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A study of the sol-gel system for the preparation of mullite

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A STUDY OF SOL-GEL SYSTEM FOR THE PREPARATION OF MULLITE

A THESIS
SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

BY
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DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA
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\[ R = \text{viii} \quad T = 65 \]
ABSTRACT

CHEMISTRY

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A STUDY OF SOL-GEL SYSTEM FOR THE PREPARATION OF MULLITE

Advisor: Dr. L. Moeti

Thesis dated December 1996

Sol-gel processing methods were used to prepare mullite ceramic powder form high purity aluminum tri-sec butoxide and tetraethylorthosilicate solutions under different processing conditions. The effects of the processing conditions on the sol to gel transition were examined by varying the water ratios, pH and temperature. Prehydrolysis of the silicon alkoxide was used since the aluminum alkoxide reacts faster than the silicon alkoxide. It was observed that the variation in temperature has the greatest effect on the time to gelation for the precursors. The rheological properties during the aging process indicated an increase in viscosity with age time, which is consistent with change in structure. Measurements of the viscoelastic properties during the sol to gel period showed a predominance of the loss (viscous) modulus over the storage (elastic) modulus in the initial stages of aging. With increased aging of the sols and gels, large elastic components were observed which is consistent with structure build-up. The changes in structural evolution were followed by Fourier Transform Infra-red spectroscopy and correlated well to changes in the rheological properties of the sol. TG/DTA and X-ray analyses were used to correlate the starting chemistry and reaction condition to the microstructure of the final mullite powder. In all experimental cases fine grain mullite powder were obtained indicating no apparent differences of the synthesis conditions on the final mullite powder microstructure.
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List Of Abbreviations

1. Tetraethylorthosilicate  TEOS
2. Aluminum tri-sec-butoxide  ATBS
3. Thermogravimetric Analysis  TGA
4. Differential thermal Analysis  DTA
5. Fourier Transform Infra-red  FT-IR
6. X-ray Diffraction  XRD
7. Scanning Electron Microscopy  SEM
CHAPTER ONE

INTRODUCTION

Mullite is an oxide ceramic material which retains its strength at high temperatures in oxidizing environments. Mullite (3Al₂O₃.2SiO₂) powders prepared in this research had a stoichiometric composition of 3:2 mole ratio of aluminum to silicon oxides. It is a stable phase in the Al₂O₃-SiO₂ binary system (Figure 1). Mullite possesses excellent high temperature properties that make it a potentially important ceramic material for high temperature structural applications. It is also attractive due to its high creep resistance¹,², low thermal expansion³ and its outstanding chemical stability. It is a high temperature structural material in an oxidizing environment in comparison to other high performance materials such as silicon nitride Si₃N₄. It is not considered as a high strength material at low temperatures because its potential becomes apparent only at elevated temperatures while the Si₃N₄ matrix ceramics start losing their strength above 1200 °C⁴.

The numerous applications of mullite derive from its favorable physical and chemical properties. For example, its use as an industrial refractory material derives from the high melting point (1890 °C), good creep resistance, low thermal expansion which yields good thermal shock resistance, high shear modulus, and good corrosion resistance. It is a major constituent of whitewares, porcelains, structural clay materials and refractory materials.
FIGURE 1. PHASE DIAGRAM FOR $\text{Al}_2\text{O}_3$-$\text{SiO}_2$
Also due to its good chemical corrosion resistance and good gas permeability, mullite ceramics find application as heat-resisting materials for crucibles, protection tubes and thermocouple tubes. The excellent creep resistance of mullite at high compressive strength at elevated temperature makes it ideal for high temperature exposed parts for mechanical testing machines. Its use as an electronic packaging material stems from its favorable thermal expansion and dielectric constant, good chemical stability, good heat resistivity, good thermal conductivity, and high mechanical strength.

The sol-gel approach was used to prepare the mullite powders in this research. Sol-gel inorganic polymer precursors can provide a route to prepare high purity ceramic materials. High purity metal alkoxides, ATSB and TEOS, were used to prepare pure mullite powders. The emphasis in this project was on developing a fundamental understanding of the physical and chemical structural evolutions occurring during the transformation from the starting materials, ATSB and TEOS, to the final dense ceramic powder. Using the sol-gel technique, the chemistry of the hydrolysis and polycondensation reactions was controlled. This was achieved by prehydrolyzing the silica precursor to avoid a poor level of chemical homogeneity since the rate of hydrolysis of the silica precursor is slower than that of the alumina precursor. Different processing conditions such as pH, TEOS:water ratio, and temperature were utilized in order to observe how these processing conditions affect the gelation process, and the structure of the gels which ultimately determine the microstructure of the final dense mullite powder. FT-IR spectroscopy, rheology, TGA/DTA, XRD, and SEM were the characterization tools to be used in this work.
CHAPTER 2

LITERATURE REVIEW

2.1 BACKGROUND

Mullite is one of the most important materials in the field of ceramic science and technology. It is a strong candidate material for advanced structural applications at high temperatures because it has high strength. It is a single phase oxide ceramic material which retains its strength at high temperature in oxidizing environments. The reactions leading to mullite formation can vary depending on the starting materials and the method of preparation. Mullite can be prepared by using conventional powder processing or colloidal routes. In order to enhance the mechanical properties and overcome the difficulty in sintering of mullite produced by the conventional techniques, alternate preparation routes, such as hot pressing, precipitation, spray hydrolysis chemical vapor deposition (CVD), powder processing and sol-gel processing have been utilized.\(^{9,10,11}\)

Processing methods used in the preparation of mullite include conventional powder, colloidal and sol-gel processing. The poor high temperature mechanical properties of existing ceramics produced by the conventional or colloidal processing can be traced to a variety of undesirable structural features such as large grain sizes, residual porosity, glassy phases, and presence of impurities. Some of the processing methods include\(^5\).
(i) CONVENTIONAL POWDER PROCESSING

