Al MAS NMR spectroscopy of the colloidal alumina used in the preparation of colloidal aluminosilicate samples heated to 500 °C. Fig. 4 shows the ^{27}Al MAS NMR spectra of the aluminosilicate prepared from this alumina heated to 500, 1050 and 1300 °C. Comparison of Figs 3 and 4 clearly shows that the aluminium environment in the colloidally prepared aluminosilicate remains similar to the aluminium environment in the precursor aluminium colloids even after heating to 1050 °C. In these figures, the peak at 5–7 p.p.m. is assigned to the octahedral site. The peak at ~ 65 p.p.m. is assigned to tetrahedral sites [20–22]. Only in the sample heated to 1300 °C do the ^{27}Al MAS NMR become characteristic of mullite.

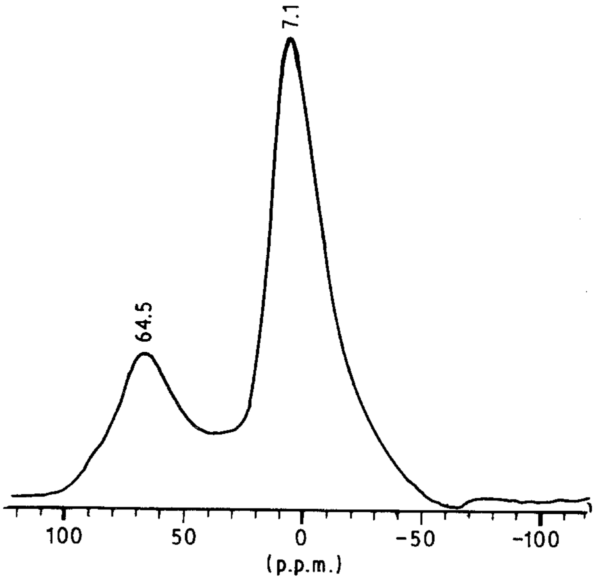


Figure 3 ^{27}Al MAS NMR spectra of precursor colloidal alumina at 500 °C.

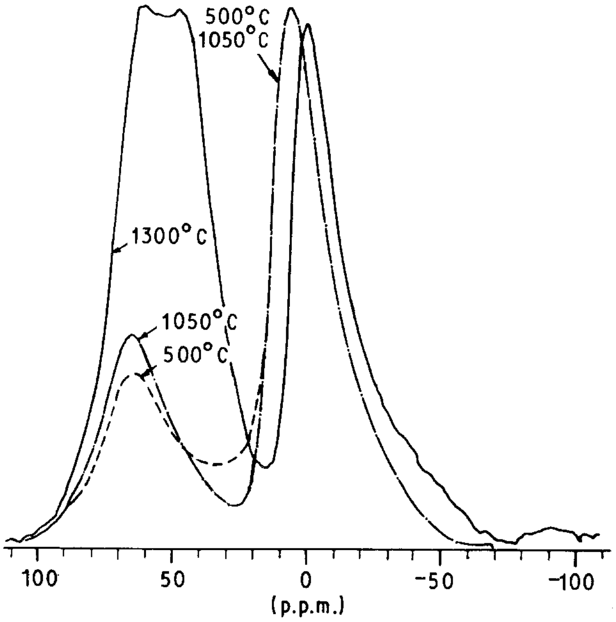


Figure 4 Aluminium environment in colloidal aluminosilicate gel as indicated by ^{27}Al MAS NMR heated to 500, 1050 and 1300 °C. Note that the aluminium environment in this structure is similar to that of colloidal Al_2O_3 at 500 and 1050 °C.

Fig. 5 shows the X-ray diffraction (XRD) patterns of the same sample heated at a rate of 10 °C min^{-1} to 950, 1050, 1200 and 1300 °C and held for 10 min. In this structure there is no hint of mullite phase at 1050 °C. The diffused peaks occurring at 46° and 67°

2θ values have been normally assigned to cubic spinel (JCPDS 10-425). They could also be assigned as the principal peaks of unreacted δ or γ-Al_2O_3 which commonly occurs in transition aluminas. These XRD peaks, however, disappear when mullite is fully developed at 1300 °C as shown in Fig. 5. In pure aluminas they would have disappeared by α-Al_2O_3 transformation.

