CHAPTER 2

PREPARATION AND CHARACTERIZATION TECHNIQUES

2.1 INTRODUCTION

This chapter describes the various synthetic methods for obtaining ultrafine alumina powders. In addition, the characterization techniques used in this work, along with the elementary theory of the techniques, are also presented.

2.2 PREPARATION OF ALUMINA POWDER

Technological development has generated a demand for materials with enhanced properties and altogether new materials. The processing developments go hand in hand to meet the challenges of making these advanced materials. In the last four decades, there has been an explosion of information on the change of properties of materials as their particle sizes reduce to nanometer dimensions, and on larger high purity materials to fabricate such fine-grained ceramic products. This has brought new designs of processing techniques resulting in a new range of materials.

The various techniques include spray pyrolysis (Johnson et al., 1979), precipitation (Shaoyan Wang et al 2008), sol-gel (Mirjalili et al 2010), thermal plasma technique (Ananthapadmanabhan et al 2004) and combustion synthesis techniques (Jiang et al 2007), that have been employed
to synthesize ultrafine Al$_2$O$_3$ powders. The vapor phase reaction for the preparation of fine $\alpha$-Al$_2$O$_3$ powder from a gas phase precursor demands high temperatures above 1200°C. The sol–gel method based on molecular precursors, usually makes use of metal alkoxides as raw material. However, the high prices of alkoxides and long gelation periods limit the application of this method. The precipitation method suffers from its complexity and time consuming nature (long washing times and aging time). The direct formation of $\alpha$-Al$_2$O$_3$ via the hydrothermal method needs high temperature and pressure. In the present work, the powders were selected from various synthesising processes, like the Bayer process, Solution combustion process, and Mechano-milling process.

2.2.1 Bayer Process

Most of the world's bauxite is converted to refined alumina by the Bayer process, which was discovered and patented by the Austrian chemist, Karl Bayer in 1893. The process involves four stages: Digestion, Clarification, Precipitation, and Calcination (Flock 1978).

In the first, step Digestion, the bauxite is ground, slurried with a solution of caustic soda (sodium hydroxide), and pumped into large pressure tanks called digesters, where the ore is subjected to steam heat and pressure. The sodium hydroxide reacts with the aluminous minerals of bauxite to form a saturated solution of sodium aluminate; insoluble impurities, called red mud, remain in suspension and are separated in the clarification step.

Following Digestion, for Clarification, the slurry is washed with fresh water in a series of large thickening tanks, to separate the caustic soda and alumina from the waste solid residue, which is pumped for storage as red mud.
The next step in the process, Precipitation, is to separate the insoluble red mud from the sodium aluminate solution. In this stage of the Precipitation process, the mud and the liquor that make up the slurry (by using a gibbsitic bauxite) are separated by settling. The liquor that is separated contains sodium aluminate, while the mud that settles at the bottom of the settling tank is removed since alumina has to be extracted from it. After addition of synthetic fluocculants in the separated red mud, the insoluble red mud solid are removed during filtration and these solids are further washed for getting sodium aluminate and residues were collected and discarded.

The process of calcination involves washing the hydrated alumina crystals before heating to ~800°C, where the water of crystallisation is driven off to leave pure alumina. Free water and water that is chemically combined are driven off, leaving commercially pure alumina—or aluminum oxide—a dry, fine, white powder, similar to sugar in appearance and consistency. It is half aluminium and half oxygen by weight, bonded so firmly that neither chemicals nor heat alone can separate them.

2.2.2 Solution Combustion Method

Most of the processing techniques involve expensive raw materials, and are associated with unmanageable processing steps.

Fortunately, the drawbacks of these methods as mentioned above, could be partially eliminated by the so called combustion synthesis (also known as self-propagating high-temperature synthesis), which has emerged as an effective powder synthesis route, as it is a simple and economic process, and yields high-purity powders with excellent homogeneity and fine particle
sizes (Singanahally et al 2008; Edrissi and Mohammad Norouzbeigi Reza 2008).

Combustion synthesis is a particularly simple, safe and rapid fabrication process, wherein the main advantages are energy and time savings. This quick, straightforward process can be used to synthesize homogeneous, high-purity, crystalline oxide ceramic powders, including ultrafine alumina powders with a broad range of particle sizes.

