Chapter 1

Introduction

Aim of the Thesis

The demand of energy is increasing day by day. At present, most of the energy needs rely on fossil fuel. The world energy consumption is made up of about 88% fossil fuel, 6% hydroelectricity, 6% nuclear power, a small fraction from biomass and solar energy sources **[1]**. Fossil fuels cause environmental pollution and are limited in nature. There is a need to find alternative sources of energy such as solar or wind energy. The solar energy is the largest carbon free energy source **[2].**

Solar cell (photovoltaic cell or photoelectric cell) is a solid state device that converts the solar energy into electricity by photovoltaic or photoelectric effect. Silicon based solar cells are environmentally clean and have high power conversion efficiency of about 20% **[3, 4]**. Silicon solar cells are very expensive as they require large amount of material for production in its purest form. Harnessing solar energy with inexpensive materials and manufacturing methods has become an important challenge. Alternate forms of solar cells are thus being heavily researched.

Michael Gratzel created a low cost dye sensitized solar cell (DSSC) with TiO_2 and obtained a solar cell efficiency of 10.4% in 1991 **[5]**. Dye sensitized solar cells are considered to be a promising alternative to conventional silicon based photovoltaic devices because of their simple assembly and low cost fabrication. The dye sensitized solar cell comprises of anode, redox electrolyte and counter electrode. Anode is a semiconducting film deposited on transparent conducting glass plate covered with the monolayer of Ru based synthetic dye. Counter electrode is a platinum coated transparent conducting glass plate.

This work is an attempt towards improving performance and lowering the fabrication cost of dye sensitized solar cells. There are several parameters which affect the efficiency of DSSC. The photo anode is the key component for enhancing the efficiency. Generally, TiO_2 is widely used semiconducting material for photo anode. A thin film of TiO_2 is coated on transparent conducting glass plate. For enhanced performance this film must possess certain structural, electrical and optical properties. The material should be of small particle size and high surface area so that more dye molecules can be adsorbed on the surface and more current can be produced. The film should be porous, so that it can accommodate large no of dye molecules. The electrical conductivity of the material should be high enough to transfer electrons generated by dye through the film and reach the conducting plate easily. A material with high refractive index is needed for making a good dye sensitized solar cell. Due to high refractive index, the material reflects incident light and thus light can travel more distance inside the material or light can stay for longer time inside the material. To generate large number of electrons large number of photons should be absorbed by material and so the optical absorption coefficient of material should be high.

In the present work main focus will be on changing material properties. The highest efficiency of DSSC has been reported for photo anode prepared with TiO_2. Attempts have been made to modify the properties of TiO_2. The particle size of TiO_2 can be varied by mixing it with another oxide. New crystallographic phases with quite different properties than the original oxides can be produced by mixing of the oxides **[6]**. It has been reported that incorporation of ZrO_2 leads to decrease in particle size of TiO_2 and increase in surface area **[7]**. TiO_2-ZrO_2 composites of different molar ratios were prepared by hydrothermal method in the present work.

The electrical and optical properties of material can be modified by doping. The addition of small amount of foreign atoms in the crystal lattice of semiconductor changes their electrical properties and produces n-type or p-type semiconductors. The porosity of the material can be also increased by doping **[8]**. Doping can change absorption properties of material by introducing new defects and energy levels. In the present work different metals were doped into TiO_2-ZrO_2 composites to modify its properties.

To prepare a low cost dye sensitized solar cell, it is required to replace expensive components with cheaper one. The expensive parts of DSSC are ruthenium based synthetic dye and platinum coated counter electrode. Ruthenium based synthetic dye is very expensive. In the present work, synthetic ruthenium dye has been replaced by natural dyes extracted from fruits, flowers as well as leaves and platinum coated counter electrode by carbon coating to lower the fabrication cost.

Since most of the DSSC preparation has TiO_2 as its base material for working electrode, a review of the structure and properties of TiO_2 becomes necessary.

