

CHAPTER I

INTRODUCTION

1.1 Background

$MgAl_2O_4$ is a well-known mineral used as a refractory material in the ceramic industry. The $MgAl_2O_4$ precursor could be synthesized via chemical process by using inexpensive preceramic precursor directly from the metal oxide or alkoxide. Chemical routes offer many advantages over traditional methods, including the potential to control product homogeneity and purity, to lower processing temperatures, and to control the size, shape, and distribution of the resulting ceramic particles, which are increasingly necessary for producing advanced ceramics. One of the simplest chemical processes, called the "Oxide One Pot Synthesis Process" (OOPS), can produce oligomeric precursors containing any combination of Al, Si, and group I or II metals in one step. (Walder *et al*, 1996 and Bickmore, 1996)

The spinel, $MgAl_2O_4$, is a pure ceramic material that has many applications. An interested one is a ceramic humidity sensor due to its better chemical resistance and mechanical strength with respect to polymeric sensors. It is well known that the electrical properties of ceramic materials are strictly related to their microstructure (Nitta, 1981 and Gusmano *et al*, 1996). The modification of the microstructure and the chemical composition of ceramic material by changing parameters in their production process permits both performance optimization in devices exploiting the electrical properties of ceramics and tailoring to specific requirement. (Traversa, 1996)

Sol-gel processing has been extensively used to prepare amorphous and crystalline materials. Sol-gel process can be done at the ambient condition and this process is inexpensive as compared to other techniques. Materials can be produced in a variety of forms, such as fine powders, thin films, monoliths and fiber. In addition, sol-gel process has ability to change or control physical characteristics, such as pore size distribution and pore volume. However, to achieve the requirements, the rate of hydrolysis and condensation reaction needs to be adjusted.

Sol-gel process

Traditional ceramic and glass processing use high temperatures to transform inorganic powders into dense objects by melting or sintering. The high temperatures and agglomeration of powders often limit control of the microstructure, properties, shape, and surface features obtained. The goal of sol-gel technology is to use low temperature chemical process to produce net-shape, net-surface objects, or composites that can be used commercially after a minimum of additional processing step.

Sol-gel technology is the preparation of ceramic, glass, or composite materials by the preparation of a sol, gelation of the sol, and removal of the solvent.

Potential advantages of the sol-gel process include:

- (1) The ability to maintain high purity
- (2) The ability to vary compositional homogeneity at a molecular level
- (3) Low temperatures of processing that lead to saving in energy
- (4) Preparation of new crystalline phases and new noncrystalline solids
- (5) The ability to produce samples in different physical forms
- (6) Ultrastructure control of materials by manipulating network formation from early stages of sol formation
- (7) Preparation of materials having improved physical properties

The handling of precursor by heat treatment is the factor needed to be considered. In general, the sol-gel process is the synthesis of an inorganic network at low temperature by a chemical reaction in solution. This technique involves the transition characterized by a relatively rapid change from a liquid (solution or colloidal solution) into a solid (gel-like state).

Sol-gel technology can be divided into two types. Firstly, colloidal method involves the suspension of solid particles in a liquid to form a sol (Schmidt, 1994). Secondly, polymeric method involves the polymerization of organometallic compounds, such as alkoxides that provide a convenient source for “inorganic” monomers to form a gel with three-dimensional network structure. The metal alkoxides, $M(OR)_n$, generally consist of metal atom, M, bonded through oxygen to one or more alkyl groups, where n is the valence of the cation. For example, spinel

precursor is an organometallic compound that consists of metal alkoxides, thus sol-gel processing for MgAl_2O_4 spinel is possible.

Generally, the precursor is dissolved in a suitable organic solvent in order to obtain a solution. The solvent must be carefully selected so that a solution with high concentration of the required component is obtained (Yi *et al*, 1991).

Sol-gel processing involves the following steps:

1. Hydrolysis of precursor
2. Polycondensation
3. Gel formation
4. Organic pyrolysis by heat treatment

The first step, starting materials (metal alkoxides) are mixed in a selected solvent system to form a solution. In the gelation process, the transition from a solution into solid, involves simultaneous hydrolysis and polycondensation of metal alkoxide precursor. Many factors influence the rate of hydrolysis and condensation because both processes often occur simultaneously. The most important variables are temperatures, nature and concentration of electrolyte, nature of solvents, and types of alkoxide precursor. The following step, pyrolysis, is necessary to convert gel into a useful form.

