# CHAPTER I
INTRODUCTION

1.1 Background

Many synthetic routes to 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 Tayaniphan et al, 1995) One of them, called the "oxide one pot synthesis (OOPS)" process, is very simple and straightforward. It provides several advantages over sol-gel, co-precipitation and other chemical techniques, for retaining purity, maintaining homogeneity and providing precursors with excellent processability. Precursors containing any combination of aluminum, silicon, with or without group I or II metals are readily produced in ethylene glycol used as solvent. It has also been found that the use of high boiling (b.p.>200 °C) amine bases, namely, triethanolamine [b.p. 335°C, $N(CH_2CH_2OH)_3$], and triethylene tetramine [b.p. 266°C, $NH_2(CH_2)_2N(CH_2)_2N(CH_2)_2NH_2$], instead of group I and II hydroxide or oxide, can be used to catalytically dissolve SiO_2 or $Al(OH)_3$. Unfortunately, attempts to react $Al(OH)_3$ with ethylene glycol (EG) and triethylene tetramine (TETA) as a catalytic or stoichiometric agent were not successful, probably because of the high Lewis acidity of the Al^{3+} species, which ties up the amine. However, reaction with approximately one mole equivalent of triethanolamine (TEA) proved quite effective in rapidly producing alkoxyalanes in 1 to 2 h (Tayaniphan et al, 1995).

The preparation of spinel oligomeric precursor proceeds as shown in the following reaction :

$$MgO + 2\ Al(OH)_3 + x's\ EG + 3\ TEA \xrightarrow{\quad 200^{\circ}C/\ -H_2O\quad}$$
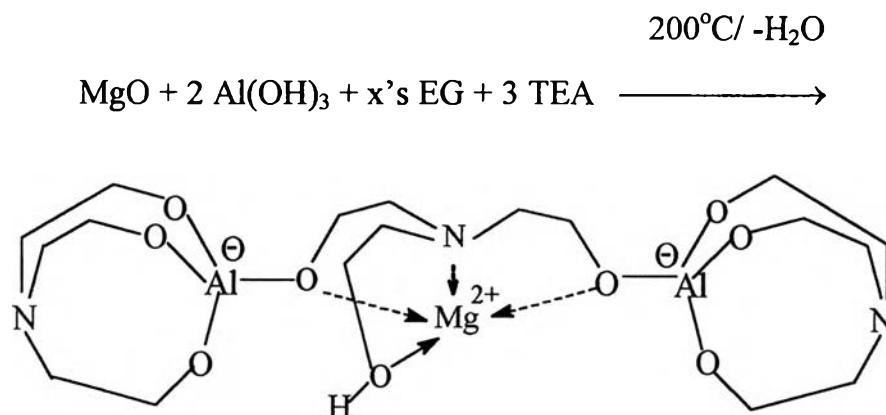
The precursors were produced by reacting mixtures of $Al(OH)_3$ and MgO [or $Mg(OH)_2$] with triethanolamine (TEA) using ethylene glycol (EG) as solvent.

The spinel precursor could be characterized by positive fast atom bombardment mass spectrometry (FAB$^+$–MS). From the mass spectral fragmentation pattern, the major peak was the parent peak at m/z = 518 (100% intensity).

After pyrolyzing the precursor, spinel forms without segregation of other phases. The XRD data for the spinel product, as compared with the powder diffraction file (Joint committee on powder diffraction standards 1990, JCPDS; file No 21-1152), showed two main peaks at the 311 hkl reflection (d = 0.244 nm, I = 100%) and the 400 hkl reflection (d = 0.202 nm, I = 60-65%). The phase evolution of crystalline spinel from the OOPS process was assessed using the method of Pasquier et al (1991). However, the integrated peak intensity ratios may be strongly affected by other factors that influence crystallization, such as degree of inversion of the spinel structure, preferential growth along specific crystallographic directions (anisotropic grain growth), and the presence of systematic defects that change in concentration with temperature. Generally, the relative intensity ratio of 400 and 311 hkl peaks (X) for the spinel is X = I (400) / I (311). At temperature $\geq 900^{\circ}C$, the peak ratio of spinel approached