In most processes of interest in ceramic technology, solid state reactions are carried out by intimately mixing fine powders. In ceramic processing, powder consolidation and sintering is the common approach for the processing of polycrystalline systems. Mullite prepared by the conventional process i.e. mixing powdered raw materials, was designated 'sinter-mullite'. Oxides, hydroxides, salts and silicates were used, as starting materials. Here mullitization takes place by solid-solid or transient liquid-phase reactions of the starting materials by aluminum, silicon, and oxygen atom interdiffusion. Therefore, mullitization temperature is controlled by the particle size of the starting powder. The starting materials of SiO₂ and Al₂O₃ components are usually of micrometer size and are not small enough to accomplish complete mullitization at relatively low firing temperature within a reasonable duration of time. The powders which are mixed, blended, granulated, crushed and synthesized can be done wet or dry. The wet process is more effective since it keeps the particles together and prevents the suspension of fine particles in air. This process can be broken down into three basic steps which are (i) processing and dispersion of powders (ii) consolidation of powders using liquid suspensions or drying processing techniques and (iii) densification of the powder compacts by heat and/or pressure.

Consolidation of the powder using liquid suspension, is a step in which a liquid is mixed with the powder in order to make a flowable fluid system thereby breaking the agglomerates down into individual particles which are dispersed throughout the liquid. The mixture of the powder and the liquid then undergoes the process of comminution i.e.,
making things more minute since small particle sizes favor more rapid densification and sintering at lower temperature. This is done by ball milling. The breakdown of the agglomerates is usually imperfect and a dynamic process in which “reagglomeration” is constantly taking place. The goal is to: (i) achieve the highest degree of intimate mixing, in powder conditioning, (ii) avoid the formation of hard agglomerates, (iii) avoid porosity, and (iv) avoid the formation of glassy phases in grain boundaries. Since the starting powder determines the ultimate quality of the mullite, there is a need to develop improved starting powders with high chemical purity and controlled particle sizes.

A sintering temperature of ~1600 to 1700 °C is required in the conventional powder techniques to produce extensive mullitization\textsuperscript{24}. Studies done by Hamano et al\textsuperscript{25} using this method showed that mullitization temperature was higher than 1400°C when quartz particles below 2μm in size and α-Al\textsubscript{2}O\textsubscript{3} particles with average particle size of 0.3μm -0.5μm were used.

The disadvantages\textsuperscript{26} of this method is that, it may result in;

1. microstructures having irregular particle shapes and ultrastructures with interphases, secondary phases, and pores between the particles.
2. unfavorable particles size, shape and distribution
3. foreign inclusions
4. hard agglomerates
5. unfavorable agglomerate size distribution (Aggregates of small particles sinter more rapidly than the surrounding particles thus opening up a flaw)
6. porosity, voids and cracks
7. varying density
8. glassy phases, and
9. rough surface

(ii) PRECIPITATION METHOD

Preparation of precipitates from a clear solution using a precipitant is the basis of this method. There are two precipitation methods, namely, coprecipitation and homogeneous precipitation. Coprecipitation involves adding a precipitant (usually ammonia solution) to a solution to form precipitates. Homogeneous precipitation involves first dissolving a precipitant such as urea or hexamethylenetramine beforehand in the solution, and subsequently forming a precipitate by varying the pH through the decomposition of the precipitant in the solution. The starting materials used as alumina sources include nitrates, sulfites, chlorides, and alkoxides while silicon alkoxides, sodium silicate, silicon chloride, and silicon acetate are used as the silicon components.

(iii) SPRAY PYROLYSIS

This method uses droplets from a solution which is sprayed into a furnace heated at high temperatures. Reactions such as evaporation of solvents, precipitation of compounds and thermal decomposition occur instantaneously in this process. The powder obtained by this process has characteristic spherical shapes with a submicrometer to micrometer size. Droplets are prepared by using an atomizer or ultrasonicators. In this method, TEOS and aluminum nitrate, for example, are dissolved in water-methanol solution and the droplets
sprayed into a furnace heated at 350 - 650 °C using borosilicate a glass atomizer with compressed air to form the droplets.

(iv) CHEMICAL VAPOR DEPOSITION (CVD) METHOD

This is a method that utilizes the vapor phase for the synthesis of mullite. Silicon and aluminum chlorides are used as starting materials. The chlorides are separately evaporated and are transported by nitrogen gas to the mixing zone which is heated by a hydrogen-oxygen combustion flame at a temperature of 1900 °C. The temperature gradually decreases through the reaction zone to about 900 °C at the exit. Spherically-shaped powders of about 40-70 nm in size can be produced. The disadvantage in this process is attributed to inhomogeneity due to either the metastable subliquidus relation between the liquid and the metastable Al₂O₃ solid solution at high temperatures or to a metastable liquid immiscibility in the Al₂O₃-SiO₂ system during the cooling process.

In this research, the sol-gel technique was used to prepare mullite powders under different processing conditions. This technique can be used for the preparation of glass, ceramic fibers, protective coatings, optical films, ultrapure monosized fine ceramic powders, and composite materials. Figure 2 shows the sol-gel process outlined for the preparation of silica glass in the bulk form, fiber, and as a coating film. The same process can also be used for preparing mullite ceramics. The various forms of silica glass can be obtained by varying the process conditions. For example, a lower water content is favorable for the formation of linear molecules and hence, fiber drawing, while higher water content is effective in making bulk glass². 
The sol-gel process has numerous advantages over the conventional melting method\textsuperscript{13, 14}. These advantages include:

1. Better homogeneity from raw materials
2. Better purity from raw materials
3. Lower processing temperature thereby saving energy, minimizing evaporation losses and air pollution, avoiding chemical reactions with the container thus ensuring purity, and by-passing phase separation and crystallization.
4. New non-crystalline solids outside the range of the normal glass formation.
5. New crystalline phase from new non-crystalline solids.
6. Better glass products from special properties of the gel
7. Ease of mixing of reactants at a molecular level
8. An ensemble of simple operations can be done without expensive facilities and still lead to final products.
FIGURE 2. Outline of the sol-gel processing route in the production of oxide ceramics
Even though the sol-gel technique has advantages compared to the colloidal route, it also has its disadvantages\textsuperscript{13} such as:

1. High cost of raw material
2. Large shrinkage during processing
3. Residual fine pores
4. Residual hydroxyl and carbon
5. Health hazard of organic solution
6. Longer processing times.

