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Structural Differences in Mullite Xerogels from Different Precursors Characterized by ^{27}Al and ^{29}Si MASNMR

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IN HONOR OF SIR JOHN MEURIG THOMAS ON HIS 60TH BIRTHDAY[1]

Mullite ($3Al_2O_3.2SiO_2$) was prepared from different precursors by multicomponent metal alkoxide and metal alkoxide–metal nitrate methods. Extreme hydrolysis conditions were used to prepare mullite gels of various degree of homogeneities. Thermal treatment of the mullite gels prepared by the multicomponent metal alkoxide method led to the crystallization of pure mullite powder at lower temperatures (≤1200°C) via a cubic spinel phase, while the gel prepared by the metal alkoxide–metal nitrate method crystallized to mullite completely only around 1300°C, via a cubic spinel and α-Al_2O_3. The nearest neighbor environments of aluminum and silicon in the gels themselves and after they were heated to various temperatures were studied by ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance (MASNMR) spectroscopy. The sequence of VI, V, and IV coordination changes in aluminum are clearly identified. The results show that there are clear differences in structure at the nearest neighbor level between nitrate–organic and purely organic derived gels. The difference between gels derived from tetraethylorthosilicate (TEOS) and tetramethylorthosilicate (TMOS) are also clearly shown. The exotherm appearing between 970 and 995°C in the differential thermal analysis (DTA) curve is discussed based on the X-ray diffraction (XRD) and MASNMR data. ^{29}Si MASNMR results indicated the presence of silica-rich regions with some Si(Al) or residual–OH groups attached to silicon in the partially crystallized samples containing the cubic spinel.

Introduction

Mullite and mullite-based ceramics have again received significant attention in recent years because of their electronic, optical, and high-temperature structural applications (*1–3*). In the Al_2O_3–SiO_2 system, the solid-state reaction between alumina and silica results, at equilibrium in the formation of mullite, the only stable phase at high temperatures (*4*). However, the reaction paths leading to the formation of mullite can be altered by the choice of alumina, silica, and various aluminosilicate precursors. This has been the subject of much research for four decades. Furthermore, chemical homogeneity of sol–gel precursors, that is the scale of mixing between aluminum and silicon can be shown to play an important role in the mechanisms and temperature range of mullite formation. Hence it offers a probe into these reaction paths.

Hoffmann *et al.* (*5*) divided sol–gel mullite precursors into monophasic and diphasic according to their scale of mixing. A single phase requiring homogeneity on the order of a few nanometer. The monophasic precursor was shown to form mullite by an exothermic reaction at about 980°C. Several authors have suggested that this exothermic peak can also be attributed to the formation

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[1] It is particularly appropriate that we dedicate this article to honor Professor J. M. Thomas, since he introduced us to MASNMR techniques, which resulted in several joint papers (see e.g., Ref. (*26*)).

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of γ-Al_2O_3 or an Al–Si spinel (*6–8*). As evidenced by a high temperature exothermic reaction (1250–1350°C), the formation of mullite in the diphasic precursor can be related to the direct reaction of alumina particle and silica-rich amorphous matrix.

Yoldas and co-workers (*9, 10*) have studied the effect of precursors and preparation conditions on the structure of monophasic aluminosilicate gels. The homogeneity of the gels are affected by the hydrolysis conditions, types of catalyst, concentration of alkoxides, amount of water, and controlled evaporation of solvent. Slow addition of water is found to be effective to avoid inhomogeneity in the resultant gels. Al-Jarsha *et al.* (*11*) prepared a dozen gels from ethyl silicate and aluminum chloride and determined the effects of organic and inorganic additives in the gels on mullite conversion. Based on the hydrolysis rate, Okada and Otsuka (*7*) classified monophasic gels prepared from tetraethoxysilane and aluminum nitrate, and the reaction paths leading to mullite were quite different for these gels. By preparing cordierite gels using different precursor methods, Selvaraj *et al.* (*12*) demonstrated that chemical modification of alkoxide precursors led to the formation of highly homogeneous gel, which exhibited the glass-transition similar to the cordierite glass and crystallized to α-cordierite at a low temperature.

