

# Phase Transformations in Polymer Al–Si Gels of Mullite Composition

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(Received 13 September 1990; accepted 5 November 1990)

## Abstract

*The sequence of phase transformations in polymer Al–Si gels of mullite composition during heating has been studied. The degree of uniformity of distribution of components in gels was different depending on the temperature of gelation. From a gel obtained at room temperature, only Al–Si spinel is formed at 980°C. From a gel obtained at 60°C, tetragonal mullite crystallizes additionally at 980°C. The degree of gel homogeneity determines the ratio of intensities of thermal effects of crystallization at 980° and 1230°C. A general scheme of phase transformation occurring during the heating of inhomogeneous Al–Si gels is proposed.*

*Es wurde die Abfolge der beim Aufheizen durchlaufenen Phasenumwandlungen in polymeren Al–Si-Oxid-Gelen mullitischer Zusammensetzung untersucht. Die homogene Verteilung der einzelnen Komponenten im Gel hing von der Gelierungstemperatur ab. Wurde die Gelierung bei Raumtemperatur durchgeführt, bildete sich bei 980°C nur ein Al–Si-Spinell. Bildete sich das Gel bei 60°C, kristallisierte nach dem Kalzinieren bei 980°C auch tetragonaler Mullit aus. Die im Gel vorhandenen Inhomogenitäten bestimmen die Intensität der bei der Kristallisation bei 980°C und 1230°C auftretenden thermischen Effekte. Für inhomogene Al–Si-Oxid-Gele wird ein allgemein gültiges Schema für die bei der Kalzinierung ablaufenden Phasentransformationen angegeben.*

*On a étudié la succession de transformations de phase intervenant lors du chauffage de gels de polymères Al–Si de composition mullite. On a trouvé que le degré d'uniformité de la distribution des composants dans les gels était dépendante de la température de gélification. Dans un gel obtenu à température ambiante, on*

*observe à 980°C la seule formation du spinelle Al–Si. Dans un gel élaboré à 60°C, on constate à 980°C la cristallisation supplémentaire de mullite tétragonale. L'homogénéité du gel détermine l'intensité des effets thermiques de la cristallisation à 980 et 1230°C. On propose également ici un schéma général des transformations de phases apparaissant au cours du chauffage de gels Al–Si inhomogènes.*

## 1 Introduction

The problem of preparation of multicomponent powders of a homogeneous composition can be solved efficiently by using sol–gel technology.<sup>1</sup> According to the classification given in Ref. 2, two versions of the sol–gel process may be distinguished: colloidal and polymeric. In the colloidal version, gelation is carried out in a solution containing a sol of one or more components. By the terminology given in Ref. 3, the resulting gel is called polyphase. The polymeric version is realized by carrying out the gelation process in solutions of organometallic compounds containing the required set of cations. Gelation takes place due to the occurrence of two elementary reactions: hydrolysis and polycondensation. Owing to the polycondensation process, a polymer gel network forms in the solution, and cations of different nature can be incorporated into the network by means of oxygen bridge bonds. In this way, intermixing of components at the atomic level is achieved. In the subsequent stage of the process, amorphous gels are transformed into crystalline powders by high-temperature heat treatment. The conditions of gelation have an essential effect on the structural and phase transformations occurring during heat treatment of gels and, therefore, on the characteristics of prepared powders.