Mullite gels can be classified, according to the scale of alumina-silica mixing, into diphasic and single phase gels. Both types of gels have been analyzed by scanning electron microscopy (SEM)\textsuperscript{16}, Fourier Transform Infra-red (FT-IR) spectroscopy\textsuperscript{17}, dynamic X-ray diffraction (DXRD)\textsuperscript{18}, and differential thermal analysis (DTA)\textsuperscript{18}. The diphasic gel is a colloidal mixture of a crystalline alumina phase and an amorphous silica phase which transforms to mullite upon heating above 1250 °C\textsuperscript{18}. DXRD results obtained by Li and Thomson\textsuperscript{18} indicated that mullite formation from the diphasic gel shows a diffusion-controlled mechanism. The SiO\textsubscript{2} phase in the diphasic gel remained amorphous throughout the heating process until it reacted with Al\textsubscript{2}O\textsubscript{3} to form mullite at about 1250° C\textsuperscript{18}.

The single phase gel has a molecular mixing of aluminum and silica through either coprecipitation of aluminum and silicon salts or hydrolysis of metal alkoxides, which can
transform to mullite at temperatures below 1000 °C\textsuperscript{19,20}. The reaction kinetics for both single phase and diphasic gel has been studied\textsuperscript{18}. A nucleation-controlled process was determined\textsuperscript{18} for the single phase gel from high temperature \textit{in situ} measurements using DXRD. Li and Thomson\textsuperscript{18} found that single phase gel appear completely amorphous up 984 °C when mullite begins to form. DTA results showed a broad exothermic peak at 300 °C which corresponds to the thermal decomposition of organic compounds. The sharp exothermic peak at 984 °C corresponds to mullite formation. FT-IR analysis\textsuperscript{18} of the single phase gel heat-treated at 500°C showed the precursor to be a mixture of amorphous SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} and at 900°C, there is evidence of Al-O-Si bond formation. The infra-red absorption of 3:2 mullite has been investigated\textsuperscript{21} in the spectral range 400 - 1400 cm\textsuperscript{-1} using the KBr powder method. Three peaks due to vibrations of the mullite specific tetrahedral units, SiO\textsubscript{4}, AlO\textsubscript{4} and Al\textsuperscript{3+}O\textsubscript{4} occurred at 1165, 1130, and 1108 cm\textsuperscript{-1} respectively.

\textsuperscript{29}Si and \textsuperscript{27}Al NMR studies\textsuperscript{22} of mullite formation from sol-gel precursors revealed the presence of Si-O-Al bonds at 75 ppm. This study also indicated that mullitization is preferred to spinel crystallization when the pentacoordinated Al sites are the predominant Al environments in the amorphous phase at 900°C. \textsuperscript{29}Si-NMR studies\textsuperscript{23} showed that alkoxysilane undergoes an alkoxy group exchange reaction in isopropanallic solution and in the presence of the chelated aluminum alkoxide. By exchanging ethoxy groups with isopropanyl groups, the reactivity of the alkoxysilane can be controlled. Also the aluminum alkoxides in solution are normally a mixture of oligomers. Information about
oligomer distribution from the different coordination spheres of the $^{27}$Al-nuclei were obtained from $^{27}$Al-NMR studies $^{21, 23}$.

2.2 APPLICATIONS OF MULLITE

Mullite is a major constituent of whitewares, porcelains, structural clay materials and refractory materials. Its use as an industrial refractory material derives from the high melting point (1890 °C), good creep resistance, low thermal expansion which yields good thermal shock resistance, high shear modulus, and good corrosion resistance. Considering all these favorable properties, mullite-based materials are used as refractories in the steel industry and mullite-based bricks which are used for lining upper parts of melting furnace, hot blast stores, hot iron runners and continuous casting furnace.

Mullite-corderite composites are used as engineering materials for heat exchangers because of their ability to retain their strength at high temperatures, good thermal shock resistance, good oxidation resistance, and good corrosion resistance. Its good creep resistance at high compressive strength at elevated temperature, enable mullite ceramics to be used for high temperature exposed parts for mechanical testing machines. Mullite crucibles, plates and tubes for various applications have been produced by a water-stabilized plasma-spraying technique. These tools display excellent shock resistance which result from their favorable microstructure and well-defined porosity. Mullite also finds application in electronic packaging. This is due to its favorable thermal expansion and dielectric constant, good chemical stability, good heat resistivity, good thermal
conductivity, and high mechanical strength. Translucent mullite ceramics are used as a window material for the mid-infra-red wavelength range from 3 to 5 μm and in the visible light range, under chemically harsh, high temperature, or mechanically stressful environments.

Mullite finds extensive applications in ceramic matrix composites, ceramic fibers, and coatings. Processing routes for preparing ZrO₂-mullite composites include sintering of conventional mixtures of mullite and ZrO₂ powders, reaction sintering of mixtures of ZrO₂ and mullite precursors (prepared by copolymerization of alkoxides), or alternatively, reaction sintering of ZrO₂, Al₂O₃, and SiO₂ and reaction sintering of zircon and Al₂O₃. One method of preparing ZrO₂-mullite composites is by a conventional mixing of fused mullite and ZrO₂ powders in an attrition mill. The samples were fired at 1610 °C. The addition of ZrO₂ to mullite is effective in enhancing densification and retarding grain growth of mullite. It is also effective in reducing the development of a glassy phase in the grain boundaries, and therefore a nearly glass-free microstructure is achieved. The microstructure development due to the addition of ZrO₂ seems to have a favorable influence on the mechanical properties such as fracture toughness, strength and thermal shock resistance.

