

Review of mullite synthesis routes by sol–gel method

Luciana S. Cividanes · Tiago M. B. Campos ·
Liana A. Rodrigues · Deborah D. Brunelli ·
Gilmar P. Thim

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Abstract The sol–gel method for the mullite synthesis is reviewed, with particular emphasis on the characterization of monophasic and diphasic gels at low, intermediate and high temperatures and the factors that influence the hydrolysis and condensation rate of the sol–gel process, which in turn determine the properties of the final material. A wide range of studies about mullite precursors synthesized via sol–gel is discussed here.

Keywords Sol–gel · Mullite · Monophasic · Diphasic · Additives

1 Introduction

Mullite is an aluminosilicate with large technological applications due to its physical and chemical properties. The sol–gel method has been widely used for mullite synthesis, generating products with high purity and

homogeneity. According to the gel homogeneity degree, sol–gel method is divided into two types: monophasic, when the aluminum and silicon are mixed at atomic level, and diphasic, when the homogeneity scale is between 1 and 100 nm. The union of monophasic and diphasic gels leads to the hybrid gel.

Many factors influence the hydrolysis and condensation rate of the sol–gel process, which in turn determine the properties of the final material. Among these factors are: pH, water amount, organic and inorganic additive addition, starting materials etc.

The behavior of gels at low and intermediate temperatures influences their behavior at high temperatures, such as the formed phases and the mullite crystallization temperature. Therefore, studying the characteristics of the gels at temperatures below the mullite crystallization is of fundamental importance.

This review presents some of the many studies about the mullite synthesis by sol–gel, selecting the most relevant and more meaningful works that characterizes mullite precursor materials at low, intermediate and high temperatures, as well as the factors influencing the crystallization of mullite and its final properties.

2 Mullite: crystalline phases, properties and application

Mullite is a refractory aluminosilicate with large technological applications. This material has been considered interesting in recent decades due to its physical and chemical properties, such as, low thermal expansion and therefore high thermal stability, low density, low thermal conductivity, good mechanical strength, creep resistance and good stability in harsh chemical environments [1, 2].

L. S. Cividanes (✉) · T. M. B. Campos ·
L. A. Rodrigues · D. D. Brunelli · G. P. Thim
Divisão de Ciências Fundamentais—IEF, Instituto Tecnológico
de Aeronáutica—ITA, Praça Marechal Eduardo Gomes,
50, Vila das Acácias, São José dos Campos, São Paulo,
SP CEP 12.228-900, Brazil
e-mail: lucianac@ita.br

T. M. B. Campos
e-mail: tiago-moreira22@hotmail.com

L. A. Rodrigues
e-mail: lika_eng@yahoo.com.br

D. D. Brunelli
e-mail: deborah@ita.br

G. P. Thim
e-mail: gilmar@ita.br

The mullite material has two stoichiometric crystalline structures: tetragonal and orthorhombic. The orthorhombic structure, more stable, has a unit cell with parameters: $a = 0.76$ nm, $b = 0.77$ nm, $c = 0.29$ nm, and the crystal has a doublet in the X-ray diffraction at 26° (2θ —CuK α), referring to the crystal planes 120 and 210 [3–6]. On the other hand, the tetragonal structure ($a = b$), metastable phase, is characterized by a single peak in the X-ray diffraction at 26° (2θ —CuK α) [3–6]. Another phase that can appear in the aluminosilicate synthesis is a spinel type intermediate phase, with a low crystallinity and peaks in X-ray diffraction at 46 and 67° [7–9]. The formation of spinel phase in the mullite synthesis is an indicative of precursor heterogeneity and its formation is due to the difficulty of controlling the hydrolysis rate of the alkoxides employed [10].

The reaction mechanisms of mullite formation can vary considerably according to the precursors and the methods employed [11]. Chemically synthesized precursors are converted into mullite in a temperature range between 850 and 1,350 °C. The scale of chemical homogeneity is the determining factor in the mullite formation mechanism and, consequently, in the crystallization temperature. When the precursor has a high degree of homogeneity, the temperature of mullite crystallization is low [12].

In literature there is a wide variety of methods for ceramic material synthesis, including mixtures of reagents in solid state, coprecipitation of mixed salts in solution, spray pyrolysis, sol–gel process etc. [11]. Each method has its peculiarity, which depending on the application and value of the final product, justifies its application. The sol–gel process has been widely used because it generates products with high purity and homogeneity, and is versatile and has good reproducibility [13].

3 Mullite synthesis by the sol–gel process: starting materials and factors that influence

The sol–gel process is a synthetic route that can generate good mixing and uniformity of the starting materials, at nanoscale, resulting in a very homogeneous distribution of components. As a result of the high degree of the precursor homogeneity, the temperature required for mullite formation is relatively low (between 1,000 and 1,350 °C), when compared with traditional methods, such as reactive powder mixture (between 1,500 and 1,700 °C) [14–17].

Different silicon and aluminum sources have been used for the mullite precursor synthesis. In general, the precursor is a metal inorganic salt (acetate, chloride, nitrate, sulfate etc.) or an organic species as a metal alkoxide. The metallic alkoxides are the largest class of precursors used in the sol–gel process [18]. Among the most common

alkoxide groups are the methoxy (OCH_3), the ethoxy (OCH_2CH_3), the n-propoxy ($\text{O}(\text{CH}_2)_2\text{CH}_3$) and the sec-butoxide ($\text{H}_3\text{C}(\text{O})\text{CHCH}_2\text{CH}_3$).

In the alkoxide group, the most used are the tetraethylorthosilicate (TEOS) and the tetramethylorthosilicate (TMOS) [19]. Roy [20] was the first to use TEOS and aluminum nitrate nonahydrate (ANN) as a source of silica and alumina, respectively. From then on, TEOS and ANN have been widely used until nowadays for the mullite precursor synthesis by sol–gel process [21].

Another silica source that has been used for the mullite precursor synthesis is the silicic acid, or an aqueous suspension of silica. Some researchers have synthesized the silicic acid by passing a solution of sodium metasilicate through an ion exchange column [22–28]. The route of the synthesis that uses the silicic acid generates lower costs compared to that one which uses the TEOS as the silica source [23]. It is important to use a freshly prepared silica sol, since the monosilicic acid, $\text{Si}(\text{OH})_4$, is very unstable. This is due to the incomplete coordination of silicon with respect to OH^- , because in hydrated form the coordination is 6. Thus, the formation of siloxane, $\equiv\text{Si}—\text{O}—\text{Si}\equiv$, occurs by the condensation of two molecules of silanol, $\equiv\text{Si}—\text{OH}$. The amounts of crystallized mullite and spinel phase formed depend on the aging of the silica sol, where the amount of crystallized mullite decreases and of spinel phase increases with the aging time [22]. In the course of time the silica polymerization occurs, forming a polymeric chain or a cluster of silica, resulting in heterogeneity in the gel.

In the sol–gel process, the addition of a solvent is necessary to increase the contact between the aluminum and silicon sources. The most sol–gel process reported in the literature, for the mullite precursor synthesis, uses ethanol as a solvent, but other solvents have also been reported: methanol, 1-propanol, 2-propanol, 1-butanol, ethylene glycol, etc. [29].