A large amount of recently published work<sup>4-9</sup> is devoted to studying the process of mullite formation in Al-Si gels. The following experimentally established facts are known. Crystallization of mullite in Al-Si gels can occur in the temperature region 950–1000°C or 1250–1300°C. In contrast to the high-temperature mullite, the mullite formed in the region 950–1000°C crystallizes with tetragonal symmetry and contains an elevated quantity of Al<sub>2</sub>O<sub>3</sub>. With an increase of temperature above 1250°C, it transforms into common orthorhombic mullite of a composition close to 3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>. The formation of mullite in the region of 950–1000°C is accompanied by an exothermic effect. The occurrence of the exothermic effect is, however, only the required, but not a sufficient condition for the formation of mullite. In many cases, no mullite is found at all in Al-Si gels exhibiting the exothermic effect in the region 950–1000°C. In that case, the material usually contains an Al-Si-O compound with a deformed cubic lattice  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which has been qualified as Al-Si spinel.<sup>5</sup> In earlier work, the appearance of an exopeak in the region 950–1000°C was treated as a result of spinodal decomposition of Al-Si gel into amorphous silica and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. It has been demonstrated convincingly in Ref. 8 that the thermal effect at 950–1000°C has a multivariant nature. The products of the phase transformation occurring with heat evolution may be tetragonal mullite, Al-Si spinel or both these phases. The nature of the phase that forms in the process depends on the structure of the initial gel, which in turn is determined by the method and conditions of gel preparation. For instance, it has been demonstrated<sup>4,7</sup> that an increase in the time of gelation (by decreasing the concentration of water in the working solution) leads to crystallization of mullite at 980°C. With a short time of gelation (a large concentration of water in the solution), Al-Si spinel forms. Crystallization of mullite is promoted by the use of solutions in which the silicon-containing compound is present in the form of monomers. A more ordered structure of gel at the molecular level is undoubtedly favourable for the appearance of mullite, rather than of Al-Si spinel. Control of the relative rates of the two elementary processes of gelation, hydrolysis and polycondensation, is an efficient way to obtain homogeneous Al-Si gels which crystallize with the formation of mullite in the temperature region 950–1000°C.

Although relative clarity has been attained as regards the products of transformation in polymer Al-Si gels at 950–1000°C, the sequence and mechanism of mullite formation in this temperature region

still have not been studied sufficiently thoroughly. There are various probable versions of realization of the process of mullite formation. The question of which of the mechanisms of mullite formation acts in each particular case can be answered by tracing the dynamics of quantitative variations in the ratio of phase components in a gel as a function of temperature, with an indispensable determination of the quantity of the amorphous phase at each stage of heat treatment. This is one of the objects of the present work. Another object is the study of the effect of the conditions of gelation on phase transformation in Al-Si gels of mullite composition. In Refs 4 and 7, the ratio of the rates of hydrolysis and polycondensation was changed by varying the concentration ratios (water content) in the system. The authors attempted to retain constant concentration ratios in the working solution and varied only the external factor, i.e. the temperature of gelation.

## 2 Preparation of Al-Si Gels

As the starting materials, tetraethoxysilane (TEOS) of extra-pure grade, Al(NO<sub>3</sub>)·9H<sub>2</sub>O (chemically pure), and absolute ethyl alcohol were used. A 1.7M solution of aluminium nitrate crystallohydrate in ethanol was initially prepared, to which TEOS was then added in an amount required to obtain the composition 3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>. After stirring for 30 min, one portion of the solution was placed into a thermostat heated to a temperature 60°C (sample M60) and another portion was left under stirring at room temperature (sample M20). In the solution kept at 60°C, gelation was completed in 6 h. For the solution kept at room temperature, 22.5 days were needed to complete gelation. The gel was vitreous and transparent in the former case and likewise vitreous, but turbid in the latter. For comparison, a gel was prepared from a solution in which hydrolysis had been effected in the basic region at an elevated rate. For this purpose, formamide in an amount equivalent in volume to the added tetraethoxysilane was added to the initial solution of the same composition as for gels M60 and M20. As is known, when heated to a temperature above 50°C, formamide decomposes with the evolution of ammonia. This property of formamide is utilized for preparation of hydroxides or basic salts in processes of homogeneous precipitation. Upon placing the solution with formamide into a thermostat preheated to 60°C, gelation was completed in 30 min. In that case, the gel was essentially a chalky sediment

