CHAPTER 2

LITERATURE REVIEW AND PROCESSING TECHNIQUES

2.1 INTRODUCTION

Ceramics are normally made from powders. These powders are consolidated and defined by sintering. A major issue in the preparation of powder precursors, especially for electroceramic applications, is chemical homogeneity. The standard conventional technique for processing precursor powders can approach homogeneity only after grinding and firing steps. A number of chemical approaches have been developed. Even though the atomic mixing level techniques involve the decomposition of salts like nitrates, sulphates and chlorides into the desired chemical form. In this chapter the most used chemical techniques are discussed.

In order to understand the properties of any solid material, it is essential to know the details of its structure. The three main categories of techniques used in structural characterization are diffraction, microscopy and spectroscopy. The X-Ray diffraction pattern (XRD), Differential Thermal Analysis (DTA), Thermo gravimetric Analysis (TGA), Infrared Spectroscopy (IR) and Scanning Electron Microscope (SEM) are the basic techniques required to find out the phase and purity of any material. In this second part of this chapter various techniques used to study the nature of ceramics are discussed.
Yttria stabilized Zirconia materials are very attractive in the field of ceramics due to their low processing temperature, homogeneity, crack-free coating, low cost, high strength, high toughness, chemical stability, high melting temperature, and high ionic conductivity. The fuel cells are preferred due to their fuel flexibility at high temperature, 800°C - 1000°C. 8mol% Yttria Stabilized Zirconia, (8YSZ) is widely used as a negative oxygen ionic conductor in Solid Oxide Fuel Cells (SOFC) and oxygen sensors (Heuer et al 1981) (Stevens et al 1986), (Li et al 2007), (Ramamoorthy et al 1999), (Badwal 1994), (Steele et al 1989). In the final part of the chapter, synthesis of 8mol% of Yttria stabilized Zirconia (8YSZ) by the sol-gel technique using metal salts of nitrate, chloride and oxalic acid, the different stages of gel preparation are explained in detail, and characterization results of 8YSZ have also been described in detail.

2.2 LITERATURE REVIEW

2.2.1 Zirconia and stabilization of zirconia

Shih Ming Ho et al (1982) studied the structure of Zirconium oxide, and the key factors of high co-valency and seven fold co-ordinations, which control the polymorphism and stabilization phenomena.

Ping Li et al (1993) studied the local structure characteristics of zirconia polymorphs by X-ray absorption studies, and observed that the Zr-O bonding was similar in monoclinic,orthorhombic and cubic zirconia, with seven fold co-ordination and comparable bond distance.

By using the X-ray absorption studies, Ping Li et al (1993) studied the Y₂O₃ addition to zirconia, and observed that the oxygen ion vacancies caused by Y doping in zirconia were preferentially located as the nearest neighbours of Zr, leaving the eight fold co-ordination to Y. The distortion of
both Zr, and Y local environments generally increased with doping. Particularly, the Zr cat ions shell in cubic zirconia was severely distorted to accommodate the ZrO$_2$ polymorphs.

Ping Li et al (1994) studied the effect of trivalent dopants on zirconia stabilization by X-ray absorption studies, and observed that the oxygen ion vacancies associated with Zr provide the stabilization for partially and fully stabilized zirconia, and also that the oversized dopants were more effective stabilizers than the undersized dopants in stabilizing the cubic and tetragonal phases of zirconia.

Stapper et al (1999) studied the structural and electronic properties of yttria stabilized cubic zirconia. It was suggested that the yttria was the preferential site for the vacancy.

Devanathan et al (2006) studied the stimulation effects and oxygen transports in yttria stabilized zirconia, and reported that oxygen vacancies preferred to be the second nearest neighbour to the yttrium dopants.

### 2.2.2 Microwave Sintering

Meek et al (1987) used microwave sintering, and studied the sintering effects of some oxide materials. Adding second phase materials to common materials enhances the densification process with microwave sintering.

Mark Jenny et al (1992) studied the microwave sintering of solid oxide fuel cell materials, namely, 8mol% Yttria Stabilized Zirconia and also reduced the sintering temperature by 100°C-150°C when compared with conventional sintering.
Sharon Nightingale et al (1997) investigated the microstructural development of 3YSZ, using the microwave sintering technique, and achieved the highly densified samples at low temperatures of 1200°C-1300°C.

Vaithyanathan et al (2008) studied the processing of nanocrystalline Yttria Stabilized Zirconia by conventional and microwave sintering, and achieved highly densified samples with smaller grain sizes.

Mazaheri et al (2008) prepared the nanocrystalline 8mol% YSZ powder by the smouldering combustion method and applied conventional, microwave-assisted, and two-step sintering methods, to study the mechanical and electrical properties.

Thridandapani et al (2008) studied the effect of microwave sintering of 8YSZ, and achieved the 90% theoretical density of the sample, and showed that the compressive strength values obtained for a 1300 °C microwave-processed sample were higher compared to those of a conventionally processed sample.

Upadhyaya et al (2001), applied the ‘Microwave Sintering technique on Cubic Zirconia, and studied its microstructure.

Ebadzadeh et al (2008) reviewed the microwave assisted sintering of zirconia study reports.

Morteza Oghbaei et al (2010) reviewed micro wave sintering versus conventional sintering of Alumina-zirconia and zirconia, and analysed the advantages and applications of microwave sintering.
2.2.3 Indentation techniques

Many investigators applied conventional sintering, the two step sintering process, and microwave sintering on the commercially available 8YSZ powder pellets, and studied the mechanical properties by using the micro indentation technique.

Dhal et al (2007) studied the densification and mechanical and electrical properties of zirconia, prepared by three different sintering techniques, ie, conventional, spark plasma, and Hot press sintering techniques, which showed that no significant differences in electrical conductivity were observed for the YSZ material with different grain sizes (from 210 nm to 12µm), and also showed that the Vicker’s hardness values do not depend on the grain size of the sample.

Mehdi Mazaheri (2008) applied the two step sintering technique on the 8YSZ material and studied the mechanical properties such as hardness and fracture toughness by applying micro indentation.

Gatee et al (2009) investigated the electrical properties of the 8YSZ, 3YSZ and 3YSZ/8YSZ composites. They found the mechanical properties for the same samples by the micro indentation technique, and showed that the addition of the 3YSZ particle to the 8YSZ matrix decreased the electrical conductivity of the matrix at higher temperature. They also showed that the Vicker’s hardness and indentation fracture toughness of pure cubic zirconia is 11.8G Pa.

Razavi Hesabi et al (2009), prepared the 8YSZ by the glycine nitrate process using by slip casting, and studied the mechanical properties by the micro indentation technique.
Razavi Hesabi (2009) prepared fully dense 8mol% yttria stabilized zirconia by conventional sintering, microwave assisted sintering and two step sintering process, to show that the considerable enhancement in electrical conductivity could be obtained, when using ultrafine-grained materials rather than coarser textures. By the reduction of grain size from 2.15µm to 295 nm, the electrical conductivity increased (> 95%) 

Masaki Fujikane et al (2007) applied the nano indentation technique on 8YSZ crystal, to show the several values of Young’s modulus and hardness of the ideal single crystal YSZ, through precise analyzing conditions.