The basis for the combustion synthesis comes from the thermochemical concepts used in the field of propellants and explosives. This technique involves the exothermic chemical reaction of a fuel (e.g. citric acid, urea, glycine, olic acid or glycol, etc.), and an oxidizer (e.g. nitrates) (Tianyou Peng et al 2006: Jiang Li et al 2007). The exothermicity sometimes appears in the form of a flame, where temperatures can be in excess of 1500°C. The large amount of gases generated during combustion synthesis rapidly cools the product, leading to the nucleation of crystallites without any substantial growth. The gas generated can also disintegrate the large particles or agglomerates, and the resulting product consists of very fine particles of friable agglomerates or nanoparticles (Xiujing Zhai et al 2006).

Actually, the mechanism of the combustion reaction is quite complex. The main parameters influencing the reaction include types of the main fuel, fuel to oxidizer ratio, the amount of oxidizer in excess, the ratio of fuels, pH of the solution and rate of calcinations. In general, a good fuel should not react violently nor produce toxic gases, and must act as a complexing agent for metal cations.

In the present research, we have introduced a new method called “microwave-assisted glycene-gel decomposition technique”, to prepare
nonocryalline alumina powders. Compared to conventional heating, microwave heating leads to a more uniform microstructure. In the microwave process, heat will be generated internally within the material, instead of originating from external sources. Because of the rapid heating of the microwave process, lower processing temperatures are needed, which in turn, provide a suitable condition for the formation of nano-sized powders.

2.2.3 Mechano Chemical Synthesis

Mechanochemical synthesis, which is also known as mechanical alloying (Sabooni et al 2010), has been recently employed to prepare nano-sized oxides and compounds. The most significant characteristic of this technique is that, the formation of the designed compounds is due to the reactions of oxide precursors which are activated by mechanical energy, instead of the heat energy required in the conventional solid-state reaction process. The novel mechanical technique is superior to both the conventional solid-state reaction and the wet-chemistry based processing routes, for several reasons. Firstly, it uses low-cost and widely available oxides as starting materials, and skips the calcination step at an intermediate temperature, leading to a simpler process (Lazarevic et al 2007). Secondly, it takes place at room temperature in well sealed containers, thus effectively alleviating the loss of the volatile components. Furthermore, due to their nanometer scale size and very high homogeneity, mechanochemically derived ceramic powders demonstrate much better sinterability, than those synthesized by the conventional solid-state reaction and wet-chemical processes.

2.3 CHARACTERIZATION TECHNIQUES

For proper understanding of the mechanism of ultrafine grained alumina and for better technological application, the structure has to be
characterized accurately. In this investigation, phase purity, and surface morphology of the samples were studied, by using the particle size analyser, Thermal analysis, X-ray powder diffraction (XRD), Fourier Transformed Infrared (FTIR) Analysis, Scanning electron microscope (SEM), and Transmission electron microscope (TEM). A brief description of the experimental techniques employed is presented.

2.3.1 Particle Size Analysis

A laser diffraction method with a multiple scattering technique was used to determine the particle size distribution of the calcined powder. To measure the particle size through the laser scattering method, the instrument correlates between the intensity and the angle of light scattered from the particle, and the particle size is calculated based on the Mie scattering theory. In order to capture the scattered light signals over this range of angles, the equipment utilizes a number of high-angle and back-scatter detectors, together with a short wavelength blue LED laser. As the particle size becomes smaller, the scattered light signal shifts to the side and rear with respect to the light source. A shorter wavelength detects the smaller particle size.

The scattered light can be measured by a series of photo detectors placed on the opposite side of the source at different angles. This is known as the diffraction pattern for the sample. As the instrument measures clouds of particles rather than individual ones, it is known as an "ensemble" technique, with the advantage that at smaller sizes (e.g. 1 micron), the system measures literally millions of particles, which gives some statistical significance to the measured results. The particles size distribution (volume percent) of the suspension was carried out in computer-controlled particle size analyzer (LA950, HORIBA Instruments, inc. U.S.A) via a software program. The powders must not be agglomerated, and must be completely dispersed in the
liquid so that they are separated into discrete unattached particles. A well-dispersed and agglomerate-free suspension was obtained, using the ultrasonic treatment of a powder well dispersed in a 0.02 mol % of Sodium Hexa meta phosphate in distilled water.

