CHAPTER 2
EXPERIMENTAL DETAILS

2.1. Introduction

The synthesis and characterization of any material is the first and foremost step during the experimental research in Condensed Matter Physics and Materials Science. The qualities of samples depend to a great extent on the synthesis method used. In addition, the proper selection of synthesis parameters helps to fabricate the samples with desired properties to be characterized along with desired potentials. Various material properties such as structural, electrical, dielectric etc. depend on method used for material synthesis. There are various methods available for the synthesis of polycrystalline bulk materials like Solid State Reaction route (SSR), Sol-Gel route, Hydrothermal method, Chemical Vapour Deposition (CVD) etc. for preparing the nanomaterials. This chapter briefly describes the methods which are generally used for the synthesis of bulk/nanomaterials and also describes the brief explanation about various characterization techniques like XRD, SEM, TEM, DSC, EPR, UV-Visible, FTIR spectroscopy etc.

2.2. Synthesis

2.2.1. Solid State Reaction (SSR) Method

Solid State Reaction (SSR) method is the most widely used method for synthesizing the polycrystalline bulk material, taking a mixture of solids as starting materials. Solid powders do not usually react together at room temperature over normal time scale so it is necessary to heat them at much higher temperature for long time duration for reaction to occur at an appreciable rate. All the bulk polycrystalline pure and doped alkali titanate samples studied during present work were synthesized using SSR method. The advantages of this method include low cost of production, available precursors, and simplicity of the processes. There are two factors, namely thermodynamic and kinetic, which are important in
solid state reaction, the former determines the possibilities of any chemical reaction to occur by the free energy considerations which are involved while the later determines the rate at which the reaction occurs [1, 2]. The atoms diffuse through the material to form a stable compound of minimum free energy. Different compounds or phases might have the lowest free energy at various temperatures or pressures or the composition of the gas atmosphere might affect the reaction. In order to prepare a single-phase sample, the conditions during any reaction are very important. During synthesis, the parameters such as temperature, pressure, gas flow and time for the reaction are needed to be varied according to the phase requirements in the sample. Mapping of all variables has to be made to find the conditions, which are the best for a particular material and phase.

The general steps involved in the solid state reaction route for synthesizing the polycrystalline alkali titanate ceramics can be summarized as follows:

[1] All starting materials should be of high purity, powders of carbonates, oxides, nitrides etc. They are preheated for appropriate time and temperature. After preheating powders are weighed for desired composition using high precision electronic weighing machine.

[2] To obtain a homogeneous distribution of components (starting materials) in required proportions of desired stoichiometry, it is very important to mix and grind the powders thoroughly for long duration for the reaction to take place homogeneously. Thorough grinding of starting materials helps to reduce the particle size of mixed powder.

[3] This powdered mixture is then heated (calcined) in air for the first time. During the first calcination, CO₂ is liberated from the mixture.
[4] After the first heating, obtained powder is again ground thoroughly for three to four hours. To maintain uniform particle size, the powder is sieved through 100 and 50 micron sieve, and then are palletized using hydraulic press.

[5] The pellets are subsequently sintered at 1000°C for 24 hours with intermittent grindings to obtain single phase samples.

The solid state reaction method has proved to be the most suitable for synthesizing such ceramic materials.

2.2.2. Sol-Gel Method

Out of several methods for synthesizing polycrystalline materials, sol-gel is the cost-effective method, easy to handle and yields stoichiometrically predefined compounds. It offers a variety of starting materials as precursors to choose. Sol-gel has become an alternative method to the conventional solid state reaction route, allowing more accurate control over the phase formation, desired stoichiometry and uniformity in particle size. In Sol-gel technique, materials are obtained from chemical solution via gelation. It is more controllable technique for synthesizing polycrystalline materials. For nanomaterials synthesis, it is necessary to have control over grain size and also on the phase formation at much lower temperature. Sol-gel method offers homogeneous particle growth having small size (at nanoscale), uniform size distribution and monodispersive nature of the particles. Figure 2.1 depicts various steps involved in the synthesis of crystalline oxides using sol-gel method.

![Figure 2.1: Typical flow chart of sol-gel method](image-url)
2.2.2.1. Sol-Gel Derived Ceramics

The intimate mixing of the elements in gel form results in very short diffusion and thereby allows formation of the target material to occur at considerably lower temperatures as compared to in conventional chemical routes. Sol-gel makes it possible to obtain low temperature modifications or metastable phases and provides good control over the stoichiometry in processing of ceramics. Another advantage of an even elemental distribution within the gel is that, unlike solid state reaction route, sol gel processing does not require any grinding procedures to achieve homogeneous single phase ceramics, thereby avoiding a potential source of contamination. This, along with the purity of the precursors, makes the sol-gel process an excellent method for making high purity materials, such as optoceramics, electroceramics and glasses for optical wave guides. The precise size control of the particles is the main strength of sol-gel processing. The particles can be used as starting materials for polycrystalline ceramic compacts. In the preparation of ceramic bodies, a controlled particle size distribution can yield very high densities, which might be sintered into fully dense bodies. Controlled particle sizes also provide better control of the microstructure during densification. For this purpose, oxide nanoparticles prepared from alkoxide precursors are of great interest, and have important technological application.