The present investigation deals with the synthesis of mullite gels by cohydrolysis of chelated aluminum alkoxide and different silicon alkoxides. Mullite gel is also prepared by a metal alkoxide–metal nitrate method. Extreme hydrolysis conditions were used in order to obtain gels of different homogeneities. The effect of homogeneity on the conversions of various gels into mullite and other intermediate phases is discussed using the DTA, XRD, and MASNMR results.

Experimental

Gel Preparation

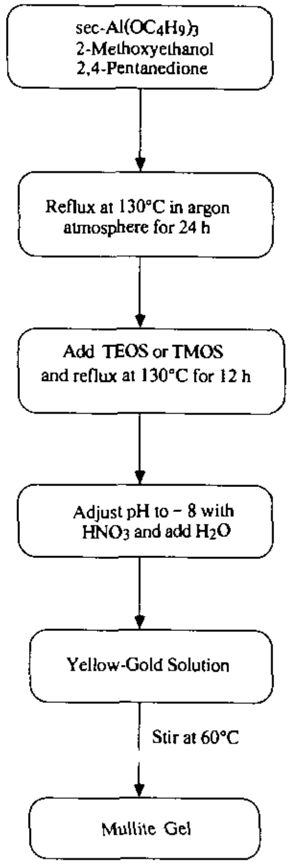

FIG. 1. Schematic diagram of the preparation of mullite gels (MG1 and MG2) from TEOS, TMOS, and $Al(OC_4H_9)_3$.

Figure 1 outlines the scheme followed to prepare mullite gels from TEOS [$Si(OC_2H_5)_4$] (Aldrich Chemical Co., Inc., WI), TMOS [$Si(OCH_3)_4$] (Aldrich) and $Al(OBu^s)_3$ (Aldrich). The mullite gel prepared from TEOS and $Al(OBu^s)_3$ is designated as MG1, while the gel prepared from TMOS and $Al(OBu^s)_3$ is designated as MG2. 0.3 *M* $Al(OBu^s)_3$ was initially dissolved in 1.5 *M* 2-methoxyethanol (Aldrich) and 0.3 *M* acetylacetone (Alpha Products, Danvers, MA), which was refluxed in argon at 130°C for 24 hr to yield the chelated alkoxide precursor $(Al(OR)_2$*acac* [*R* may be either Bu^s or $(CH_3O)CH_2CH_2$]. The complex solution was refluxed with appropriate quantities of either TEOS or TMOS to obtain the mullite precursor solution.

The pH values of these refluxed solutions were adjusted with concentrated HNO_3

from ~10.5 to 8. These acidified solutions were hydrolyzed with water diluted with 2-methoxyethanol (molar ratio of water: 2-methoxyethanol was 1:5). The water content used was twice the stoichiometric amount of water required for complete hydrolysis. Transparent yellow gels were obtained by keeping these solutions at 60°C with continuous stirring.

Mullite gel was also prepared by the following metal alkoxide–metal nitrate method, originally devised by Roy and Osborn (*13*) in the first utilization of the sol–gel method in 1948. The metal alkoxide precursor solution was prepared by partially hydrolyzing 0.2 *M* TEOS in 200 ml of ethanol, 1 M water, and 0.01 *M* concentrated HNO_3. The metal nitrate precursor solution was prepared by dissolving 0.6 *M* aluminum nitrate nonahydrate (Aldrich) in 600 ml of ethanol and 1 *M* water. These solutions were mixed and stirred at 60°C to obtain the mullite gel (MG3).