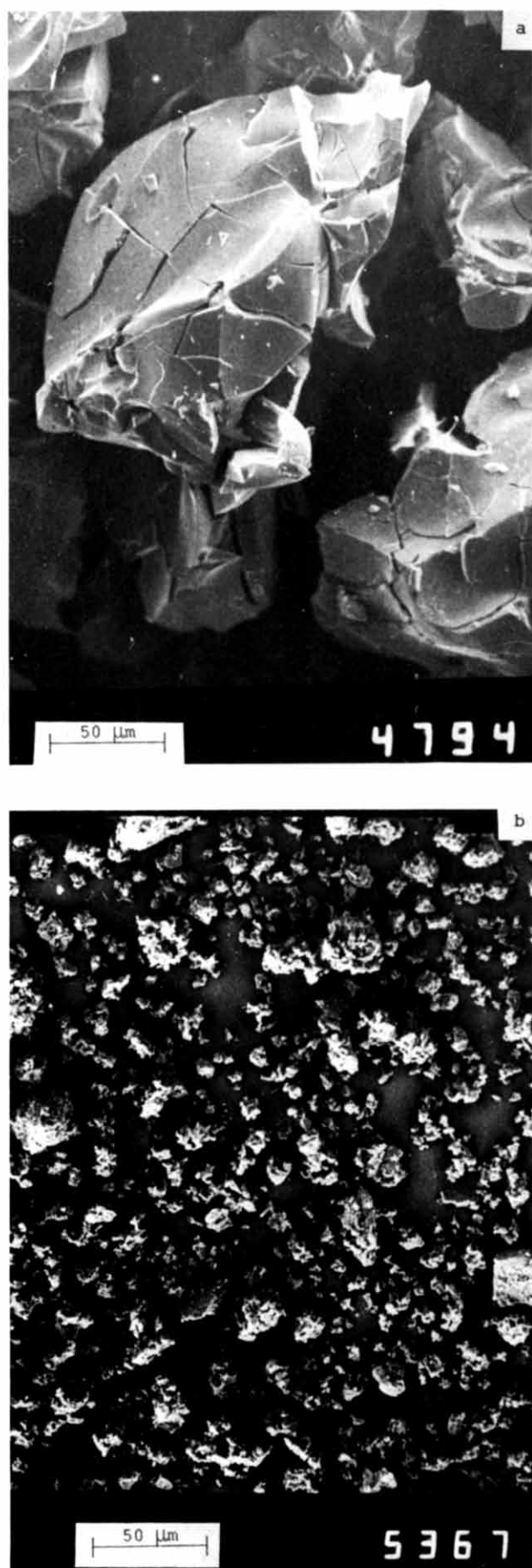


Fig. 1. Structure of Al-Si gels. (a) M60 and (b) MF.

with a distinct boundary between it and the solution. In this case, the term 'coprecipitation' seems to be more correct than 'gelation'. This gel is designated the MF sample. An indication of the morphological peculiarities of the gels may be given by the micrographs in Fig. 1.

The gels were dried at 100°C and then subjected to heat treatment at a temperature of 700, 950, 1000, 1100, 1200, 1300 or 1500°C. The ageing time at each temperature was equal to 3 h.

### 3 Experimental Methods

X-Ray photographs were taken by means of a DRON-3M diffractometer with  $\text{CuK}_\alpha$  emission. Quantitative phase analysis was made by a variation of the internal standard method which is called the matrix flushing method.<sup>10</sup>  $\text{CaF}_2$  was used as the internal standard. The method makes it possible, along with quantitative determination of crystalline phases, to estimate the concentration of amorphous phase in the material. IR spectra were recorded in a UR-20 spectrophotometer. Powder specimens (KBr plates) were suspended in vaseline oil. Differential thermal and thermogravimetric analysis was made in a Paulic-Paulic thermoanalyser model Q-1500. The temperature was raised to 1400°C at rates of 7.5 and 15°C/min. The mass of sample in each experiment was constant and equal to 700 mg. This made it possible to judge the ratio of thermal effects by the ratio of intensities of peaks in DTA curve. For more accurate identification of the products of phase transformations, some samples were taken for phase analysis after heat treatment in the thermoanalyser immediately before or after the appearance of thermal effect.

### 4 Results and Discussion

Curves of differential thermal and thermogravimetric analysis are shown in Fig. 2. Samples of gels M20 and M60 exhibited an exothermic effect at 980°C, whereas no exopeak was observed for the MF sample in this temperature region. The M20 gel had an additional exoeffect at 1230°C. The MF gel showed the thermal effect in the low-temperature region (230°C). At this temperature, a sharp loss of mass of the MF gel was observed. According to the results of thermogravimetric analysis, the change in mass ( $\Delta m$ ) was the highest for the M20 gel at  $\Delta m = 65\%$ ;  $\Delta m = 43.5\%$  for the M60 gel and  $\Delta m = 52.5\%$  for the MF gel.