The choice of starting materials, of course, influences the steps of the sol–gel process, generating different final-products. Fujio Mizukami et al. [30], for example, studied the influence of the alumina source in the mullite formation. In this study, they synthesized mullite by polymeric sol–gel from TEOS, organic polydentate ligands and two sources of alumina: ANN or dibutoxyethylacetatoacetoaluminum ($\text{Al}(\text{OBu})_2(\text{Ac}(\text{AcEt}))$). These authors showed that mullite was formed more easily from the ANN than from ($\text{Al}(\text{OBu})_2(\text{Ac}(\text{AcEt}))$). This is because the ANN, in the presence of water, leads to the formation of a complex structure, which contains one aluminum and six water molecules in the form of a regular octahedron, where the ion is the central element and the water molecules the ligands. However, as the ($\text{Al}(\text{OBu})_2(\text{Ac}(\text{AcEt}))$) is bidentate it can produce much stronger coordination bonds than ANN, which is unidentate, and difficult to be replaced [30].

Vol'khin et al. [31] also studied the effect of different alumina sources in the mullite precursor synthesis. They synthesized mullite by colloidal sol–gel from sols containing γ -AlOOH and SiO₂ nanoparticles, and also replaced the γ -AlOOH sol by Al(NO₃)₃. They showed that the mullite amount formed when they used Al(NO₃)₃ was lower than when the γ -AlOOH sol was used, indicating a greater degree of aluminum hydroxide particles aggregation, which reduces their reactivity [31].

In order to achieve mullite precursor samples with good homogeneity the following experimental conditions should be strictly controlled: the hydrolysis rate, the amount of water added for hydrolysis, the pH, the solvent and the temperature [2], since the xerogel physical properties also depend on the hydrolysis and condensation rates of the sol–gel process [32].

Studies have shown that the greater the water amount present in the medium reaction, the higher the mullite crystallization temperature and the spinel formation occurrence [33–35]. Regarding the influence of the pH, the particle sizes increase with the pH, while an acidic environment promotes the formation of smaller particles [36]. For example, the synthesis in an acid medium and with low water content generally produces dense materials with smaller pores, while basic solutions with a greater amount of water produce materials that are more porous. This is because under acidic conditions, condensation occurs preferably between the silanol groups located in monomers or at the end of the polymer chains. This condensation leads to the formation of gels composed of linear polymer chains, which, after drying, form a matrix of low pore volume. However, under basic conditions, condensation occurs preferably between highly branched oligomers, which lead to the formation of particulate gels that, after drying, produce materials with high porosity. Regarding the water amount present in the medium, a minimum quantity is necessary for the hydrolysis step, however, water in excess leads to the achievement of heterogeneous materials, with extensive phase segregation. One way to prevent this phase segregation caused by the large water amount is the slow release of water by chemical or physical processes, such as by ambient humidity, allowing the control over the water concentration and, consequently, on the hydrolysis of metal oxide precursors [7, 37–39]. Another possibility to avoid the presence of water in the reaction medium is usually called non-hydrolytic chemical or non-aqueous chemical. In this case, the oxygen comes from donors such as ethers, alcohols or alkoxides, which leads to completely different chemical reactions, based on the reactivity of the carbon–oxygen [37]. The M–O–M bond formation occurs through the condensation reaction between the ligands coordinated to two different metal centers followed by the elimination

of an organic fragment [40–42]. The size of the alkoxide group also influences the hydrolysis and condensation reactions rate due to steric factors. An increase in the size of the alkoxide group decreases the hydrolysis rate [43–45].

The biggest problem of sol–gel method is based on the control of hydrolysis and condensation reaction rates of the precursors. The difference in the reactivity of metal alkoxides makes it difficult to control the composition and homogeneity of the material obtained by the sol–gel, generating phase segregation [18].

The hydrolysis and polycondensation rates of silicon alkoxides, for example, are very low if compared with that of the aluminum alkoxides [2]. In this case, a significant polymerization of aluminum alkoxide will cause heterogeneity in the precursor, and crystallization of mullite will occur at higher temperatures. Therefore, many researchers have replaced the more reactive alkoxide by a hydrated salt, so the water molecules from the salt promote the hydrolysis of the less reactive alkoxide, resulting in a homogeneous copolymerization of the silica and the alumina. The salt commonly used is the ANN. However, the rapid hydrolysis rate can generate heterogeneity in the samples and it must be avoided, by the control of the excess of water, basic conditions or insufficient time to co-hydrolysis [2].

The sol homogeneity level can be controlled by the action of chemical additives such as urea, citric acid, ethylenediaminetetraacetic acid (EDTA), among others. These additives affect the synthesis process by controlling the steps of complexation, hydrolysis and condensation of the starting materials, by changing the ceramic materials crystallization kinetics [20, 46, 47].

Another alternative to reduce and adjust the precursor reactivity is the use of organic additives, such as carboxylic acids, β -diketones or functional alcohols, which act as chelating agents and modify the precursor reactivity [48–52].

Table 1 summarizes some reagents for the mullite synthesis by sol–gel found in the literature, further than the description of the phases formed by heating and the orthorhombic mullite crystallization temperature in each case. Table 1 shows that the crystallization temperature and the crystallized phases differ greatly according to the solvent type, the silicon and aluminum sources used, the presence or absence of additives, etc.

The choice of reagents and synthesis conditions of the mullite precursor by sol–gel gives rise to different gels, which have been divided into two types: monophasic, when the aluminum and silicon are mixed at atomic level, and diphasic, when the homogeneity scale is between 1 and 100 nm [2, 62, 63]. There is still a third type, not much studied, the hybrid gel, which is the union of monophasic and diphasic gel [64, 65].

Table 1 Summary of methods for obtaining mullite by sol–gel

Reagents	T(°C)	Formed phases	References
TEOS + sec-Al(OC ₄ H ₉) ₃ + (alcohol + ketone) or + (alcohol + water)	1,200	Spinel → orthorhombic mullite	[53, 54]
TEOS + ANN + water	1,300	Spinel → α -alumina + spinel → orthorhombic mullite + α -alumina (1,200 °C) → orthorhombic mullite	[53]
TEOS + ANN + ethanol	980	Tetragonal mullite	[54–56]
TEOS + ANN + ethanol + NH ₃	1,200	Spinel → tetragonal mullite	[56]
TEOS + ANN + water + NH ₃	1,300	Tetragonal mullite + spinel (1,200 °C) → tetragonal mullite	[54]
TEOS + ANN + water + urea	1,300	Tetragonal mullite (980 °C) → orthorhombic mullite	[14, 57]
TEOS + ANN + AIP + water	1,000	Tetragonal mullite (traços) → mullite tetragonal	[56, 58]
TEOS + AIP + ethanol + water	1,200	Spinel + orthorhombic mullite (1,000 °C) → orthorhombic mullite	[59]
TEOS + boehmite + water	1,250	Spinel → orthorhombic mullite	[60]
TEOS + AlCl ₃ .6H ₂ O + water + alcohol + NH ₃	1,350	Baierita → δ -alumina → (δ, θ)-alumina → mullite ^a + (δ, θ)-alumina (1,250 °C) → mullite ^a	[9]
Colloidal silica + ANN + water	1,200	θ -alumina → mullite ^a + cristobalite	[61]
Silicic acid + ANN + urea	1,300	Tetragonal mullite (980 °C) → orthorhombic mullite	[2]
TESPA + ANN + water + citric ac. + NH ₃	1,300	Tetragonal mullite (980 °C) → orthorhombic mullite	[2]