1.1 Titanium Dioxide

Titanium dioxide (TiO_2) is a wide band gap semiconducting material. TiO_2 is chemically inert, cheap and easy to synthesize. It is a naturally occurring mineral. TiO_2 exists in three different crystal structures namely Anatase, Rutile and Brookite. Among these, the Anatase and Rutile phase has major applications as they can be synthesized easily **[9]**. In recent years, it has been reported that Brookite also exhibits good photo catalytic properties **[10]**.

Anatase TiO_2 has bandgap of 3.2 eV, Rutile 3.0 eV, where as Brookite TiO_2 has bandgap between 3.0 eV and 3.2 eV **[11]**. The Rutile phase is thermodynamically stable while Anatase and Brookite are metastable phases and can be easily transformed into Rutile on heating **[12]**. Anatase transforms to equilibrium phase at temperatures between 550° and 1000 °C. The transformation temperature depends on the impurities or dopants as well as on the morphology of the material. Rutile TiO_2 is widely used in white pigments because of its high refractive index. Rutile TiO_2 is optically positive where as Anatase TiO_2 is optically negative. The different physical parameters are listed in Table 1.

Table 1: Physical properties of the TiO_2 phases.

Phase	Refractive Index	Bandgap (eV)	Density (gm/cm^3)
Rutile	2.609	3.00	4.23
Anatase	2.488	3.20	3.78
Brookite	2.583	Between 3.00 and 3.20	4.08

1.1.1Crystal structure of TiO_2

Among the three phases of TiO_2, Rutile and Anatase have tetragonal crystal structure. These crystals are formed by chains of distorted TiO_6 octahedra. The unit cell of most stable Rutile phase contains two TiO_2 units. The titanium cations have a coordination number of 6. They are surrounded by an octahedron of 6 oxygen atoms via two apical and four equatorial bonds of length 1.976 A° and 1.946 A°

respectively **[13]**. The oxygen anions have a co-ordination number of 3 resulting in three coplanar titanium cations via one apical and two equatorial bonds. The unit cell of metastable Anatase phase contains four TiO_2 units whereas unit cell of Brookite contains eight TiO_2 units. The Ti – Ti distance in Rutile is shorter than in Anatase. These structural changes lead to the change in mass density. Anatase phase is 9% lesser dense than Rutile. Two surfaces (101) and (001) of Anatase crystal are exposed. The (101) surface is most stable and constitutes 94% of the crystal surface. Three different surfaces (110), (101) and (001) of Rutile crystal are exposed. The most stable (110) surface forms 56% of the total crystal surface **[13]**. The unit cells of different structure of TiO_2 are shown in figure 1.