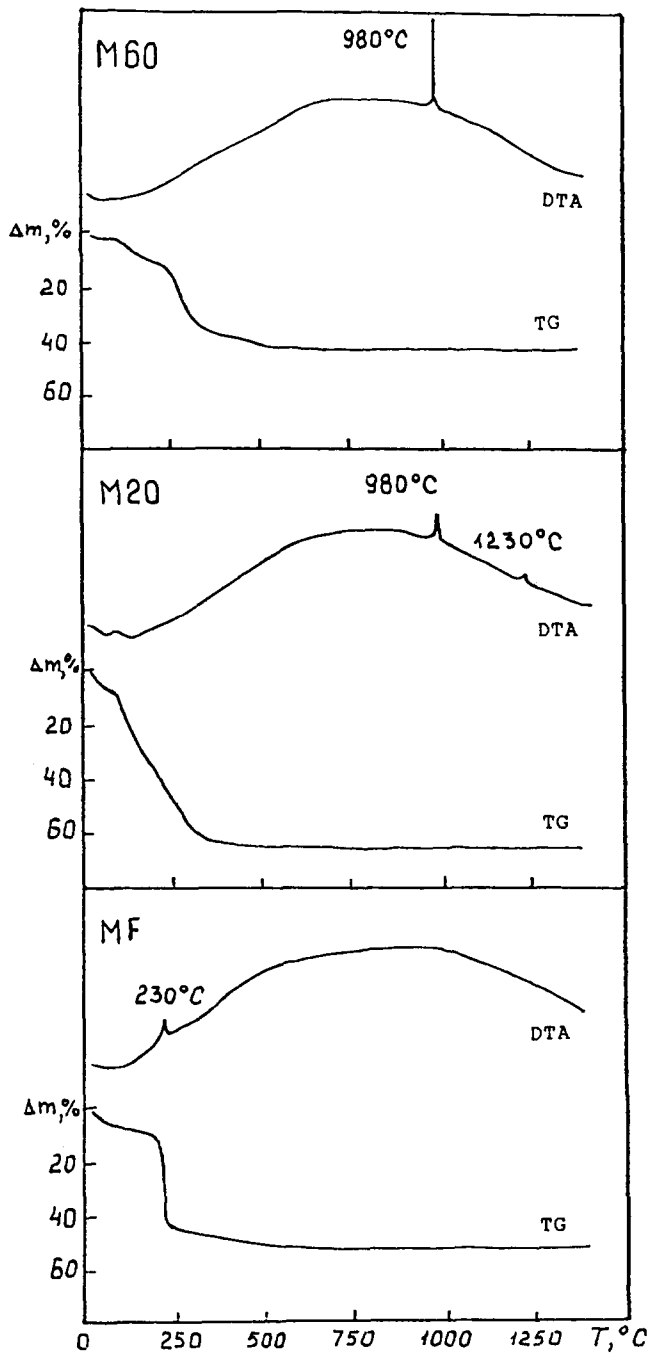


Fig. 2. DTA and TG curves for Al-Si gels. Rate of temperature rise 7.5°C/min.

The results of phase analysis are summarized in Table 1. The polymer gels M20 and M60 have a similar sequence of phase transformations. The first crystalline phases appear at 950°C. For the M20 gel, this phase is Al-Si spinel, whereas tetragonal mullite is additionally present in M60. With a further increase of the ageing temperature, the concentration of tetragonal mullite in these samples increases and the Al-Si spinel disappears. At the same time, an increase of the quantity of the amorphous phase is observed, which is retained up to 1300°C. The appearance of  $\theta$ - and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was recorded in the M60 gel at 1100°C, and in the M20 gel at 1200°C. Orthorhombic mullite forms at a temperature above 1300°C. It should be noted that the phase transformations in M20 occur by the same scheme as in M60, but with a lag of temperature.

Crystalline phases appear in polymer gels after a 3-h ageing at a temperature below the temperature of the thermal effect in the DTA curve (980°C). The appearance of Al-Si spinel and tetragonal mullite on long ageing at temperatures below 980°C was also remarked upon earlier.<sup>8,11</sup> This indicates a mixed nature of  $A \rightleftharpoons AS$  and  $A \rightleftharpoons Mt$  transformations. These transformations can be realized by either diffusionless or diffusion processes. The same is proved by the strong sensitivity of the temperature of the thermal effect to the heating rate. An increase in the rate of temperature rise from 7.5 to 15°C/min leads to a displacement of the maximum of the exopeak from 980 to 1025°C for the M60 gel and to 1020°C for the M20 gel. The phase composition of the samples extracted from the thermoanalyser after the occurrence of the thermal effect was similar to that of the samples subjected to 3-h ageing at 1000°C. Samples extracted from the thermoanalyser upon attaining the temperature of 970°C (before the exopeak) were amorphous.