DTA and XRD Analyses

Gel powders heated to 800°C for 8 hr were used for DTA and XRD analyses. Phase transformations of these gel powders were studied using a Perkin-Elmer (Model DTA 1700, Perkin-Elmer, Norwalk, CT) differential thermal analyzer interfaced with a computerized data acquisition and manipulation system. Phases crystallizing in the heat treated samples were identified using a Scintag (Model DMC 105, Scintag, Inc., Santa Clara, CA) USA PAD-V Diffractometer with Ni filtered Cu*Kα* radiation.

^{27}Al and ^{29}Si MASNMR Spectra

^{27}Al MASNMR spectra were recorded on a spectrometer (Model HX-360, Bruker, Rheinstetten-FO, Germany) operating at 8.45 T. The samples were spun at frequencies between 9 and 10 kHz. Approximately 4500 scans were accumulated before Fourier transformation. A 2-μs pulse was used with a repetition time of 300 ms between pulses. The chemical shift values were assigned relative to the reference, 1 *M* aqueous $AlCl_3$ solution. Increasing chemical shift values indicate increasing resonance frequencies or decreasing shielding constants.

^{29}Si MASNMR spectra were recorded on a spectrometer (Bruker AM-270, Bruker) operating at 53.76 MHz, with a sample spinning speed of approximately 4.0 kHz. Approximately 500 scans were accumulated before Fourier transformation. Spectra were obtained using 5-μs pulses with a repetition time of 60 s and a spectral width of 10 kHz. Chemical shifts of the broad peaks were reproducible to ±1 ppm, and are reported with respect to the external standard, tetramethylsilane (TMS).

Results and Discussion

DTA and XRD Analyses

Figure 2 shows the DTA curves for MG1, MG2, and MG3 gels previously heated in air at 800°C for 8 hr. Sharp exothermic peaks appeared at about 990 and 985°C for MG1 and MG2 gels, while a broad and less intense exotherm appeared at 970°C for MG3 gel. For MG1, MG2, and MG3 gels, the values of enthalpy of crystallization determined from the area under the DTA exotherms, are −44.0, −48.0, and −27.3 cal/g, respectively. These DTA results are in agreement with numerous earlier studies (*5, 10, 14, 15*), Yoldas and co-workers (*9, 10*) synthesized amorphous mullite powder by varying hydrolysis conditions. These authors related the occurrence of the exothermic peak at approximately 980°C to the crystallization of mullite and also the intensity of the exotherm with the extent of reaction occurring between aluminum and silicon alkoxides to form the –Si–O–Al– linkages. By spray pyrolysis technique, Kanzaki and Tabata (*14*) prepared amorphous mullite powder, which exhibited a sharp exotherm at 970°C. Hoffmann *et al.* (*5*) synthesized single phase mullite gel that exhibited a sharp exotherm at 960°C and the intensity of the exotherm decreased for gel formed from a larger volume of ethanol. Furthermore, the single

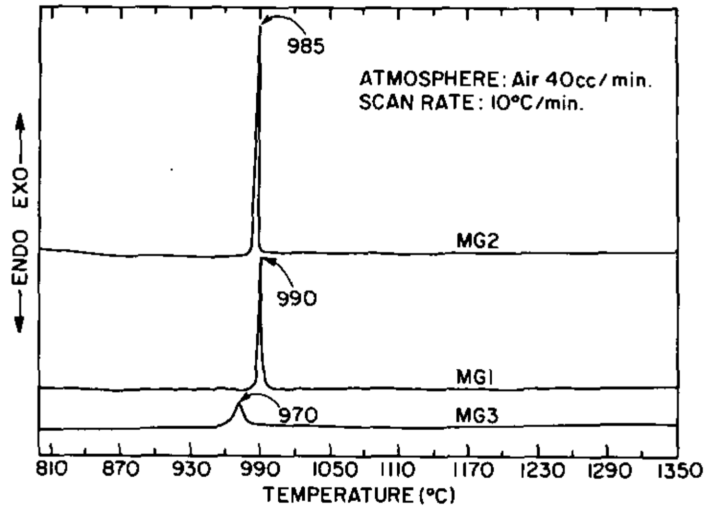

FIG. 2. DTA curves for MG1, MG2, and MG3 gels of same weight.

phase mullite gel prepared by Li and Thomson (*15*) under different hydrolysis conditions exhibited peaks of varying characteristics; gels synthesized by slow hydrolysis showed sharp peaks, while gels produced by rapid hydrolysis displayed diffuse peaks.