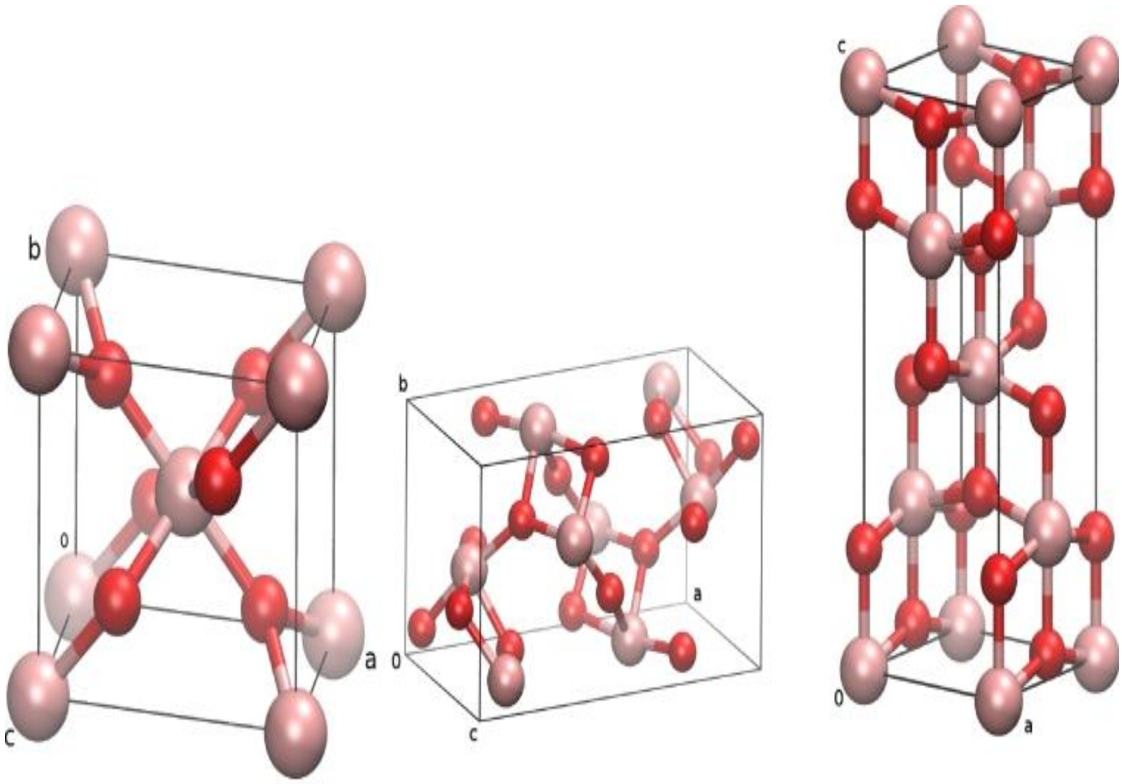

Figure 1: Unit cell of different TiO_2 structures (a) Rutile, (b) Anatase and (c) Brookite (from left to right)[14]

1.1.2 Applications of TiO_2

TiO_2 has wide applications. Some of the prominent ones are given below.

(1) Pigment

The most important constituent of paint is titanium dioxide. Titanium dioxide (TiO_2) is the most important inorganic white pigment used in the coating industry because of its high refractive index, brightness and opacity. Rutile TiO_2 is preffered because it scatters light more efficiently, is more stable and durable. It is also used as a refractive optical coating for dielectric mirrors **[15]**. Earlier, toxic Lead was used in paints for high gloss and rich depth of color. TiO_2 being a non toxic, opaque and inert substance has replaced it. It has also been used in food colouring and crayons **[16]**. Nearly 95% of the TiO_2 production is supplied to the pigment industry .

(2) Photocatalyst

The word photocatalysis is composed of two parts, “photo” and “catalysis”. Photocatalyst is the substance which can modify the rate of chemical reaction using light. Titanium dioxide is a photocatalyst under ultraviolet radiation. Anatase phase of TiO_2 is more active as a photocatalyst compared to Rutile. When TiO_2 is excited by UV, the electrons absorb energy and move from valance band to conduction band. Hence an electron hole pair is generated. These free radicals recombine with oxygen, water or pollutants adsorbed on the surface of TiO_2 and decomposes them **[17]**.TiO_2 can act as a hydrolysis catalyst and can break water molecule into hydrogen and oxygen. Hydrogen can be collected and used as a fuel. TiO_2 can be also used as a self cleaning or anti fogging coating. The photocatalytic propety of TiO_2 is useful in water purification and photodegradation of pollutants.

(3) Cosmetics

Skin protection against ultraviolet radiation has become essential in current life style. TiO_2 has been used for years in cosmetics and sunscreens for UV protection. Being a wide band gap material TiO_2 absorbs UV radiations. Generally sunscreens are composed of mixture of organic and inorganic UV filters. TiO_2 based material can be used for UVB protection and replaces organic UV filters.TiO_2 based UV absorbants also impart whitening effect when applied to the skin**[18]**. TiO_2 does not have side effects or drawbacks of organic UV filters. The particle size of TiO_2 influences UV absorption. The sunscreen composed of TiO_2 nanoparticles will help to make thin uniform layer of it on the skin, which will be more efficient against UV radiations. The whitening effect is due to the scattering of visible light. It has been reported that the scattering of visible light decreases with decreasing particle size but UV – absorption ability is mintained as light scattering and light absorption is differently dependent on particle size. The particle size of TiO_2 in typical UV filters is in the range of 15–50 nm.