^{27}Al MAS NMR spectra of the polymeric aluminosilicate gel heated to 500, 950 and 1050 °C are shown in Fig. 6. Here an entirely different aluminium environment is indicated. In this structure, the majority of aluminium sites are pentahedrally coordinated. As the material is heated a slight increase in the number of 4- and 6-coordinated sites appears to occur. More importantly, a fundamental transformation between 950 and 1050 °C is indicated. During this transformation, 5-coordinated aluminium sites are eliminated and the material exhibits the characteristic mullite MAS NMR spectra. The precise nature of this structural transformation is elucidated by the XRD patterns shown in Fig. 7. Here it is shown that the amorphous phase at 950 °C has transformed to the fully developed crystalline mullite phase at 1050 °C. Again we see diffused XRD peaks at 2θ 46° and 67°. These peaks can be assigned to cubic spinel or trace amounts of unreacted transition aluminas. It was noticed that a slightly excessive amount of silica tends to eliminate these peaks.

The differential thermal analyses of these gels are shown in Fig. 8. In the polymeric structure, the crystallization temperature of mullite from the amorphous phase is pinpointed with a strong exothermic peak at

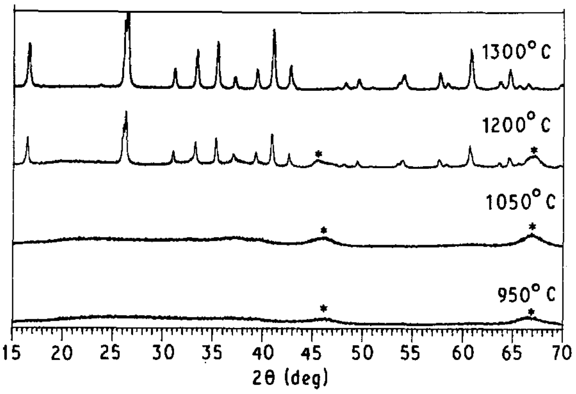


Figure 5 XRD patterns of colloidal aluminosilicate gel heated to 950, 1050, 1200 and 1300 °C. The two peaks on each pattern marked by asterisks do not belong to mullite.

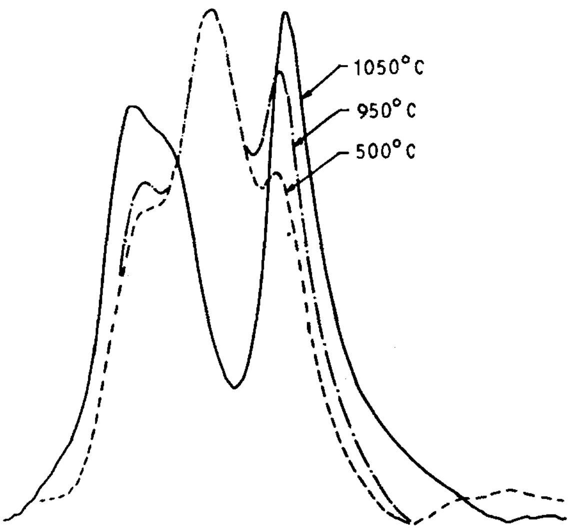


Figure 6 ^{27}Al MAS NMR indicating an entirely different aluminium environment in polymeric $Al_6Si_2O_{13}$ gels. It also shows that a fundamental transformation occurs between 950 and 1050 °C where pentahedral sites, 30 p.p.m., are eliminated. The structure exhibits characteristics of mullite NMR spectra, after the transformation.

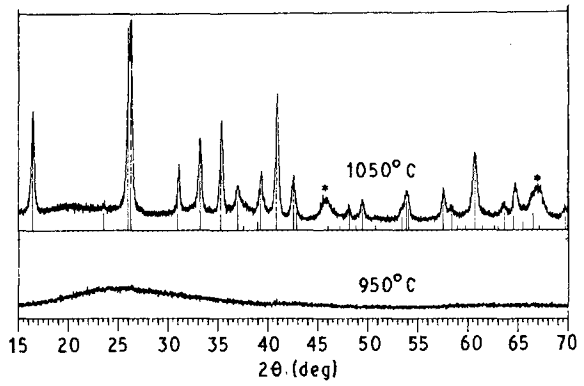


Figure 7 XRD patterns showing the amorphous polymeric $Al_6Si_2O_{13}$ gel at 950 °C crystallizes to mullite when heated to 1050 °C. (Bars indicate mullite pattern, JCPDS 15-776.)