Mullite is promising as a protective coating for silicon-based ceramics in aggressive high-temperature environments. This is because of its environmental durability, chemical compatibility, and coefficient of thermal expansion similar to that of SiC. A plasma-spraying process has been developed which produces fully-crystalline mullite. In this process, the precipitation of amorphous mullite is prevented by heating the substrate
above the crystallization temperature. The fully crystalline mullite coating exhibited excellent adherence and a dramatically improved crack resistance compared to conventional mullite coatings under thermal cycling.

Various kinds of continuous fibers, chopped fibers or whiskers, platelets and particles have been used to reinforce mullite matrices to enhance the mechanical properties or to improve the low temperature sinterability and special physical properties such as thermal expansion and dielectric constant for possible application as substrate materials for electronic packaging. Silicon carbide (SiC) fibers and carbon fibers are used to prepare fiber-reinforced-mullite composites. Continuous mullite fibers have been manufactured by the 3M company. A solution containing aluminum ions was prepared by dissolving aluminum metal powder in a solution obtained by mixing equivalent amounts of formate and acetate. The concentration of aluminum ions was adjusted to an aluminum/carboxylate ratio of 1:2. Commercial silica sol and boric acid were added to the solution and mixed. Fibers were spun from this solution, which was concentrated to a suitable viscosity. The cross-section of the fibers obtained was oval and 10 - 15 \( \mu \text{m} \) in diameter. Typically produced fibers are Nextel 313 (62wt% \( \text{Al}_2\text{O}_3 \), 14 wt% \( \text{B}_2\text{O}_3 \), 24wt% \( \text{SiO}_2 \)) and Nextel 480 (70 wt% \( \text{Al}_2\text{O}_3 \), 2wt% \( \text{B}_2\text{O}_3 \), 28 wt% \( \text{SiO}_2 \))\(^6\). These are used as textile materials above 1000\(^\circ\)C and as reinforcement for resin matrices, particularly ceramic matrices\(^8\).
CHAPTER THREE

RESEARCH OBJECTIVES

The objectives of this research were to:

- use the sol-gel process to prepare mullite precursor under different processing conditions such as pH, temperature, water/TEOS ratio and to see how these conditions affect the microstructure of the final, dense mullite. The chemistry of the reactions was controlled by varying the processing conditions.

- use rheological measurements to correlate the structure build-up in the precursors as a function of aging by following both the steady shear rotational flow and oscillatory shear flow behaviors. The steady state flow behavior of the sols was followed by studying the relationship between shear stresses and shear strains to gain information on how the fluid will behave under various processing conditions. Two methods were used to characterize the flow behavior, namely, time linear ramps (to quantify the degree of hysteresis of the thixotropic behavior of the sols) and equilibrium flow curves (to determine to determine equilibrium behavior). The viscoelastic properties
were studied by measuring the changes in storage and loss moduli as a function of aging of the sols.

- use thermal analysis e.g. TG/DTA to establish heating profiles for sintering in order to achieve dense mullite with reduced porosity. The thermal behavior of the dried powders was studied in air using a heating rate of 10 deg/min from room temperature to 1200 °C. TGA was used to provide information on weight losses occurring in the sample during heat-treatment, while DTA provided information on the enthalpies of transition occurring as a result of chemisorption, physisorption, decomposition reactions and mullitization.

- use X-ray diffraction to determine amorphous and crystalline phases.

- use scanning electron microscopy to study the microstructure of mullite.

- perform qualitative FT-IR studies on the precursor sols to follow the structural evolution in the mixed alkoxide sols, resulting from the occurrence of the hydrolysis and polycondensation reactions, as a function of aging of the sols. A possible mechanism for the reactions was postulated.
CHAPTER FOUR

EXPERIMENTAL APPROACH AND PROCEDURE

4.1 SYNTHESIS OF ALKOXIDE-DERIVED GELS

Sol-gel synthesis was carried out using high purity commercially available metal alkoxide precursors. The objective of this approach is to determine the effect of the starting chemistry and how it affects the microstructure of the resulting mullite. Tetraethylorthosilicate (TEOS) was used as the precursor sol for silica while aluminum tri-sec butoxide (ATSB) was used as the precursor for alumina. Hydrolysis of the sols was carried out in an acidic environment using concentrated hydrochloric acid (catalyst) and 2-propanol (solvent). 17 ml of TEOS was mixed with 5 ml of 2-propanol and allowed to stir in a parafilm-covered beaker for one hour after which acidified water was added. The resulting solution was allowed to stir for 24 hrs in order to prehydrolyse the TEOS before the addition of ATSB. This was necessary since the alumina source reacts faster than the silica source. After 24hrs, aluminum tri-sec butoxide dissolved in 2-propanol was then added and the mixture was allowed to stir vigorously.

The following processing conditions were used.

(i) Temperatures of 40°C and 65°C.

(ii) Water:TEOS molar ratios of 1.5, 2.0 and 3.0

(iii) pH’s of 1.5, 1.7 and 2.0

(iv) TEOS : 2-propanol ratio of 10
4.2 RHEOLOGICAL AND STRUCTURAL STUDIES

Various characterization techniques were used to monitor the formation of mullite by the sol-gel process from the initial alkoxide sols to mullite. This is to better understand the chemical and physical changes occurring during the hydrolysis and polycondensation reactions at the molecular level. Techniques such as Fourier transform-infrared spectroscopy (FT-IR), thermogravimetric analysis/differential thermal analysis (TGA/DTA), scanning electron microscopy (SEM), rheology and X-ray diffraction (XRD) were employed to gain insight into the structural evolution of mullite from the metal alkoxide precursors.