(4) Dye Sensitized Solar Cell

The most important application of TiO_2 is in dye sensitized solar cell. Dye sensitized solar cell(DSSC) is third generation solarcell, it was invented in 1991 by Professor Michael Graetzel and Dr Brian O'Regan**[19]**. DSSC works on the principle of photosynthesis.The details of Dye Sensitized Solar Cell is given in Chapter 2.

1.2 Zirconium Dioxide

Zirconium dioxide (ZrO_2) is a refractory material. It is also called as Zirconia. ZrO_2 has a great potential for technological applications because of its electrical and mechanical properties **[20]**. ZrO_2 is one of the most studied ceramic materials. It has excellent properties such as high melting point, high refractive index, good thermal and chemical stability, high fracture toughness, high density, high hardness and good resistance against oxidation **[21]**. ZrO_2 exists in three different polymorphs namely Monoclinic, Tetragonal and Cubic. At room temperature it remains in Monoclinic phase. As temperature increases, it transforms into Tetragonal and then Cubic phase. The Tetragonal phase is stable at 1170°C and Cubic phase at 2370°C. The volume of crystal expands as cubic phase transforms to tetragonal and then to monoclinic phase. The cubic phase of ZrO_2 can be stabilized at room temperature by doping with different oxides like MgO, CaO, and Y_2O_3 **[22]**. ZrO_2 is an insulating material with a bandgap of 6 eV. However, it behaves as a semiconductor when prepared by sol gel method or doped with transition metal **[23]**.

1.2.1 Crystal Structure of ZrO_2

ZrO_2 exists in three different crystal structures namely Monoclinic, Tetragonal and Cubic. Monoclinic and Cubic are stable phases whereas Tetragonal is a metastable phase ZrO_2. Figure 2 shows different phases of ZrO_2 **[24]**.

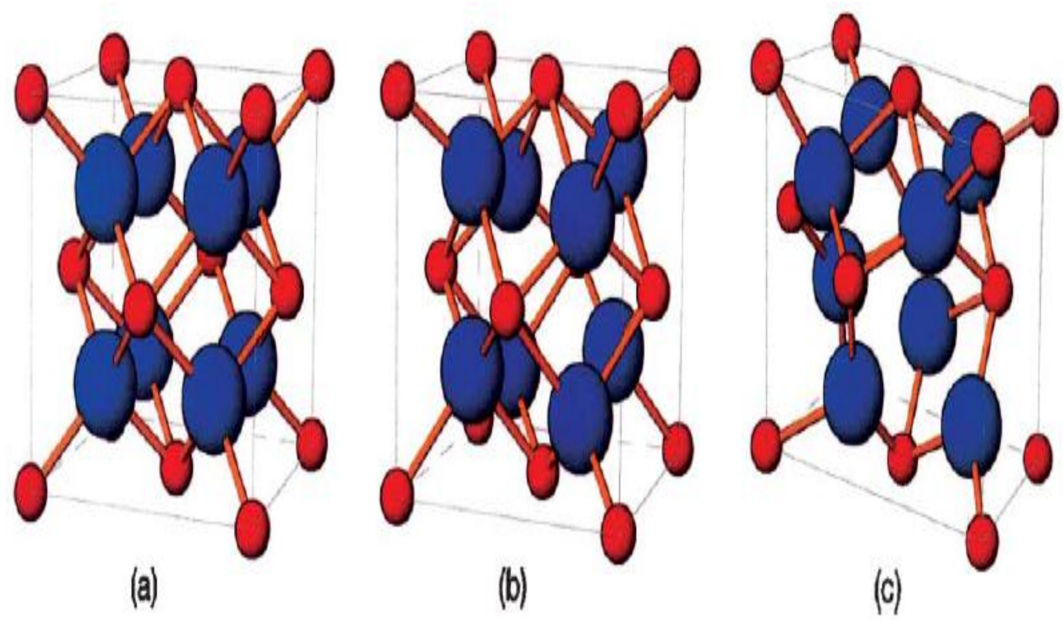

Figure 2: (a) Cubic ZrO_2, (b) Tetragonal ZrO_2, (c) Monoclinic ZrO_2.