Wellman et al (2004) applied the Nano and micro indentation studies of bulk zirconia and EB PVD TBC, and showed differences in the results obtained when using the two different tests, relating them to the interactions between the indent and the columns of the EB PVD TBC microstructure. It was found that the individual columns had a hardness of 14 GPa, measured using nano indentation, while the hardness of the coating, using micro indentation decreased from 13 to 12.4 GPa as the indentation load increased from 0.1 to 3N. This decrease in hardness was attributed to the interaction between the indenter and a number of adjacent columns, and also the ability of the columns to move laterally under indentation.

Soyez et al (2000) found the mechanical properties of polycrystalline YSZ films by using the Nano indentation technique.

Voevodin et al (2001) fabricated YSZ/Au nano composite films evaluated their mechanical behaviour by the nano indentation technique.
Gaillard et al (2009) applied the nano indentation technique on the yttria stabilized zirconia crystal to analyse the phase transformation of the single and polycrystal.

Anoo Mukhopadhyay et al (2009) applied the nano indentation technique, to calculate the nano hardness of pressure less sintered alumina samples.

Winnubst (2004) found the coefficient of friction of CuO doped 3Y-TZP sample to be $\mu=0.2$.

Shen Ran et al (2009) studied the Dry-sliding self-lubricating ceramics: CuO doped 3Y-TZP.

2.2.4 Electrical Conductivity Studies of YSZ


Ghatee et al (2011) investigated the electrical and mechanical properties of tetragonal/cubic composite electrolytes for commercial 8 mol % and 3 mol% Yttria Stabilized zirconia powders.

Fonesca et al (2009) studied the impedance of Yttria stabilized Zirconia-magnesia composites in the (0-30 mol%) range collected the impedance diagram at 800 C-1400 C, and found the micro structural
features associated with both sintering processes, solid solution formation of YSZ- m Mg O.

Schouler et al (1983) analysed the merits of the Impedance spectroscopy technique for studying the sintering process of yttria stabilized zirconia and observed the possibility of the behaviour of the separating the grain from the grain boundaries, during thermal cycles (300 C-600 C), and found the grain boundary formation evolution for different firing conditions.

Dhal et al (2007) prepared the 8YSZ Samples by the glycine - nitrate smouldering combustion method, and applied different sintering techniques, viz, conventional, spark plasma, and hot press, and also showed that the spark plasma sintered sample has the highest electrical conductivity 82 ms/cm at 900 C than other conventional sintering techniques.

Li et al (2007) prepared the 8YSZ, nano ceramics by sol-gel method, and proved that the conductivity of the high pressure sintered nano crystalline sample was comparable with that of the microcrystalline sample; they found that the electrical conductivity of the nano crystalline sample is one order of magnitude lower than that of the microcrystalline sample. This may be attributed to the grain boundary effect of the nano crystalline material.

Qigen Wang et al (2008) prepared 8YSZ by the glycine nitrate process and showed that the amount of glycine had effects on the total conductivity and also the grain boundary and bulk contribution, and observed that the maximum electrical Conductivity was 0.0275 S/Cm at 800 C for YSZ prepared with 80% glycine.

Vladimir et al (2001) prepared 3 mol% yttria stabilized zirconia by the so-gel technique, and the A.C. conductivity of the sintered 3YSZ
pellets was measured in air by the four probe impedance analyzer from 20Hz - 3MHz, in the temperature range 75 - 825°C, and observed the conductivity increasing with temperature; the highest value of about $10^{-3}$ S / Cm was measured at 677°C.

### 2.2.5 Zirconium Tin Titanate


Yung-Shou Ho (2005) et al prepared nano Zirconium tin titanate by the sol gel technique, and studied its microwave dielectric properties.

Nedelcu et al prepared Magnesium doped Zirconium Tin titanate by the solid state reaction method. Samples were sintered in the temperature range 1270°C, and it was proved that the addition of MgO improved the sintering process and showed the minimum pores in the SEM structures.

Xiong, et al 2003 prepared (Zr,Sn) TiO$_4$ nano powders by Hydrothermal synthesis. The prepared powder particle size was 10-120 nm. and the pressed pellets were sintered at 1200°C - 1300°C, and found the microwave dielectric properties.

Kudesia et al 1993 analysed the structural study of Zirconium tin titanate, and investigated the crystal structure of (Zr$_{0.8}$ Sn$_{0.2}$) TiO$_4$ ceramics, using the extended X-ray absorption fine structure spectroscopy (EXAFS), neutron powder diffraction, and Raman spectroscopy techniques. They conclude that the (Zr$_{0.8}$ Sn$_{0.2}$) TiO$_4$ possesses α-PbO$_2$ structure, and the average cation distance is 2.066Å.
2.3 PROCESSING TECHNIQUES OF CERAMICS

Chemical homogeneity is the main property for the structural and electrical applications of 8YSZ. The conventional powder preparation method has firing and grinding steps. In order to improve the mixing of properties at the atomic level, various chemical methods have been developed.

Freeze drying, spray drying, sol-gel process, Pechini process, and solution combustions are used to get a homogeneous, fine grained and highly pure powder. Out of these, the following techniques are frequently used.

1. Sol-gel method
2. Spray drying
3. Freeze drying
4. Pechini process

2.3.1 Sol-Gel Process

There are various wet chemical routes available for the synthesis of 8YSZ, namely, the Solution Combustion Route (Mridula Biswas 2011), Polymerized Complex Method (Ch Laberty 2001), Gel Combustion Method (Jua Arez 2000, Jagadish Ray 2001), and Co-Precipitation Method (Tsoga 1999). The Hydrothermal Synthesis (Dell’s Agli 2000) Solid State Reaction Methods are used to prepare bulk amounts of ceramic powder. It requires long time heat treatment and also for milling. The Pyrolysis method requires a high reaction chamber, and handling the waste product is also difficult. In the co-precipitation technique, a controlled reaction condition, and repeated washing processes are needed to eliminate reacting salt wastes; this method is a time consuming one. The sol-gel method is useful to synthesise nano 8YSZ (Kim 1998).
The main advantages of the sol-gel techniques are its high chemical purity, and lower processing temperature. Sintering can have considerable influence on the densification and grain growth of nanopowders.

Sol–gel processing was developed in the mid-1960’s for nuclear fuel applications. The main requirement of the sol–gel process is that, the oxide component should be capable of forming a concentrated colloidal sol of the metallic oxides or hydroxides, and converting this sol to a gel. The shape and size of the final oxide product is determined at the gelation stage, which is therefore crucial to the whole process. The classification of the sol-gel is given in Figure 2.1, based on the availability of the starting materials and the characteristic nature of the formation of the sol and the gel (Johnson 1985).

![Figure 2.1 The classification of the sol-gel Process](image)

1. The Sol gel process is an alternative method to conventional ceramic processing. This is main reason for the atomic molecular scale mixing and low densification temperature. The Sol-gel Method was widely used to prepare highly interactive ceramics. The sol may be defined as the dispersed colloidal particles in a liquid. The gel is a solid in a liquid medium, with a low elastic modulus (Florry 1986).
2. The Sol-gel method is a promising processing technique because of its inherent advantage, controlled particle size, shape and distribution, desired composition, relatively low temperature sinterability, molecular level mixing, extreme purity, perfect stoichiometry, nanoparticle size and distribution and fine spherical shape. A high surface area, high surface reactivity, and low processing temperature requirements are the advantages of the Sol-gel method. High cost starting materials, and long processing time are the disadvantages of this method.

