“CHAPTER 2: EXPERIMENTAL TECHNIQUES”

“2.1. PRECURSOR PREPARATION”

Several methods can be used for the preparation of ceramic powders. The methods can be divided into two categories: (i) mechanical methods and (ii) chemical methods. In the mechanical methods, small fine particles are produced from coarse and granular ones by mechanical forces, a process referred to as comminution. The process of comminution involves operations such as crushing, grinding, and milling. Powders of traditional ceramics are generally prepared by mechanical methods. However, a wide range of chemical methods exists for the preparation of ceramic powders, which have received a high degree of interest and have undergone considerable changes in the last 30 years or so. Chemical methods can be classified into three main categories, (i) Solid state reactions, (ii) Precipitation from the solutions, and (iii) Vapour phase reactions.

In the present work, the precursor powders for doped ceria have been prepared by the mixed oxide method (mechanical method).

2.1.1 Mixed Oxide Method

Gadolinium-doped ceria (GDC) was chosen as the base of the electrolyte. Cobalt, Calcium and Yttrium -doped Cerium gadolinium electrolytes were prepared by the mixed oxide method. Doped ceria were prepared by mixing the oxides or carbonates for over 8 hrs in acetone as medium using ball milling process in polypropylene bottle and yttria stabilized zirconia balls mixture obtained was then dried at room temperature and after adding binder again dried, pressed into pellets at 340 MPa Pressure using stainless steel die with diameter 12.80-mm die of high carbon content steel. Pressed pellets were sintered using microwave energy. The specimens were sintered using microwave energy at different temperatures 900°C ,1000°C, 1100°C, 1200°C, 1300°C, 1350°C & 1400°C to different soak over periods. Conventionally sintered specimens were fired in a muffle furnace at 1300°C & 1400°C for 8 hrs.
“2.2. BALL MILL”

A vertical ball mill was fabricated in the laboratory as shown in figure 2.1(a), has been used for the milling and mixing of the powders at different stages. The powders were ball milled in a polythene bottle using the zirconia balls and acetone as a grinding medium for 6 hours.

“2.3. CONSOLIDATION OF MATERIALS”

The powders of different compositions were mixed with the 4% PVA binder. A uniaxial hydraulic press as shown in figure 2.1(b) was used to consolidate the powder in the form of the cylindrical pellets using a 12.80-mm diameter die of high carbon content steel. The pellets were made at the various pressures. However, the pellets made at a pressure of 340 MPa were chosen for the further study, as their green densities were found to be the maximum. The mass of each pellet was kept 2.00 g. A stearic acid based lubricant solution was developed in the laboratory itself. It was applied over the inner walls of the die for the uniform distribution of pressure over powdered materials during their consolidation.

“2.4. MICROWAVE PROCESSING”

2.4.1 Fabrication of microwave furnace

Microwave processing system consists of a microwave source, an applicator, and a system to control the heating. An applicator is a device (cavity) that provides a mean for applying the microwave energy from the generator to the work piece to be processed. The main purpose of the applicator is to focus the microwave energy to the material load and to provide impedance matching in order to efficiently transfer the microwaves into the load.
## Table 2.1 Samples Details

<table>
<thead>
<tr>
<th>Sample</th>
<th>Abbreviation</th>
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<tr>
<td>Ce$<em>{0.80}$Ca$</em>{0.20}$O$_{1.8}$</td>
<td>CCO</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Gd$</em>{0.1}$Y$<em>{0.1}$O$</em>{1.9}$</td>
<td>CGYO</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Gd$</em>{0.2}$O$_{1.9}$</td>
<td>CGO</td>
</tr>
<tr>
<td>Co Ce$<em>{0.8}$Gd$</em>{0.2}$O$_{1.9}$</td>
<td>Co CGO</td>
</tr>
</tbody>
</table>
“Figure 2.1 (a). Vertical Ball Mill [Fabricated in Laboratory]

(b) : Hydraulic press [Uniaxial]”
Microwave cavities can be either single-mode or multimode (Sutton, 1989; 1992). A multimode applicator is a cavity, typically an enclosed metal box as the home microwave oven. It is the most commonly used applicator in the microwave processing. Its main drawback is that the electrical field distribution inside it is non-uniform which may cause inhomogeneous heating. The use of a mode stirrer or a turn table, which moves the work piece in the field, provides a more uniform heating pattern in the cavity. When microwaves propagate in a cavity, they establish a standing wave pattern. By properly choosing the dimensions of the cavity, a fundamental standing wave pattern can be produced. Such a cavity is said to be single-mode cavity. The single-mode applicator provides the precise and the desired control of the fields within the work piece. Such an applicator maximizes the field strength at the work piece location so that the rapid and uniform heating of the sample can be achieved. However, the heating volume is limited and the homogeneous heating of the large sample is difficult to achieve.