4.2.1 FT-IR SPECTROSCOPY

FT-IR spectroscopy was used to follow the structural evolution in the mixed alkoxide sols, resulting from the occurrence of the hydrolysis and polycondensation reactions, as a function of aging of the sols. FT-IR data of the mullite precursors, pure silica and ATSB were obtained using a Nicolet Impact 400 FT-IR Spectrophotometer. The Impact optical bench is equipped with an Ever-Glo mid-IR source. The laser source is a He/Ne laser of wavelength 632.8 nm. The optical bench comes with a DTGS detector and KBr beamsplitter. Data analysis was carried out with Omnic version 1.2 software. Spectra were collected at times $T_0$ (i.e. $T_0$ is the time when ATSB is added to the prehydrolyzed
silica), after 24, 48, and 96 hrs. Infrared absorption spectra of the silica and mullite precursor samples at various aging times were recorded between 500 cm\(^{-1}\) to 4000 cm\(^{-1}\).

4.2.2 THERMAL ANALYSIS

The TGA/DTA results were used to establish a heating profile for sintering in order to achieve dense mullite with reduced porosity. Thermal measurements were done using a Seiko TG/DTA 320 Thermal Gravimetric Analyzer. Heating was carried out in air at a rate of 10 deg/min. from room temperature to 1200 °C. Differential thermal analysis was used to gain information on enthalpic transitions occurring, as a result of changes in sample such as physico-chemical reactions, phase changes, crystalline structure inversions etc., during heat treatment. Generally, phase transition and dehydration effects produce endothermic effects while crystallization, oxidation, and some decomposition reactions produce exothermic effects. Information on the weight loss as a function of temperature was obtained from thermogravimetric analysis.

4.2.3 RHEOLOGY

Changes in the rheological properties of the sol during aging reflects the structural evolution from a dilute sol to the development of the structure of the mullite precursor gel. Steady shear flow measurements was used to study viscosity changes of the precursor sols with aging. Several flow behaviors such as Newtonian, shear thinning, shear thickening,
and thixotropy were observed. The dynamic response of viscoelastic materials to cyclic stresses and strains is important, partly because cyclic motion occurs in many processing operations and applications, and partly because so much rheological information can be gained from dynamic measurements. Rheological studies on the precursor sols were accomplished using a Haake RheoStress RS100 Rheometer. A concentric cylinder Z20 DIN sensor, having minimum and maximum stresses of 0.0482 and 482 Pa respectively, was used for the steady shear and oscillatory flow measurements. The flow behavior of the sols was followed by studying the relationship between shear stresses and shear strains to gain information on how the rheological properties correlate to the starting chemistry. Two methods were used to characterize the flow behavior, viz.

(i) time linear ramps to quantify the degree of hysteresis of the thixotropic behavior of the sols.

(ii) equilibrium flow curves to determine to determine equilibrium behavior.

4.2.4 X-RAY DIFFRACTION

X-ray diffraction provides information about the crystallinity and phase identification. Powder diffraction data were collected at room temperature using a Philip’s X’Pert Materials Research diffractometer. The mullite samples were irradiated with CuKα x-rays (λ = 5.406 Å). A scan rate of 2 deg/min was utilized over a diffraction angle of 10 to 85 deg(2θ). Data were collected on samples pre-heated to 900, 1000, 1100, 1300, and
1500 °C in a tube furnace. Data analysis was carried out using the Total Access Diffraction Database.

4.2.5 SCANNING ELECTRON MICROSCOPY

SEM was used to gain information about the microstructure of the mullite powders. Information on the grain size and particle distribution were obtained.
CHAPTER FIVE

5.0 RESULTS AND DISCUSSION

5.1 SYNTHESIS CONDITIONS AND GELATION TIME

The gels were prepared under different experimental conditions such as mole ratio of TEOS:Water, acidity and temperature as seen in Table 1. Precipitation of colloidal particles was encountered on adding ATSB to the partially hydrolyzed silica precursor. In all cases studied, the gels obtained were clear and transparent. Tables 1 and 2 show the synthetic conditions used to prepare the mullite precursors and the gelation conditions. The values used in obtaining Figure 3, were taken from Tables 3 and 4. From Figure 3 it can be inferred that variation in temperature has a pronounced effect on the gelation time. This is to be expected since the rate of hydrolysis and condensation reactions increase with increase temperature and, hence, a decrease in the time to reach the gelation point.

The gelation time was found to be dependent on the Water:TEOS ratio. Increase in Water:TEOS ratio caused a decrease in gelation time as shown on both graphs (Figure 3). The increase in water content caused an increase in the hydrolysis reaction, hence, a decrease in gelation time. The HCl content had less of a pronounced effect on the time to gelation.
Table 1: Effect of Synthesis Condition on Gelation Time and Appearance of Mullite Precursor Gel

<table>
<thead>
<tr>
<th>Gel #</th>
<th>HCl</th>
<th>H₂O</th>
<th>ATSB</th>
<th>Temp (°C)</th>
<th>TEOS:H₂O</th>
<th>Gel Time</th>
<th>Appearance of gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>0.009</td>
<td>0.03</td>
<td>0.1</td>
<td>40</td>
<td>1.5</td>
<td>39</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>1-2</td>
<td>0.009</td>
<td>0.03</td>
<td>0.1</td>
<td>65</td>
<td>1.5</td>
<td>32</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>1-3</td>
<td>0.006</td>
<td>0.03</td>
<td>0.1</td>
<td>40</td>
<td>1.5</td>
<td>39</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>1-4</td>
<td>0.006</td>
<td>0.03</td>
<td>0.1</td>
<td>65</td>
<td>1.5</td>
<td>10</td>
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<tr>
<td>1-5</td>
<td>0.003</td>
<td>0.03</td>
<td>0.1</td>
<td>40</td>
<td>1.5</td>
<td>26</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>2-1</td>
<td>0.009</td>
<td>0.04</td>
<td>0.1</td>
<td>40</td>
<td>2.0</td>
<td>21</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>2-2</td>
<td>0.009</td>
<td>0.04</td>
<td>0.1</td>
<td>65</td>
<td>2.0</td>
<td>24</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>2-3</td>
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<td>0.04</td>
<td>0.1</td>
<td>40</td>
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</tr>
<tr>
<td>2-4</td>
<td>0.003</td>
<td>0.04</td>
<td>0.1</td>
<td>65</td>
<td>2.0</td>
<td>11</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>3-1</td>
<td>0.009</td>
<td>0.06</td>
<td>0.1</td>
<td>40</td>
<td>3.0</td>
<td>35</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>3-2</td>
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<td>0.06</td>
<td>0.1</td>
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<tr>
<td>3-3</td>
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<td>0.06</td>
<td>0.1</td>
<td>65</td>
<td>3.0</td>
<td>10</td>
<td>clear, transparent</td>
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<tr>
<td>3-4</td>
<td>0.006</td>
<td>0.06</td>
<td>0.1</td>
<td>40</td>
<td>3.0</td>
<td>21</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>3-5</td>
<td>0.006</td>
<td>0.06</td>
<td>0.1</td>
<td>65</td>
<td>3.0</td>
<td>9</td>
<td>clear, transparent</td>
</tr>
</tbody>
</table>