2.3.1.1 Polymerized alhoxides route

To prepare a single component oxide material using its corresponding alhoxide. Initially the alhoxide is partially hydrolysed as given below.

\[ M(OR)_x + yH_2O \rightarrow M(OR)_{x-y}(OH)_y + yROH \]  \hspace{1cm} (2.1)

where ‘R’ represents an alcoholic group, and ‘M’ the cation. The partially hydrolysed species are allowed to form a M-O-M linkage by a polymerization or condensation of reaction. This continuous condensation leads to the polymerised sol.

2.3.1.2 Colloidal sol

Sol-gel processed from colloidal sols fit the common definition sol, a stable dispersion of colloidal particles in a liquid. The inter particle surfaces forces a three dimensional net work, to form the span of the sol, which finally forms a semi rigid mass called a gel. This type of gelation is known as physical gelation. The Sol-gel process can be further classified into (i)
colloidal sols, formed by a precipitation peptisization, and (ii) formed by the
dispersion of very fine particles.

2.3.1.3 Hydrolysis

The Metal oxide hydrolysis mechanism is complex and depends on
the experimental condition. The hydrolysis rate of metal oxides depends on
the characteristics of the metal, and the loss of the alkyl group. However, in
the initial stage one water molecule interacts with the alhoxides and the other
molecule of alcohol is also expelled. The alhoxides water reaction in which
the hydroxyl ion is attached to the metal atom is also termed as hydrolysis.

\[ M(OR)_{z} + H_2O \rightarrow M(OR)_{z-1}OH + ROH \]  \hspace{1cm} (2.2)

2.3.1.4 Effect of the catalyst

The Sol-gel transition depends on the catalyst used to promote the
rate of hydrolysis. HCl, and HNO\textsubscript{3}, are the two acid catalysts used to promote
hydrolysis through electrophoilici reaction. The rate of hydrolysis increases
when the pH of the starting mixture decreases from 7. Further, the
condensation reaction occurs around pH equal 2. Hence, a sol prepared by
an acid catalyst requires a very long gelling time, and the resulting gel
undergoes large shrinkage during sintering.

2.3.1.5 Sol-gel Transformation

The sol to gel transformation can be achieved in three different
ways. At the very beginning the polymeric molecules growth cross-links
randomly to form three dimensional net works. Then, individual particles
grow together and become larger. In the final process, stabilization of the
colloids by surface changes occurs, due to the change of Zeta potential and
inter-particles condensation process. The Sol-gel transformation is shown in Figures (2.2 - 2.4).

**Figure 2.2** Schematic diagram of sol-gel inorganic network formation

**Figure 2.3** Schematic diagrams of gels (a) with significant branching and cross-linking (b) with little branching and cross-linking
2.3.1.6 Poly condensation

Poly condensation is a process, in which the linking of smaller and partially hydrolysed molecules into a large molecule takes place

\[
\text{M (OR)}_{z-1}\text{OH} + \text{M(OR)}_z \rightarrow \text{(RO)}_{z-1}\text{M-O-M(OR)}_z + \text{ROH} \quad (2.3)
\]

This poly condensation results in the formation of the semi solid phase. The gel contains water in the structural cavities. Further, the ‘sol’ is heated; water and the alcohol molecules are eliminated.

2.3.2 Spray Drying

This method is energetically expensive and is mostly suitable for bulk ceramic powder preparation. The pressure of 300-500 KPa is applied to a small drop of salt solution which is atomized to a fine spray. Then, the uniform droplets are rapidly dried, by the upward flowing hot gas. (Johnson et al 1979).

2.3.3 Freeze Drying

The freeze drying technique has three steps. The concentrated solution is atomized into fine droplets, and then the droplets are rapidly frozen.
by allowing them into chamber cooled liquid nitrogen. Finally, the spheres are
dried by evacuating the chamber. After calcinations, the obtained ceramic
powder crystalline size was 0.1 and 0.5 µm. (Alessandra Bianco et al 1999).

2.3.4 Pechini Process

In this Pechini Process method, an aqueous solution of a suitable
oxide is mixed with Citric Acid. Complex ring shaped compounds around the
metal cations will be formed in this solution. Then, poly hydroxyl alcohol is
added to the solution mixture and heated to 150° - 250°C to allow the chelates
to polymer or to form a long cross linked net work. The excess water is
removed by heating, which gives a polymer resin. At a higher temperature
of 500°C-600°C, the resin decomposed or charred, and mixed oxide is
obtained. Fine powders are obtained in this route.

2.4 CONSOLIDATION

There are different methods available for shaping ceramic powders,
such as pressing the powder into a pellet form, slip casting, tape casting,
injection moulding, extrusion, hot iso static pressing, etc. Organic binders,
such as PVA, PEG (Poly vinyl alcohol, poly ethylene glycol) are added to
give sufficient strength; hence this is easy to handle the green body before
sintering.

2.4.1 Tape Casting

This method of tape casting is mostly suitable for forming
traditional ceramics. Here, the ceramic powder slurry is continuously cast on
a moving carrier made of smooth non-stick Teflon material. A knife edge
smoothly spreads slurry to the required thickness. Then the solvent is
evaporated and a fine ceramic tape is obtained. In general the Tape Casting Method is used to make a substrate for IC and multilayer capacitors.

2.4.2 Injection Moulding

Initially, the prepared ceramic powder is mixed with a thermo plastic polymer; then the ceramic mixture is injected into the injection moulding machine under certain pressure, and the material hardens to the desired shape.

2.5 COMMINUTION

Usually the desired particle size and size distribution cannot be achieved simply by screening, and classifying the raw materials. Particle size reduction is necessary. Comminution is a process, by which a larger particle is reduced to smaller size using mechanical forces.

The operations involved in comminution are crushing, milling and grinding. The high compression roller mills, Jet mills, and Ball mills are the most important milling systems. Ball mills are categorized into different types based on the method used to impart motion to the balls (e.g. vibration and agitation.). In general the used mills for grinding ceramic materials are, called ball mills, vibratory mills, attrition mills, fluid energy mills and roller mills.

2.5.1 Hammer Milling

Hammer milling is a rapidly rotating rigid bar or plate. The particles are dropped in the bar and fragmented by the impact. Further, the fragmentation occurs as the particle strikes the walls of the mill. A hammer mill is capable of producing a large particle around to about 0.1mm.
2.5.2 **Roller Milling**

It is an alternative for the Hammer Milling technique. In this method, the ceramic particles are directed to hard fused rollers which rotates in opposite directions, such that the ceramics are pinched between them, though the process is unsuitable for the production of particle sizes below 10µm. The two advantages of roller milling are: the energy utilization is fairly good for the production of particles of the same size from a stock of coarse particles, and only a small amount of material makes contact with the roller; so the wear is fairly low.

2.5.3 **Jet Milling**

The operation consists of the interaction of one or more streams of high-speed gas, bearing the stock of coarse particles, with another high-speed stream. Communition is achieved by collisions between the particles in the high-speed stream and a wall (fixed or movable) within the mill. The milled particles leave the mill in the emergent fluid stream, and are usually collected in a cyclone chamber outside the mill.

2.5.4 **Attrition Milling**

Attrition Milling is similar to “ball milling”. It is cylindrical in shape and contains balls. The very small balls are agitated by a series of stirring arms mounted on an axial shift. Attrition milling is much quicker than ball milling, and less contamination are the advantages of attrition milling, which is used for producing sub-micron powders, hard refractory oxides, carbides, nitrides, titania pigments and paper grade kaolin.
2.5.5 Vibratory Milling

This is entirely different from ball milling and attrition milling. The energy for comminution is supplied through vibration rather than tumbling or mechanical stirring. The powder is placed in the stationary chamber of the mill, together with the suitable grinding media and a liquid. In the process, the vibration is transmitted through the chamber into the media and the powder.