Figure 3 shows the XRD patterns for MG1 gel isothermally heat treated at different temperatures for 6 hr. To identify the phases, the observed *d*-spacings and intensities were matched to the Joint Committee on Powder Diffraction Standards (JCPDS) index files. The gel remained amorphous until 900°C. Peaks corresponding to a cubic spinel (JCPDS 10-425) and mullite (JCPDS 15-776) developed upon heating the gel at 950°C. The gel heated at 1200°C crystallized to pure mullite. Although the intensity and sharpness of the exotherm for MG2 gel in DTA is slightly higher than that of MG1 gel (Fig. 2), MG2 gel exhibited XRD patterns similar to those shown in Fig. 3 under identical isothermal heat treatment conditions. In addition, MG1 and MG2 gels heated at a rate of 10°C/min to a temperature just above the exotherms in DTA and quenched in air crystallized to the cubic spinel and mullite of almost identical intensities in XRD. On the other hand, MG3 gel exhibiting a diffuse and weak DTA peak, transformed into pure mullite only at 1300°C (Fig. 4). Heating this gel in DTA to just above the exotherm, led to the crystallization of a cubic spinel only. Dynamic XRD measurements of single phase mullite gel (*15*) indicated that the 970°C exotherm was due to the formation of both the spinel and mullite. On isothermal heating at different temperatures for 6 hr, the MG3 gel crystallized to the cubic spinel at 950°C, cubic spinel and α-Al_2O_3 at 1050°C,

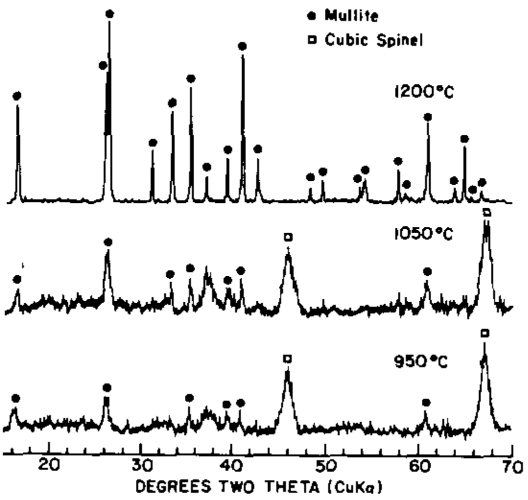

FIG. 3. XRD patterns of MG1 gel heat treated at different temperatures for 6 hr.

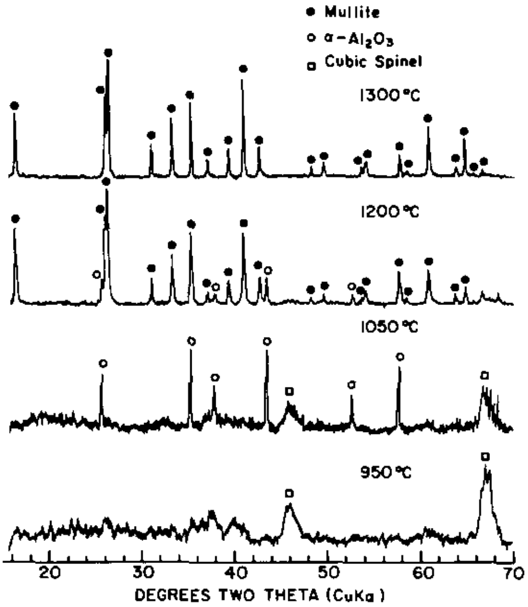

FIG. 4. XRD patterns of MG3 gel heat treated at different temperatures for 6 hr.