ATSB = Aluminum tri-sec-butoxide (C₂H₅CH(CH₃)O)₃Al {80% v/v};
Table 2. Effect of Temperature on Gelation Time

<table>
<thead>
<tr>
<th>Gel #</th>
<th>Temp</th>
<th>Gelation time</th>
<th>Appearance of gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>40</td>
<td>39</td>
<td>clear, transparent</td>
</tr>
<tr>
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<tr>
<td>1-3</td>
<td>40</td>
<td>39</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>1-4</td>
<td>65</td>
<td>10</td>
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<tr>
<td>1-5</td>
<td>40</td>
<td>26</td>
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</tr>
<tr>
<td>2-1</td>
<td>40</td>
<td>21</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>2-2</td>
<td>65</td>
<td>24</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>2-3</td>
<td>40</td>
<td>45</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>2-4</td>
<td>65</td>
<td>11</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>3-1</td>
<td>40</td>
<td>35</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>3-2</td>
<td>65</td>
<td>8</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>3-3</td>
<td>40</td>
<td>30</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>3-4</td>
<td>65</td>
<td>10</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>3-5</td>
<td>40</td>
<td>21</td>
<td>clear, transparent</td>
</tr>
<tr>
<td>3-6</td>
<td>65</td>
<td>9</td>
<td>clear, transparent</td>
</tr>
</tbody>
</table>

Table 3. Effect of Water:TEOS ratio on gelation time (at 40 °C)

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Water:TEOS mole ratio</th>
<th>Gelation Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-4</td>
<td>1.5</td>
<td>39</td>
</tr>
<tr>
<td>4-5</td>
<td>2.0</td>
<td>35</td>
</tr>
<tr>
<td>4-6</td>
<td>3.0</td>
<td>21</td>
</tr>
</tbody>
</table>
Table 4  Effect of Water TEOS ratio on gelation time (at 65 °C)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water TEOS mole ratio</th>
<th>Gelation Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>1-5</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>1-6</td>
<td>30</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 3  Graphical representation of the effect of TEOS H₂O ratio on gelation time at 40 and 65 °C
5.2 RHEOLOGY

The rheological properties of the sol to gel transition of the precursor sols were studied by both steady state shear and dynamic viscosity. Figure 4a shows the variation of the steady state viscosity with aging of the precursor sols for sample 2-1 prepared at 40 °C. As expected, the viscosity was found to increase with aging time. Up to the 5th day, there was only a minimal change in viscosity with aging as depicted in the curve. This is an indication of increased condensation growth and agglomeration of the interacting species leading to the gradual formation of a 3-dimensional network structure. A similar trend was found for sample 2-4 prepared at 65 °C as shown in Figure 4b. Figure 5 shows the steady state flow curves (shear stress vs shear rate) of sample 2-1 at various aging times. Initially the sols exhibited a Newtonian flow behavior (viscosity is independent of shear rate). This is attributed to the minimal particle-particle interactions existing in the dilute sol. The sols also showed slightly shear thickening behavior as shown in Figure 6 which is a plot of the viscosity vs shear rate at different aging times. This behavior is attributed to increased particle-particle interactions resulting from condensation growth and agglomeration of the species. Also with further aging of the sols, the sample exhibited a yield stress as shown in the linear scale plot in Figure 7. This yield stress is indicative of the elastic character of the species forming the 3-dimensional network structure.

The sols exhibited thixotropy as shown by the flow curve forming an hysteresis loop in Figure 8. This is an indication that the 3-dimensional network structure is broken
down as the shear rate is increased, but full recovery does not occur during the time period over which the shear rate is decreased. The degree of thixotropy, calculated from the area under the thixotropic loop, was found to vary with aging of the precursor sols. From Figure 8, the degree of thixotropy was calculated to be 940 Pa.s for the curve R211 (day 1) and 290 Pa.s for curve R214 (day 4). Thus, as the gelation point is approached the degree of thixotropy is reduced, which is consistent with the development of extensive 3-dimensional network structure.
FIGURE 4a. Viscosity as a function of aging of precursor sol sample 2-1

FIGURE 4b. Viscosity as a function of aging of precursor sol sample 2-4
FIGURE 5. Steady state flow behavior of mullite precursor sol at different aging times (shear stress shear rate curve)
FIGURE 6. Steady state flow behavior of mullite precursor sol at different aging times (viscosity-shear rate curve)
FIGURE 7. Steady state flow behavior of mullite precursor sol at different aging times (shear stress shear rate curve on linear scale)
FIGURE 8. Thixotropic flow behavior of mullite precursor sol sample 2-1
is reduced, which is consistent with the development of extensive 3-dimensional network structure.