2.2.3. Hydrothermal Method

The term hydrothermal usually refers to any heterogeneous reaction in the presence of aqueous solvents or mineralisers under high pressure and temperature to dissolve and recrystallise materials that are relatively insoluble under ordinary conditions [3]. Hydrothermal synthesis is typically carried out in a pressurized vessel called an autoclave with the reaction in aqueous solution [4]. The temperature in the autoclave can be raised above the boiling point of water, reaching the pressure of vapour saturation. Hydrothermal synthesis is widely used for the preparation of metal oxide nanoparticles which can easily be
obtained through hydrothermal treatment of peptized precipitates of a metal precursor with water [4, 5]. The hydrothermal method can be useful to control grain size, particle morphology, crystalline phase and surface chemistry through regulation of the solution composition, reaction temperature, pressure, solvent properties, additives and aging time [6].

2.3. Heat Treatment

Heat treatment process is an important step for the preparation of the oxide products. The drying of the samples causes the collapse of the network structure and shrinkage to produce materials with smaller surface areas.

2.3.1. Calcination

Calcination is a heat treatment process where the decomposition of the precursor or the degradation of the impurities in the product occurs with the liberation of gases (H₂O and CO₂, or other gaseous products of degradation) in the oxidizing atmosphere (air, oxygen, nitrous oxide, or ozone). Metal oxides prepared by wet chemical methods are usually contaminated with organic residues from the organic components involved in the synthesis, such as physisorbed solvent, ligands. Studies on different aerogels showed that calcination at 300-500ºC is necessary to remove these organic residues, but it is still possible that a small amount is present in pores and on the surface of the aerogel [7]. Application of oxidative atmospheres such as air or oxygen helps to burn off the organic residuals and remove them in the form of CO₂ gas. The oxide powder characteristics such as particle size, particle shape, surface area, crystallinity, phase purity are dependent on the conditions of calcination. The presence of organic residuals on the surface can significantly influence the physical and chemical properties of an aerogel. They can cover active sites of the material and decrease the reactive and catalytic activity of the aerogel.
2.3.2. Sintering

Heating the powders at high temperatures causes the particles of the powders to fuse together, as well as decreasing the pore sizes and voids between particles. Further heat treatment leads to the production of dense solid material in a process called sintering. Sintering is an important process for producing different materials like ceramics and ironware. However, in case of the nanoparticles, the sintering process is undesirable because it will cause the increase of the particle sizes and the decrease of surface areas. Particles in the powder have an excess of surface free energy. During heating, they try to decrease this free surface energy by decreasing the total surface area. Particles join together and transport mass to decrease the surface of particles (figure 2.2). Surfaces within particles have different chemical potentials based on the curvature. The convex surface has a positive surface energy, while the concave surface has a negative free energy. Mass transport goes through the diffusion process from the concave particle surface to the concave interparticle surface (necks or pores). The driving force of sintering is greater for smaller particles, and nanoparticles undergo significant increase in particle sizes and decrease of surface areas. The driving force for mass transport is the diffusion of mass flow depending on different vacancy concentrations. Diffusion goes through two main paths, which are surface diffusion and volume diffusion. In the surface diffusion, vacancies go from the neck surface to the convex surface, so the mass flow goes oppositely from the convex surface to the neck (figure 2.2, path 1). In the volume diffusion, vacancies in the grain boundaries and/or dislocations in the grain matrix move in the volume to the surface while the mass flow tend to fill the place of moved vacancies (figure 2.2, path 2).

Figure 2.2: Sintering by diffusion (path 1 - surface diffusion, path 2 - volume diffusion)
2.4. Characterization Techniques

2.4.1. X-Ray Diffraction (XRD)

Diffraction occurs when waves interact with a regular structure whose repeat distance is about the same as the wavelength of X-ray waves. X-rays have wavelengths of the order of a few angstroms, the same as typical interatomic distances in crystalline solids so they can interact with atoms and can gain the information at atomic level. Crystalline materials can be described by their unit cell which is the smallest unit describing the material. In the material, this unit cell is then repeated over and over in all directions. This will result in planes of atoms at certain intervals. Figure 2.4 shows the schematic representation of X-ray diffractometer. X-ray powder diffraction is a powerful non-destructive testing method for determining a range of physical and chemical characteristics of materials. It is widely used in all fields of science and technology. The applications include phase analysis, i.e. the type and quantities of phases present in the sample, the crystallographic unit cell and crystal structure, crystallographic texture, crystalline size etc. X-ray diffraction results from the interaction between X-rays and electrons of atoms. Depending on the atomic arrangement, interferences between the scattered rays are constructive when the path difference between two diffracted
rays differ by an integral number of wavelengths. This selective condition is described by the Bragg equation, also called “Bragg’s law”:

\[ n \lambda = 2 d_H \sin \theta_H \]

Where \( d_H \) = inter planar distance (d-spacing), \( \theta_H \) = half angle between incident and reflected beam (or the angle between the incident/reflected beam and particular crystal planes under consideration), \( n \) = order of reflection (integer value), \( \lambda \) = wave length of X-rays. \( H \) describes the Miller indices triplet (h k l) of each lattice plane as shown in figure 2.5.