and mullite and α-Al_2O_3 at 1200°C (Fig. 4). The formation of a small percentage of α-Al_2O_3 ($\leq 10\%$), delayed the transformation of MG3 gel to pure mullite until 1300°C. However, the peaks due to the reaction between α-Al_2O_3 and mullite were not detected in DTA (Fig. 2). Okada and Otsuka (*7*) observed a similar cubic spinel to α-Al_2O_3 transformation in SiO_2–Al_2O_3 xerogels around 1150°C using XRD.

^{27}*Al MASNMR Spectra*

Figure 5 shows the ^{27}Al MASNMR spectra of MG1, MG2, and MG3 gels dried at 60°C. These spectra are not complicated by the overlap of spinning side bands due to fast sample spinning as has been previously observed for many aluminosilicates (*16*). The peak in the region of 50 to 60 ppm is attributed to 4-coordinated aluminum present in the gel network (*16*), whereas the peak around -5 to 10 ppm is assigned to 6-coordinated aluminum. A weak peak appearing ~ 30 ppm for MG1 gel can be attributed to 5-coordinated aluminum. Risbud *et al.* (*17*) observed 5-coordinated aluminum in roller-quenched, phase separated aluminosilicate glasses. In anodically formed amorphous alumina, Dupree *et al.* (*18*) observed 5-coordinated aluminum. Gilsion *et al.* (*19*) showed the generation of 5-coordinated aluminum in crystalline and amorphous aluminosilicates after heat treatments. Also, dealuminated clays and calcined kaolin clays (*20*) exhibited 5-coordinated aluminum peaks due to the formation of metakaolin ($Al_2Si_2O_7$).

No attempts have been made to calculate the exact intensities of 4-, 5-, and 6-coordinated aluminum in these gels due to the overlap of signals arising from the presence of aluminum in a wide range of local environments (*21*) and because of the possibility

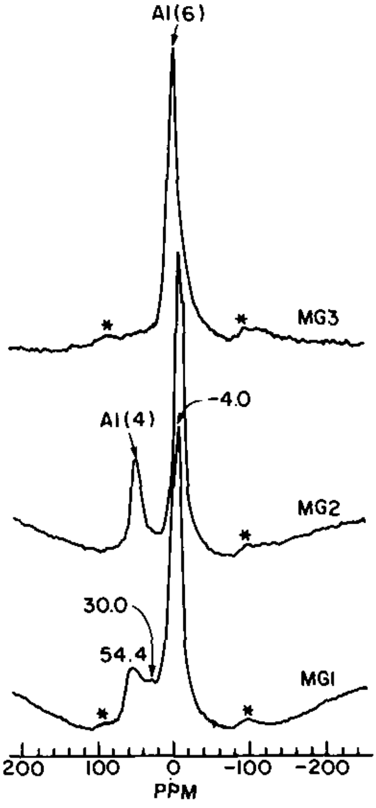

FIG. 5. ^{27}Al MASNMR spectra of MG1, MG2, and MG3 gels dried at 60°C. The spinning side bands are indicated by asterisk.

that significant signal is likely to be lost from a given site. Nevertheless, the following trends are noticeable in MG1, MG2, and MG3 gels dried at 60°C. The relative intensity of 4-coordinated aluminum in MG1 and MG2 mullite gels dried at 60°C is appreciable, while in the MG3 gels there is no detectable peak due to 4-coordinated aluminum. This suggests that more aluminum becomes part of the inorganic network as $[AlO_4]^-$ in MG1 and MG2 gels and $[SiO_4]$ tetrahedra in silica gel. The charge balance as a result of aluminum entering into the network is achieved by the interstitial octahedral Al^{3+} ions (*22*). Similar phenomenon in zeolites has also been reported by Fyfe *et al.* (*23*) using ^{27}Al NMR. The formation of –Si–O–Al– linkages before and during gelation can be due to the following types of condensation reactions:

$$Si(OR)_4 + (HO)Al(OR')acac \rightarrow (RO)_3Si\text{–}O\text{–}Al(OR')acac + ROH$$

$$Si(OR)_3OH + (HO)Al(OR')acac \rightarrow (RO)_3Si\text{–}O\text{–}Al(OR')acac + H_2O$$

where $R = C_2H_5$ or CH_3, $R' = sec\text{–}C_4H_9$. The group $(CH_3O)CH_2CH_2$ of 2-methoxyethanol may replace either R or R' due to the exchange reactions between the solvent and the alkoxide precursors. The relative intensity of 4-coordinated aluminum in MG2 gel is higher than that of MG1 gel probably because of the higher condensation reaction rate of TMOS as compared to TEOS (*24, 25*). Since the hydrolysis and condensation reactions are carried out under diluted conditions, the self-polymerization leading to the formation of Al–O–Al linkages are minimized (*10*).

As more aluminum enters into the network in MG1 and MG2 gels during gelation, the homogeneity of mixing, that is, the extent of formation of –Si–O–Al– linkages is higher when compared to MG3 gel. Similar behavior was observed in cordierite gels (*12*) prepared by two different precursor techniques. The molecular level of mixing was found to be higher in cordierite gel prepared by multicomponent metal alkoxide method than that in metal alkoxide–metal nitrate method.

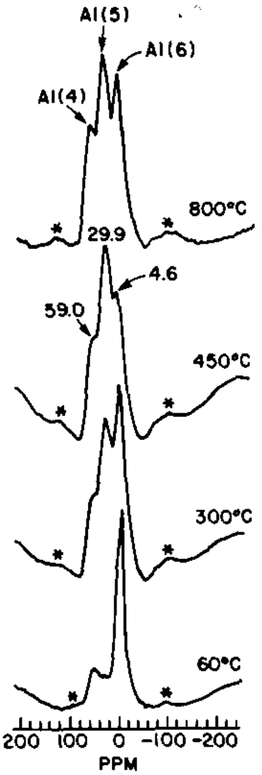

FIG. 6. ^{27}Al MASNMR spectra of the MG1 gel heat treated at different temperatures for 8 hr. The spinning side bands are indicated by asterisk.

^{27}Al MASNMR spectra of MG1 and MG3 gels heated at various temperatures for 8 hr are shown in Figs. 6 and 7, respectively. XRD patterns of these heat treated samples were characteristic of amorphous materials. The heat treated gels also exhibited peaks attributed to 5-coordinated aluminum, besides 4- and 6-coordinated aluminum. Nearly similar spectra were obtained for MG1 and MG2 gels heated at various temperatures. The relative intensity of 4- coordinated aluminum increased in both MG1 and MG3 gels (Figs. 6 and 7) on heating, indicating more aluminum becomes part of the inorganic network. For MG1 gel (Fig. 6), the relative intensity of 5-coordinated aluminum increased as the gel was heated

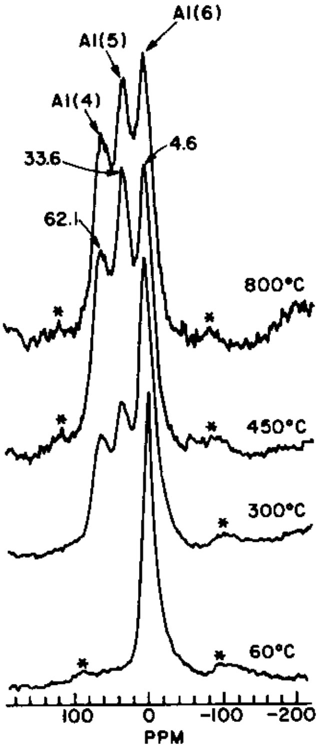

FIG. 7. ^{27}Al MASNMR spectra of the MG3 gel heat treated at different temperatures for 8 hr. The spinning side bands are indicated by asterisks.

between 60 and 450°C and thereafter it remained almost constant until 800°C. However, the relative intensity of 6-coordinated aluminum increased for gels heated between 450 and 800°C. This may be due to the segregation of alumina-rich region or the formation of Al–O–Al linkages. For MG3 gel (Fig. 7), the relative intensity of 6-coordinated aluminum was found to be higher than 4- and 5-coordinated aluminum between 60 and 800°C.