Analysis of the quantitative data on the concentrations of amorphous and crystalline phases in

Table 1. Phase composition of Al-Si gels after three hours heat treatment

Temperature (°C)	Gel		
	M60	M20	MF
700	A(100)	A(100)	A(64) + $\gamma$ (36)
950	A(7.6) + AS(83.3) + Mt(9.1)	A(70.2) + AS(29.8)	A(16.7) + $\gamma$ (83.3)
1000	A(13.7) + AS(68.4) + Mt(17.9)	A(36.2) + AS(63.8)	A(22.8) + $\gamma$ , AS(77.2)
1100	A( ) + $\alpha$ , $\theta$ ( ) + Mt( )	A(32.2) + AS(55.6) + Mt(12.1)	A( ) + $\theta$ ( )
1200	A(61.6) + Mt(38.4)	A( ) + $\alpha$ , $\theta$ ( ) + Mt( )	A( ) + $\alpha$ , $\theta$ ( )
1300	A(11.6) + Mt(88.1)	A(24.9) + Mt(75.1)	Mo(52.5) + $\alpha$ (47.5)
1500	Mo(100)	Mo(100)	Mo(67.5) + $\alpha$ (32.5)

A = Amorphous phase; AS = Al-Si spinel; Mt = tetragonal mullite; Mo = orthorhombic mullite;  $\alpha$ ,  $\theta$ ,  $\gamma$  =  $\alpha$ ,  $\theta$ ,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; numbers in brackets give concentrations of phases, % by mass; empty brackets imply that quantitative analysis was not carried out for the given sample.

the polymer gels M20 and M60 (see Table 1) shows that, in the course of transformations in the temperature interval 1000–1200°C, the Al-Si spinel formed at 980°C decomposes, with the separation of amorphous  $\text{Al}_2\text{O}_3$  and tetragonal mullite. (In the composition of Al-Si spinel, the amount of  $\text{Al}_2\text{O}_3$  is substantially higher than that required for its simple transformation into tetragonal mullite  $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ . According to the data of Ref. 4, the composition of Al-Si spinel is  $6\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ .) In the temperature range 980–1230°C, amorphous  $\text{Al}_2\text{O}_3$  transforms into  $\theta$ - and  $\alpha$ - $\text{Al}_2\text{O}_3$ . Amorphous silica and  $\theta, \alpha$ - $\text{Al}_2\text{O}_3$ , which are present in the system, react at 1230°C with each other and form secondary mullite. This process is accompanied by heat evolution. Depending on the concentration of amorphous silica and  $\theta, \alpha$ - $\text{Al}_2\text{O}_3$  in the system, the thermal effect may turn out to be sufficiently high to appear in the DTA curve. In the present case, this has been observed for the M20 gel (see Fig. 2). With a higher quantity of tetragonal mullite formed directly from the amorphous gel at 980°C, the thermal effect should be more substantial at 980°C and less substantial at 1230°C, since little of the free  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  remains in the system.

The phase transformations in coprecipitated (biphasal) MF gel differ substantially from those in the polymer gels M20 and M60. They proceed by the common scheme which is realized by solid-phase reaction in a mixture of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  powders.  $\gamma$ - $\text{Al}_2\text{O}_3$  is already formed at 700°C. With a further rise in temperature, the concentration of the amorphous phase decreases continuously due to the formation of  $\gamma$ - $\text{Al}_2\text{O}_3$ . In contrast to the polymer gels M20 and M60, diffractograms of the two-phase MF gel after heat treatment at 1300°C clearly show reflexes of orthorhombic mullite (doublet in the region  $2\theta = 26^\circ$ ).

MF gel calcined at 1500°C contains an appreciable amount of  $\alpha$ - $\text{Al}_2\text{O}_3$ . The cause of such substantial deviation from the initial composition lies in incomplete precipitation of one of the elements, silicon. In the presence of formamide in the solution, soluble silicon complexes are probably formed, which cannot pass over to the precipitate. The latter contains a compound which is the product of reaction of formamide and aluminium aqua-complex. The occurrence of the exothermic effect at 230°C in the MF gel can be explained by decomposition of this compound.