The lattice parameter for crystallographic systems in the present study can be calculated from the following equation using the (hkl) parameters and the interplanar spacing \( d \) from XRD data.

\[
\frac{1}{d^2} = \frac{h^2}{a^2 \sin^2 \beta} + \frac{k^2}{b^2 \sin^2 \beta} + \frac{l^2}{c^2 \sin^2 \beta} - \frac{2hl \cos \beta}{ac \sin^2 \beta}
\]

[2.1]
2.4.2. Scanning Electron Microscopy (SEM)

Electron microscopes are scientific instruments that use a beam of energetic electrons to examine objects on a very fine scale. Electron microscopes were developed due to the limitations of light microscopes which are limited by the physics of light. In the early 1930's this theoretical limit had been reached and there was a scientific desire to see the fine details of the interior structures of organic cells (nucleus, mitochondria etc.). This required 10,000X plus magnification which was not possible using existing optical microscopes. Scanning electron microscopy (SEM) can provide a highly magnified image of the surface and the composition information of near surface regions of a material [8].

An electron microscope forms a three dimensional image on a cathode ray tube by moving a beam of focused electrons across an object and reading both the electrons scattered by the object and the secondary electrons produced by it. High powered indirect microscope produces an image by bombarding a sample with a beam of high energy electrons. The electrons emitted from the sample are then scanned to form a magnified image which allows
the examination of the structure and morphology of materials. In addition to its great magnification, the SEM also has a great depth of field. Most SEM also have a facility to analyze the X-rays given off by the target as a result of its bombardment and, as each element in the periodic table produces its own X-ray spectrum, this can be used to determine the elemental content of the sample. Scanning electron microscope (SEM) is used for studying the surface topography, microstructure, and chemistry of metallic and non-metallic specimens at magnifications from 50 up to ~ 100,000 X, with a resolution limit < 10nm (down to ~ 1nm) and a depth of focus up to several μm (at magnifications ~ 10,000 X). In SEM, a specimen is irradiated by an electron beam and data on the specimen are delivered by secondary electrons coming from the surface layer of thickness ~ 5nm and by backscattered electrons emitted from the volume of linear size ~ 0.5μm. Due to its high depth of focus, SEM is frequently used for studying fracture surfaces. High resolving power makes SEM quite useful in metallographic examinations. Sensibility of backscattered electrons to the atomic number is used for the detection of phases of different chemistry. Electron channeling in SEM makes it possible to find the orientation of single crystals by electron channeling pattern (ECP) or of grains by selected area channeling pattern (SACP). Accelerated electrons in an SEM carry significant amount of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD) that are used to determine crystal structures and orientations of minerals, photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light and heat.
Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples. Characteristic X-rays are produced for each element in a mineral that is excited by the electron beam. SEM analysis is considered to be "non-destructive"; that is, X-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly. The schematic block diagram of SEM is shown in figure 2.6 indicating the interaction of the electron beam with a sample producing secondary, reflected electrons, X-rays, etc. Depending on the type of the detector, the radiation emitted by the sample is transformed into electrical signals which, after amplification, are used to modulate a cathode-ray tube display where an image of the sample surface is formed.

2.4.2.1. Field Emission Scanning Electron Microscopy (FESEM)

The field emission scanning electron microscope (FESEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of
electrons. The electrons interact with the shells in atoms that make up the sample producing signals that contain information about the sample's surface topography and composition. The spot size in a Field Emission SEM is smaller than in conventional SEM and can therefore produce very high-resolution images, revealing details in the range of 1 to 5 nm in size.

2.4.3. Transmission Electron Microscope (TEM)

The transmission electron microscope (TEM) uses a high voltage electron beam to create an image. The electrons are emitted by an electron gun, commonly fitted with a tungsten filament cathode as the electron source. The electron beam is accelerated by an anode typically at +100 keV (40 to 400 keV) with respect to the cathode, focused by electrostatic and electromagnetic lenses, and transmitted through the specimen that is in part transparent to electrons and in part scatters them out of the beam. When it emerges from the specimen, the electron beam carries information about the structure of the specimen that is magnified by the objective lens system of the microscope. The spatial variation in this information (the "image") is viewed by projecting the magnified electron image onto a fluorescent viewing screen coated with a phosphor or scintillator material such as zinc sulfide. The image can be photographically recorded by exposing a photographic film or plate directly to the electron beam, or a high-resolution phosphor may be coupled by means of a lens optical system or a fibre optic light-guide to the sensor of a CCD (charge-coupled device) camera. The image detected by the CCD may be displayed on a monitor or computer.

Resolution of the TEM is limited primarily by spherical aberration, but a new generation of aberration correctors has been able to partially overcome spherical aberration to increase resolution. Software correction of spherical aberration for the High Resolution TEM (HRTEM) has allowed the production of images with sufficient resolution to show carbon atoms in diamond separated by only 89 picometers and atoms in silicon at 78 picometers at magnifications of 50 million times. The ability to determine the positions of atoms within
materials has made the HRTEM an important tool for nano-technologies research and development. Generally, the image resolution of an SEM is about an order of magnitude poorer than that of a TEM.