AIP: aluminum isopropoxide (Al(OC₃H₇)₃), boehmite: γ -AlOOH, TESPA: (C₂H₅O)₃Si(CH₂)₃NH₂, ANN: Al(NO₃)₃.9H₂O

^a It does not specify the type od mullite

4 Monophasic gel

Monophasic gels are formed when aluminum and silicon are mixed at the atomic level. These gels are formed by the replacement of silicon that comes from the silica three-dimensional network, by atoms and/or hydrolysed aluminum molecules, leading to bonds Al–O–Si similar to those formed during the mullite crystallization stage [2–11, 14, 15]. Monophasic gels crystallize orthorhombic mullite (the more stable phase) without the crystallization of intermediate phases at a temperature of about 980 °C [11, 16, 56, 66, 67]. The mullite crystallization process is controlled by the nucleation stage, since the speed of this process depends on the presence of nucleating agents [24, 68]. The activation energy to crystallize mullite from monophasic gels is in the range from 290 to 400 kJ/mol [11] although some authors have already determined higher activation energy values for monophasic gels. Okada, in 2008 [69], showed an activation energy for mullite nucleation-growth of 1,400 kJ/mol for precursors that formed mullite at 1,000 °C. In this study, Okada showed that the increase in the activation energy is directly proportional to the increase in the mullitization temperature until 1,000 °C, and from this temperature, the activation energy starts to decrease as the temperature increases. The mullitization process for monophasic gels, according to Okada, has three stages: nucleation, nucleation-growth and coalescence, as the heating temperature increases [69].

A silica and alumina mixture at the atomic scale can occur by slow hydrolysis of alkoxides and salt solution

mixtures [11]. Monophasic mullite precursors are obtained using TEOS, ANN and ethanol with slow hydrolysis.

Another possibility for obtaining monophasic mullite precursors is the use of AIP (aluminum isopropoxide) with the ANN in aqueous solution. [58, 70, 71]. Leivo [58] showed the tetragonal mullite formation, at temperatures below 1,000 °C, as the only crystalline phase without the intermediaries phases formation, using AIP with ANN as the aluminum source. They observed that AIP and ANN form partially hydrolysed and stable nanoparticle polycondensates at temperature of 60 °C for gel formation. These nanoparticles have many Al–O–Si links, where Si is generally linked to three Al^{VI} via oxygen bridges [58].

Chakravorty [22] succeeded in synthesizing monophasic gels from a freshly prepared silica sol and aluminum sulphate hydrate, at pH 4.5, showing the tetragonal mullite formation at 980 °C and the spinel phase presence [22].

4.1 Monophasic gel: characterization at low temperatures

Chakraborty [21] studied precursors prepared by sol–gel from TEOS and ANN using different concentrations of alumina and silica. By controlling the temperature of the sol during gelatinization, he observed that the temperature increased with time in different proportions, depending on the content of silica and alumina in the sol. The highest temperature observed was 110 °C, and it occurred at the sol with the mullite stoichiometric composition. This sample also showed an exothermic DTA peak around 110 °C, and

it was the only one that did not separate phases of silica and alumina when fired at temperatures above 1,000 °C, as occurred with the samples synthesized with silica and alumina in excess. The peak around 110 °C does not appear in the DTA of pure TEOS and ANN. In other words, this peak should be related to an interaction between the TEOS and ANN. According to Chakraborty, nitrate radicals from the solution of aluminum nitrate oxidize the ethoxy groups of TEOS forming NO₂ groups and create links between silicon and aluminum via oxygen atoms. This interaction between TEOS and ANN also explains the increase at the temperature of the sol during gelatinization [21]. According to Schneider et al. [11], this exothermic reaction between the nitrate group and the organic material facilitates the organization (pre-arrangement) between the chains of silicon and aluminum due to the heat released. This organization facilitates the mullite crystallization at lower temperatures [11]. Therefore, if there is a greater amount of organic material in a sample, this reaction is more intense, until a certain limit. Chakraborty has proven this hypothesis by comparing DTA analysis in samples formed by TEOS, ANN and ethanol, with samples without the addition of ethanol to the reagents used previously. He noted the increased intensity of the exothermic peak at 110 °C in the DTA curve of the sample prepared with ethanol addition.

Many authors who synthesized mullite by sol–gel process using TEOS and ANN as precursors, obtained orthorhombic mullite as the only phase crystallized at approximately 1,000 °C. Chakraborty [21] obtained the tetragonal phase with the spinel at 1,000 °C, but the phase of orthorhombic mullite appeared only at 1,250 °C. This possibly occurred because the gelatinization temperature used by Chakraborty was 80 °C, which was a high temperature, so the ANN crystallization water evaporated in short time, and the total hydrolysis of TEOS did not occur. The other authors usually use a gelatinization temperature of 60 °C. However, temperatures lower than 60 °C for the gelatinization of monophasic gels prepared with ANN, TEOS and ethanol, are not recommended. This is because the aluminum nitrate is much less soluble in ethanol at 25 °C than at 60 °C. The aluminum nitrate solubility in ethanol at 60 °C increases about seven times compared to its solubility at 25 °C, as observed by Okada et al. [72]. In this study, they showed that sols, prepared with TEOS, aluminum nitrate and ethanol, crystallized a very small amount of mullite at 1,000 °C when kept at temperatures equal or below 50 °C during the drying process, opposite to what happened when the sols were kept at temperatures of 60 °C, as illustrated in Fig. 1. This fact is directly related to the higher solubility of aluminum nitrate in ethanol at 60 °C, which means that the samples have a much greater

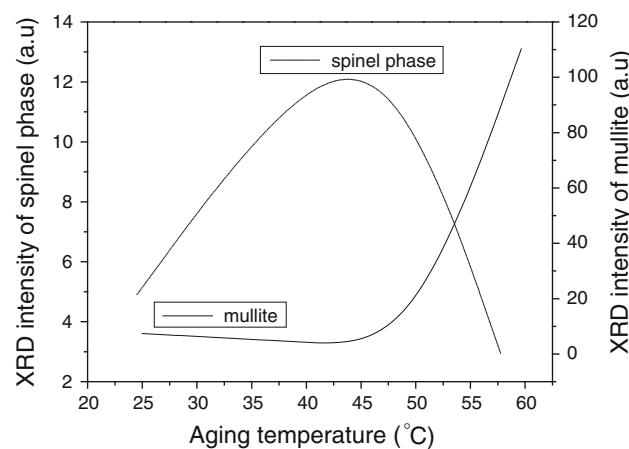


Fig. 1 XRD intensity of mullite and spinel phase in the samples fired at 1,000 °C, previously aged at various temperatures; figure slightly modified from [72]

homogeneity when the drying occurs at this temperature than at lower temperatures [72].

Some authors have shown the mullite formation at temperatures lower than 900 °C [56, 71, 73]. Ban et al. [56] obtained mullite at 450 °C (small amount) from precursors prepared with ANN, AIP and TEOS, and pre-calcined at 250 °C for 16 h. The same precursors, which were not pre-calcined at 250 °C, formed mullite only at 1,000 °C. Therefore, the treatment at 250 °C was essential for the mullite formation at much lower temperatures. This treatment caused dehydration and decomposition of part of the nitrate and alkoxyl groups, which led to regions with a small heterogeneity and with a slightly different chemical composition in the precursor particles. Thus, the interfaces between these regions are energetically active and act as the heterogeneous nucleation sites. However, the amount of mullite formed is small, because the mullitization process occurs only at the interface between regions with different compositions [56].