Monoclinic phase is a natural form of Zirconia. It is also known as baddelyite. Zr^{+4} ions of monoclinic ZrO_2 have coordination number of seven for the oxygen. The average distance between the Zirconium ion and three of the seven Oxygen ions is 2.07 A° while between Zirconium ion and other four Oxygen ions is 2.21 A°. In Tetragonal phase, Zr^{+4} ions have coordination number of eight. The distance between the Zirconium ion and four Oxygen ions is 2.065 A° and that between Zirconium and other four oxygen ions is 2.455 A°. The Cubic structure of ZrO_2 is also known as fluorite. It can be represented by a cubic lattice with eight oxygen ions which are surrounded by a cubic arrangement of cations **[24]**. The single crystal of Cubic ZrO_2 has low fracture toughness and strength but very high thermal shock resistance. The atomic density of Monoclinic phase is 96% of that of Cubic phase and 97% that of Tetragonal phase. The transformation from Monoclinic to Tetragonal and then to Cubic phase is results into toughening of the material **[25]**. Tetragonal to Monoclinic transformation can also be triggered by applying stress. Hence strain will be produced in structure. The reverse transformation also leads to toughening and depends on volume expansion as well as shear strain when tetragonal phase transforms to monoclinic phase.

1.2.2 Applications of ZrO_2

Zirconia has extraordinary thermal, electrical, optical and mechanical properties. Because of these properties, it is used in refractory materials, insulations, catalyst, anti-corrosion coating, oxygen sensors, fuel cell membranes, high temperature induction furnace susceptors and for clinical purpose. Zirconia is one of the best insulating material. It has approximately 5 times the insulating value of alumina or magnesia. Some of ZrO_2 applications are listed below.

(1) Biological Applications

It has been confirmed that Zirconia is a highly biocompatible material when it is purified of its radioactive content **[26]**. Instead of Titanium and Aluminium, ZrO_2 can be used as a new material for hip replacement **[27]**. Zirconia is chemically inert and produces no adverse reactions in tissues. In vitro tests have proved that Zirconia has lower toxicity than Titanium.

Zirconia has emerged as a promising material for dental ceramics due to its excellent mechanical properties. The mechanical property of ZrO_2 is similar to stainless steel and hence it has been called as ‘Ceramic Steel’ by Gravie **[28]**.The Cubic phase of Zirconia transforms to Monoclinic phase on cooling, causes approximately 5% volume expansion and produces cracks. This volume expansion may fracture Zirconia at room temperature. Due to this, pure Zirconia is not used in dentistry application. However, mixed phases of Zirconia are used. A mixture of Tetragonal phase along with Yttrium stabilized Zirconia or Magnesium stabilized Zirconia is widely used for dentistry application **[2]**.

(2) Refractory material

Zirconia is an excellent material for high temperature applications because of high melting point, excellent corrosion resistance, high mechanical properties and small thermal expansion co efficient. Zirconia can withstand high temperature up to 2700°C. Zirconia is an ideal material for the melting of precious metals and super-alloys which have melting point higher than 1800°C.

1.3 Mixed Oxides

Mixed oxides are oxides that contain more than one cation. The combination of Titania – Zirconia has been extensively studied in recent years. TiO_2 and ZrO_2 exhibit good catalytic properties. It has been extensively mentioned in literature that mixing of two dissimilar oxides form a new stable compound having different physiochemical and catalytic properties. The structural and optical properties are greatly influenced by mixing oxides.

The Anatase phase of TiO_2 can be stabilized by mixing ZrO_2 **[30]**. Mixing of ZrO_2 with TiO_2 decreases particle size of TiO_2 and increases surface area because of dissimilar nuclei size **[31]**. The photo catalytic activity of TiO_2 can be changed by doping it with transition metal oxides **[32]**. The photo catalytic activity of TiO_2 is seen to be improving by mixing ZrO_2 **[33]**. The acid – base or redox properties of oxides can be altered by mixing two of them which is beneficial for catalytic applications. The surface acidity of TiO_2–ZrO_2 mixed oxide is improved compared to pure Zirconia and pure Titania which will enhance the catalytic property **[34]**. The mixed oxides have been used for various purposes like fuel cell, gas sensors, catalyst, ceramic technologies etc. **[35]**.