**Figure 2.7:** Layout of components in TEM

**Figure 2.8:** Picture of Transmission Electron Microscope setup
2.4.4. Ultraviolet and Visible (UV-Vis) Absorption Spectroscopy

The word ‘spectroscopy’ is used as a collective term for all the analytical techniques based on the interaction of light and matter. Spectrophotometry is one of the branches of spectroscopy where we measure the absorption of light by molecules that are in a gas or vapour state or dissolved molecules/ions. Spectrophotometry investigates the absorption of the different substances between the wavelength limits 190 nm and 780 nm (visible spectroscopy is restricted to the wavelength range of electromagnetic radiation detectable by the human eye, that is above ~360 nm; ultraviolet spectroscopy is used for shorter wavelengths). In this wavelength range the absorption of the electromagnetic radiation is caused by the excitation (i.e. transition to a higher energy level) of the bonding and non-bonding electrons of the ions or molecules. A graph of absorbance against wavelength gives the sample’s absorption spectrum. Modern spectrophotometers draw this automatically. The measured spectrum is continuous, due to the fact that the different vibration and rotation states of the molecules make the absorption band wider.

Spectrophotometry is used for both qualitative and quantitative investigations of samples. The wavelength at the maximum of the absorption band will give information about the structure of the molecule or ion and the extent of the absorption is proportional with the amount of the species absorbing the light. Quantitative measurements are based on Beer’s Law (also known as “Lambert-Beer Law” or even “Bouguer-Lambert-Beer Law”) which is described as

\[ A = e \cdot c \cdot l \]  

where, \( A \) = absorbance [no units, because it is calculated as \( A = \log_{10}(I_0/I) \)], 
\( I_0 \) is the incident light’s intensity and \( I \) is the light intensity after it passes through the sample. 
\( e \) = molar absorbance or absorption coefficient [in \( \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \)] 
\( c \) = concentration (molarity) of the compound in the solution [in \( \text{mol dm}^{-3} \)] 
\( l \) = path length of light in the sample [in cm]
The instruments used for spectrophotometry are called photometers or spectrophotometers as shown in figure 2.9. The difference between them is that we can only make measurements at a particular wavelength with a photometer, but spectrophotometers can be used for the whole wavelength range.

**Figure 2.9:** Photograph of Spectrophotometer used for the study

Both types of instruments have suitable light sources, monochromator (that selects the light with the necessary wavelength) and a detector. The solution is put into a sample tube (called a “cuvette”). The light intensity measured by the detector is converted into an electric signal and is displayed as a certain absorbance on the readout as shown in the figure 2.10.

**Figure 2.10:** Optical diagram for UV-Vis Spectrophotometer
2.4.5. Fourier Transform Infra Red (FTIR) spectroscopy

FT-IR stands for Fourier Transform Infra Red, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). FT-IR Spectrometer collects and digitizes the interferogram, performs the FT function, and displays the spectrum. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample.

FT-IR can provide the following information:

- It can identify unknown materials.
- It can determine the quality or consistency of a sample.
- It can determine the amount of components in a mixture.

An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each material is a unique combination of atoms, no two compounds produce exactly same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present.

With modern software algorithms, infrared is an excellent tool for quantitative analysis. The specimen’s transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks. The resulting FTIR spectral pattern is then analysed and matched with known signatures of identified materials in the FTIR library. FTIR spectroscopy does not require a vacuum, since neither oxygen nor nitrogen absorbs infrared rays. FTIR analysis can be applied to very small quantities of materials, whether solid, liquid, or gaseous. FTIR spectroscopy uses Michelson
interferometer to produce an interferogram. IR spectrum and the interferogram are related by a mathematical operation called Fourier transformation.

Figure 2.11: Schematic Diagram of FTIR spectrometer

Michelson interferometer consists of a beam splitter and two mirrors, one fixed and the other movable. The IR radiation emitted by a source is split into two beams of equal intensity, one having a fixed length and the other a variable length. Either one beam or both are passed through the sample and depending on the movable mirror's relative displacement, the beams are recombined either constructively or destructively. The combination of the two beams produces an interference pattern known as interferogram. This is converted to a plot of transmission versus wave number by the Fourier transformation, with the help of a built-in computer in the machine.

Figure 2.12: FTIR Spectrometer Lay out
2.4.6. Measurement of Dielectric Constant, Dielectric Loss and AC Conductivity

A substance whose basic electrical property is the ability to be polarised and in which, an electrostatic field can exist is known as a dielectric material. These materials offer a very large resistance to the passage of electric current under the action of applied voltage and sharply differ in their basic electrical properties from conductive materials. Conducting materials and dielectrics are equally important, because in order to prevent the flow of current through undesirable routes dielectrics are needed. The most important property of dielectrics is their ability to be polarised under the action of an external electric field. The amount of polarization produced is characterised by a parameter called permittivity, dielectric constant or dielectric coefficient. This is an extremely important parameter of a dielectric, depends on the temperature, particle size, and frequency of the applied ac electric field. When an electric field acts on any matter a certain quantity of electric energy is transformed into heat energy. The amount of power losses in a dielectric under the action of the voltage applied to it is known as dielectric loss. The dielectric constant and dielectric loss are frequency dependent. It also depends on temperature and size of the particle involved. Hence the contribution of quantum size effect of nano particles in dielectric constant, ac conductivity and dielectric loss has been carried out at different ac frequencies and temperatures. Dielectric constant, dielectric loss and ac conductivity measurements were carried out using a LCR HI-Tester (HIOKI 3532-50).