4.2 Monophasic gel: characterization at intermediate and high temperatures

The work done by Jaymes et al. [2] in 1996, using mullite precursor powder from mono and diphasic gels, showed changes in the coordination number of Si and Al atoms during the mullite crystallization process. Jaymes et al. found that the type of transformation depends on the arrangement involved around the aluminum atoms. The analysis of precursor powders, obtained from monophasic gels, showed that the concentration of hexa-coordinate aluminum cations decreased significantly—increasing the tetra-coordinated—around 980 °C and that the orthorhombic mullite crystallization occurred at this temperature [2].

The work of Beran et al. [74], as well as the work of Jaymes et al. [2], showed that, at low temperatures, hexacoordinate AlO_6 structures prevail in relation to tetra-coordinated AlO_4 , and by increasing the temperature, the opposite occurs. According to Beran, this is related to the dehydration process, which occurs between middle and high temperatures of network condensation, starting at around 400 °C, and it shows the inhibiting role of H_2O and OH in the formation of AlO_4 structures [74].

Voll et al. [75] synthesized mullite monophasic gels by sol-gel process from TEOS, aluminum sec-butoxide and isopropanol. They showed that monophasic gels have a strong increase of the OH/ H_2O ratio up to 600 °C and a recombination of OH groups to H_2O molecules above 600 °C. They suggested, from FT-IR analysis, a mechanism of monophasic precursor dehydration. According to them, the water molecules that are in the pores and adhered to the precursor surface leave the network by the evaporation together with the organic material at above 400 °C. Between 600 and 700 °C, the thermal energy is high enough for dehydroxylation precursor of the network and the recombination of OH groups to H_2O molecules occur. Part of this ‘recombination-produced’ H_2O is trapped in closed pores. Above 800 °C, microfracturing of the precursors occurs because the high vapour pressure of the entrapped H_2O , and so, it enables H_2O to evaporate rapidly along the micropores. Then, at 900 °C, the precursor becomes nearly free of H_2O [75].

Monophasic and diphasic precursors synthesized by Beran et al. [74] showed FT-IR spectra between 1,400–400 cm^{-1} of samples fired up to 800 °C very alike, due to the similar arrangement of the structure Al–O–Si in both of them. However, significant differences were noted between the two spectra after burning at 900 °C. At this temperature, the diphasic precursor FT-IR spectra remain similar to that one presented at 800 °C, while the monophasic showed FT-IR spectra similar to the mullite one. The FT-IR bands were shifted, and the XRD pattern of the monophasic precursor burned at 900 °C showed the formation of an amorphous substance. FT-IR and XRD analysis indicated the increasing in the network condensation degree and changes in the Si–O distances, which changes to SiO_4 tetrahedra dimensions, similar to those that occur in mullite. For diphasic gels, there is no change in the FT-IR spectra between 800 and 900 °C, but only at 1,000 °C, due to the formation of $\gamma\text{-Al}_2\text{O}_3$ [74].

Sola et al. [76] studied monophasic gels and observed a continuous increase in the intensity ratio of FT-IR bands at 1,160 and 1,130 cm^{-1} with the increase of the temperature from 900 °C, showing that the crystallized mullite becomes increasingly rich in SiO_2 . Other studies [77, 78] with monophasic and diphasic gels also showed that the intensity ratio of the bands in 1,170 and 1,130 cm^{-1} in the

FT-IR spectra, which appears after firing at high temperatures, has a linear relationship with the mullite composition, defined as $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$. In this formula, x represents the oxygen vacancies amount per unit cell. The value of x is related to the replacement of silicon ions (Si^{4+}) by aluminum ions (Al^{3+}) in the tetrahedral sites of the material structure and the simultaneous formation of oxygen vacancies. Its value varies depending on the molar concentration of Al_2O_3 , according to Eq. 1 [79]:

$$x = 10 - 6[(m^* + 200)/(m^* + 100)] \quad (1)$$

where m^* is the mole percent of alumina.

Orthorhombic mullite has the value of x equal to 0.25, and the tetragonal has x equal to 0.4. For the tetragonal mullite, the FT-IR band at 1,130 cm^{-1} is more intense than the band at 1,170 cm^{-1} , and for the orthorhombic phase, the opposite occurs [78].

In another study performed by Sola et al. [80], they have shown that the monophasic gels crystallized orthorhombic mullite directly from the amorphous gel at 900 °C, and, with increasing temperature, alumina-rich phase reacts with the silica to form mullite with higher silica content. The X-ray patterns of monophasic gels showed the two characteristic peaks of orthorhombic mullite at 26° being separated gradually more after heating the gels at temperatures between 1,000 and 1,600 °C, as shown in Fig. 2 [80].

Some studies about the mullite FT-IR spectra and the assignment of IR vibrational modes were made. The assignment of each peak present in the mullite FT-IR spectra, according to Schneider et al. [77], is shown in Table 2. However, Voll et al. [81], in 2002, suggested a new assignment, shown in Table 3.

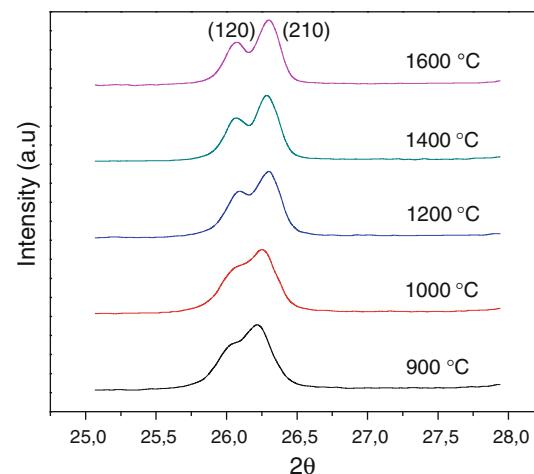


Fig. 2 XRD patterns of gels fired at various temperatures: the splitting of peaks (1 2 0) and (2 1 0) are observed with increasing temperature; figure slightly modified from [80]

Table 2 Band locations and assignments for the various vibrational modes for mullite by Schneider et al. [77]

Band locations (cm^{-1})	Band assignments
1,125–1,165	Si–O stretch
950–988	Si–O stretch
830–909	Al–O stretch (AlO_4)
730–737	T–O–T bend (TO_4), onde T = Al or Si
620	Al–O bend (AlO_4)
548–578	Al–O stretch (AlO_6)
482–498	Si–O bend

Table 3 Band locations and assignments for the various vibrational modes for mullite by Voll et al. [81]

Band locations (cm^{-1})	Band assignments
1,168	Si–O stretch (SiO_4), in-plane
1,131	Si–O stretch (SiO_4), in-plane
988	Si–O stretch (SiO_4), out-of-plane
909	Al–O stretch (AlO_4), out-of-plane
828	Al–O stretch (AlO_4), in-plane
737	T–O–T bend (TO_4), in-plane onde T = Al or Si
620	O–A–O bend (AlO_4)
578	Al–O stretch (AlO_6)
482	O–Si–O bend (SiO_4) and Al–O–Al bend (AlO_6)

In-plane and out-of-plane vibrations are related to the (0 0 1) plane of the structure

Stretch: stretching vibration, bend: bending vibration

4.3 Monophasic gel: pH influence

Chakravorty [22] studied the effect of the pH on the formation of mullite synthesized by sol–gel from a silica sol. He showed that when the pH was between 3 and 4.5, the formation of monophasic precursors occurred, with the mullite crystallization at 980 °C. However, if $\text{pH} \leq 1$ or $\text{pH} \sim 14$, the formation of diphasic precursors occurs, with the mullite crystallization at higher temperatures and the formation of intermediate phases at 980 °C. This happens because when the pH is smaller or equal to 1, the silica sol loses its stability and rapidly gels due to the diminution of the negative charge of the sol by Al^{3+} . In the case of a pH between 3 and 4.5, by mixing an aluminum salt and a silicic acid sol, the reaction between one silicic acid molecule with three aluminum atoms takes place, forming a simple unit of aluminosilicate complex. Two of these molecules are polymerized in the next step [22].