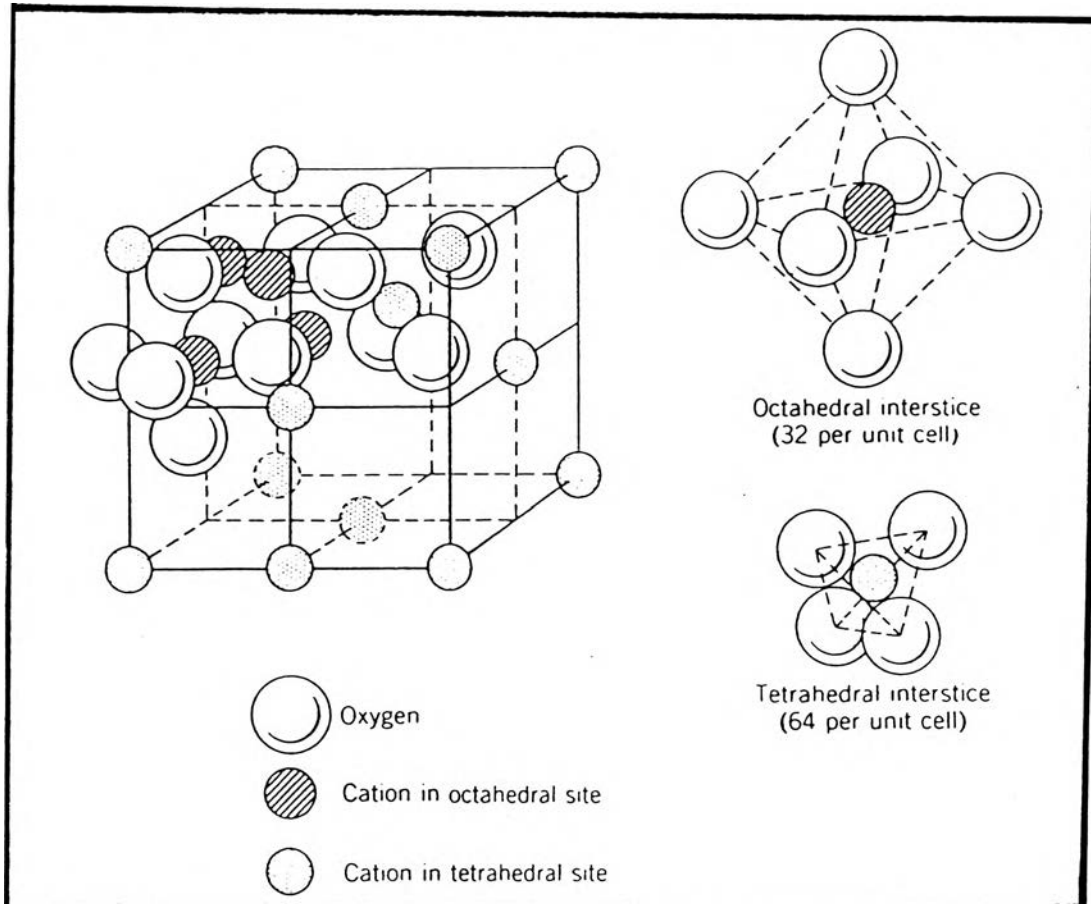constant value, 0.55, as the materials transform to pure spinel (Tayaniphan et al, 1995).

Figure 1.1 Spinel structure (Kingery et al, 1975).

MgAl$_2$O$_4$, mineral spinel, belongs to the class of the mixed oxides having general formula AB$_2$O$_4$. The spinel class of oxides crystallize in a cubic structure that can be viewed as a combination of the rock salt and zinc blende structures. The oxygen ions are face-centered cubic close packed. As shown in Figure 1.1, for a subcell of this structure there are four atoms, four octahedral interstices, and eight tetrahedral interstices. This makes a total of twelve interstices to be filled by three cations (B^{3+}), one divalent and two trivalent (A^{2+}). Each elementary cell is arranged to form a unit cell containing 32

oxygen ions, 16 octahedral cations and 8 tetrahedral cations (Kingery et al, 1975). $MgAl_2O_4$ is called normal spinel which is also observed in $ZnFe_2O_4$, $CdFe_2O_4$, $FeAl_2O_4$, $CoAl_2O_4$ etc. Additionally, system can also be found that is called inverse spinel, formulated as $B(AB)O_4$. The A^{2+} ions and half of B^{3+} ions are on the octahedral sites; the other half of the B^{3+} are on the tetrahedral sites. Examples of inverse spinels are $FeMgFeO_4$, $FeTiFeO_4$, $ZnSnZnO_4$, $FeNiFeO_4$ and many other ferrites of importance for their magnetic properties (Kingery et al, 1975).