**Figure 2.13:** LCR Hi Tester (HIKOI 3532-50) used for the present study
The instrument can directly measure the parameters $|Z|$, $|Y|$, $\theta$, $R_p$, $R_s$, $\text{ESR}$, $G$, $X$, $B$, $C_p$, $C_s$, $L_p$, $L_s$, $D (\tan \delta)$, $Q$. The variation of dielectric constant with temperature can give information about the ferroelectric/diffused phase or any other transition of the material and on the behaviour of localized electric charge carriers leading to greater understanding of the mechanism of dielectric polarization.

The dielectric constant is related to capacitance ($C_p$) given as

$$\varepsilon' = \frac{C_p \times d}{\varepsilon_0 \times A} \quad [2.3]$$

Where $d$ is thickness, $A$ is the area of sample and $\varepsilon_0$ represents permittivity for vacuum.

The complex dielectric constant ($\varepsilon''$) of the sample was calculated using the relation:

$$\varepsilon'' = \varepsilon' \tan \delta \quad [2.4]$$

Where $\tan \delta$ is the dielectric loss tangent, proportional to the loss of energy from the applied field into the sample (this energy is dissipated as heat) and therefore denoted as dielectric loss.

Then ac conductivity can be calculated using the relation:

$$\sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan \delta \quad [2.5]$$

where $\omega (\omega = 2\pi f)$ is the angular frequency of applied field.

2.4.7. Introduction to Photocatalytic Analysis

Environmental contamination, which is growing around the world or in our daily life, is serious social problem and can not be neglected. Examples of such contamination can be listed as follows:

- Water pollution caused by industrial and household wastes.
- Respiratory diseases caused by air pollutant such as $\text{SO}_x$ or $\text{NO}_x$.  

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• Room air contamination caused by organic compounds emerging from newly
developed building materials.
• Dioxin emerging from resin during incineration.

The fact that using energy to eliminate such environmental contamination increases
emission of CO₂ resulting in more global warming. Under such circumstances, we have come
to the conclusion that we need a new material that can gently harmonize the contaminated
environment to restore original conditions by using natural energy which is a part of the
environment and low cost energy supplied to our daily home life. One solution to that
problem is our proposal, photocatalyst.

2.4.7.1. What is Photocatalyst?

Photocatalyst produces surface oxidation to eliminate harmful substances such as organic
compounds or nearby bacteria, when it is exposed to light. The function of photocatalyst can be
divided into few major categories as follows:
• Purifying water.
• Preventing contamination.
• Anti-bacterial action
• Deodorizing.
• Purifying the air (dissolving NOₓ).

The energy that the earth receives from the Sun is gigantic: 3 ×10²⁴ joules, which is about
10,000 times more than the global population currently consumes [9]. In other words, if we
could only exploit 0.01% of this incoming solar energy for the profit of humankind, we could
solve the problem of energy shortage. Any improvement in the utilization of sunrays will
make a profound positive effect on modern science and technology. In 1972, Fujishima and
Honda discovered the photocatalytic splitting of water on a semiconductor (TiO₂), which is
the first photocatalyst suitable for water splitting and the beginning of a new era of modern
heterogeneous photocatalysis [10]. Thereafter, a great deal of effort has been devoted to photoelectrochemical process such as splitting of water [11, 12], reduction of carbon dioxide for the conversion of solar energy into chemical energy [13, 14] and wet-type solar cells [9]. In addition to applying photocatalysts for energy renewal and energy storage, applications of photocatalysts to environmental cleanup have been one of the most active areas in heterogeneous photocatalysis [15-17]. This is inspired by the potential application of TiO$_2$ based catalysts for the complete destruction of organic contaminants in polluted air and waste water [18]. The power of semiconductor based photocatalyst, such as TiO$_2$, is due to their charge separation ability (figure 2.14).

![Figure 2.14: Schematic illustration of the charge separation theory of semiconductor upon a photoexcitation](image)

The photocatalytic mechanism is activated by light of energy greater than that of the semiconductor band gap. Upon photo-activation, an electron-hole pair is produced that reacts with adsorbed species to produce radical species. These radicals are powerful oxidising agents and will oxidise organic contaminants to CO$_2$ and H$_2$O. The separated hole has strong oxidation power to obtain electron from absorbed species. The separated charge and hole can
also recombine to release energy in the form of heat. To enhance the photocatalysis, electron-hole pair recombination must be suppressed. This can be achieved by trapping either the photogenerated electrons or the photogenerated holes at trapping sites in the structure. The band gap of a semiconductor determines its working wavelength. The semiconductors with either too large or too narrow band gaps are not suitable for practical use. The reason is that larger band gap will not cause any reaction while narrow band gap materials will have to face the problem of light erosion. Till now TiO\(_2\) (anatase, bandgap ~3.2 eV) is the most extensively studied material for photocatalysts because of its strong oxidizing power, low toxicity, and long-term photostability [17, 15]

2.4.7.2. Mechanism of Photocatalysis

2.4.7.2.1. Electronic Processes

The term photocatalysis is always used to describe the process that semi-conductor materials such as TiO\(_2\) undergo when irradiated by light of a certain wavelength. It is a term that implies photon assisted generation of catalytically active species.