Figure 3 shows the IR spectra of M20 and M60 gels subjected to heat treatment at 700, 1000 and 1500°C, which have been recorded in the region of wave numbers  $\nu = 1000$ – $1200 \text{ cm}^{-1}$ . In this region,

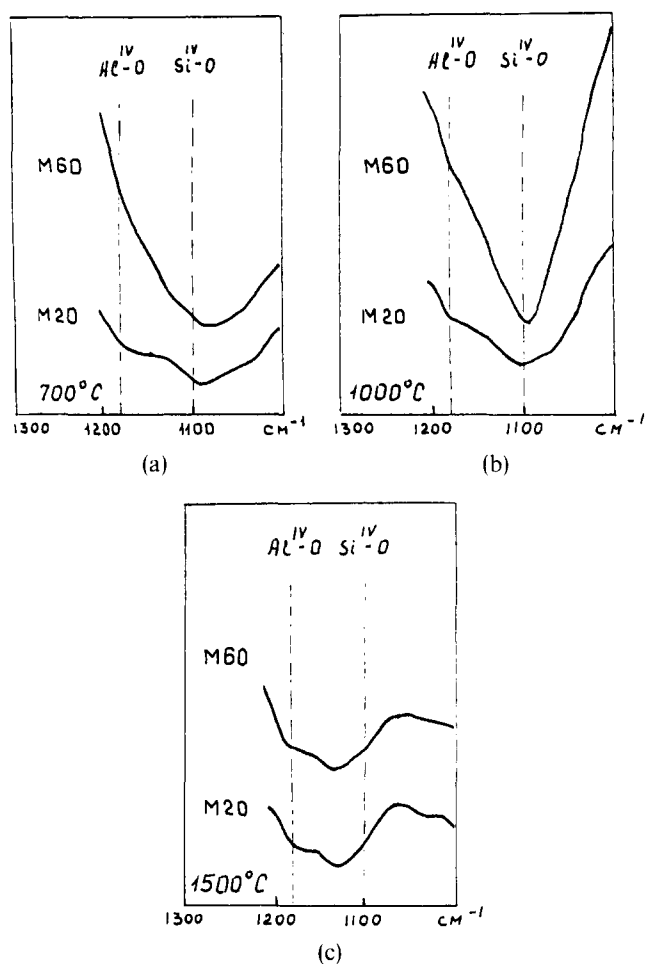


Fig. 3. IR spectra of Al-Si gels M60 and M20 corresponding to heat treatment at (a) 700°C, (b) 1000°C and (c) 1500°C.

an absorption band appears at  $\nu = 1100 \text{ cm}^{-1}$ , which corresponds to stretching vibrations of  $\text{Si}^{\text{IV}}\text{-O}$  bonds in silicon-oxygen tetrahedrons of the Al-Si gel, along with an absorption band at  $\nu = 1180 \text{ cm}^{-1}$ , corresponding to stretching vibrations of  $\text{Al}^{\text{IV}}\text{-O}$  bonds.<sup>12,13</sup> By comparing the IR spectra of gels calcined at 700 and 1000°C, it may be seen that the absorption band corresponding to the stretching vibrations of  $\text{Al}^{\text{IV}}\text{-O}$  bonds has a stronger resolution in the spectrum of the M60 gel. This is an indication that this gel has a higher concentration of four-coordinated aluminium ion which can be substituted for silicon in silicon-oxygen tetrahedrons. At 1500°C, the IR spectra of M20 and M60 gels become identical. As has been demonstrated in Ref. 4, the concentration of  $\text{Al}_2\text{O}_3$  in mullite can be judged from the ratio of intensities of absorption bands  $1100 \text{ cm}^{-1}$  and  $1180 \text{ cm}^{-1}$ . This concentration corresponds to 71 mol%, which exceeds the concentration of  $\text{Al}_2\text{O}_3$  in stoichiometric orthorhombic mullite. The latter fact implies that the process of ordering from tetragonal to orthorhombic mullite is still not fully complete at 1500°C.