4.4 Monophasic gel: use of additives

Some studies have used organic polydentate ligands in the mullite precursor synthesis by sol–gel to control the hydrolytic polymerization by the ligants ability to produce complex substances. Fujio Mizukami et al. [30] synthesized samples from TEOS and ANN or dibutoxyethylacetatoaluminum ($\text{Al(OBu)}_2(\text{Ac}(\text{AcEt}))$), and used: ethylene glycol, 1,3-propanediol, 1,3-butanediol, 2-methyl-2,4-pentanediol, diethylene glycol monoethyl ether and ethoxyethanol as ligands. All of the ligands used, ethylene glycol proved to have a more positive effect in the mullite formation. This is because the ethoxy group of TEOS can easily replace the hydroxyl groups of ligands and coordinate the aluminum ion. Therefore, the ligands can act as a bridge between aluminum and silicon. NMR spectra of the precursor prepared with ethylene glycol suggested the existence of $\text{Al}-\text{OCH}_2\text{CH}_2\text{O}-\text{Si}$ bond. According to Stefanescu et al. [82] the presence of ethylene glycol in the silica matrix occurs in three forms: chemically bonded in the silica network, hydrogen bonded with the silanol groups and free in the hybrid matrix pores.

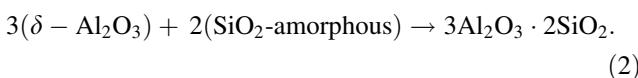
Urea is another additive used in the mullite precursor synthesis. Jaymes et al. [57] synthesized mullite monophasic gels from ANN aqueous solution, silicic acid and urea. This solution was maintained at 80–100 °C, for the ammonia formation. The production of ammonia has two purposes, first, to promote the polycondensation of silicic acid into silica gel by raising the pH, and second, the hydrolysis and polycondensation of aluminum. With the slow addition of ammonia, the copolycondensation of Al and Si species occurs. These precursors, when washed free of ammonium nitrate, form tetragonal mullite at 980 °C [57].

Some authors have tried to add inorganic additives in mullite monophasic precursors prepared by sol–gel process in order to reduce the mullite crystallization temperature. Simendi and Radonji [83] added fluorine acid to polymeric sols prepared from TEOS and aluminum nitrate nanohydrate. The fluoride ion was added from 2 to 5% (weight). They showed that the addition of fluoride ions decreased the mullite crystallization temperature from 980 to 890 °C for the fluorine concentration of 3.5%(weight). This fluoride mass concentration was the one that caused the lowest mullite formation temperature. The effect of fluoride ion is related to its contribution to breaking oxygen bonds in mullite gel structure, reducing the homogeneity scale of the precursors to the molecular level. Moreover, breaking that structure should provide conditions for heterogeneous nucleation [83].

5 Diphasic gel

Diphasic gels are formed when the homogeneity scale between aluminum and silicon is between 1 and 100 nm. For this precursor type, a transient phase formation usually occurs before the mullite crystallization, which commonly occurs at temperatures around 1,300 °C. For this type of gel, the activation energy for mullite crystallization is about 1,000 kJ/mol [11]. Hoffman et al. [84] initiated the synthesis of mullite diphasic gels, by sol–gel process in 1984, and used aqueous silica sol and boehmite sol as starting materials.

Wei et al. [62] showed, in 1988, that diphasic gel crystallized mullite around 1,200 °C, from the following reaction:



The Wei's study resulted in a model for the crystallization process based on the formation of a mullite interface between the alumina and silica grains, and the growth mechanism was controlled by diffusion of silicon and aluminum in this interface (Fig. 3). Only in 2001, Kleebe et al. [68] have clearly shown, through electron microscopy transmission, the formation of this interface between the particles.

In 1991, Sundaresan et al. [15] proposed that the mullite crystallization process starts with the step of alumina dissolution in the amorphous silica phase. When the alumina concentration reaches the mullite solubility limit, precipitation occurs, starting at these points the mullite nucleation. Therefore, the growth rate of mullite grains would be controlled by the rate of alumina dissolution in the amorphous matrix [15, 85].

Studies by Wei [62] and Sundaresan [15] showed that the amorphous matrix crystallized directly into tetragonal mullite and then to orthorhombic mullite

[15, 62]. On the other hand, several authors have described the formation of an aluminosilicate intermediate phase, concomitantly with the tetragonal mullite formation, which precedes the orthorhombic mullite formation [8, 86]. According to Okada [69], the steps that control mullitization in diphasic precursors at higher temperatures change at higher temperatures from being dominated by the transfer of alumina from γ - Al_2O_3 to amorphous silica, to diffusion-controlled processes. Tkalcec et al. [87] investigated diphasic gels and identified two stages of mullite formation: nucleation and growth of mullite and a slow conversion of 2:1 mullite composition for 3:2. This second slow stage is accelerated in the precursor with small size of alumina particle, what does not happen in the sample with alumina derived from boehmite (γ - AlOOH). If the morphology is in a very fine scale, the conversion of 2:1 composition mullite starts even in the first stage of transformation [87].

Diphasic gels can also be formed by rapid hydrolysis of alkoxides or saline solutions [7, 11], by using colloidal silica and boehmite [88], or colloidal silica and ANN [89].

Table 4 summarizes different studies that investigated the mullite formation kinetic. They are separated in relation to the mole percentage of Al_2O_3 present in each study, activation energy and mullite crystallization temperature found.

5.1 Diphasic gel: characterization at low temperatures

Mullite precursor gels prepared by an aqueous route are often diphasic gels. Unlike monophasic gels, these diphasic gels are obtained by keeping the sols at room temperature until the gel formation. This is because the drying process at room temperature for aqueous routes results in increased elasticity of the gel, decreasing the volume and causing the absence of fluid exudation with the cut, maintaining its homogeneity [89, 93].

The exothermic peak at low temperatures (between 110 and 200 °C) that occurs in the DTA analysis of the monophasic gel does not occur for the diphasic gel, synthesized, for example, from TEOS, ANN and water [21, 34, 35, 94]. This observation is due to the low concentration of organic matter in this diphasic gel. Therefore, there is not enough organic material to react with TEOS in the diphasic gel synthesized from TEOS, ANN and water. This is one of the reasons that diphasic gels crystallize mullite only at higher temperatures. The chemical reaction between the nitrate group and the organic material releases heat enough to facilitate the organization of the silicon and aluminum chains [11, 35].