![Figure 2.15: Schematic of photocatalytic mechanism](image)

In photocatalysis, light of energy greater than the band gap of the semiconductor, excites an electron from the valence band to the conduction band (figure 2.15). In the case of anatase (TiO\(_2\)), the band gap is 3.2 eV, therefore UV light (< 390 nm) is required to initiate the
photocatalytic process. Light (< 390 nm) excites an electron (e\textsubscript{CB}) to the conduction band generating a positive hole (h\textsubscript{VB}) in the valence band (Scheme 2.1).

Photocatalyst (e.g. TiO\textsubscript{2}) + h\nu \rightarrow h\textsubscript{VB} + e\textsubscript{CB} \quad \text{[Scheme 2.1]}

Alternatively the charge carriers can migrate to the catalyst surface and initiate redox reactions on the adsorbates [19]. Positive holes generated by light get trapped by surface adsorbed H\textsubscript{2}O. The H\textsubscript{2}O gets oxidised by h\textsubscript{VB} producing H\textsuperscript{+} and OH• radicals (Scheme 2.2.1), which are extremely powerful oxidants (table 2.1). The hydroxyl radicals subsequently oxidise organic species from the surrounding environment to CO\textsubscript{2} and H\textsubscript{2}O (Scheme 2.2.3) [20] and in most cases these are the most important radicals formed in TiO\textsubscript{2} photocatalysis.

**Table 2.1: Oxidation potentials of various oxidants relative to normal hydrogen electrode**

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Oxidation Potential (V)</th>
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<tbody>
<tr>
<td>OH• (hydroxyl radical)</td>
<td>2.80</td>
</tr>
<tr>
<td>O\textsubscript{3} (Ozone)</td>
<td>2.07</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2} (hydrogen peroxide)</td>
<td>1.77</td>
</tr>
<tr>
<td>HClO (hypochlorous acid)</td>
<td>1.49</td>
</tr>
<tr>
<td>Cl (chlorine)</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Electrons in the conduction band can be rapidly trapped by molecular oxygen adsorbed on the particle. Trapped molecular oxygen will be reduced by excited electrons to form superoxide (O\textsubscript{2}•) radicals (Scheme 2.2.2) that may further react with H\textsuperscript{+} (Scheme 2.2.4), to generate peroxide radicals (•OOH) and H\textsubscript{2}O\textsubscript{2} (Scheme 2.2.5) [21, 22].

**2.4.7.2.2. Recombination**

Recombination is a major limitation in semiconductor photocatalysis as it reduces the overall quantum efficiency of the photocatalyst because of the high recombination rate of photo induced electron-hole pairs at the surface of the photocatalyst [23]. The photocatalytic efficiency can be significantly enhanced if recombination is reduced. Doping with ions, [24,
heterojunction coupling [26-28] and nanosized crystals [29-30] have all been reported to promote separation of the electron-hole pair, reducing recombination and therefore improving the photocatalytic activity of the semiconductor material. When recombination occurs, the excited electron reverts to the valence band without reacting with adsorbed species (Scheme 2.2) [31]. Radiation may be emitted when an excited electron recombines with the valence band. As such, photoluminescence may be successfully employed to monitor recombination and in general, low intensity photoluminescence signals indicate lower recombination rates [23].

\[
e_{\text{CB}} + h_{\text{VB}} \rightarrow \text{energy} \quad \text{[Scheme 2.2]}
\]

\[
H_2O + h_{\text{VB}} \rightarrow \cdot \text{OH} + H^+ \quad \text{[Scheme 2.2.1]}
\]

\[
O_2 + e_{-\text{CB}} \rightarrow O_2^- \quad \text{[Scheme 2.2.2]}
\]

\[
\cdot \text{OH} + \text{VOC} \rightarrow H_2O + CO_2 \quad \text{[Scheme 2.2.3]}
\]

\[
O_2^- + H^+ \rightarrow \cdot \text{OOH} \quad \text{[Scheme 2.2.4]}
\]

\[
\cdot \text{OOH} + \cdot \text{OOH} \rightarrow H_2O_2 + O_2 \quad \text{[Scheme 2.2.5]}
\]

\[
O_2^- + \text{VOC} \rightarrow CO_2 + H_2O \quad \text{[Scheme 2.2.6]}
\]

\[
\cdot \text{OOH} + \text{VOC} \rightarrow CO_2 + H_2O \quad \text{[Scheme 2.2.7]}
\]

Scheme 2.1.1 – 2.1.7 schematisate the whole process [20, 32, 38]. Hydroxyl radicals produced by the photocatalytic process will oxidise the majority of volatile organic compounds (VOC) until complete mineralization. Recombination competes strongly with the photocatalytic process. It may occur on the surface in the bulk and is in general catalysed by impurities, defects, or all factors which introduce bulk or surface imperfections into the crystal [39]. The fact that the process can only be initiated by UV light is also a limiting factor in the process. It is desirable to produce a photocatalyst that can be activated by visible light to make full use of the solar spectrum.
2.4.7.2.3. Physical Effects