2.5.6 Fluid Energy Milling

In fluid energy milling, reduction is achieved by the particle-particle impact in a high velocity fluid. The fluid can be compressed air, CO, super heated stream, water or any other gas. The powder is added to the compressed fluid and accelerated to sonic (or) near sonic velocity, through jets leading in to the grinding chamber. The grinding chamber is designed to maximize the particle-particle impact, and minimize the particle-wall impact, achieving minimum contamination. In this method, the particle size is reduced to 1 µm.

2.5.7 Ball Milling

In ball milling, the particle is placed in a closed cylindrical container, with balls or rods as the grinding media, and rotating the cylinder horizontally on its axis, so that the medium is cascaded. Ball milling is suitable for wet or dry milling. Wet ball milling has an advantage over dry milling in that its energy utilization is higher (10-20%). It also has the ability to produce a high fraction or fine particles.
2.5.7.1 High-energy ball milling

A ball mill is a cylindrical device used in grinding (or mixing) materials like ores, chemicals, ceramic raw materials and paints. Ball mills rotate around a horizontal axis, partially filled with the material. Different materials are used as the media, including ceramic balls, flint pebbles and stainless steel balls. An internal cascading effect reduces the material to a fine powder. Industrial ball mills can operate continuously fed at one end, and discharged at the other end. Large to medium-sized ball mills are mechanically rotated on their axes, but small ones normally consists of a cylindrical capped container that sits on two drive shafts (pulleys and belts are used to transmit the rotary motion). Ball mills are also used in pyrotechnics and the manufacture of black powder, but cannot be used in the preparation of some pyrotechnic mixtures such as flash powder because of their sensitivity to impact. High-quality ball mills are potentially expensive, and can grind mixture particles as small as 5 nm, enormously increasing the surface area and reaction rates. The grinding works on the principle of critical speed. Critical speed can be understood as the speed, after which the steel balls (which are responsible for the grinding of the particles) start rotating along the direction of the cylindrical device, thus causing no further grinding.

Ball mills are used extensively in the mechanical alloying process, in which they are not only used for grinding but for cold welding as well, with the purpose of producing alloys from powders.

The ball mill is a key piece of equipment for grinding crushed materials, and it is widely used in production lines for powders such as cement, silicates, refractory materials, fertilizers, glass ceramics, etc. as well as for ore dressing of both ferrous and non-ferrous metals. The ball mill can
grind various ores and other materials either wet or dry. There are two kinds of ball mills, the grate type and over fall type, due to different ways of discharging the material. There are many types of grinding media suitable for use in a ball mill, each material having its own specific properties and advantages. The important properties of the grinding media are their size, density, hardness and composition. The interplay between these forces produces the high and very effective degree of size reduction of the planetary ball mill.

2.5.7.2 Planetary ball mill

Planetary Ball Mills are used wherever the highest degree of fineness is required. In addition to well-proven mixing and size reduction processes, these mills also meet all the technical requirements for colloidal grinding, and provide the energy input necessary for mechanical alloying. The extremely high centrifugal forces of Planetary Ball Mills result in very high pulverization energy in a short grinding times.

2.6 SINTERING TECHNIQUES

2.6.1 Sintering Mechanism

Sintering is an important factor for preparing a good ceramic product. During the sintering process, the heat is used to convert the powder compact into dense crystalline material. In general, sintering methods can be classified as solid state sintering, liquid phase sintering, pressure-less sintering, and pressure assisted sintering.

Sintering plays an important role in the fabrication of ceramics. In general, all ceramic bodies should be sintered at elevated temperatures to give
a fine microstructure with good properties. There are two main functions of sintering powder compacts (i) atomic bonding between the particles to give strength (ii) pore’s elimination. The following points must be considered before sintering the green body:

1) A mechanism for material transport
2) A source of energy to activate and sustain the material transport.

The Sintering process is different for polycrystalline and amorphous materials. There are six different mechanisms of sintering polycrystalline ceramics, as shown in Figure 2.5. All these lead to neck growth between the particles, and by increasing the strength of the compacts during sintering. In the densification or sintering mechanism, matter is removed from the grain boundary [mechanism 4, 5 of the figure] or from dislocation within the neck region (mechanism 6); mechanisms (1-3), do not cause densification, and are known as non-densifying mechanisms. But, they reduce the curvature of the neck and also the rate of sintering. In general, sintering occurs in three stages (i) Initial stage (ii) Intermediate stage (iii) final stage. Here, each step represents an interval of time or density, over which the microstructure is considered to be well defined. Table.2.1 shows the sintering mechanism in a polycrystalline and amorphous solid.
Figure 2.5 Sintering mechanism

1. Surface diffusion
2. Lattice diffusion
3. Vapour transport
4. Grain boundary diffusion
5. Lattice diffusion (from the grain boundary)
6. Plastic flow
Table 2.1 Mechanism of sintering in a polycrystalline and amorphous solid

<table>
<thead>
<tr>
<th>Types of solid</th>
<th>Mechanism</th>
<th>Source of matter</th>
<th>Sink of matter</th>
<th>Densifying</th>
<th>Non-Densifying</th>
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<td>Surface Diffusion</td>
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<td>Surface</td>
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<td></td>
<td>X</td>
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<td>Vapor transport</td>
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<td>Neck</td>
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<td>Grain boundary</td>
<td>Neck</td>
<td></td>
<td>X</td>
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<tr>
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<td>Un specified</td>
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<td>x</td>
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</tbody>
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Table 2.2 Different mechanisms of sintering

<table>
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<th>Type of sintering</th>
<th>Material Transport</th>
<th>Driving Energy</th>
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<tr>
<td>Vapor-phase</td>
<td>Evaporation condensation</td>
<td>Difference in Vapor pressure</td>
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<tr>
<td>Solid-state</td>
<td>Diffusion</td>
<td>Difference in free energy or chemical potential.</td>
</tr>
<tr>
<td>Liquid-phase</td>
<td>Viscous-Diffusion</td>
<td>Capillary pressure, surface tension.</td>
</tr>
<tr>
<td>Reactive liquid</td>
<td>Viscous-flow, solution precipitation</td>
<td>Capillary pressure, surface tension.</td>
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Table 2.3 various stages of sintering and their process

<table>
<thead>
<tr>
<th>Initial stage</th>
<th>Intermediate stage</th>
<th>Final stage</th>
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<td>Rearrangement</td>
<td>Grain growth</td>
<td>Growth</td>
</tr>
<tr>
<td>Neck formation</td>
<td>High shrinkage</td>
<td>Discontinuous</td>
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</tbody>
</table>

2.6.1.1 Solid State Sintering

The neck growth between the contacting particles is an important factor in solid state sintering, which improves the powder compact. There are three steps involved in the solid state sintering process, namely, the Initial stage, intermediate stage and the final stage. In the first stage, the particles come close, a neck is formed between the contacting particles, and in minor level densification occurs; in the intermediate stage, which determines the property of the sintered compact, pore rounding densification and grain growth occur. Finally, there are simultaneous, coarsening events that improve densification. Then the pores are attached to the grains giving the ideal fine sintered sample. Various stages of sintering and its process are shown in Table 2.2, and the stages of sintering are also illustrated in the following Figure 2.6.
2.6.1.2 Vapour phase sintering

In this sintering the driving energy has the difference in vapour pressure and also in the function of the surface curvature. The material is transported from the surface of the particle, which has a positive and negative vapour pressure. The vapour phase transport changes the shape of the pores, achieves bonding between the adjacent particles, increases the strength of the
materials, and decreases the permeability due to open porosity. However, it does not give shrinkage and cannot produce densification.