Figure 8 shows the ^{27}Al MASNMR spectra of MG1 gel heated at 950°C and 1300°C for 6 hr. The gel heated at 950°C exhibited peaks attributed to 4- and 6-coordinated aluminum. The peak assigned to 5-coordinated aluminum was not detectable in this region. The mullite gel was amorphous until 800°C. The partial crystallization of this gel at 950°C to cubic spinel and mullite (as evidenced from XRD (Fig. 3)) appear to convert the 5-coordinated aluminum to either 4- or 6-coordination. The gel heated at 1300°C (Fig. 8) displayed peaks characteristic of mullite (*26*).

^{29}*Si MASNMR Spectra*

Figure 9 shows the ^{29}Si cross polarization (CP) MASNMR spectra of MG1, MG2, and MG3 gels dried at 60°C. Spectra were also obtained without CP, which showed no noticeable changes except decreased signal to noise ratio. These spectra are quite broad, indicating silicon is present in a wide range of local environments (*27*). Amorphous gels prepared as zeolite precursors (*28*, *29*) also exhibited broad signals, due to a wide range of Si(mAl) [$m = 0$ to 4] environments caused by –Al–O–Si– linkages. The broad peak in MG3 gel is centred at −101 ppm. For MG1

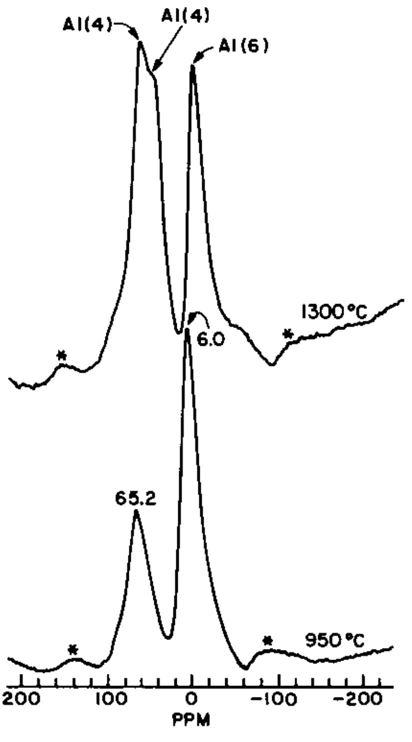

FIG. 8. ^{27}Al MASNMR spectra of MG1 gel heated at 950 and 1300°C for 6 hr. The spinning side bands are indicated by asterisks.

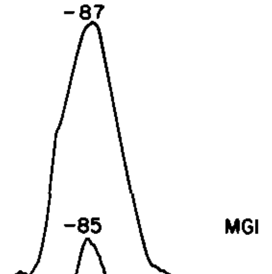

FIG. 9. ^{29}Si CP MASNMR spectra of MG1, MG2, and MG3 gels dried at 60°C.

and MG2 gels the corresponding peaks are shifted to the downfield (Fig. 9). This further substantiates the ^{27}Al MASNMR results which indicated that more -Al-O-Si- linkages were formed before and during gelation in MG1 and MG2 gels.