However, the most obvious reason to explain the mullite crystallization at higher temperatures is the lack of homogeneity that exists in the diphasic sol. This can occur,

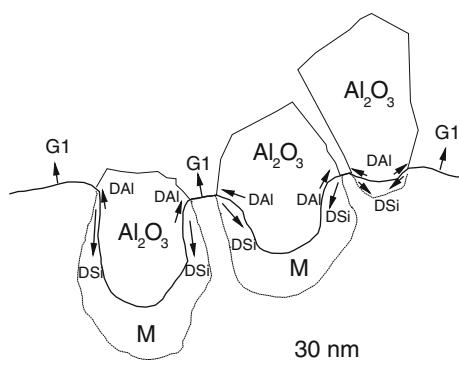


Fig. 3 Diffusion of silicon and aluminum in the mullite interface; figure slightly modified from [62]

Table 4 Kinetic parameters of mullite precursors synthesized by sol-gel

Gel type	Mol (% Al ₂ O ₃)	Ea (kJ/mol)	Temperature (°C)	Reference
Gel monofásico	60.0	330 ± 30	980	Li and Thomson [63]
Gel monofásico	60.0	1,202 ± 27	969–998	Okada [90]
Gel monofásico	60.0	1,385 ± 145	973	Douy [91]
Gel difásico	60.0	1,034 ± 63	1,300–1,390	Li and Thomson [4]
Gel difásico	60.0	1,070 ± 200	1,200–1,300	Wei and Halloran [62]
Gel difásico	60.4	950 ± 82	1,200–1,300	Lee and Yu [92]
Gel difásico	59.7	891 ± 17	1,275–1,315	Lee and Yu [92]
Gel difásico	73.0	932 ± 29	1,275–1,315	Lee and Yu [92]
Gel híbrido	60.0	960 ± 91	1,200–1,275	Huling and Messing [8]

for example, due to the large size of the particles present in the sol. A study by Vol'khin et al. [31] showed that the smaller the particle size of the mullite precursors, the lower the mullitization temperature [31]. Furthermore, the extensive condensation of alumina and silica, generating clusters and segregation phase, also cause heterogeneity and increases the mullite crystallization temperature. This heterogeneity was shown by Padmaja et al. [60], who studied, by FT-IR, diphasic precursors prepared from a boehmite sol and TEOS (gelatinization occurred at 60 °C) burned at various temperatures between 60 and 1,400 °C. The FT-IR spectra of the gel and of the gel fired at 200 °C were very similar. The FR-IR analysis also showed Si–O–Si and Al–O–Al bonds for the gel and for the precursor calcined at 200 °C, but did not show the formation of Si–O–Al bond for both, indicating the lack of homogeneity of the precursors [60].

Volllet et al. [95] characterized diphasic gels synthesized from a colloidal sol of boehmite and a hydrolyzed TEOS solution. They observed that the wet gel, which was almost clear and monolithic, lost its transparency in drying, when syneresis ended and crack occurred. The transparency is recovered upon water re-absorption from a saturated atmosphere. The gel XRD pattern was found to be compatible with a diphasic system, composed of an amorphous silica phase, and a colloidal crystalline phase of boehmite [95].

5.2 Diphasic gel: characterization at intermediate and high temperatures

FT-IR studies of diphasic gels synthesized from boehmite sol and TEOS, in the temperature range between 400 and 1,000 °C, done by Padmaja et al. at [60] showed the presence of nanostructured Al₂O₃, SiO₂ and Al₂O₃–SiO₂ agglomeration in the amorphous state. That study also showed the presence of tetra-coordinated and octa-coordinated aluminum atoms just before 1,000 °C, indicating the formation of the spinel phase, which was characterized by DTA and XRD. At 1,200 °C, they showed the mullite

formation by shifting the Si–O–Si and Si–O–Al bands to higher wave numbers. The end of the orthorhombic mullite formation was shown by the FT-IR spectra of the precursor calcined at 1,250, 1,300 and 1,400 °C, which are almost equal. The reversal of the relative intensity of the bands around 1,190 and 1,130 cm⁻¹ is an indicative of the increased amount of Si–O–Si bonds compared to Si–O–Al, which is explained by the reabsorption of silica during the transformation of the spinel into mullite [60].

Jaymes et al. [2] have shown that mullite precursor powders obtained from diphasic gels led to the formation of an intermediate aluminosilicate (spinel) exhibiting a higher concentration of hexa-coordinated aluminium at 980 °C when compared with the monophasic gel [2]. Fig. 4 shows the differences in the amounts of each type of aluminium coordination for monophasic and diphasic gels calcined at various temperatures.

Beran et al. [74] synthesized monophasic and diphasic gels of mullite by sol-gel process from TEOS and aluminum sec-butoxide using isopropanol as a solvent for the monophasic precursor, and isopropyl alcohol and water in

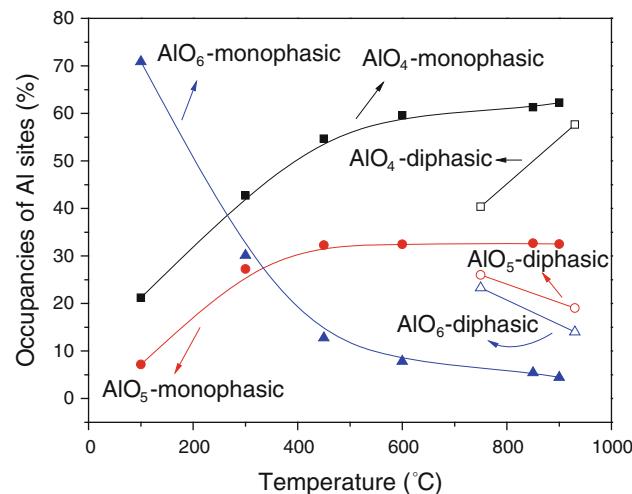


Fig. 4 Estimated occupancies of Al₄, Al₅ and Al₆ in monophasic and diphasic precursor; figure slightly modified from [2]

basic pH for the diphasic precursor. In this study, the diphasic gels showed the OH/H₂O ratio continuously increasing as the temperature increases between 100 and 1,000 °C, unlike the monophasic gels, which showed a strong increase of the OH/H₂O ratio up to 600 °C and a recombination of OH groups to H₂O molecules above 600 °C, as shown in Fig. 5 [74, 75].

For the diphasic gels, according to this study, the dehydration is in contrast with monophasic gels. This is because the diphasic precursors show a slight and continuous increase of the OH/H₂O ratio until only 400 °C, above this temperature, this ratio remains constant, or; in some cases, one can see a slight decrease in it. In addition, the diphasic gels showed essential amounts of H₂O molecules and OH groups at 1,000 °C. Structural changes of the

diphasic precursors occur at temperatures higher than the monophasic precursors, due to the strong retention of H₂O and OH of the diphasic gels between 400–700 °C [74].

Vollet et al. [95] studied the sequence of phase transitions that take place in diphasic gel synthesized from colloidal sol of boehmite and a hydrolyzed TEOS solution. In this study, the mullite is formed at 1,300 °C after the formation of alumina intermediate phases, closely following the same transition sequence as in pure alumina [95].