Sol-gel process can be done at the ambient condition (vacuum is not needed). Another advantage of this process is inexpensive as compared to other deposit techniques. Materials can be produced in a variety of forms, such as fine powders, thin films, monoliths and fiber. However, some drawbacks of the sol-gel process are excessive shrinkage that can cause cracking.

At present, metal alkoxides are used as precursors for polymeric gel in sol-gel processing. These precursors are readily used with a suitable organic solvent, which is usually alcohol. The metal alkoxide bond is in general extremely susceptible to hydrolytic reaction leading to metal hydroxides or hydrated oxide. The choice of an alkoxide can be considered by many factors including metal content, reactivity, availability, cost, and sensitivity to moisture and decomposition temperature.

A compound with less organic content and high metal content is a proper precursor. Less organic solvent content causes in less volumetric shrinkage during

drying and annealing. Therefore, film has fewer tendencies to crack. However, a compound with high metal content is usually much more reactive, it may be difficult to prepare a stable solution. For alkoxides with different alkyl groups, the reactivity usually increases in the order of methyl > ethyl > propyl > butyl > higher order alkyl groups (Kwok *et al*, 1993).

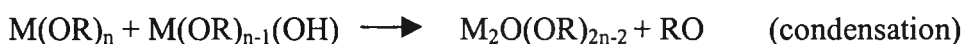
The gelation process:

There are two important reactions in polymeric gel formation. These reactions are partially hydrolysis, followed by condensation polymerization. Polymerization steps via hydrolysis and condensation reaction are illustrated in reactions (1.1) - (1.3).

Reaction (1.1)



Reaction (1.2)



Reaction (1.3)



The M-O-M network product is formed by polycondensation reactions as in reactions (1.2) and (1.3) which alcohol and water are produced as the by-products. Many applications of controlled hydrolysis to obtain a desired molecular structure.

Other parameters that need to be considered are aging of gel, removal of solvent, and heat treatment.

Aging represents the time between the formation of a gel and the removal of solvent. As long as the pore liquid remains in the matrix, a gel can undergo many transformations. For alkoxide derived gels, condensation between surface functional groups continue to occur after the gel point. This process can actually be desirable because it leads to a more cross-linked network that is mechanically stronger and easier to handle.

Drying is a process of evaporating solvent from a gel network. Similar to aging, a gel is not static during drying and, for that reason, drying can be viewed as part of the overall aging process. The properties of product are thus dependent on the drying method and condition.

Calcination/Sintering often is done in the presence of a reactive gas (e.g. flowing air, oxygen, or hydrogen) in order to burn off any residue organics or to oxidize (or reduce) the sample. Exposing the sample to a high temperature over an extended period of time leads to sintering and consequently a decrease in surface area. The process can also cause the material to crystallize into different structure forms. Thus, the physical characteristics of the product depend on parameters, such as temperature, heating rate, time and gaseous environment.

Other critical parameters need to be considered are viscosity, and rheological properties of the solutions. Therefore, many applications of controlled hydrolysis to obtain a desired molecular structure and appropriate viscosity of the solution are used to improve spinning and coating ability. In addition, the solution concentration, viscosity, surface tension of the solution and the deposition technique determine the film thickness and uniformity.

Traditional method of $MgAl_2O_4$ spinel is prepared by fusion of a mixture of the two components. Spinel has been synthesized hydrothermally using commercially available hydroxide reactants. This is usually a high temperature reaction and this method has many starting material left (Alak *et al*, 1989).

These magnesium aluminate spinels can be prepared by other three different techniques, which are thermal co-condensation, co-precipitation, and co-gel formation (Bhattacharyya *et al*, 1989).

Co-condensation uses the sintered mixture of pseudoboehmite alumina and magnesium oxide. The reaction is shown in reaction (2.1)

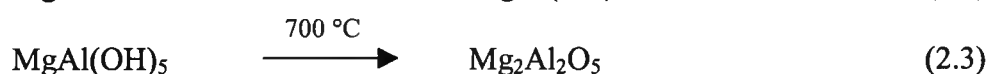


This method needs high sintering temperature and the repetitive of pulverization and calcination steps are required to produce high quantity and quality spinel.