Both noble and inverse spinels have been widely studied, especially for humidity sensing. Humidity critically affects many industrial and agro-industrial processes. As a consequence, a vast numbers of humidity sensors, operating according to different working principles, have been developed and are commercially available (Kulwicki, 1991). The trend towards using automated control systems has recently gained importance in environmental control because of the falling cost of interface circuits and microprocessors, their improved reliability, and broadening applications (Yagi, 1993). Humidity sensors that respond via exhibiting changes in one or more electrical parameters are needed for these purposes (Ichinose, 1985).

In recent years humidity control systems have been used increasingly in the quality control for production processes and products in a wide range of industries, such as the production of electronic devices, precision instruments, textiles, food stuffs (Arai et al, 1992). Many domestic applications have also increased, such as intelligent control of the living environment in buildings, where humidity sensors are used to maintain a comfortable humidity level and for cooling (Toyota et al, 1992).

As humidity is a major factor in our environment, measurements and/or control of humidity are important not only for human comfort, but also for a broad spectrum of industries and technologies. Among the different types of humidity sensors, those based on electrical properties, such as impedance (or resistance) and capacitance are best suited to modern automatic control systems. Generally speaking, a humidity sensor has to fulfill the following requirements to satisfy the widest range of applications; good sensitivity in a wide humidity range; quick response; good reproducibility and no hysteresis; fitness to circuitry; tough durability and long life; resistance to contaminants; insignificant dependence on temperature; simple structure, and low cost. Each field of application requires different operating conditions, and therefore different kinds of humidity sensors have been developed in order to meet the different requirements (Yamazoe et al, 1986).

Nearly all existing humidity sensors can be grouped into one of the following four classes: (i) Hygrometric sensors, where the sensor response is generated by the charge of a physical property of the material on the adsorption/desorption of water vapour. Examples are based on the measurement of a dimensional change of natural or synthetic fibres, the detection and measurement of a change in conductivity or electrical capacity of a sensing material, the measurement of the shift in oscillation frequency of a crystal covered by a humidity adsorbing layer, etc. (ii) Psychrometric sensors, where the sensor response is based on the implementation, in one way or another, of the classical 'wet and dry bulb" method. (iii) Dew point sensors, where the humidity content of a gaseous environment is deduced from the dew formation on a cooled surface. (iv) Radiation absorption sensors, where the humidity content of a sample is deduced from the attenuation of the intensity of electromagnetic radiation in the IR or microwave range. All sensors and sensing techniques have their specific advantages, disadvantages and areas of applications (Huyberechts et al, 1993).

A wide variety of materials has been studied as sensing elements in humidity sensors and used for commercial devices. They are roughly classified into three groups: electrolytes, organic polymers, and ceramics (Yamazoe et al, 1986). A representative electric humidity sensor is the LiCl electrolyte humidity sensor, which was developed by Dunmore in 1938 and has been used for over 40 years (Dunmore, 1939), being the only electric humidity sensor available. It operates on the principle that lithium chloride solution immersed in a porous binder changes its ionic conductivity depending on the relative humidity of the surrounding atmospheric air. However, this sensor has drawbacks, such as leaching of lithium chloride which is triggered by condensation, resulting in extremely poor accuracy and slow response times at low temperatures, and inability to operate in an ammonia and organic solvent atmosphere. Thus, there are many applications where this type of sensor will not work.