Thus, under comparable conditions, an increase in

the temperature of gelation favours the formation of Al–O–Si bonds at the stage of hydrolysis before the beginning of intensive polycondensation. This results in a more uniform distribution of aluminium atoms in the structure of the gel and leads to a more complete formation of mullite at 980°C. By suppressing quick polycondensation and forming favourable conditions for an elevated reaction capacity of the silicon-containing compound, it may be achieved that aluminium atoms will be distributed uniformly in the whole volume of the gel and the latter will crystallize at 980°C with the formation of mullite only. This behaviour of the Al–Si gel has been demonstrated, for instance, in Ref. 14 where a solution containing partially hydrolysed tetramethoxysilane and aluminium ions was sprayed into a furnace heated to 400°C. In that case, evaporation of the solvent took place before the beginning of polycondensation, so that only mullite was crystallized on heating the gel up to 1000°C.

## 5 Conclusion

The results given demonstrate that polymer Al–Si gels should not be regarded as being homogeneous at the molecular level of the system. Local inhomogeneities of the composition may lead to different courses in the process of mullite formation in individual microvolumes. The degree of this inhomogeneity depends on the conditions of gelation and introduces certain corrections into the integral picture of phase transformations occurring during heat treatment of gels.

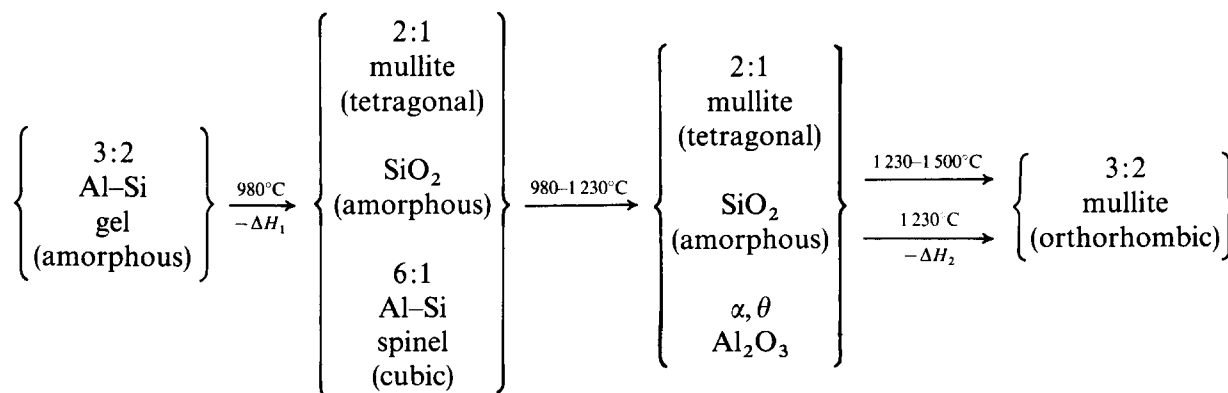
Proceeding from the results obtained and from analysis of experimental data of other researchers, it is possible to suggest the following general scheme of phase transformations in inhomogeneous Al–Si gels of mullite composition.

At 980°C, amorphous 3:2 Al–Si gel crystallizes with a thermal effect into tetragonal mullite of the

composition 2:1 and Al–Si spinel which has a higher concentration of Al<sub>2</sub>O<sub>3</sub> compared with mullite (6Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub> according to Ref. 4). The material also contains a certain quantity of amorphous silica. In the temperature range 980–1230°C, Al–Si spinel gradually decomposes with the formation of tetragonal mullite. Excessive Al<sub>2</sub>O<sub>3</sub> separates from Al–Si spinel as an amorphous phase and further transforms into  $\theta, \alpha$ -Al<sub>2</sub>O<sub>3</sub>. At 1230°C, orthorhombic mullite is formed as a result of reaction of amorphous silica and amorphous Al<sub>2</sub>O<sub>3</sub> which has separated on the decomposition of Al–Si spinel, or on reaction with  $\theta, \alpha$ -Al<sub>2</sub>O<sub>3</sub>. The process occurs with evolution of heat. As the temperature is raised further above 1230°C, tetragonal mullite transforms into the orthorhombic form by solid-phase reaction with the residual silica. Depending on the ratio between the quantities of mullite and Al–Si spinel formed at 980°C (i.e. depending on the degree of homogeneity of gel), the ratio of the intensities of heat evolution at 980 and 1230°C may be quite different.

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