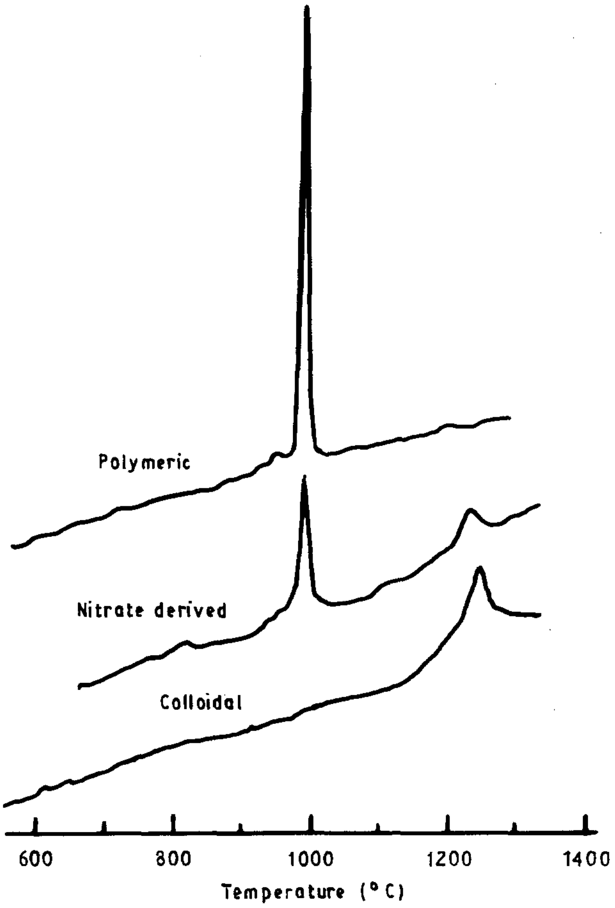


Figure 8 DTA curves of the aluminosilicate gels showing the exothermic peaks associated with mullite crystallization in these structures.

~ 980 °C. There is no peak at 1200 °C which is normally associated with the presence of free alumina in the system. The material exhibits significant densification during this transformation. The thermal energy associated with the enthalpy change in this transformation apparently is not expanded on large structural arrangements. Thus it becomes available for sintering. Colloidal gel shows no 980 °C peak. A diffused DTA peak, with one-tenth of the intensity of the 980 °C peak of the polymeric system occurs between 1200 and 1300 °C. This peak reflects the gradual formation of mullite in this ultrastructure.

Finally, the question arises whether the spontaneous crystallization of mullite at ~ 980 °C is prompted by the higher degree of homogeneity in the polymeric gels, or whether the presence of an inorganic network also plays a role. The X-ray results shown in Fig. 9 indicate that some mullite crystallization has already occurred at 1050 °C in the precursor, providing molecular level homogeneity without the network linkage. However, the crystallization is not as extensive in this case as it is in the polymeric structure under the same heat-treatment condition. The degree of mullite crystallization in this structure is also reflected by the relative intensities of the 980 °C DTA peaks shown in Fig. 8. Again, there are diffused XRD peaks at 2θ 46° and 67° at 1050 °C. These peaks, however, disappear by 1200 °C when the fully developed mullite crystallinity is exhibited. The ^{27}Al MAS NMR spectroscopy of this material indicates that initially the aluminium environment is similar to that of the polymeric structure due to the similarly high degree of homogeneity. However, as the material is heated close to ~ 1000 °C, alumina appears to coalesce to a state similar to the colloidal one prior to mullite crystallization (Fig. 10), presumably due to the absence of chemical linkage between silicon and aluminium. Fig. 11 compares the relative stages of mullite crystallinity in the three aluminosilicate ultrastructures under the same 1050 °C heat-treatment condition.