2.3.2 Thermal Analysis (TGA & DTA)

The thermal analysis technique is an excellent device for determining the presence and quantity of hydrated water, which also aids to determine the oxygen content. Additionally, it can give an idea about the decomposition behaviour, phase transitions, formation of products etc. from precursor powders synthesized through different chemical routes. Thermo Gravimetric (TG) and Differential Thermal Analysis (DTA) analyses were carried out in (STA 409C) air, from room temperature to 1000 °C at a heating rate of 10°C per minute. For TGA, the sample was loaded onto an accurate balance, and heated at a controlled rate, to record the weight loss at different temperatures. When a material undergoes physical or chemical change, it absorbs or releases thermal energy which is a characteristic of the range. The temperature difference of a sample with respect to a reference inert material during heating or cooling is shown in a DTA as the deviation from the zero base line. Exothermic or endothermic changes are shown in opposite directions of the baseline.

2.3.4 X-ray Diffraction Analysis

From the literature it was quite clear, that the four major peaks in the X-ray diffraction patterns of aluminium would be in the 2θ range of 20° to 80°. For this reason, the patterns were recorded for the above 2θ range with a step size of 0.05°, and a scanning rate of 1.5 degrees/minute. The wavelength
used to compute the d – spacing is that of a Cu Kα₁ (λ₁ = 0.154056 nm). The tube current and the voltage were kept at 30 mA and 30 kV respectively. The X-ray diffraction equipment, General Engineering X-ray diffractometer (model GE-110T), was used. The diffraction condition is described by Bragg’s law, which relates the wavelength of the X-ray beam to the spacing of the atomic planes. The actual equation is of the form:

\[ \lambda = 2d \sin \theta \]  \hspace{1cm} (2.1)

where

\( \lambda \) - wavelength of incident wave
\( d \) - spacing between the planes in atomic lattice
\( \theta \) - angle between incident ray and scattering plane

The above equation is extremely important in the determination of the crystal structure of the materials. It is assumed that the diffracted beam makes the same angle \( \theta \) with the atomic planes as with the incident beam; \( d \) is the spacing between the planes when the higher order reflections are considered as the first order reflections. The diffraction patterns are recorded with the intensity of the peaks on the Y axis, and the measured diffraction angle \( 2\theta \) along the X axis. The experimental diffraction patterns were compared with the standard patterns of alumina, and the results are discussed in the later chapters.

**Crystallite Size Determination by XRD**

The crystallite sizes of the calcined powders were determined from the X-ray line broadening, using Scherrer’s equation as follows (Cullity 1978):
\[ d = \frac{0.9\lambda}{B \cos \theta} \]  

\( d \) = Crystallite size, Å

\( \lambda = \) wavelength of X-ray = 1.542 Å

\( B = \) full width at half maximum, radians

\( \theta = \) position of X-ray peak

Silicon was also employed as an external standard for correction, due to instrumental broadening.

2.3.5 Fourier Transform Infrared (FTIR) Analysis

Fourier transformation is a mathematical operation used to translate a complex curve into its component curves. In a Fourier Transformation Infrared instrument, the complex curve is an interferogram, or the sum of the constructive and destructive interferences generated by overlapping light waves, and the component curves are the infrared spectrum.

An interferogram is generated because of the unique optics of an FTIR instrument. The key components are a moveable mirror and a beam splitter. The moveable mirror is responsible for the quality of the interferogram, and it is very important to rotate the mirror at constant speed. For this reason, the moveable mirror is often the most expensive component of an FTIR spectrometer. A beam splitter is just a piece of semi-reflective material, usually a mylar film sandwiched between two pieces of IR-transparent material. The beam splitter splits the IR beam 50/50 to the fixed and moveable mirrors, and then recombines the beams after being reflected in each mirror. The standard infrared spectrum is then calculated from the
Fourier transformed interferogram, giving a spectrum in percent transmittance (%T) vs. Light frequency (cm\(^{-1}\)). The Fourier transformation infrared analyses of calcined powders were done at a resolution of 4 cm\(^{-1}\). Chemical groups on the surface of the calcined powders were analyzed by Diffuse Reflectance Infrared Fourier Transformation (Perkin Elmer-Spectrum RS 1) in the wave number range of 400 to 4000 cm\(^{-1}\). A small amount of sample (0.2 to 0.5 gm) was thoroughly mixed with the ground KBr in an agate mortar, and a disc was prepared in vacuum, maintaining a pressure of 33 kg/cm\(^2\). The spectrogram of the sample is observed on a video monitor and a graphic representation of the spectra was taken. Each analysis consisted of a minimum of 64 scans and the resolution was ± 4 cm\(^{-1}\).