1.4 Effect of doping

Doping is a process of introducing impurities in a pure semiconductor in order to modify its structural, electrical and optical properties. In luminescent or phosphor materials, doping is known as activation. The number of electrons and holes in a semiconductor can be changed by doping. The addition of small amount of foreign atoms in the crystal lattice of semiconductor changes their electrical properties and produces n-type and p-type semiconductors. The conductivity of a semiconductor material can be increased in n-type material by increasing number of electrons and in p-type material by increasing number of holes.

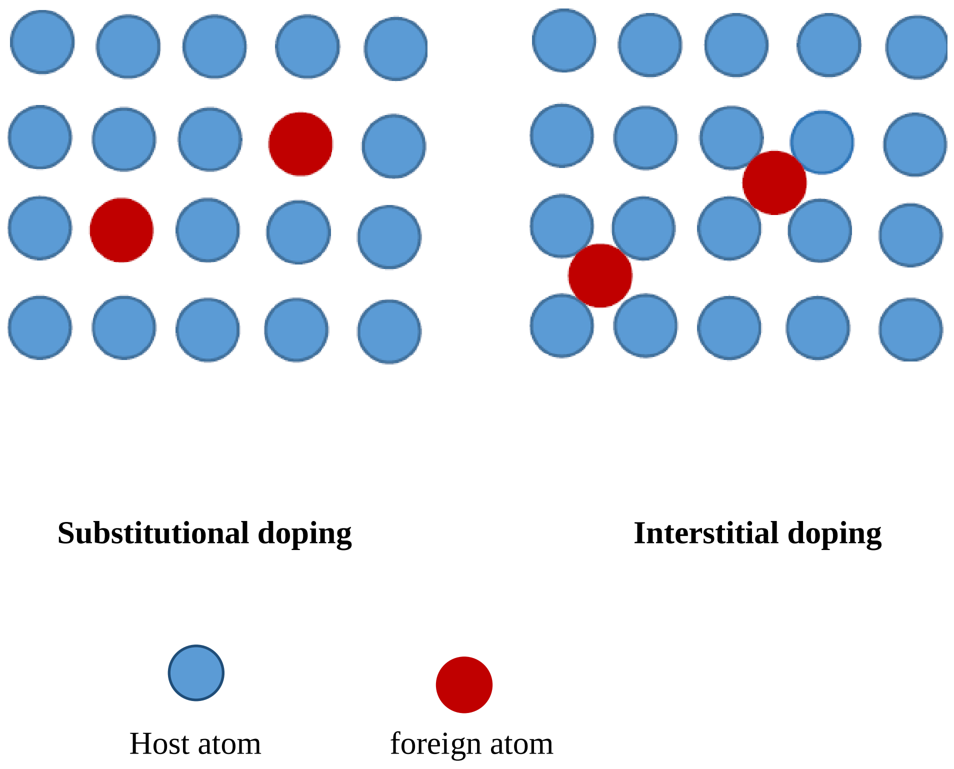

Figure 3: Doping in semiconductors

Doping can be either substitutional or interstitial or both. In substitutional doping the foreign atom takes its position in crystal lattice by replacing an atom from host material. If an atom takes its position in available voids or space in a crystal lattice of host material, such a doping is called interstitial doping. These are illustrated in figure 3.

The electrical, optical and structural properties are greatly influenced by doping. The phase transformation of TiO_2 depends on impurities, types of dopant and amount of dopant. The doping of iron increases porosity in TiO_2 **[8]**. The dopants are more likely to enter lattice in a substitutional manner if the ionic radius of dopant is smaller than the host atom and inhibit the crystal growth. If the ionic radius of dopant is larger than host atom, it enters into interstitial space and breaks the crystal.

Semiconducting material with varying bandgap has significant applications in optoelectronic devices. The bandgap of material can be varied by either changing particle size or by adding impurities. Transition and rare earth metal ions shift the absorption edge towards visible region and increase photo reactivity of TiO_2 in the visible region **[36, 37, 38, 39, 40]**. The metal and rare earth ions produce new energy levels within the bandgap of TiO_2.

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