Another method of $MgAl_2O_4$ preparation bases upon thermal decomposition of precursors. The mixtures of hydroxides were prepared by co-precipitation reaction from Mg and Al nitrate solution, stoichiometric to the spinel formation. The Mg-Al hydroxide mixtures were prepared by adding drop by drop of Mg and Al nitrate. Hydroxide mixtures with different phase distribution were investigated, prepared by varying the precipitation procedure. The thermal decomposition of co-precipitated

hydroxide mixtures leads to MgAl_2O_4 formation at a temperature as low as $400\text{ }^\circ\text{C}$. However, the product obtained contains $\text{Mg}(\text{OH})_2$ in the mixture separately from MgO (Gusmano *et al*, 1991).

For co-gel formation method, a gel was prepared using aqueous slurries of pseudoboemite alumina, MgO , and an acid. This method yielded the homogeneous mixture of Mg^{2+} and Al^{3+} . The reactions of this method are shown in reactions (2.2) and (2.3):

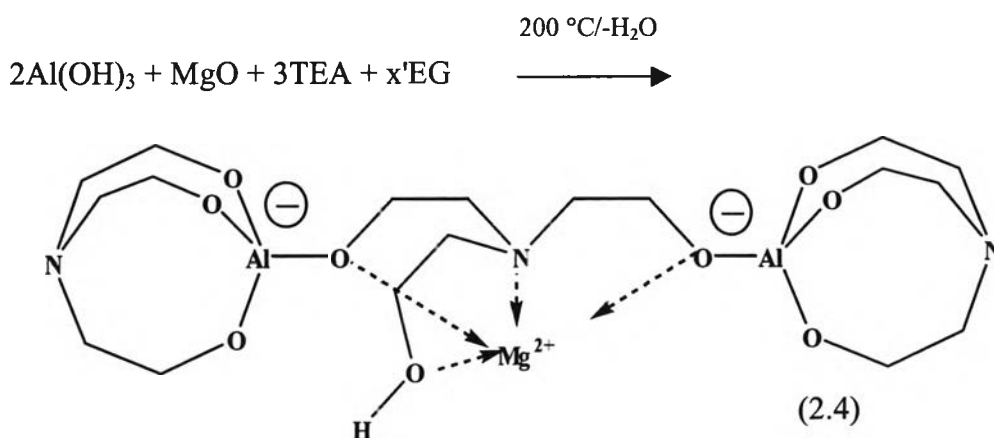


This technique gave quite similar physical properties to co-precipitation but MgO did not occur.

Chemical routes to ceramics offer many advantages over traditional methods, including the potential to control product homogeneity and purity, to lower processing temperatures, and to control the size, shape, and distribution of the resulting ceramic particles. These are necessary for production of advanced ceramics (Messing *et al*, 1993 and Gurav *et al*, 1993). Additionally, chemical techniques can often be used to process thin films and fibers. Typical chemical processing methods include sol-gel, spray drying, and freeze drying of salts and alkoxide solution; co-precipitation of metal salts; and hydrothermal processing. The most disadvantage of these processing methods is the cost of starting materials relative to the cost of the minerals (Tayaniphan *et al*, 1996).

Therefore, many syntheses focused on using a wide variety of inexpensive preceramic polymers directly from the corresponding metal oxides or hydroxides have been described in previous reports (Laine *et al*, 1993, 1994 and Tanyaniphan *et al*, 1996). One of them is called the oxide one pot synthesis (OOPS) process. Precursors containing any combination of aluminum, silicon, with or without group I or II metals are readily produced in ethylene glycol (EG) solvent. High boiling point amines, namely triethanolamine or TEA (b.p. $335\text{ }^\circ\text{C}$) can be used as a catalyst instead of group I or II metal oxide or hydroxide (Apirat *et al*, 2000).

The structure of oligomeric spinel precursor prepared from reaction (2.4) is shown below:



The precursor product was yellow, transparent, and brittle solid at room temperature and melted to a polymer-like, viscous liquid on heating to $\approx 150^\circ\text{C}$. The structure of the spinel precursor was proposed to be a trimetallic species, consisting of one TEA group per metal center. It was assumed that the Mg^+ was actually enfolded by the third TEA, in term of charge separation. This structure reasonably minimizes charge separation and appears to be the most stable for the di-positive cation. Thus, the electrostatic interaction is diminished.

Many analytical instruments were used to characterize this structure. Those are positive fast atom bombardment mass spectroscopy, ^1H -NMR, ^{13}C -NMR and FTIR. (Tayaniphan *et al*, 1996)

Ultrafine spinel powders were prepared using flame spray pyrolysis. Metal alkoxide precursor from OOPS was injected and converted to a ceramic powder. This process minimizes impurities and give production rate as high as 50-100g/hr from a simple bench-top apparatus (Bickmore *et al*, 1996).