The materials currently used to replace electrolyte humidity sensors are mainly organic polymer films and porous ceramics. However, each of these materials has its limitations. Polymer films cannot operate at high temperatures and high humidities, and show hysteresis, slow response times, long-term drift and degradation upon exposure to some solvents or to electric shocks. They also require temperature compensation. Nevertheless, recent developments have improved the characteristics of these materials (Furlani et al,1992; Sakai et al, 1993; and Matsuguchi et al, 1993), and several polymeric capacitive sensors are commercially successful (Matsuguchi et al, 1991 and Kuroiwa et al, 1993).

Metal oxide ceramics have been studied for a long time because of their physical, chemical and thermal stability. Ceramic humidity sensors are mainly porous sintered bodies, prepared by traditional ceramic processing. The porosity allows water vapour to pass easily through the pores and to condense in the capillary-like pores between the grain surfaces.

Ceramic materials possess a unique structure consisting of grains, grain boundaries, surfaces and pores, which make them suitable for use as chemical sensors when they have a controlled microstructure (Shimizu et al, 1985). Compacts with a given microstructure can be produced by controlling the different steps of the ceramic production process spinel in particular provides useful sensors (Gusmano et al, 1991).

Spinel (magnesium aluminate, $MgAl_2O_4$) was first recognized by Ryshkewitch (Gitzen, 1970) as a pure ceramic material (Kingdon et al, 1991). Alais described the preparation of spinel by electrofusion and casting (Gitzen, 1970). It is characterized by high refractoriness and exceptional dielectric properties. Navias (Gitzen, 1970) also described the preparation and some properties of spinel synthesized by the vapor transport of MgO from periclase in a hydrogen atmosphere at $1500°$ to $1900°C$.

$MgAl_2O_4$ has been successfully fabricated by standard ceramic processing methods, such as casting, extrusion, or cold pressing, followed by sintering at temperature of $1650°$ to $1850°C$ (Kingdon et al, 1991). It is used as a refractory material in the ceramic industry partly because of its low density (3.58 g/cm^3) (Kingdon et al, 1991) and because it is stable in harsh environments (Sharafat et al, 1993). It has been suggested for use as a fusion reactor power core insulating material due to its radiation stability (Cousin et al, 1990).

The constituent materials of spinel, alumina from bauxite and magnesia from brucite, are inexpensive and relatively abundant (Cousin et al, 1990). Fully dense, polycrystalline spinel is transparent both optically and in 3-5 μm infrared regions, if grain size is less than the wavelength of light to be transmitted (Kingery et al, 1975; Cranmer, 1991; and Carts, 1992).

Additionally, in recent years $MgAl_2O_4$ has been proposed as a sensor material for use in humidity detection devices (Gusmano et al, 1993), with interesting results in terms of sensitivity, stability and response time. As well-known, different levels of environmental humidity are associated with changes in impedance or capacitive response of porous oxides. Two factors affect the humidity-sensitive electrical characteristics of porous ceramics; adsorption, and the capillary condensation of water.

The conduction mechanism of porous $MgAl_2O_4$ in humid environments, which is similar to that of many other ceramic oxides, is ionic, with a transport of protons by a Grotthuss chain reaction (Yamazoe et al, 1986). When the dry ceramic oxide is exposed to humid atmosphere, a layer of water-vapor molecules on its surface is first chemisorbed with the formation of surface hydroxyl ions. In this stage, charge transport occurs first by a hopping mechanism between hydroxyl groups of protons coming from the hydroxyl dissociation. Subsequent layers of water molecules are physically adsorbed on the hydroxyl layers. The easy dissociation of physisorbed water, due to the high electrostatic fields in the chemisorbed layer, produces protons which are responsible for the electrical conduction by hopping between water molecules (Anderson et al, 1968).

The humidity-sensitivity of ceramics is mainly dependent on their microstructure. The presence of open porosity permits greater conductivity due to water condensed in the capillary pores. Electrolytic conduction occurs in the liquid-like layers, in addition to the protonic transport, resulting in an increase in porous ceramic conductivity (Kulwicki, 1984). The quantity of condensed water depends on the available pore sizes and their distribution. It is possible to estimate the pore radius at which capillary condensation occurs as a function of partial pressure of the saturated vapour (Jankowska et al, 1991). This

relationship is based on the Kelvin equation, which gives the maximum radius of pores for capillary condensation :

$$r_k = \frac{2\gamma M}{\rho RT \ln(Ps/P)}$$

where r_k is the Kelvin radius, γ is the surface tension of water, ρ is the density of water, M is molecular weight of water, Ps is the saturated vapor pressure and P is the water vapor pressure in the surrounding environment (Shimizu et al, 1985 and Jankowska et al, 1991). The functioning of the humidity-sensing elements made of oxide ceramic materials is based on the dependence of their impedance on the quantity of the absorbed moisture.