Single mode and multimode cavities may both be tuned to produce a desired mode pattern. Tuning is usually accomplished with the aid of a sliding shoring plunger, which changes the dimension of the cavity. A kitchen multimode microwave oven (LG MS-285SD 1200W, Frequency 2.45 GHz, 900W RF magnetron output power) with dimensions of the inner cavity as 34.4cm x 34.4cm x 22.5cm was modified to work as the microwave furnace as shown in figure 2.2(a) To make this kitchen microwave oven suitable for the high temperature firing/sintering experiments, following modifications were made:

1. An insulating packet transparent to microwaves was made to fire the work piece to prevent the loss of radiations and to sustain the cavity temperature during firing.
2. An aluminum plate was placed below the sintering packet to prevent the cavity from being overheated.
3. Two variacs were added to the power supply of the magnetron to control the heating rate and to achieve the required temperature for the desired exposure time.
4. A hosepipe of copper was soldered onto the outside surface (under the outer shell) of the top of the cavity for the continuous water circulation to efficiently cool the magnetron and to maintain the cavity at low temperature so as to avoid excess heat transfer from the cavity to the magnetron.
5. A small hole was drilled at the centre of the roof along the vertical axis of the fabricated furnace for insertion of the thermocouple.

6. A digital display (Pyrotron) was connected to the S type thermocouple (Pt-10% Rh/Pt) to measure the cavity temperature with an accuracy of ± 1°C during processing.

2.4.2 Insulating packet

The insulating packet was made of an alumina crucible, zirconia cylinder (Zircar Products, Inc. Florida, NY), silicon carbide (SiC) rods, and thermal insulating AL-25/1700 (Zircar Products, Inc. Florida, NY) as shown in figure 2.2(b). Zircar alumina insulation type AL-25/1700 is a combination of the high purity alumina fibers, refractory fillers and inorganic ceramic binders. The typical chemical composition of the thermally insulating AL-25/1700 board is 80% Al₂O₃ and 20% SiO₂ with density 0.44 g/cc, modulus of rupture 1.38 MPa, compressive strength 0.24 MPa and thermal conductivity 0.27W/m°C at 1650°C. As claimed by the manufacturer, Al-25/1700 offers low thermal conductivity, high temperature stability, good hot strength, dimensional stability, excellent resistance to thermal shock and chemical attack, and is not affected by oil or water. It can withstand temperatures up to 1700°C for continuous use. AL-25/1700 is pre fired, contains no organic binders and produces no smoke or odor when heated. The zirconia cylinder vertically surrounding the samples functions both as a microwave susceptor and as an insulator. As a susceptor, it absorbs and converts microwaves to heat, thus preheats the sample if the sample does not absorb microwaves significantly at low temperatures. As an insulator, it prevents heat of the samples from dissipation to the surroundings. Also SiC rods were used as a susceptor. These rods help in combination with the zirconia cylinder in preheating of the sample.

2.4.3 Temperature measurement in microwave processing

The temperature measurement in the microwave sintering/heating is one area which is very critical and is a matter of concern for its accuracy and reliability. The
“Figure 2.2 (a). Schematic display of the sintering packet in microwave processing
1. Turntable
2. Zirconia cylinder
3. Samples
4. Thermocouple
5. AL-25/1700 insulator
6. SiC rods;
7. Microwave port

(b) Insulating packet in Microwave furnace”
microwave sintering/heating in ceramics usually has been reported as improving the ceramic properties at a relatively lower processing temperature or at the same temperature (Sutton, 1989; Fang, 1994). Hence the precise temperature measurement is essential for the comparison of results obtained by the microwave and the conventional processing methods. In a microwave field, the interference of the microwave with the electromotive force of the thermocouple makes the temperature readings random or erroneous (Satapathy et al, 2005). To avoid the microwave interference with the thermocouple, the thermocouple was properly shielded and grounded to get the reliable temperature readings. In the present study, a platinum shielded S-type Pt-10%Rh/Pt thermocouple was used to measure the temperature within the accuracy of ± 1°C. The thermocouple was fitted in the microwave so that the tip of the thermocouple was nearly 1mm away from the work piece in the sintering packet.

“2.5. CONVENTIONAL PROCESSING”

The precursors of doped Ceria were prepared for conventional processing also. The green pellets of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, $\text{CoCe}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, $\text{Ce}_{0.80}\text{Ca}_{0.20}\text{O}_{1.8}$, $\text{Ce}_{0.8}\text{Gd}_{0.1}\text{Y}_{0.1}\text{O}_{1.9}$ were fired conventionally at 1300°C and 1400°C for 8 hrs. The maximum temperature of 1300°C and 1400°C was achieved in 3 hours in a programmable furnace and an S type (Pt-10% Rh/Pt) thermocouple measured the temperature with an accuracy of ± 1°C.