These studies indicate that both the homogeneity and the presence of pre-polymerized inorganic networks promote mullite crystallization. When both conditions exist a spontaneous mullite crystallization occurs at ~ 980 °C with a strong exothermic reaction.

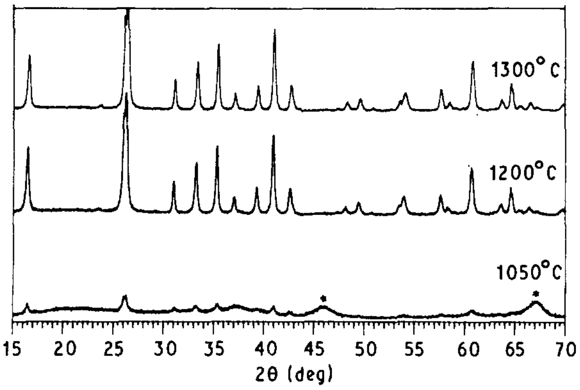


Figure 9 XRD patterns of nitrate-derived $3Al_2O_3 \cdot 2SiO_2$ gel showing that mullite crystallization in this structure is not as spontaneous or as extensive as in the polymeric structure at 1050 °C.

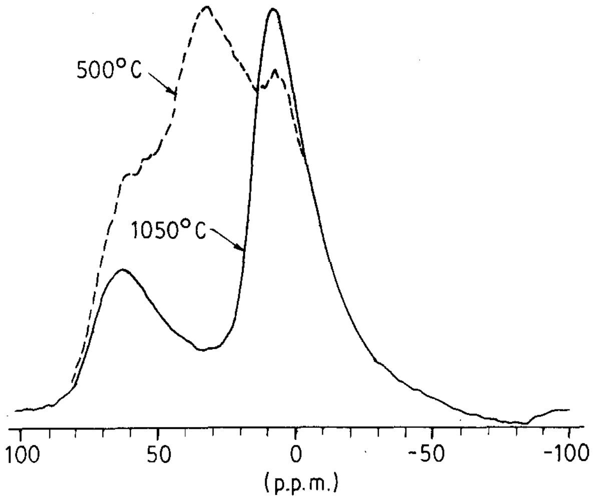


Figure 10 ^{27}Al MAS NMR spectra of nitride-derived $3Al_2O_3 \cdot 2SiO_2$ gel at 500 and 1050 °C.

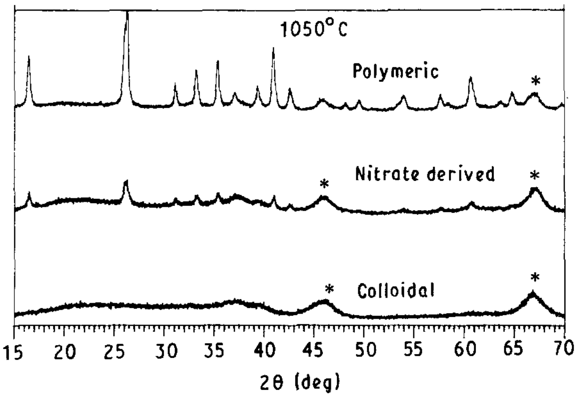


Figure 11 Comparison of relative mullite crystallization in three ultrastructures at 1050 °C. The top pattern represents 100% crystallization (the two peaks marked by asterisks do not belong to mullite).

4. Conclusion

It has been demonstrated that aluminosilicates prepared by different chemical methods crystallize differently. Crystallization in this system is fundamentally affected by chemical bonding, homogeneity, molecular size and morphology in the ultrastructure. In chemically condensed networks, the structural properties are determined as much by the condensation parameters as by the chemical composition. Thus, what crystalline phase that will emerge when a chemically condensed aluminosilicate network becomes thermodynamically unstable, at ~ 1000 °C, appears to be strongly dependent on the nature of the ultrastructure. A spontaneous crystallization of mullite at ~ 980 °C, appears to require both a high degree of homogeneity and the presence of polymerized aluminium–silicon networks. A sol-gel preparation method that provides these conditions in the ultrastructure is given.

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