Application of MgAl_2O_4 spinel:

The controlling environmental humidity is receiving ever-wider attention, mainly for comfort and for industrial processes. Humidity sensor technologies are amenable to widespread application in electronic control system, such as microwave oven, dryer, and etc (Nitta, 1981). This technology is becoming even more important, principle in control system for industrial process due to many experiences that humidity changes make the variable results (Bernard, 1991).

The trend towards using automated control systems has recently gained importance in environmental control because of the falling cost of interface circuits and broadening application. For this purpose, humidity sensors using changes in electrical parameters are needed.

There are three groups of materials which have been proposed as sensing elements for humidity devices. They are electrolytes, organic polymers, and porous ceramics. The use of electrolytes, such as lithium chloride, produces sensors which are highly stable but which have slow response to humidity: moreover, they have short lifetime in highly humid environments. Humidity sensors using polymeric films have limited applications since they exhibit low heat resistance and mechanical strength, and do not accurately perform over the whole humidity range. (Gasmano *et al*, 1992) Furthermore, polymer films show hysteresis, long term drift, and degradation upon exposure to some solvent or to electrical shocks. The discussion focuses on sensors which are amenable to both low-cost manufacture and use in electronic control application (Nitta, 1991). Ceramic sensors, in particular metal oxide, have the advantages of better mechanical characteristics, resistance to chemical attack and easier heat cleaning. Ceramic humidity sensors show better chemical and mechanical strength with respect to polymeric sensors. Ceramics have been studied for use in humidity sensors mainly as porous sintered bodies, prepared by traditional ceramic processing, in order to allow water vapor to pass through the pores and water condensation in the capillary like pores between the grain surfaces. Ceramic materials possess a unique structure consisting of grains, grain boundaries, surface and pore, which makes them suitable for chemical sensors when they have a controlled microstructure. Nevertheless, commercial humidity sensors are mainly based on polymeric films. The market for ceramic humidity sensors, based on porous sintered oxide, is shrinking and contains many contaminants (oil, dust) due to the conventional ceramic technology used for their production. Thus, other process need to be added to solve the problems, which make ceramics far more expensive than polymeric film fabrication (Enrico *et al*, 1996).

$MgAl_2O_4$ has been proposed as a sensitive material for humidity detection devices, with interesting results in terms of sensitivity, stability and response time.

(Gusmano *et al*, 1993) Many researchers focus on MgAl_2O_4 films or pellet prepared from traditional process for humidity sensing material.

In year 1992, Gusmano *et al*, studied MgAl_2O_4 spinel prepared by thermal decomposition of either nitrate and hydroxides. The samples were formed into pellets and sintered at 1100 °C and 1300 °C. The pellets were analyzed using a.c. impedance spectroscopy at different temperatures and relative humidities. They found that MgAl_2O_4 spinel has good characteristics for use as humidity sensing elements. It showed linear relationship between impedance and relative humidity. In addition, the electrical properties of the pellets were correlated with their microstructure. However, the impedance was very high because of the pellet geometry adopted, particularly at low relative humidity values.

In year 1993, Gusmano *et al*, studied a MgAl_2O_4 thin film. Thin film was deposited on Si/SiO₂ substrates. This film showed interesting characteristics in terms of their use in humidity measurement devices. The different behavior of pellets and thin films is due to the different microstructure. MgAl_2O_4 pellet is crystalline, while it is disordered in thin-film form. The electrical response of MgAl_2O_4 film depends on the number of water molecules present on their surface. Thin film showed good adhesion to the substrate, which may be related to the interaction of Mg, Al, and Si at the interface. The compatibility made MgAl_2O_4 film possible to use. However, many parameters need to be compromised and improved.

In year 1995, Enrico showed the mechanism and effect of electrical response of ceramic sensors. This paper illustrated many factors that influence the sensing properties. Both total open porosity and pore size distribution have a great influence on the resistance versus humidity sensitivity of spinel compacts. Best results were shown by sample with a distribution of pore in the range 20-500 nm. The response time was influenced by the microstructure. The presence of micropores caused slow response time, while the absence of micropores results in a fast response time due to the easy adsorption and desorption of water molecules.