2.3.6 Scanning Electron Microscopy (SEM)

The microstructural aspect of the materials can be analyzed using a Scanning Electron Microscope (SEM). The SEM was used to study the microstructural feature of the samples, as it had a much higher resolution power compared to an optical microscope. In the SEM, a hot tungsten filament electron gun under vacuum emits electrons, which pass through a series of electromagnetic lenses. The sample is then bombarded with a fine beam of electrons having acceleration potentials in the range of 1-30 KV. A part of the beam is reflected as back scattered electrons (BSE), along with low energy secondary electron emission (SE), cathode luminescence, and X-ray excitation beam and electron transmission also takes place. Images formed from the (SE) beam were studied in the extrinsic mode of the SEM.

The emitted secondary electrons are detected and displayed on a scanning TV display. A bright image will be the result of high secondary electron emission, while the primary influence on high emission is the surface
structure of the specimen. The end result is, therefore, brightness associated with surface characteristics, and an image which looks very much like a normally illuminated subject.

**Sample Preparation for SEM**

Sample surfaces were ground with the help of a series of diamond grinding pads from 1200 μm to 15 μm, on a polishing machine. The samples were polished with 8 μm diamond paste on a rotating disk. The final polishing was done with 6, 2 and 1 μm diamond pastes to create a mirror finish on a lapping machine. The polished surfaces were analyzed in the scanning electron microscope. Prior to the microscopic analysis, the samples were thermally etched at 50°C less than the respective sintering temperatures. The thermally etched samples were heated at the rate of 10°C/min, whereas the rate of cooling was 10°C/min initially upto 1000°C/min, and subsequently at 5°C/min up to room temperature. The thermally etched samples were mounted on a metal stub with carbon paint. The samples were thin coated with palladium-gold under vacuum of 0.01 torr, to make the surface conducting easy for viewing through SEM. Thermally etched, worn-out and fractured specimens were sputtered with gold, to avoid the charging effect under the SEM. The mounted specimens were studied by SEM (TESCAN VEGA3 SBU) for surface morphology analysis.

**2.3.6 Transmission Electron Microscopy (TEM)**

Transmission Electron Microscopy (TEM) was used to estimate the particle size of the powders, and to observe the morphology and the state of agglomeration of the powder. TEM observations were performed in an instrument equipped with a tungsten filament operating at 120 kV (Model JEM-1200EX II, JEOL, Japan), and a point-to-point resolution of 5Å. The
powders were dispersed in ethanol using an ultrasonic treatment. A drop of the resulting suspension was placed on carbon-coated copper grids, and then the particle dimensions were measured from micrographs taken with the TEM.

2.4 PROPERTY EVALUATION STUDIES

The sintered discs were used to determine the physical properties, such as densification behaviour and phase analysis. The sintered billets were used to determine the Electrical and mechanical properties.

2.4.1 Dielectric Property Evaluation

Alumina is a very good dielectric material, and hence, it is important to study its dielectric behaviour at different frequencies. The dielectric properties of alumina depend on several factors, including the method of preparation. The dielectric constant and loss tangent can be measured by using the LCR meter.

The surfaces of each sintered pellet diameter of 10 mm were carefully polished and then coated with silver paint. Before conducting the experiment, the surfaces were checked for good contact. The computerised LCR Bridge (HIOKI 3532-50 Hi tester) has been used in the current investigation. It can measure the dielectric properties in the frequency ranges from 350 Hz to 3MHz at room temperature (25°C ± 5°C). Operation was made extremely simple, by the interactive touch panel. The following parameters θ, Rp, Rs, G, X, Lp, Ls, Cs, D (tanδ) and Q can be measured. It can be externally controlled by a computer, by installing an RS-232C Interface. The measured data is captured by the computer into standard spread
sheet software and the results can be presented graphically. The following dielectric parameters were determined from the captured data.