The structural changes that result from the condensation growth and agglomeration of the species are also reflected in the measurements of the viscoelastic properties during the sol-gel aging period. Figures 9 to 12 show the storage and loss moduli ($G'$ and $G''$) respectively and the loss tangent ($\tan \delta$) at various stages in the aging process for sample 2-1 while Figure 13 shows the variation of $G'$ and $G''$ with aging at a frequency of 0.6 rad/s. Frequencies of 0.1 and 0.9 rad/s, corresponding to the initial and final stages of the experiment, were also utilized. From the dynamic viscosity measurements for all the stated frequencies, the precursor sols showed a small elastic component during the early stages of aging. During this period of Newtonian flow behavior, the loss (viscous) modulus dominates. This is a reflection of the minimal particle-particle interactions in the dilute sols. With increased aging of the sols and gels, larger elastic components are observed which is consistent with the build-up of structure. Figure 14 shows the variation of the loss tangent with aging time. As expected, the loss tangent decreased with aging time since the elastic nature of the sols ($G'$) increased as the sols aged.
FIGURE 9. Variation of $G'$, $G''$, and $\tan \delta$ with $\omega$ for sample 2-1 (day 1)
FIGURE 10. Variation of $G'$, $G''$, and $\tan \delta$ with $\omega$ for sample 2-1 (day 3)
FIGURE 11. Variation of $G'$, $G''$, and $\tan \delta$ with $\omega$ for sample 2-1 (day 5)
FIGURE 12. Variation of $G'$, $G''$, and $\tan \delta$ with $\omega$ for sample 2-1 (day 7)
FIGURE 13. Variation of $G'$, $G''$ with aging time for sample 2-1
FIGURE 14. Variation of $\tan \delta$ with aging time for sample 2-1
5.3 FT-IR SPECTROSCOPY

Figure 15 shows the FT-IR spectra of mullite precursor sols as a function of aging. The condensation reactions are seen to increase as a function of aging as observed by the decreasing presence of the C-O bond at 2200 - 2300 cm\(^{-1}\). Both the Si--O-Al and Si-O-Si linkages occurred at 910 - 920 cm\(^{-1}\). The changing peak intensities is indicative of structure build-up in the sols with aging. Because of the close proximity of the Si-O-Si and Si-O-Al linkages in the FT-IR spectra, individual spectral assignments proved extremely difficult. The larger peak at 1360 is attributed to Si-OH bonds on the silica skeleton.

Shown in Figure 16 is a postulated mechanism for the structure build-up in the mullite precursor sols.
FIGURE 15. FT-IR of mullite precursor during aging
POSTULATED MECHANISM

The reactions involved are hydrolysis and polycondensation. TEOS is partially hydrolyzed (because silica has a slower rate of hydrolysis than alumina) and catalyzed by the addition of an acid. In the reaction, low pH level (1-3 ) is used to form linear molecule (occasionally crosslinked).

Hydrolysis occurs by electrophilic attack on the alkoxide group (the oxygen atom has a high electron density owing to its strongly electronegative character and the polarizing effect of the alkyl groups ). The oxygen possess two pairs of unshared electrons making a very favorable site for undergoing co-ordination with proton $H^+$ from the acid. This situation where the oxygen attracting high electron density, leaves the connected atom partially deficient and thus positively charged. In this case the electrophilic reagent is hydrochloric acid ($H^+$ ) and the nucleophilic reagent is water (OH). Both hydrolysis and condensation may occur by bimolecular nucleophilic substitution reaction. (rapid deprotonation of the -OR or OH substituents bonded to the silicon atom$^{15}$).

In the partially hydrolyzed TEOS (acid catalyzed), there is abundant residual silanol (OHís ) and a few -OC$_2$H$_5$ groups bound to Si. If another alkoxide is added this will react with the silanol to form a soluble metallosiloxane.

\[
(RO)_3SiOH + M(OR)X \rightarrow (RO)_3Si-O-M(OR)_{x-1} + ROH
\]

As the concentration of TEOS reduces, the silanol and the product increases as a function of time$^5$. 

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Factors that can affect the rate of the reactions are:

(i) Size of the alkyl group. The rate of reaction depends on the chain length and degree of branching of the alkyl group. This effect is known as the steric effect or crowding effect. As the size increases, repulsion between the groups increases thereby increasing the energy of the reaction. This causes the rate of the reaction to decrease.

(ii) The rate of reaction decreases with higher alkyls and increases with increasing degree of alkyl substitution.

Studies done by Pouviel and Boilot\textsuperscript{23} using \textsuperscript{29}Si NMR results, showed, to a greater extent, that proton and water concentration have an effect on the overall reaction. After 20 hrs and using a low water concentration the room temperature NMR spectrum exhibited peaks (starting mixture consist of TEOS, ethanol, HCl and water). These peaks corresponded to silanol, tetraethylorthosilicate and disilicic ester. The reactions were summarized to be hydrolysis (nucleophilic substitution reaction) and condensation. Discussing the effect of water content, they indicated that with substiochiometric amounts of water, the condensation takes place very slowly by the reaction between Si-OR and Si-OH group with loss of R-OH. With medium water concentration, during the hydrolysis step, the peaks obtained in the NMR spectrum corresponded to four silanol groups. The time evolution of the silanol species suggests that the rate constant are different. Assuming that the rate concentration of the water remains constant in the first stages of the hydrolysis, it can be concluded that the kinetics is first order and the rate constant ratio can be estimated. Showing that the hydrolysis rate depends strongly on the degree of substitution of monomers.
In this research the amount of water used can be estimated to be medium concentration. After 24hrs of hydrolyzing the silica source the predominant constituent of the mixture is assumed to be silanol. Using these as a guide, the postulated mechanism for the reaction is as depicted in Figure 16. This proposed mechanism shows the dominant reactions occurring. Although the dominant product formed is indicated in the mechanism, other reaction products such as (OH)Si(OR)_3, (OH)_2Si(OR)_2, (OH)_3Si(OR) are also formed.
PROPOSED MECHANISM

i. Prehydrolysis of Tetraethyorthosilicate
R Represents C₂H₅

\[ R-O-Si-O-R \xrightarrow{H^+} R-O-Si-OH \xrightarrow{H₂O} \]

\[ \xrightarrow{-H^+ - ROH} \]

\[ \{ R-O-Si-OH \} \]

\[ \xrightarrow{H^+} \]

\[ R-O-Si-OH \xrightarrow{H₂O} \{ R-O-Si-OH \} \xrightarrow{-ROH - H^+} R-O-Si-OH \]

\[ \xrightarrow{H^+} \]

\[ R-O-Si-OH \xrightarrow{-ROH - H^+} R-O-Si-OH \]

\[ \xrightarrow{H₂O} \{ R-O-Si-OH \} \]

\[ \xrightarrow{H^+} \]
ii. Addition of ATSB (after prehydrolyzing the silica source for 24hrs)
Acid catalyzed condensation, where R' represents C₂H₅(CH₃)
5.4 THERMAL ANALYSIS

Thermal analysis of the various gels were carried out after the gelled samples were oven dried for 3 hrs at 45 °C using TG/DTA. Typical TGA and DTA curves of the dried samples, recorded at a heating rate of 10°C/min are presented in Figures 17 and 18 below.