The concept of the electrical impedance was first introduced by Oliver Heaviside in the 1880s and was soon after developed in terms of vector diagrams and complex representation by A.E. Kennelly and especially C.P. Steinmetz (Macdonald, 1987). An impedance is a vector quantity of the magnitude and direction of a planar vector in a righthand orthogonal system of axes to be expressed by the vector sum of the components Z' and Z" along the axes, that is, by the complex number:

$$Z = Z' + iZ''$$

where Z' and Z" are the real and imaginary components of impedance, respectively. They can be plotted in the plane with either rectangular or polar coordinated, as shown in Figure 1.2. Here the two rectangular coordinate values are clearly

$$\text{Re}(Z) \equiv Z' = |Z|\cos(\theta) \quad \text{and} \quad \text{Im}(Z) \equiv Z'' = |Z|\sin(\theta)$$

with the phase angle

$$\theta = \tan^{-1}(Z'' / Z')$$

and the modulus

$$|Z| = [(Z')^2 + (Z'')^2]^{1/2}$$

This defines the Argand diagram or complex plane, widely used in both mathematics and electrical engineering. In polar form, Z may now be written as $Z(\omega) = |Z| \exp(i\theta)$, which may be converted to rectangular form through the use of the Euler relation $\exp(i\theta) = \cos(\theta) + i\sin(\theta)$. In general, Z is frequency-dependent. It will be noticed that the original time variation of the applied voltage and the resulting current have disappeared, and the impedance is time-invariant.

In most cases the equivalent circuit of a sensing element of spinel type could be represented as a parallel connection of a resistor and a capacitor. The total resistance of the circuit is determined according to

$$Z = R / (1 + j2\pi fRC)$$

where Z is the total impedance, R and C are the direct-current resistance and capacity of the element, respectively, and f is the frequency of the voltage (Nenov et al, 1992).
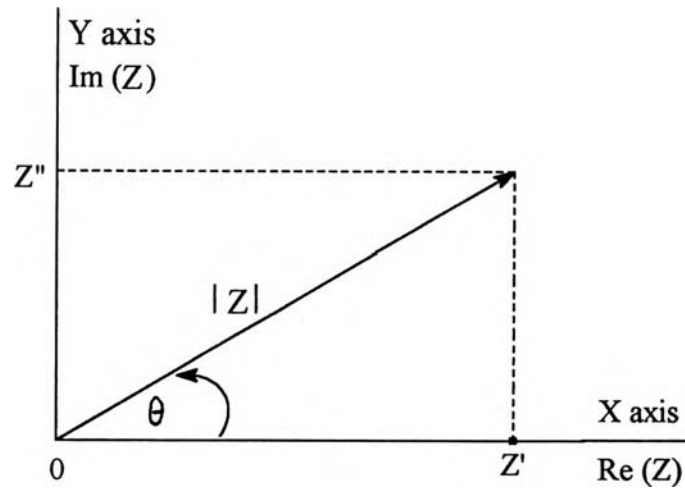
Figure 1.2 Impedance Z plotted as a planar vector using rectangular and polar coordinates (Macdonald, 1987).

1.2   Research Objectives

This research therefore targets the development of $MgAl_2O_4$ spinel humidity sensing elements, produced by the OOPS process, as shown by K.F. Waldner (1996) and Tayaniphan (1995).   Characterization of the product is carried out using TGA, SEM, BET, and XRD.   The focus of this work is to investigate the humidity-sensitive electrical properties of spinel in bulk form by a.c. impedance spectroscopy.

Further objectives include studying the effects of sintering on pellet microstructures of as a function of conductivity.