### 2.6.1.3 Liquid phase sintering

Rapid and uniform densifications are the advantages of liquid phase sintering. In this method, a small amount of liquid form between the particles, and the rapid re arrangement of the solid particles takes place. The special feature of liquid phase sintering is the homogeneous packing of the particles. The liquid phase sintering has three stages, (i.e) particle rearrangement, solution preparation and, Oswald ripening. And the factors that control the liquid phase sinterings are: Particle size, Viscosity and Surface tension.

In the first stage, a liquid is formed between the particles and it rapidly rearranges the particles under the action of the surface tension forces, to produce more stable packing. In the solution preparation stage, it was assumed that the solid particles are soluble in the liquid and coarsening and the grain shape will be formed.

In the final stage, microstructural coarsening by the solute preparation mechanism is involved, and the excess liquid present in the packed region flows into the isolated pores, and leads to densification.

### 2.6.1.4 Pressure assisted sintering

The powders are pressed into the required shape at high temperature. The pressure increases the driving force for the densification and also decreases the temperature needed for sintering. Finally, the shape forming and densification will occur in a single step (McDonough et al 1978, Shi et al 1989).
2.6.1.5 Rapid heating

Plasma sintering and microwave sintering comes under rapid heating techniques. Plasma sintering can be performed in ionized gases. (Ciachi et al 1996, Alessandra Bianco et al 1999).

2.6.1.6 Conventional sintering

In conventional sintering, the heat is transferred between the samples by the conduction, convection, and radiation processes. During the conventional sintering process the sample surface is first heated. Then the heat moves inward and there is the temperature gradient from the surface to the inside of the sample. (Dhal et al 2000). But the microwave initially heats the material and then heats the entire volume of the specimen. Enhanced diffusion process, rapid heating rate, reduced sintering temperature, and low hazards, are the salient features of the microwave processing technique.

2.6.1.7 Microwave sintering

Microwave energy is a form of electromagnetic energy with the frequency range of 300 MHz to 300 GHz. Microwave heating is a process, in which the materials couple with microwaves, absorb the electromagnetic energy volumetrically, and transform it into heat. This is different from conventional methods, where heat is transferred between objects by the mechanisms of conduction, radiation and convection. In conventional sintering, the material surface is first heated followed by the heat moving inward. This means that there is a temperature gradient from the surface to the inside. However, microwave heating generates heat within the material first, and then heats the entire volume. This heating mechanism is advantageous due to the following facts; enhanced diffusion process, reduced energy consumption, very rapid heating rates, considerably reduced processing
times, decreased sintering temperature, improved physical and mechanical properties, simplicity, unique properties and fewer environmental hazards. (Mark Jenny et. al 1992). Micro wave energy wave length is in between 1 mm and 1 m. Microwaves are used for heating purpose in the frequency of 9.5 MHz and 2.45 GHz. In microwave sintering, the ceramic samples couple with the microwaves, and absorb the electromagnetic energy volumetrically, and transform it to heat. Microwave processing is purely based on two factors: (1) Power absorption (P) and Depth of penetration (D).

In the Microwave sintering technique the power absorbed per unit volume can be calculated as follows,

\[ P = 2f \varepsilon'' |E|^2 \]
\[ = 2\pi f \varepsilon'' \varepsilon' \tan \delta |E|^2 \]  
(2.6)

where

- \( E \) – Magnitude of the internal electrical field
- \( \varepsilon'' \) – relative effective dielectric factor
- \( \varepsilon_0 \) – permittivity of free space
- \( f \) – microwave frequency
- \( \varepsilon' \) – Relative dielectric constant
- \( \tan \delta \) – Energy loss required to store a given quantity of energy

The absorbed Microwave power converted to heat within the material is given by \( \Delta T/\Delta t = P_a/p(C_p) \cdot C/sec \)  
(2.7)

where

- \( P_a \) = Power of microwave
- \( P \) - density of the ceramic Kg/m³
\[ C_p = \text{Specifc heat (KJ/Kg)} \cdot C \]

The penetration depth was given by

\[ D = 3 \lambda_0 / 8.686 \pi \tan \left( \frac{\zeta}{\zeta_0} \right)^{1/2} \]  

(2.8)

Where

\[ \lambda_0 = \text{Incident wave length} \]

\[ \zeta, \zeta_0, \tan \delta = \text{Dielectric constants}. \]

2.7 MATERIAL CHARACTERIZATION TECHNIQUES

The different types of instruments used for the characterization of the materials, used to identify the phase formation and structural aspects (FTIR, DTA/TGA, XRD, TEM, SAED), and the morphology, and salient features of these techniques are described in detail below.

2.7.1 Fourier Transform Infra Red Spectroscopy (FTIR)

Infrared spectroscopy gives information about molecular vibrations that cause a change in the dipole moment of the molecules and offers a fingerprint of the chemical bonds present within materials. The Michelson interferometer technique was used in the FTIR spectrometer. A beam of radiation from the source is focused on a beam splitter, where half the beam is reflected in a fixed mirror, and the other half of the beam is transmitted to a moving mirror, which reflects the beam back to the beam splitter. From there it travels, recombined with the original half beam, to the detector. The IR intensity variation with the optical path difference (interferogram) is the Fourier transform of the (broadband) incident radiation. The IR absorption spectrum can be obtained, by measuring an interferogram, with and without a sample in the beam, and transforming the interferograms into spectra. The scanner modulates the radiation from the source or from the sample, and the
analog to digital (A/D) conversion board digitizes the analog signals from the detection system, and sends them to a computer for further processing. The scanner and data acquisition are controlled through software using the respective hardware. Two corner cubes and a retro-reflector make the system immune to tilt and shift, with the minimum realignment requirements. Moreover, the Scanning Mirror Control System is based on two in-quadrature He-Ne laser interferograms, that provide the position and direction information. Fine-tuning is available to position the ZPD (zero path difference), exactly in the centre of the scan. The FTIR (MIR8300) provides both the transmission and reflection spectra in the range of 1.7 µm to 28 µm. Generally the FTIR suits liquid and solid bulk materials, and requires some sample preparation. In this study the Attenuated Total Reflection (ATR) accessory was employed for the sample preparation. In this work, KBr was used as the solvent. The output spectrum was obtained by subtracting the background due to the solvent.