The composition of the spinel intermediate phase, formed during heating diphasic precursors, is controversial. Schneider et al. [96] re-examined the composition of spinel phase at temperatures between 350 and 1,150 °C and concluded that above 350 °C, this phase contains about 12% (mol) of SiO₂, and up to 750 °C the composition remains constant. However, above this temperature, the content of SiO₂ increases gradually until it reaches 18% at 1,150 °C.

5.3 Diphasic gel: pH influence

The pH of the mullite precursor influences the type of the phase formed at each temperature, as well as the morphology of the mullite formed. Studies by Jae-Ean Lee et al. [61] with samples prepared from ANN and colloidal silica sols showed that when the pH was less than 2, the synthesis of needlelike mullite occurred, while for pH greater than 8, rodlike or granular mullite occurred. The mullitization temperature was about 1,200 °C for the acid samples and above 1,200 °C for the basic samples. In addition, basic precursors generate opaque gels, and acid precursors generate transparent gels due to the size of the particles that are lower in acid precursors [61].

Osawa et al. [25] produced mullite from alumina and silica sols at different pH, with the mullite stoichiometric composition and with silica excess. They showed that the pH did not influence the mullite formation from precursors prepared with silica excess (molar ratio Al:Si = 1:3). In this case, the silica excess determined its distribution around alumina, leading to the formation of a tetragonal mullite, following the Sundaresan and Aksay mechanism. However, the pH influenced the mullite formation from precursors prepared with the stoichiometric composition (molar ratio Al:Si = 3:1). While at pH 1 octa-coordinated Al³⁺ ions were predominant in the alumina sol, at pH 6 tetra-coordinated ions were predominant. The minimum mullite crystallization temperature was determined by the interactions between the silica and alumina particles and their distribution in the precursors [25].

Huang et al. [97] synthesized mullite precursor diphasic gels from TEOS, water and aluminium chloride hydrate (AlCl₃·6H₂O) at different pH. They showed that, at pH 1.5,

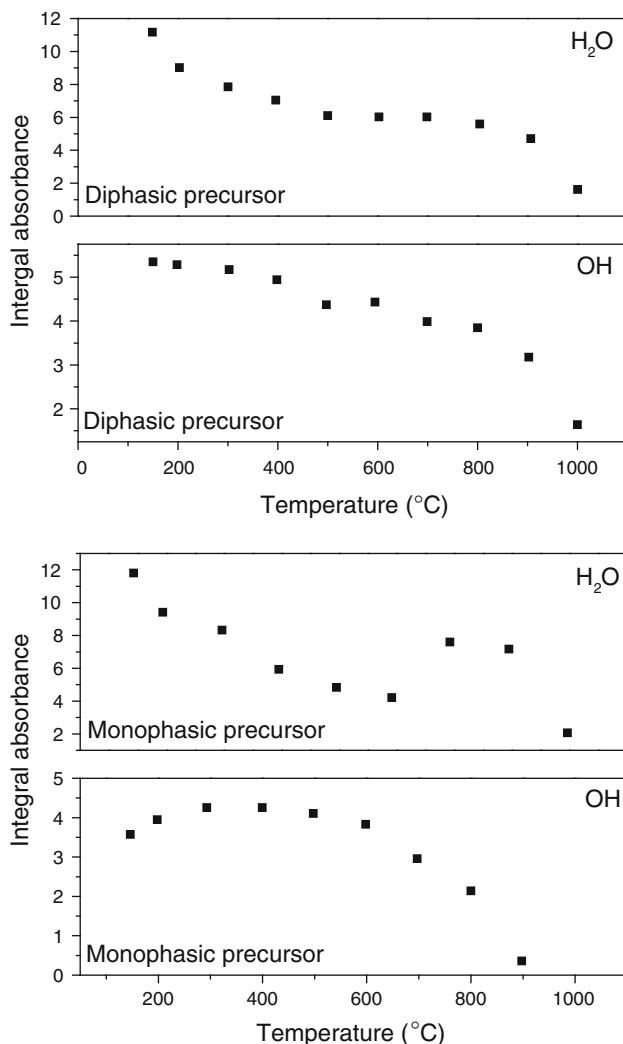


Fig. 5 Integral absorbance values of the mullite precursor, preheated at different temperatures, of the H₂O combination band centered at 5,160 cm⁻¹, and of the (Si, Al)-OH combination band at 4,540 cm⁻¹, for monophasic and diphasic gel; figure slightly modified from [74, 75]

the mullite formation occurs at 1,200 °C, while at pH 11.5 the mullite formation occurs only at 1,350 °C. This is because, under acidic conditions, the hydration of the OH⁻ groups on the surface of the silica particles can decrease the particles agglomeration. In addition, the Al(OH)₃ particles react with acid to form Al³⁺ ions, which can act as counterion absorbing on the surface of the silica particles. This brings the Al³⁺ and SiO₂ particles next to each other, and the gel becomes more homogeneous. In the case of basic pH, the base addition leads to condensation reactions between Al(OH)₃ particles, Al(OH)₃ and SiO₂ particles, and SiO₂ particles, resulting in segregations of alumina and silica [97].

5.4 Diphasic gel: use of additives

Thim and co-authors [98], in 2001, studied mullite precursors xerogels obtained from gels prepared with silica sol, aluminum nitrate and urea. They found, through analysis of ²⁷Al nuclear magnetic resonance (NMR), the presence of peaks indicating the presence of Al atoms in different chemical environments, as shown in Fig. 6. Mathematical calculations, using Monte Carlo, showed that urea replaces two water molecules in the first coordination sphere of aluminum at room temperature [98].

Further studies, conducted by Campos et al. [24] showed that precursors synthesized with silicic acid, aluminum nitrate and urea in the proportion of urea/Al³⁺ equal to 3/1, crystallized mullite with activation energy of 730 ± 150 kJ/mol, at temperatures close to 1,200 °C, through the spinel type aluminosilicate formation [24]. Another study of the mullite crystallization kinetics performed by our group using similar samples, showed an activation energy of 919 ± 24 kJ/mol [26, 99]. In this study, we used the isoconversional, non-isothermal, Flynn–Wall–Ozawa method, unlike the study by Campos

et al., who used the Johnson–Mehl–Avrami–Kolmogorov (JMAK) method. In the work [27, 99] mullite precursors from polymeric and colloidal sol were synthesized using molar ratios of urea/Al³⁺ equal to 0/1, 1/1 e 3/1. In this study, we showed that urea has a positive effect on the mullite crystallization when the precursor is colloidal and a negative effect when the precursor is polymeric. In addition, the crystallized mullite amount increased with the urea content in the colloidal gels, and the colloidal gel with higher urea concentration formed mullite at 1,100 °C and was the only sample that did not segregate the phase α -alumina. It is believed that the positive effect of urea on the colloidal gels is related to its participation in the hydrolysis and condensation steps of aluminum and silicon, avoiding the intense phase segregation. This study also suggested that the negative effect observed in the polymeric samples might have occurred due to competition between aluminum nitrate, silanol, and urea by the few water molecules present in the polymeric precursors.