FIGURE 17. TG/DTA of mullite precursor gel prepared at 40°C
FIGURE 18. TG/DTA of mullite precursor gel prepared at 65 °C
For the sample prepared at 40°C, a total weight loss of ~33% was calculated while the sample prepared at 65°C showed a total weight loss of ~31%, indicating as whole no significant difference in total weight loss between the two temperatures. From the TGA curve it was found that significant weight loss occurred in the temperature range from room temperature to ~300°C.

Three endothermic and two exothermic peaks were present in the DTA curve. All samples showed basically the same DTA pattern. The 1st endotherm at ~80°C is due to evaporation of the 2-propanol solvent. The 2nd endothermic peak at ~193°C is attributed to loss of residual or physically absorbed water, 2-propanol solvent and tetraethylorthosilicate entrapped in the micropores of the gels. The 3rd endothermic peak at ~235°C in the DTA is attributed to the loss of structural water (chemisorb) by dehydration condensation of the hydroxyl groups. The 1st exothermic peak at ~331°C is attributed to oxidation of residual organics. The second exothermic peak at ~1000°C is ascribed to mullitization (conversion of the mullite precursor to the mullite ceramic or crystallization of the amorphous material).

5.5 X-RAY DIFFRACTION

The heat-treated samples were subjected to powder x-ray diffraction at room temperature for phase identification and order. The x-ray diffractograms (Figures 19&20) show that the samples preheated to 900°C are amorphous. This was evident by the existence of broad peaks. For the samples preheated to 1000°C, the X-ray diffractogram shows sharp
peaks (Figure 21) indicating the onset of crystallization or mullitization. The subsequent Figures 22, 23 and 24 show the x-ray diffractograms of sample 2-4 preheated to 1100°C, 1300°C and 1500°C respectively. Fully crystalline mullite is obtained at 1100°C indicated by the existence of sharp distinct peaks in the diffraction patterns. This also indicates that the degree of crystallinity increases as the temperature is raised to 1500°C. The X-ray results correlate well with TGA/DTA studies. Most of the peaks identified in the diffraction patterns were typical of mullite peaks. However, there were some peaks due to alumina occurring at d-spacings of 69.7 and 71.4 Å suggesting that the powders were alumina-rich mullite samples.
Figure 19.  X-ray pattern of mullite (sample 2-1) heated to 900 °C
[sample prepared at 40°C]
Figure 20. X-ray pattern of mullite (sample 3-1) heated to 900 °C
[sample prepared at 65°C].
FIGURE 21. X-ray pattern at 1000°C
FIGURE 22. X-ray pattern of mullite heated to 1100 °C

[Caption: Sample prepared at 65°C].
FIGURE 23. X-ray pattern of mullite heated to 1300 °C

[Caption: Sample prepared at 65°C].
FIGURE 24. X-ray pattern of mullite heated to 1500 °C

[sample prepared at 65°C].
5.6 SCANNING ELECTRON MICROSCOPY

The SEM micrographs of the mullite powders heat-treated to 1100, 1300, and 1500 °C are shown in Figures 25, 26 and 27 respectively. The SEM micrographs show fine grain sizes.

FIGURE 25. SEM micrographs of mullite heat-treated to 1100 °C
FIGURE 26. SEM micrographs of mullite heat-treated to 1300 °C
FIGURE 27. SEM micrographs of mullite heat-treated to 1500 °C
CHAPTER SIX

CONCLUSIONS

Sol-gel processing methods were used to prepare mullite ceramic powders from aluminum tri-sec butoxide and tetraethylorthosilicate under a variety of experimental conditions. The effects of the processing conditions on the sol to gel transition were examined by varying the water ratios, catalyst content, and temperature. It was observed that the variation in temperature has the greatest effect on the time to gelation for the precursors.

The rheological properties during the aging process indicated an increase in viscosity with aging time, which is consistent with changing structure. Measurements of the viscoelastic properties during the sol to gel aging period showed a predominance of the loss (viscous) modulus over the storage (elastic) modulus in the initial stages of aging. With increased aging of the sols and gels, larger elastic components were observed which is consistent with the build-up of structure. The changes in structural evolution were followed by Fourier Transform Infra-red spectroscopy and correlated well to changes in the rheological properties of the sol.

Conversion of the starting materials, gelled under various reaction conditions, to mullite was conducted. TG/DTA and X-ray analyses were used to correlate the starting chemistry and reaction conditions to the microstructure of the final mullite powder. X-ray diffraction studies suggested the presence of alumina-rich mullite. In all
experimental cases fine grain powders were obtained indicating no apparent differences of the synthesis conditions on the final mullite powder microstructure.
CHAPTER SEVEN

RECOMMENDATIONS FOR FUTURE WORK

1. Future work should be carried out to control the chemistry of the hydrolysis and polycondensation reactions by using other methods other than prehydrolysing the silica to slow down the reactivity of ATSB. For example, the use of chelating complexes to slow down the reactivity of the ATSB used.

2. The sol-gel synthesis should be carried out using 2-butanol as solvent instead of 2-propanol used in this work. This will help to understand the effect of solvent on the precursor gel properties and hence, the final mullite powder.
REFERENCES