“2.6. DENSITY MEASUREMENT”

The specimens were cylindrical in shape. The green and sintered densities of the pellets were measured by making weight and geometrical measurements. An electronic balance (CITIZEN 279 x 400 pixels) with precision of ±0.0001g measured the weight. The diameter and thickness of the pellets were measured by vernier caliper MITITYOYO with an accuracy of ±0.02 mm and the corresponding volume was calculated using formula $\pi r^2 h$. The sample pellets were weighed after the microwave and the conventional heating schedule. The density of the sintered pellets
of all the compositions were also measured by the Archimede’s principle/technique in temperature range of 20° to 25° using distilled water.

“2.7. X-RAY DIFFRACTION”

When x-rays are incident on a sample, the electrons in the sample atom start to oscillate and when an electron decelerate (loses energy) it produces new x-ray. This process of absorption and reemission of electromagnetic radiation is called scattering. Interference is the overlapping of two or more scattered waves producing a resultant wave that is a sum of various amplitudes at each point. A constructive interference of more than one scattered wave is diffraction.

Normally scattered x-rays are out of phase and cancel each other, but at certain distances between the atom planes in the sample the scattered waves will be in phase. This relationship is given by Bragg’s law

\[ n\lambda = 2d \sin \theta \]

Where n is an integer, \( \lambda \) is the wavelength of the incident of the incident x-ray, \( \theta \) is the half the deflection angle and d is the distance between the atom planes. When Bragg’s Law is fulfilled the x-rays leaving the sample are in phase and the beam is diffracted.

In a diffraction pattern the recorded intensity is plotted against the deflection angle 2\( \theta \).

In the present work, powder x-ray diffraction studies were carried out for phase identification of different samples. The equipment used in this study was X-ray Diffractometer (X-ray Diffractometer, Model: Bruker AXS, D-8 Advance, Switzerland and Model: Phillips PW1710). The continuous scan at a rate of 2\( ^\circ \)(2\( \theta \))/minute was carried to obtain the X-ray diffractograms in the 2\( \theta \) range of 20° to 80°.

“2.8. SCANNING ELECTRON MICROSCOPY (SEM)”

Conventional light microscopes use a series of glass lenses to bend light waves and create a magnified image. Scanning electron microscope (SEM) gives the morphological and topographical information of the solid surfaces that is necessary in understanding the behavior of the surfaces. In SEM the sample is bombarded with wavelength an electron beam. The short wavelength of electron creates better
resolution and the samples with higher magnifications can be recorded (Skoog et al., 1998).

For the electrons to pass through the sample, the sample should be conductive. In case of nonconductive sample a layer of gold is sputtered on the surface of the sample.

The electron beam, emitted from the filament in the electron gun, is accelerated towards the sample and focused by several condenser lenses. When the focused beam hits a point on the sample, numerous collisions between the electrons from the beam and atoms in the sample will occur. As a result of these collisions some of the outer most electrons will be detached from the sample. These electrons, called secondary electrons, have relatively low kinetic energy and can easily be detected by the detector. The detector counts the number of electrons emitted from the small area and the result is displayed as appoint on a computer screens. A magnified image of the sample is created by scanning the electron beam over a small area and detecting and displaying the number of electrons originating from each point. Both the topography of the sample and the atom numbers affect the number of secondary electrons emitted and these factors are therefore represented in the picture. The resulting image has shadows and perspective, much like ordinary photograph and is easy to interpret (Watt, 1997).

In the present work, the microstructures of the fractured surfaces were observed with a digital scanning electron microscope (JEOL, Model: JSM 6100). Before carrying on the microscope observation, selected sintered pellets were polished using alumina and were coated with gold by sputtering method to avoid electric charging.

“2.9. VICKER’S HARDNESS MEASUREMENTS”

Hardness was measured on conventional microhardness machine with Vickers diamond indenters. The basic principles of operation of the Vickers hardness test are illustrated in Fig.2.3 where it can be seen that the load is applied to the indenter by a simple weighted lever. All Vickers ranges use a 136° pyramidal diamond indenter that forms a square indent.

1. The indenter is pressed into the sample by an accurately controlled test force.
2. The force is maintained for a specific dwell time, normally 10 – 15 seconds.

3. After the dwell time is complete, the indenter is removed leaving an indent in the sample that appears square shaped on the surface.

4. The size of the indent is determined optically by measuring the two diagonals of the square indent.

5. The Vickers hardness number is a function of the test force divided by the surface area of the indent. The average of the two diagonals is used in the following formula to calculate the Vickers hardness.