The photocatalytic efficiency of a photocatalyst does not only depend on the electronic properties of the materials. The availability of active sites on the material surface also plays a major role in the ability of the photocatalytic material to degrade organic contaminants [33]. A photocatalyst can produce an infinite amount of oxidising species to no effect unless the resulting radicals migrate to the photocatalyst surface where they can initiate the oxidation of the organic species from the surrounding environment. Therefore, properties such as crystal size and structure, pore size/volume, density of OH groups, surface charge, number and nature of trap sites and absorption/desorption characteristics all play an important factor in the photocatalytic activity of a semiconductor [33, 34]. Large surface areas will result in an increase in the number of active degradation sites available for degradation reactions. A delicate balance between surface area and recombination must be achieved in order to produce an effective photocatalyst. Smaller crystal sizes will result in larger surface areas but a spectral blue shift can be observed with crystal sizes below 10 nm. This is believed to be the result of the quantum size effect. The quantum size effect is believed to produce a blue shift in the absorbance band edge as a consequence of exciton confinement with decreasing particle size [35]. Recombination is also promoted with larger surface areas. This is usually because increased amounts of crystal defects are present with larger surface areas. The surface defects will act as recombination centres for the photoinduced electron/hole pair [33]. Surface hydroxyl groups also affect the photocatalytic efficiency of the materials. Surface hydroxyl groups participate in the photocatalytic process in a number of ways. They trap photoexcited electrons and produce OH• radicals and they can also act as active absorption sites for pollutants [33].
2.4.7.2.4. Methyl Orange Degradation

The photocatalytic activity of the synthesised material was investigated by degrading an organic dye (methyl orange). Methyl orange is one of the generally accepted organic pollutants for degradation studies and is used as an industrial standard. The standard protocol in our laboratory is as follows; in a typical experiment, potassium hexatitanate (titania based compound) powder was added to methyl orange. The suspension was allowed to stir in the dark for 30 min to obtain adsorption-desorption equilibrium, eliminating any error caused by initial adsorption. The suspension (under continuous stirring) was then irradiated by light in a Q-sun Xenon solar simulation chamber (0.68 W/m² at 340 nm). Aliquots (5 mL) were removed at timed intervals and the absorption spectra were recorded using a Perkin-Elmer Lambda 35 UV-Vis spectrometer (figure 2.9). The rate of degradation was found to obey (pseudo) first order kinetics and hence the rate constant for degradation, \( k \), was obtained from the first-order plot of kinetic analysis according to the following equation:

\[
\ln \left( \frac{A_0}{A} \right) = kt [2.6]
\]

Where, \( A_0 \) is the initial absorbance, \( A \) is the absorbance after a time ‘t’ of the methyl orange dye degradation, and \( k \) is the psuedo first order rate constant (min\(^{-1}\)). The rate constant, \( k \) can be derived from a plot of \( \ln(A_0/A) \) versus time.

2.4.8. Electron Paramagnetic Resonance (EPR)

Electron Paramagnetic Resonance (EPR) or Electron Spin Resonance (ESR) is a spectroscopic technique, which detect species that have unpaired electrons. A surprisingly large number of materials have unpaired electrons. (e.g. free radicals like NO•, CH3• etc. and many transition metal ions such as V, Mn, Fe, Co, Ni, Cu etc. EPR alone yields inconvertible evidence of free radicals and has the unique power of identifying the paramagnetic species. The partially filled electronic shell is favourable to the occurrence of paramagnetism in the compounds or crystals containing the transition metal ions. The phenomenon of electron spin
resonance spectroscopy can be explained by considering the behaviour of a free electron. According to quantum theory the electron has a spin which can be understood as an angular momentum leading to a magnetic moment. Consequently, the spinning electron constitutes a circulating electric current. The circulating current induces a magnetic moment $S$, which if the electron is subjected to a steady magnetic field $B_0$ parallel to $z$-axis, causes the electron to experience a torque tending to align its magnetic moment with the field. The relation between the magnetic moment and the spin vector is

$$\mu_s = -\frac{g\beta}{h} S$$ \hfill [2.7]

Where $\beta$ is the Bohr magneton and $g$ is the Lande's factor given by

$$\beta = \frac{eh}{4\pi mc} \quad \text{and} \quad g = 1 + \frac{1}{2J(J+1)} \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

In the above relations $J$ is total angular momentum, $L$ is the orbital angular momentum, $S$ is the spin angular momentum, $e$ is electronic charge, $h$ is Planck’s constant, $c$ is speed of light and $m$ is electronic mass.