2.7.2 X-ray Diffraction (XRD) Analysis

The X-ray Diffraction (XRD) technique can be used to study the crystal structure of solids, microstructural properties such as the grain size, grain orientations, and residual stress and strain in the lattice, preferred orientations, and order-disorder transformations in crystals. According to Bragg’s law, the incident X-ray is diffracted from atoms arranged in successive planes of the crystal lattice of the material under investigation. The size of the particle, inter-atomic distance, crystal structure, etc, are obtained from the X-ray diffraction pattern. In this study, the Seifert X-ray diffractometer (M/s Seifert Inc., Germany) has been employed to study the synthesized nano particles. It comprises of a Cu $K_{\alpha 1}$ radiation source. The wavelength ($\lambda$) of 1.5406 Å is filtered using bent quartz monochromators.
The grain size of a polycrystalline material is of the nanometre size, the crystals cause a broadening of the diffracted beam, due to diffraction at angles close to the Bragg’s angle. The crystalline size (D) and the full-width at half-maximum (FWHM) of the diffracted line β (in radian) are related by the Scherrer formula given in Equation (2.4)

\[ D = \frac{0.9 \lambda}{\beta \cos \theta_p} \] (2.4)

where, \( \lambda \) is the wavelength of the X-ray used, and \( \theta_p \) is the Bragg’s angle of the diffraction peak in degree. The Gaussian fitting is used to account for the instrumental line broadening. The presence of strain in the lattice will also cause the XRD line broadening. In such cases, the Warren-Averbach method of curve-fitting can be used to evaluate the grain size.

### 2.7.3 Particle Size Analysis

The particle size is one of the important parameters, which can alter the property of the final product. In general, the particle is defined as the diameter of the particle. This definition is possible entire particle in the prepared powder is spherical (regular shape) in nature. According to the nature of preparation, the shape may change. The powder prepared by spray drying is almost spherical in shape with the same particle size. In the case of the Sol gel method, the powders are obtained only after many processing steps like gel drying, calcinations and milling. Hence, the final powder may contain regular and irregular shaped particles. For irregular shaped particles; the size cannot be taken as the diameter of a single particle; instead, the particle size distribution is measured and the mean particle size is considered as the size of the particle.
2.7.4 Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) is used to study the surface structure of the material. In the SEM analysis, the sintered sample is irradiated with the electron beam, because the electrons have shorter wavelengths compared to the photons. The resolution of the Scanning Electron Microscope is very high, compared to that of the optical Microscope. For these reasons, SEM has a high magnifying power, and it has a very powerful technique to explore the free surfaces of materials. The microstructure of the sintered 8YSZ sample was observed by Scanning Electron Microscopy (SEM). The scanning electron microscope produces detailed photographs, which give the information about the surface structure and morphology (Singh 1984, Yin Sheng & Nicolsen 1988). The mean grain size is determined by the linear intercept method, from the SEM micrographs taken of the polished microwave sintered sample’s. The microstructure of the sintered samples surfaces are polished with SiC carbide paper (grades from 600 and 1500) and diamond paste, down to 1 pm, analysed by the scanning electron microscope, (HITACHI Model S-3400 JAPAN).

2.7.5 Thermal Analysis

2.7.5.1 TGA (Thermogravimetric Analysis)

TGA is one of the simple analytical techniques used to measure the weight loss or weight gain of a material, as a function of a temperature, and it is an effective tool to measure the changes in the physical and chemical properties of a given material. The thermal analysis study of ceramics is used to understand thermal decomposition and phase transition. The TGA is used to determine the decomposition process, decomposition-synthesis steps, and temperature of final crystallization, time duration of the stages, and the weight losses at each stage. (Sproson et al (1988)). The DTA analysis is used to
determine the thermal effects of the decomposition and crystallization stages
Sun et al (1988). The TGA & DTA (Perkin Elmer-thermal analyser) analyses
were carried out in a nitrogen atmosphere with the temperature range of
40°C to 1000°C at a heating rate of 5°C.

The TGA provides a quantitative measurement of the thermal
stability (mass change/weight loss), oxidation kinetics, and gas solid reaction
in materials, associated with the transition temperature of thermal
degradation, and it records the changes in mass from dehydration,
decomposition and oxidation of the sample with time and temperature.

2.7.5.2 Differential thermal analysis (DTA)

The DTA is used to heat or cool a test sample and an inert reference, under identical conditions, while recording the temperature difference between the sample and the reference. This temperature difference is plotted against time (or) against temperature. Temperature changes depend mainly on endothermic (or) exothermic reactions, such as those caused by the melting point, crystallization, phase transition, thermal stability, and gas-solid reaction. In general, more heat is required for the sample. The temperature difference between the sample and the reference is recorded as a function of temperature.

2.7.6 Transmission Electron Microscope (TEM)

The TEM study was used to determine the particle size and morphology of the nano particles. The basic reasons for using this non-optical technique for nano material characterizations are, to be achieved through higher spatial resolutions than optical systems, and to probe the internal structure of materials, which are opaque at optical wavelengths, and to
determine the physical parameters, which cannot be measured by electromagnetic radiation.

The Transmission Electron Microscopy (TEM) is a versatile technique used to characterize the microstructure of materials with very high spatial resolution. The transmission electron microscope uses a high energy electron beam transmitted through a very thin sample, to image and analyze the microstructure of materials with an atomic scale resolution.

In this study, the (JEOL) high-resolution transmission electron microscope was employed and the representative wavelength ($\lambda$) with a resolution of 0.14 nm can be computed from the non-relativistic de Broglie expression, given in Equation 2.5.

$$\lambda = \frac{h}{\sqrt{2Em_e}} \quad (2.5)$$

Where $m_e$ is the electronic mass.

The electrons are focused with electromagnetic lenses, and the image is observed on a fluorescent screen, or recorded on film or a digital camera. The electrons are accelerated at several hundred kV, giving wavelengths much smaller than those of light. This high resolution imaging mode of the microscope gives the crystal lattice of a material, as an interference pattern between the transmitted and diffracted beams, which allows observing the planar and line defects, grain boundaries, interfaces, etc, with atomic scale resolution. The bright field/dark field imaging modes of the microscope, which operate at intermediate magnification, combined with electron diffraction are invaluable tools for getting information about the morphology, crystal phases, and defects in a material. TEM is also capable of forming a focused electron probe, as small as 20.0 Å, which can be positioned
on very fine features in the sample, for micro diffraction information or analysis of X-rays for compositional information. In the present investigation, the TEM images and selected area diffraction patterns were recorded using [JEOL-1200 EX II operated at 120 kV (max)] the Transmission Electron Microscope.

### 2.7.6.1 TEM and SAED

Selected Area Electron Diffraction (abbreviated as SAD or SAED), is a crystallographic experimental technique that can be performed inside a Transmission Electron Microscope (TEM).

In the TEM, a thin crystalline specimen is subjected to a parallel beam of high energy electrons. As TEM specimens are typically ~100 nm thick, and the electrons typically have energy of 100–400 kilo electron volts, the electrons pass through the sample easily. In this case, the electrons are treated as wave-like, rather than particle-like. Because the wavelength of the high-energy electrons is a few thousands of a nanometer, and the spacing between the atoms in a solid is about a hundred times larger, the atoms act as a diffraction grating to the electrons, which are diffracted. That is, some fraction of them will be scattered to particular angles, determined by the crystal structure of the sample, while others continue to pass through the sample without deflection.

As a result, the image on the screen of the TEM will be a series of spots and the selected area diffraction pattern, SADP, each spot corresponding to a satisfied diffraction condition of the sample's crystal structure. If the sample is tilted, the same crystal will stay under illumination, but different diffraction conditions will be activated and different diffraction spots will appear or disappear.
SAD is referred to as "selected", because the researcher can easily choose from which part of the specimen to obtain the diffraction pattern. Located below the sample holder on the TEM column is a selected area aperture, which can be inserted into the beam path. This is a thin strip of metal that will block the beam. It contains several different sized holes, and can be moved by the user. The effect is to block the entire electron beam except for a small fraction passing through one of the holes; by moving the aperture to the section of the sample the user wishes to examine, this particular area is selected by the aperture, and only this section will contribute to the SADP on the screen. This is important, for example, in polycrystalline specimens; it is useful to select a single crystal for analysis, at a time.