In year 2000, Apirat showed that MgAl_2O_4 ceramic spinel made from inexpensive materials exhibited good humidity sensors. In his work, the precursor was prepared via the OOPS process and pyrolyzed in a furnace at 1100°C for 2 h and

1300°C for 8 h. The sample was characterized using XRD to find the crystalline region, SEM to identify the microstructure of the powder, and BET method with N₂ as adsorbate to determine the surface area. Then, the samples were prepared into a pellet form and used a.c. impedance spectroscopy to study humidity sensor.

The specific surface area of the 1100°C spinel powder was measured by BET analysis to be 11.2 m²/g. The equivalent spherical diameter predicted from the BET surface area was 150 nm.

The mercury porosimetry was used to characterize the pore size, pore distribution in MgAl₂O₄ pellet and confirmed SEM micrographs. The results indicated that the variation in the sintering temperature and time affected not only the total open porosity but also the pore size distribution. The fired pellet at 1100°C, 2h had a total porosity of 40% with 60.5% of the pores being <100 nm and 39.5% of pores in the 100-1000 nm range. Whereas, the fired pellet at 1300°C, 8 h had total porosity 29.1% with 21.1% of the pore smaller than 100 nm, while the remaining is in range 100-1000 nm.

The results of impedance spectroscopy showed that the fired pellet at 1100°C has lower impedance when compare with 1300°C fired pellet. That means, microstructure, both pore size and pore distribution influence in humidity sensitivity as well. Increasing total porosity, homogeneous pore distribution and specific surface area will improve humidity sensor.

The conduction mechanism of MgAl₂O₄ ceramic spinel

Humidity sensor ceramics are porous, permitting free access to the air, and the resistance is modulated by selective adsorption of water vapor from the atmosphere. Control of the size and distribution of micropores is important in achieving reproducible, optimal sensor response (Bernard, 1991).

The role of resistive potential barrier layers at the grain boundaries in the conduction mechanism is somewhat complex. The conductivity will increase with increasing chemisorption, physisorption, and/or capillary condensation of water within the pore structure (Gusmano *et al*, 1993). In case of MgAl₂O₄, semiconductor is *p*-type, donor molecule, such as hydroxyl groups become attached at the surface by chemisorption of water molecules at elevated temperature and subsequent reaction

with oxygen present in the previously adsorbed layer or the atmosphere. Further absorption of water molecules occurs in stages. Initially, H_3O^+ ions are produced, assisted by high electronic charge density in the neighborhood of the hydroxyl sites, and protonic conduction to adjacent sites becomes possible. At high humidity, condensation of water in the capillary-like pores leads to a liquid like layer, and electrolytic conduction ensues.

A comprehensive examination of the characteristics of wide range of different humidity sensor materials concluded all operations by means of the same physical mechanisms. At low humidity, small ions (e.g. Li^+ , Mg^{2+} or Cr^{3+}) present in the surface area of the grains, process high local charge density, strong electrostatic field and present very good sites for the chemisorption of water molecules. Upon exposure to the atmosphere, strongly bound water molecules quickly occupy the available sites. This layer, once formed, is not further affected by exposure to humidity, but it can be thermally desorbed.

Once the first layer has been formed, subsequent layers of water molecules are physically adsorbed. The physisorbed water dissociates because of the high electrostatic fields in the chemisorbed layer:



Charge transport occurs when H_3O^+ releases a proton to a neighboring water molecule while releasing another proton, and so forth. This is known as the Grotthuss chain reaction (at high humidities). It is true to represent the conduction mechanism in liquid water as well as in the surface layers of humidity sensor. (Sun *et al*, 1989)

Thus, the charge transport mechanism depends on the surface coverage of the physisorbed water molecules. The proton hopping from one water molecule to the others when the water layer is continuous (at low humidities) also governs it. The activation energy required to dissociate water is lower than that needed to dissociate hydroxyl groups, resulting in higher conductivity or lower resistivity at the high relative humidity. A higher carrier concentration is therefore found when more adsorbed water layers are present on the pettlet surface (Nitta, 1981; Sadaoka *et al*, 1987; Yeh *et al*, 1990; and Kawicki, 1991).

From the study of Apirat (2000), the humidity was also found to be related to their microstructure. At different relative humidity (RH) values, the presence of pores is not only effective in increasing the specific surface area, but also in permitting capillary condensation of water in the pores, which results in electrolytic conduction in addition to protonic conduction.