The citric acid addition to the mullite precursors sols has also been studied by Campos et al. [28], who synthesized mullite precursors from silicic acid, ANN and citric acid in molar ratios of citric acid/Al³⁺ equal to 0/1, 1/1, 2/1 and 3/1. The citric acid helped in the mullite crystallization, and the best effect was seen for the sample with molar ratio of citric acid/Al³⁺ equal to 1/1 pre-calcined at 450°C for 120 h. According to Bertran et al. [100], citric acid acts as a chelator of Al³⁺ ions, controlling the phase segregation during the drying stage and the initial heat treatment of the gel. Inorganic additives can also be added to diphasic gels to reduce the mullite crystallization temperature. Hong and Messing [101] synthesized diphasic gels prepared from boehmite and silica doped with boria, introduced to the aqueous dispersion as boric acid. The mullite crystallization temperature was reduced from 1,345 °C for non-doped sample to 1,260 °C for sample doped with boria (3%-wt). This reduction in the mullite crystallization temperature is related to the fact that boria enhanced the densification by reducing the viscosity and by forming a fine grain microstructure [101].

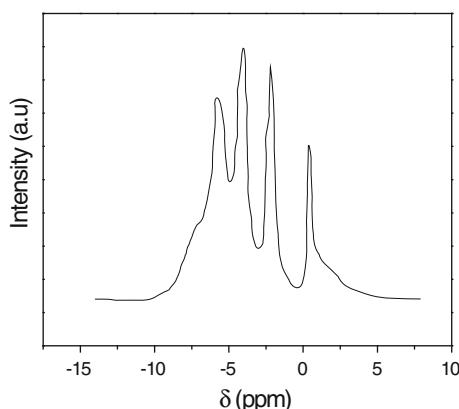


Fig. 6 ²⁷Al NMR spectrum for an aqueous solution containing aluminum nitrate salt and urea in high concentration, $\delta = 0$ ppm for hexa-coordinated aluminum; figure slightly modified from [98]

6 Hybrid gel

Huling and Messing [64] were the first to introduce the concept of hybrid gel, in 1989, as a mixture of polymeric and colloidal sols. In this work, they synthesized hybrid gels from a colloidal boehmite-silica sol and a polymeric aluminum nitrate-TEOS sol. The polymeric gel crystallizes mullite first, and acts as nuclei of nucleation for the mullite crystallization of the gel hybrid colloidal component. The hybrid gel with 30% of polymeric component formed mullite as the main crystalline phase after being heated at 1,230 °C for 2 h [64].

Zhao et al. [65], in 2003, synthesized a hybrid gel composed of a relatively small amount of monophasic gel in a diphasic gel matrix. The diphasic gel was synthesized from AlOOH and SiO₂ and heated at 700 °C for 7 h. The mullite formation temperature was more than 1250 °C, showing that the diphasic component, which is in higher proportion, controls the mullite crystallization mechanism of the hybrid gel. In this study, the apparent activation energy for mullitization was 846 kJ/mol [65].

7 Properties of the mullite obtained

The final matrix porosity and the material surface area can be controlled by monitoring the kinetics of hydrolysis and polycondensation [101] of silicon alkoxides by a precise control of the pH [102, 103], organic additives addition [104, 105] or metals addition [106]. For example, urea can avoid one of the most serious problems in the gel production synthesized from sol-gel process, which is the fracture and breakage of the sample during the conversion of gel to xerogel. This fracture is due to capillary forces that appear during the drying. The use of additives such as formamide, oxalic acid and urea can efficiently control the pores formation during the drying process. The gels prepared with these additives have a uniform pore distribution, preventing further fractures that could be caused by the difference in capillary forces in the pore walls [89, 93].

Although the monophasic gel crystallizes mullite at a lower temperature than the diphasic gel, the densification of ceramics induced by sintering is more difficult to occur in this material. This difficult is related to the very slow mullite diffusion rate, where the time required for mullite densification process of a sample obtained from monophasic gel is much higher than the crystallization time. However, this kind of difficult is not observed in the mullite densification process of samples obtained from diphasic gels, since they require long crystallization time [77, 88, 107]. A complete densification, with fine microstructure and without any glassy phase is very important to achieve very good mechanical properties [88]. For monophasic gels, the temperature required for complete densification is greater than 1,500 °C. However, diphasic precursors have a complete densification at temperatures between 1,250–1,500 °C, due to the formation of a silica-rich viscous phase that helps in the densification process. Nevertheless, this segregated phase usually remains in the final product, which deteriorates the optical and mechanical properties of the material [108]. Moreover, the presence of γ-Al₂O₃ in the structure of the mullite precursor initially promotes densification, but the sintering rate is very low after the mullite crystallization [54].

Despite the complete densification is required for applications where you need a material with excellent mechanical properties, mullite ceramics with high porosity have also application. They are used for high temperature catalysis and separations, and can be synthesized from aerogels made by supercritical drying [88].

Another mullite application is the fibers manufacture. Mullite fibers have been synthesized by sol-gel, especially using AIP, TEOS and aluminum nitrate as starting reagents, because AIP gives the spinning viscosity necessary to synthesize mullite fiber, due to its polymerization [109–111]. However, AIP is expensive. In the study carried out by Zhang et al. in 2009 [111], they showed the mullite fibers synthesis with smooth surface and no cracks from cheaper reagents: ANN, TEOS and polyvinyl butyral (PVB) as binder.

Hrvoje Ivankovic et al. studied the properties of mullite obtained from gels synthesized from TEOS, ANN and water and also from TEOS and γ-Al₂O₃, and TEOS and boehmite, fired at high temperatures (greater than 1,400 °C) [112]. SEM micrographs showed that mullite obtained from ANN had a bimodal grain size distribution; whereas those obtained from γ-Al₂O₃ or boehmite had a monomodal grain size distribution. Mullite obtained from γ-Al₂O₃ or ANN, had a grain size much smaller (0.5–0.7 μm) than those obtained from boehmite (1.3 μm). The microstructure of mullite obtained from ANN is typical of a liquid flow sintering, in other hand, the microstructures of mullite prepared from γ-Al₂O₃ and boehmite had equiaxial morphologies, indicating a solid state sintering. Mullite obtained from ANN had higher strength, higher Vickers hardness and smaller fracture toughness than that prepared from γ-Al₂O₃ and boehmite. The sample prepared with γ-Al₂O₃ had the highest creep rate, while the sample prepared with boehmite had the lowest creep rate. The samples prepared with ANN had intermediaries creep rate values. Mullite prepared from boehmite showed the highest activation energy value for creep ($Q = 742$ kJ/mol), while mullite obtained from γ-Al₂O₃ and ANN showed similar values ($Q = 563\text{--}603$ kJ/mol) [112].

8 Conclusions

As could be seen, the characteristics of the sol and the gel, at low and intermediate temperatures, strongly influence the mullite behavior at high temperatures, and therefore influence the morphology and properties of the final material. Following are described two characteristics that differs monophasic from diphasic gels and their behavior at high temperatures:

- The exothermic reaction between the nitrate group and the organic material, at around 110–200 °C, is observed during the heating a monophasic gel, but it is not observed during the heating of a diphasic gel. This reaction releases heat, facilitating the organization of silicon and aluminum chains.
- Samples prepared from diphasic gel shows higher concentration of hexa-coordinated aluminium at 980 °C than samples prepared from monophasic gel. This hexa-coordination leads to the formation of spinel phase, rather than mullite.

There are many works and studies about the characterization of mullite precursors synthesized by sol-gel at high temperature, but not so many characterizing these precursors at lower temperatures. Thus, it is important to encourage additional studies of monophasic and diphasic mullite precursors at lower temperatures for a greater understanding of their behavior at high temperatures.

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