As a diffraction technique, SAD can be used to identify crystal structures and examine crystal defects. It is similar to X-ray diffraction, but unique in that, an area as small as several hundred nanometers in size can be examined, whereas X-ray diffraction typically samples areas several centimeters in size.

A diffraction pattern is made under broad, parallel electron illumination. An aperture in the image plane is used to select the diffracted region of the specimen, giving a site-selective diffraction analysis. SAD patterns are a projection of the reciprocal lattice, with lattice reflections showing as sharp diffraction spots. By tilting a crystalline sample to low-index zone axes, SAD patterns can be used to identify crystal structures and measure lattice parameters. SAD is essential for setting up dark-field imaging conditions. Other uses of SAD include the analysis of lattice matching, interfaces, twinning and certain crystalline defects.

SAD is used primarily in material science and solid state physics and is one of the most commonly used experimental techniques in field of crystal structures.
2.8 EXPERIMENTAL PROCEDURE

In the sol-gel process, Zirconium Oxychloride (ZrOCl$_2$8H$_2$O) (CDH), Yttrium nitrate hexa hydrate [ Y(NO$_3$)$_3$.6H$_2$O], (CDH), and oxalic acid (C$_2$H$_2$O$_4$) (CDH), were used as the starting materials (Kumar et al (2000)). These respective salts were dissolved in 200 ml of Millipore water in the stoichiometric ratio of 1M. The initial solutions of the precursors were mixed under constant stirring by a magnetic stirrer, until a transparent viscous gel was formed. The obtained gel was dried in a hot air oven at 45ºC for five days. The dried gel was calcined at 600ºC for 3 hrs and ground well in a planetary mill for 5 hrs in an ethanol medium, at a rotational speed of 300 rpm.

The planetary jar mill and grinding balls were made of tungsten carbide material. The milled powder was dried in air at 60°C for 24 hrs and the powder was characterized by X-ray diffraction (XRD, Seifert 3000P) with Cu - K$_\alpha$ radiation ($\lambda$ = 1.5406 Å). The XRD patterns were recorded in the 2$\theta$ scanning range of 10° – 80°. The phase formation of the nano 8YSZ was analysed by the XRD and the particle morphology was analysed by the Transmission Electron Microscope (TEM) [JEOL-1200 EX II operated at 120 kV (max)]. The milled powder was mixed with the Poly Vinyl Alcohol (PVA) binder, and pressed in to pellets (10 mm in diameter) at a pressure of 40MPa, using a uniaxial press. The 8YSZ green samples were sintered in a microwave furnace (V. B. C. C India) at 1500 ºC at a 1.1 kW and 2.45 GHz frequency, at a heating rate of 100 ºC / min for three different holding times, viz 5, 10 and 15 minutes. In the microwave sintering furnace, a special susceptor is designed to generate heat against the microwave at a heating rate of 100ºC/min. A non-contact optical sensor (RAYTEK, USA) was used to measure the temperature in the range of 600ºC - 1600ºC. The time temperature profile is programmed by the Eurotherm temperature indicator cum programmer. The density of the samples was measured by the
Archimedes method. The microstructure of the sintered and polished samples was analysed by the scanning electron microscope (SEM) (HITACHI Model S-3400 JAPAN). The average grain size of the sintered samples was measured by the linear intercept length method. The flow chart for the processing of 8mol% Yttria Stabilized Zirconia is shown Figure 2.7.

Figure 2.7  Shows the typical flow chart for the processing of 8mol% Yttria stabilized zirconia
2.8.1 Procedure for the Sample Preparation

The precursors of the 8YSZ powder were calcined at 600°C for 3 hrs at a constant heating rate of 5°C/min, and ground well in a planetary mill for 5 hrs in an ethanol medium at a rotational speed of 300 rpm. The planetary jar mill and grinding balls were made of tungsten carbide material. The milled powder was dried in air at 60°C for 24 Hrs. The dried powders were uni axially pressed in to pellets of diameter 10 mm at a pressure of 40 M Pa. The pressed compacts were oven dried at 100°C for 24 hours. Then the dried compacts were sintered at 1500°C in a microwave furnace at a heating rate of 100°C/min for various dwelling times of 5, 10, and 15 minutes.

From the microwave sintering results, three types of sintered samples of different densities were obtained; i.e, Sample A (Density 92%), Sample B (Density 95%), Sample C (Density 98%) corresponding to the 5, 10 and 15 minute’s holding time respectively. The surface morphology of the microwave-sintered 8YSZ samples A, B, C has been depicted in Figure 2.12 (a), (b) and (c).

2.8.2 Compaction Behaviour of Uniaxial Pressed Powder

The precursors of the gel powder were calcined at 600°C, and dried and then added to a suitable binder. Binders provide bridges between powder particles. A large number of organic substances are used as binders. Some of the binders are soluble in water. The remaining are soluble inorganic liquids only. The applications of the different type of binders have been reviewed by Onoda (1978). Further, the classification of binders is according to how effectively they increase the viscosity of the solution. Low, medium, high viscosity grades are normally used for specific binders. PVA (Polyvinyl
alcohol), and PEG (Poly Ethylene glycol) are the most used binders in the 8YSZ sample preparation. In this processing technique, PVA is used as a binder. Then the powder mixed with the binder by using pestle and mortar without agglomerates, then pelletized by applying 40MP, using the uni axial 10 Ton press. The green density of the uni axially pressed samples were measured by the volumetric method. The green density of the sample was 48%.

2.8.3 Densification

In the densification process, the particle size remains as such, but the grain boundary replaces the surface energy, and the shape of the particle changes. During this process, the atoms are removed from the grain boundary, and deposited on the most concave parts of the free surface. This process occurs in the initial and final stages of sintering, by lattice diffusion or boundary diffusion.

2.8.4 Micro Structural Analysis (SEM)

The Micro Structural Analysis of a sintered sample is a very important characteristics technique in the analysis. So, it is necessary to control the microstructure and this can be achieved by controlling the atomic ratios, addition of selective cations, varying the additive concentrations, and modifying the sintering profile. The densified ceramic samples microstructure/phase distribution also depends on (1) the initial processing technique, (2) selection of raw materials, (3) phase changes due to reaction kinetics, and (4) Grain growth (Hsuch et al 1982). In general, the following microstructural characteristics determined, (i) the identification phases present, (ii) relative amount of each phase present, and (iii) the grain size
measurement, shape and orientation. The grain growth in the dense material is incorporated in the grain boundary motion.

The structural and electrical property of the 8YSZ depends on the microstructure of the sintered sample. The size, and shape of the grains, the amount of porosity, pore size, the distribution of any second phase, and that of the pores, are remarkable features of the microstructure which is fully dependent on the processing methods. Uniform packing is very important factor in the green sample preparation. Non-uniformity in the green sample produces voids or large pores between the dense regions. So, we have to take the necessary steps, precautions to prepare the green samples. There are two possible types of grain growth in densified ceramic samples namely the normal and abnormal. In the normal grain, the grain size and shapes are in the narrow region. Abnormal grain growth has a few large grains at the expense of smaller ones.