The energy of the system depends upon the projection of the spin vector along $B_0$. Quantum theory stipulates that only two values are permitted for an electron $S_z = \pm \frac{\hbar}{2}$ which means that the electron magnetic moment can only assume two projections onto the applied field as shown on figure 2.16. Consequently,

$$\mu_z = \pm \frac{1}{2} g\beta$$ \hfill [2.8]

and the ensemble of energy levels therefore reduce to the two following values

$$E_{\pm} = \pm \frac{1}{2} g \beta B_0$$ \hfill [2.9]

If electromagnetic radiation is applied at a frequency that corresponds to the separation between the permitted energies equal to

$$\Delta E = E_+ - E_- = g \beta B_0 = \hbar \nu$$ \hfill [2.10]
energy is absorbed from the electromagnetic field, where $\nu$ is the frequency of microwave radiation.

![Figure 2.16: Schematic representation of splitting of energy levels (Ref. 40)](image)

For electrons bound into an atom or a molecule, the phenomenon of EPR may not be observed at all, because electron spins pair off in atomic or molecular orbitals so that virtually no net spin magnetism is exhibited and the material is said to be diamagnetic. When an atom or a molecule has an odd number of electrons, however, complete pairing is clearly not possible and the material is said to be paramagnetic. In that case EPR can be observed.

Electron Paramagnetic Resonance (EPR) is a sensitive spectroscopic method for the determination of the geometric and electronic structure, the dynamics and the spatial distribution of paramagnetic species in materials. EPR directly focuses on the unpaired electrons and nuclei in their vicinity and is therefore the method of choice for studying free radicals, compounds with transition metal and rare earth ions and defect centers. It is a particularly useful technique for analysing orientationally disordered systems such as powders or frozen solutions where standard diffraction methods fail.

For the present study, EPR studies have been pursued far more extensively in perovskite and perovskite like crystals than in hydrogen-bonded crystals. This is because in perovskite, a lifting of the degeneracy of the spin levels can detect even very small deviations from the cubic paraelectric phase. The accuracy of EPR method is very impressive in such
circumstances and the location of the pseudo-quaternary axes in the perovskite can be achieved to better than one tenth of degree. EPR measurements have also provided accurate and valuable information concerning static phenomenon close to transition points. In most ferroelectrics, however anomalies occur near Tc and readily measured by conventional dc or ac techniques, so that information obtained from EPR often tends merely to confirm existing results.

The EPR spectra were recorded at RT on a Bruker EMX Biospin spectrometer operating at X band frequencies (9.8 GHz) with 100 kHz and 10 G modulations with maximum calibrated power available being 0.201 mW. Conventional first derivative of absorption signals were recorded between 0.08-1.0 T range. The high frequency modulation field amplitude ranged typically from 0.005-0.5 mT with E-231 rectangular cavity at 100 kHz field modulation. The samples were kept in 4 mm quartz tube. An incident microwave power level of 10 mW was used to achieve levels of $10^5$.

![Figure 2.17](image)

**Figure 2.17:** (a) Bruker EMX X-band EPR Spectrometer used in the study (b) Block diagram of a typical X-band EPR Spectrometer
2.4.9. Differential Scanning Calorimetry (DSC)

A differential scanning calorimeter measures heat into (endothermic reaction) or out (exothermic reaction) of a sample relative to a reference with a linear temperature ramp. Differential scanning calorimetry (DSC) monitors heat effects associated with phase transitions and chemical reactions as a function of temperature. In a DSC the difference in heat flow to the sample and a reference at the same temperature, is recorded as a function of temperature. The reference is an inert material such as alumina, or just an empty aluminum pan. The temperature of both the sample and reference are increased at a constant rate. Since the DSC is at constant pressure, heat flow is equivalent to enthalpy changes.

\[
\left( \frac{dq}{dt} \right)_p = \left( \frac{dH}{dt} \right)
\]

[2.11]

Here \( \frac{dH}{dt} \) is the heat flow measured in mcal sec\(^{-1}\). The heat flow difference between the sample and the reference is:

\[
\Delta \frac{dH}{dt} = \left( \frac{dH}{dt} \right)_{\text{sample}} - \left( \frac{dH}{dt} \right)_{\text{reference}}
\]

[2.12]

It can be either positive or negative. In an endothermic process, such as in most phase transitions, heat is absorbed and, therefore, heat flow to the sample is higher than that to the reference. Hence \( \Delta dH/dt \) is positive. In an exothermic process, such as crystallization, some cross-linking processes, oxidation reactions, and some decomposition reactions, the opposite is true and \( \Delta dH/dt \) is negative.

![Schematic diagram for DSC](Ref. 41)

Figure 2.18 (a): Schematic diagram for DSC (Ref. 41)
Generally speaking, physical phenomena like phase transitions, vaporization, dehydration, sublimation, reduction, some decomposition reaction etc. produce endothermic effects, whereas crystallization, grain growth, adsorption, polymerization etc. produce exothermic effects. Any phenomenon that produces enthalpic change or a change in heat capacity can be detected by DSC technique. The shape of the peaks, and also the peak maximum and peak minimum temperatures are controlled basically by the reaction kinetics, although they are also influenced by the sample packing and geometrical parameters, the heating rate, the furnace atmosphere, and the reference temperature source. Even more subtly, the changes of baseline can be related to the change in specific heat of the sample; which is an important parameter. For the analysis of the samples in the present study, a Dupond 910 DSC was used.

2.18 (b): Typical DSC curve (Ref. 41)
References


[41] www.pslc.ws/macrog/dsc.htm