Figure 10 shows the ^{29}Si MASNMR spectra of MG1 gel heated at different temperatures for different times. The position of the central peak shifted from −87 to −92 ppm on heating the gel between 60 and 600°C. This indicates that, as the gel is heated, more number of silanol groups are converted to Si–O–Si linkages and as discussed above alumina-rich regions are formed. The chemical shift value (−92 ppm) of the gel heated to 600°C is in the range expected for silicon surrounded by two or three aluminum ions (Si(2Al) or Si(3Al)) in the second coordination sphere (*21*). The gel heated at 950°C exhibited a relatively strong peak at −108 ppm, due to a silica-rich region, and a weak peak at −87 ppm, due to mullite (*24*). The peak at −108 ppm corresponds to a deshielded silicon as compared to the ~111 ppm for pure SiO_2 glass. This suggests that the silica-rich region probably contains some Si(Al) or residual -OH groups attached to silicon. The intensity of the −87 ppm mullite peak increased for the MG1 gel heat treated at 1050°C. Partially crystallized glass containing crystalline mullite–silica glass mixture also exhibited peaks in this region (*24*). Figure 11 shows the ^{29}Si spectra of MG3 gel heated at 950 and 1050°C for 6 hr. The gel heated at 950°C showed peaks at −87 and −105 ppm. In the gel heated at 1050°C, the −87 ppm peak intensity decreased slightly and the other peak shifted to −108 ppm, suggesting the segregation of silica- and alumina-rich regions. XRD results indicated the formation of α-Al_2O_3 in this region (Fig. 4).

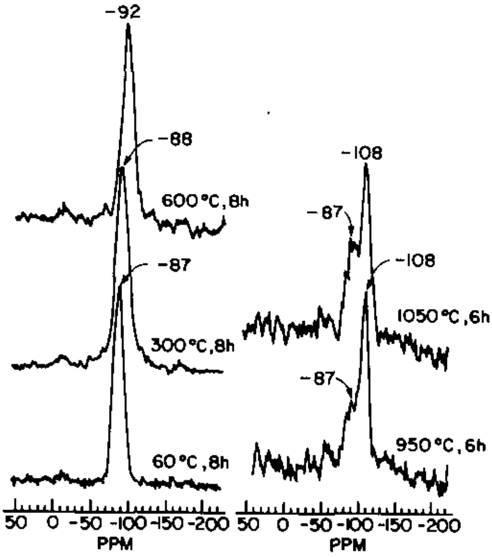

FIG. 10. ^{29}Si MASNMR spectra of MG1 gels heat treated at different temperatures for different times.

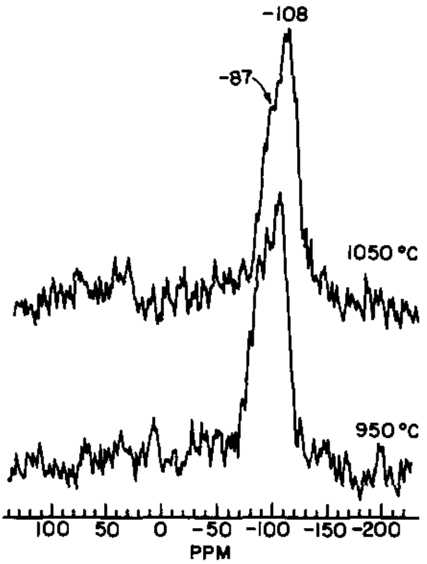

FIG. 11. ^{29}Si MASNMR spectra of MG3 gel heated at 950 and 1050°C for 6 hr.

Conclusions

Different precursor gels for mullite were prepared by using various techniques. Gels prepared using aluminum and silicon alkoxides (TEOS and TMOS) crystallized to mullite via a cubic spinel, while gel prepared from aluminum nitrate nonahydrate and TEOS crystallized to mullite through a cubic spinel and α-Al_2O_3. ^{27}Al and ^{29}Si MASNMR results showed that the molecular scale mixing, before and during gelation, was better in the gels prepared exclusively from chemically modified metal alkoxide precursors. In the gel prepared from aluminum nitrate nonhydrate and TEOS, 4-coordinated aluminum was not detectable, indicating little or no aluminum became part of the Si–O network during gelation.

Acknowledgment

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