Sol-gel derived nano 8mol% Yttria Stabilized Zirconia samples were sintered in a microwave furnace at 1500°C for different dwelling times of 5, 10 and 15 minutes respectively. These microwave sintered samples were polished by SiC sheets of mesh sizes 800, 1000, 1200, and 2000, followed by 1/0 and 2/0 grades, and then polished by 3/0, 4/0 grade alumina coated sheets. The micro structural features of the polished microwave sintered samples were studied by the Scanning Electron Microscope (SEM).
2.9 RESULT AND DISCUSSION

2.9.1 TGA/DTA Analysis

Figure 2.8 shows the TGA-DTA plot of the precursors of the sample. The thermal curve shows that a slight weight loss was observed from 100°C to 250°C, which is due to the evaporation of water in the dried precursor gel. The exothermic and endothermic peaks at 275°C and 330°C in the DTA, and the weight loss from 250°C to 375°C in the TGA, were due to the removal of the oxalate and the structural hydroxyl group. The broad exothermic range of 375°C to 475°C, and the corresponding weight loss may be due to the crystallization of 8YSZ. There is no considerable weight loss above 600°C. This analysis illustrates the optimum calcination temperature for 8YSZ around 600°C. (Suciu et al 2008) , (Vatansever1 et al 2010).

Figure 2.8 Thermo gravimetric and differential thermal analysis of 8YSZ dried-gel at 45°C

2.9.2 X-ray Diffraction
The XRD pattern of the nano 8YSZ sample was calcined at 600°C for 3 hrs, as shown in Figure 2.9. The corresponding diffraction peaks coincide with the JCPDS file number: 82-1246 (Kumar C, 2007). The average crystalline size of the 8YSZ sample has been calculated, using the Debye–Scherrer formula given in Equation (2.2)

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]

where, \( D \) is the average particle size in nm, \( \beta \) is the full width half maximum (FWHM) of the X-ray reflection expressed in radians, and \( \theta \) is the position of the diffraction peaks in the diffractogram. The average crystalline size of the nanocrystalline 8YSZ was found to be 15 nm.

![XRD pattern of 8YSZ nano powder calcined at 600°C](image)

**Figure 2.9 XRD pattern of 8YSZ nano powder calcined at 600°C**

### 2.9.3 TEM Analysis

The particle morphology of the 8YSZ nano powder was analysed by the Transmission Electron Microscope (TEM). The TEM study confirms
that the average particle size was 15nm. The sol-gel derived nano 8YSZ particle size was very small, compared to the same particles prepared by the co-precipitation technique (Keshmiri .M et al 2006).

The TEM micrograph of the Sol gel derived nano 8YSZ sample is shown in Figure 2.10. It reveals better crystallinity, and the crystals have an average size of less than 15 nm, and this result agrees well with the reported results calculated from the XRD Pattern. There are three continuous diffraction ring patterns obtained in the SAED image, corresponding to the diffraction planes (111), (2 2 0) and (4 0 0) respectively (Singh et al 2007).

The XRD as well as SAED d-spacing (d_{hkl}) results confirm the cubic structure of nano 8YSZ. The SAED image demonstrates the well resolved diffraction fringes of the d-spacing (d = 2.97 Å, 1.82 Å, and 1.28 Å), as shown in Figure 2.11. A comparison of the interplanar spacing (d_{hkl}) and average grain size of both XRD and SAED is presented in Table 2.4.

Table 2.4 Comparison of the inter-planar d_{hkl} spacing and average grain size obtained from the XRD and TEM studies

<table>
<thead>
<tr>
<th>d_{hkl} (Å)</th>
<th>d_{hkl}(Å)</th>
<th>Diffracting plane (h k l)</th>
<th>Average Grain size in (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD</td>
<td>SAED</td>
<td>XRD</td>
<td>TEM</td>
</tr>
<tr>
<td>30.19°</td>
<td>2.97 Å</td>
<td>2.977 Å</td>
<td>(111)</td>
</tr>
<tr>
<td>49.86°</td>
<td>1.82 Å</td>
<td>1.835 Å</td>
<td>(220)</td>
</tr>
<tr>
<td>73.74°</td>
<td>1.28 Å</td>
<td>1.320 Å</td>
<td>(400)</td>
</tr>
</tbody>
</table>
Figure 2.10  TEM image of the Nano 8YSZ powder Calcined at 600°C for 3hrs

Figure 2.11 Selected area electron diffraction pattern of 8YSZ
2.9.4 Densification and SEM Results

From the microwave sintering study, three types of sintered samples of different densities were obtained; i.e, A (Density 92%), B (Density 95%) and C (Density 98%) corresponding to 5, 10 and 15 minutes holding time respectively. The surface morphology of the microwave-sintered 8YSZ samples A, B, C has been depicted in Figure 2.12 (a), (b), (c).

The densities of the microwave sintered samples were increased, due to the increase in the sintering temperature or holding time. Because of the holding time during the microwave sintering process, the sintered sample (C) shows higher density (98%) with an average grain size of (< 900nm) than the other two samples ‘A’ and ‘B’. The SEM image of the sample ‘A’ shows the maximum pores and agglomerates. Sample ‘B’ appeared with minimum pores. From this analysis, it can be concluded, that the minimum holding time during sintering is responsible for the poor densification and pores appearing in the microstructure of the samples A and B. Mehdi Mazaheri et al, prepared 8YSZ nanopowder with an average particle size of 30 nm, by the smouldering combustion technique and applied microwave sintering on 8YSZ green samples, and achieved 98% density with a uniform grain size of 2.35µm. Rajeswari et al used commercially available 8YSZ powder (TZ-8Y Tosh.Tokyo,Japan) with an average particle size of 205 nm; then performed microwave sintering and got high density samples (98%) with an average grain size of 2.77 µm. Here, the microwave sintering study results revealed that the obtained grain size was (< 900nm) smaller in size compared to the previous researcher’s reports. The main reason for this minimum size grain (< 900nm) present in the microstructure of the sample, was the nano sized particle (15 nm) which confirmed the particle size influences, the grain size, and the microstructure of the sample.
2.10 CONCLUSION

In this Chapter, the fundamental processing techniques of ceramic materials, and the various material characterization techniques have been clearly analysed. Then the 8YSZ nano-powders were synthesized by the Sol-gel method. The thermal properties of the gel are analysed using simultaneously the TGA/DTA measurement; It shows, the step by step partial removal of water, oxalate and hydroxyl group, in the temperature range of 50ºC - 375ºC. The thermal curve showst a slight weight loss was observed from 100ºC to 250 ºC, which is due to the evaporation of water in the dried precursor gel. The exothermic and endothermic peaks at 275ºC and 330ºC in the DTA and the weight loss from 250ºC to 375ºC in the TGA were due to the removal of oxalate and the structural hydroxyl group. The broad exothermic range of 375ºC to 475ºC and the corresponding weight loss may be due to
the crystallization of the 8YSZ. There is no considerable weight loss above 600°C. By using the TGA/DTA, the optimum calcination temperature for 8YSZ around 600 °C is calculated.

The prepared material was calcined at 600 °C for 3 h, and its phase formation was confirmed by the XRD. The particle size was analysed by the TEM and SAED, and the average particle size was 15 ±0.7 nm. The 8YSZ green samples were sintered in a microwave furnace 1500°C at a 1.1 kW 2.45 GHz frequency, at a heating rate of 100 °C / min for three different holding times (i.e) 5, 10, and 15 minutes, and three sintered samples of different densities 92%, 95% and 98% were obtained respectively. The microwave sintered 8YSZ sample exhibits submicron grains (< 900 nm) with less pores.