2.4.1.1 Dielectric constant

The dielectric constant measurement, also known as relative permittivity, is used to evaluate insulators, such as rubber, plastics and ceramics etc. It is used to determine the ability of an insulator to store electrical energy. The complex dielectric constant consists of a real part ($\varepsilon'$), which represents the storage capability, and an imaginary part (D), which represents the loss.

The dielectric constant ($\varepsilon'$) was evaluated from the formula,

$$\varepsilon' = \frac{C}{C_0} \quad (2.3)$$

where $C$ and $C_0$ were the capacitance values with and without sample, respectively, $C_0$ is given by $\frac{(0.08854 \text{ A})}{d} \text{ pF}$; where $A (\text{cm}^2)$ is the area of the electrodes and $d (\text{cm})$ is the thickness of the sample.

2.4.1.2 Dielectric loss

The imaginary part of the dielectric constant ($\varepsilon''$) is a measure of the absorption of energy by the dielectric from the alternating field. The dielectric loss factor can be calculated by using the relation

$$\tan \delta = \frac{1}{2\pi} \frac{R_p C_p}{R_p C_p} \quad (2.4)$$

where, $\tan \delta$ is the loss angle, $f$ is the frequency, $R_p$ is the equivalent parallel resistance, $C_p$ is the equalent parallel capacitance. The dielectric loss is also measured in terms of the loss tangent ($\tan \delta$) defined by the relation
$$\varepsilon_r'' = \tan \delta \quad \varepsilon_r'$$  \hspace{1cm} (2.5)

### 2.4.1.3 Resistivity

The d.c. conductivity of the ultrafine alumina sample was calculated by using the following relation:

$$\sigma_{\text{d.c.}} = \varepsilon_0 \omega \varepsilon_r' \tan \delta$$  \hspace{1cm} (2.6)

$$\rho_{\text{d.c.}} = \frac{1}{\sigma_{\text{d.c.}}}$$  \hspace{1cm} (2.7)

where $\tan \delta$ is the dissipation factor, $\omega$ is the angular frequency, which is equal to $2\pi f$ (where $f$ is the frequency) and $\varepsilon_0$ is the relative permittivity of free space.

### 2.4.2 Mechanical Property Evaluation

#### 2.4.2.1 Hardness

The hardness of the materials was calculated from the size of the impression produced under load, by a pyramid-shaped diamond indenter. The indenter employed in the Vickers test is a square-based pyramid whose opposite sides met at the apex at an angle of 136°. The diamond is pressed into the surface of the material at loads of 4.903 N (HV0.5). The load was applied for 14 sec on the sample. The indentation time was maintained constant. The size of the impression was measured with the aid of an optical microscope, with a magnification of x 400, and the same is captured in a programmed
computer. The computerised MicroHardness Tester, Schimadzu, Model HMV-2, has been used in the current investigation.

The Vickers number (HV) was calculated using the following formula:

\[
HV = 1.854 \left( \frac{P}{d^2} \right) \quad (2.8)
\]

- \(P\) - Applied load (measured in Kgf)
- \(d^2\) - Indentation diagonal length (mm)

2.4.2.2 Fracture toughness

The Fracture toughness (\(K_{IC}\)) of the samples was measured, using the indentation technique (Niihara et al 1982; Evans 1990; Cook and Pharr 1990). Depending upon the type of cracks developed around the indentation impression, different expressions have been used. However, a widely used equation for the measurement of fracture toughness has been developed by Evans and Charles (1976), and is given as:

\[
K_{IC} = 0.016 \ H_V \ a^{1/2} \ (c/a)^{3/2} \quad (2.9)
\]

where,
- \(K_{IC}\) - fracture toughness (MPa.m\(^{1/2}\))
- \(H_V\) - Hardness (GPa)
- \(c\) - indentation crack length (mm)
- \(a\) - diagonal radius (mm)