The square pyramidal indenter created smaller, deeper impressions on polished mirror planes of the sintered pellets with a load of 0.5Kg and 5 Kg as shown in Fig.2.3. To evaluate mechanical properties, the hardness of the sintered samples was determined from Vickers indentations obtained with load of 0.5 and 5 Kg for 10sec using Vickers hardness tester technique (Shimadzu- 341-64278 Type-M). Hardness values were determined for each indentation site by means of the expression:

$$H = 0.47 \frac{P}{a^2}$$

(Lawn and Marshall, 1979)

where: \(a\) = half the diagonal of the indentation (m), and \(P\) = applied load (Kg).

The apparent fracture toughness was calculated by means of the following formula:

$$K_{IC} = 0.016 \left(\frac{E}{H}\right)^{1/2} \frac{P}{C^{3/2}}$$

(Anstis et al., 1981)

where: \(E\) = Young's modulus (GPa),

\(P\) = applied load (Kg),

\(H\) = Vickers hardness (GPa), and

\(c\) = max lateral extent of crack (m).
“Figure 2.3. Vickers hardness testing methodology”
2.10. MEASUREMENT OF ELECTRICAL CONDUCTIVITY

The electrical conductivity can be defined as:

\[ \sigma = \frac{G}{l/A} \quad (2.3) \]

where \( G \) is the conductance, \( l \) the thickness and \( A \) the cross sectional area of the sample. The electrical conductivity measurement is generally performed by attaching suitable electrodes at two opposite faces of the solid electrolyte pellet or crystal. Hence, the electrical conductivity data of the solid electrolyte does not only show the characteristic of the bulk material but also includes the effects caused by the electrode-electrolyte interfaces. Further, the dc. measurement of the electrical conductivity is not useful for a solid electrolyte because the unidirectional flow of the current results in the formation of polarization clouds at the electrodes and ultimately concentration gradient within the electrolyte that opposes the effect of the applied field. Hence, the a.c. measurement of the electrical conductivity of the solid electrolyte is preferred to. For the evaluation of the bulk conductivity, the complex impedance spectroscopy is used.

In complex impedance spectroscopy, a low amplitude a.c. signal (sinusoidal) is applied to the cell consisting of the solid electrolyte. The real and the imaginary parts of the impedance/admittance are measured over a wide frequency range. The impedance (\( Z \)) / admittance (\( Y \)) is a complex quantity and can be written

\[ Z(\omega) = Z'(\omega) - jZ''(\omega) \quad (2.4) \]
\[ Y(\omega) = G(\omega) + jB(\omega) \quad (2.5) \]

where \( Z' \) and \( Z'' \) are the real and the imaginary parts of the impedance, \( G \) is the conductance, and \( B \) the susceptance. Hence, when the measured real and imaginary parts of impedance/admittance are plotted in a complex plane, it gives rise to the frequency dispersion curves. These frequency dispersion curves possess information about the effects of electrode-electrolyte interface, the bulk resistance, and the grain boundary. The overall behavior can be idealized using lumped circuit elements as shown in figure 2.4.

The intersection of the low frequency and the high frequency dispersion curves to the real axis gives the bulk resistance/conductance of the sample.

If the grain boundaries are also present (as in the case of polycrystalline samples), the conductivity may either increase or decrease depending upon whether
the activation energy for the grain boundary conduction is less or more than that of the bulk conduction. The grain boundaries are effective at high frequencies and their contribution to the conductivity can be derived from the high frequency intercept of the high frequency dispersion curve to the real axis.

Several other approaches for the impedance/admittance response of the electrochemical cell are available in the literature (Kleitz et al, 1995; Macdonald, 1987; Gabrielli, 1984; Raistric, 1986; Badwal, 1997). In the present investigation, the bulk conductivity was derived from the complex impedance plots based on Bauerle’s (1969) approach. Electrical conductivity measurements were made on the polished sintered sample pellets by the complex impedance spectroscopy method in the frequency range of 100Hz to 5 MHz using LCR METER (HIOKI 3532-50 LCR Hi TESTER, Japan) Silver paste as electrode was applied on both sides of the polished pellets and the conductivity measurements were taken from the 200°C to 700°C. The variation of temperature was ±1°C. The experimental arrangement along with the sample holder used is shown in figure 2.5.
“Figure 2.4. Schematic of an idealised complex impedance plot and associated Equivalent circuit. ($R_{gi} =$ grain interior resistance, $R_{gb} =$ apparent grain boundary resistance, $R_{el} =$ electrode polarization resistance, $C_{gi} =$ grain interior capacitance, $C_{gb} =$ grain boundary capacitance, $C_{el} =$ electrode capacitance.)”
"Figure 2.5. Experimental set up for electrical conductivity measurement"