Chapter 1

Introduction

1.1 Introduction

Every day, the worldwide demand for energy rises. Currently, fossil fuels contribute to a large portion of energy use. Around 83% of the world's energy comes from fossil fuels, with hydroelectricity and nuclear power accounting for about 10%. Around 7% comes from biomass and different forms of unconventional energy, including solar power, which accounts for roughly 2% according to Global Primary energy consumption by source, 2022 **[1]**. Environmental pollution is a significant issue caused by fossil fuels, which are also limited in their availability. Consequently, there is a need to explore alternative energy sources, such as solar and wind energy. Among these, solar energy stands out as the most abundant source of carbon-free energy **[2].**

Silicon-based solar cells are known for their relatively high-power conversion efficiency. They have evolved over the years, with the best models achieving around 20%. **[3, 4]**. Apart from Silicon, Cadmium Telluride (CdTe), Copper Indium Gallium Selenide (CIGS) and Amorphous Silicon (a-Si) have been also used for making solar cells and are clubbed as the second generation Solar Cells. However, the conventional silicon solar cell still remains prevalent. The production of silicon solar cells involves high costs, primarily due to the processing expenses and the quantity of material needed. Consequently, there is a significant scope in capturing solar energy using more cost-effective materials and manufacturing techniques. This has led to the exploration and development of alternative types of solar cells. These are also referred to as the third generation solar cells. They include Dye Sensitized Solar Cells (DSSCs), Organic Solar Cells (OSCs), Perovskite Solar Cells and Quantum Dot Solar Cells. The fourth generation would involve the concepts of Multi-Junction Solar Cells, Tandem Solar Cells, Nanostructured Solar Cells and Integrated Solar Cells.

A detailed description of solar cells is given in Chapter 2.

This work is on Dye Sensitized Solar Cells.

Michael Gratzel fabricated the first low-cost TiO_2 based Dye Sensitized Solar Cell (DSSC)in 1970 and subsequently obtained a solar cell efficiency of 10.4% in 1991 [5].

Dye Sensitized Solar Cells (DSSCs) are a category of solar cells which can cater to certain low power applications using solar energy. Compared to traditional silicon-based photovoltaic devices, they have a straightforward assembly and cost-effective fabrication process.

These cells consist of three primary components: an anode (also called photo anode or working electrode), a redox electrolyte, and a counter electrode **[6]**. Anode consists of a layer of semiconducting material deposited on transparent conducting glass plate generally covered with the monolayer of Ruthenium based synthetic dye or any other dye to absorb light and produce electron hole pairs. Iodide solution is generally used as the redox electrolyte. Counter electrode is generally a Platinum coated transparent conducting glass plate.

The most commonly used semiconductor material for the photo anode in DSSCs is TiO_2. It is applied as a thin film on a transparent conducting glass plate. To achieve better performance, this material needs to exhibit appropriate structural, electrical, and optical properties. It is crucial for the TiO_2 to have a small particle size and a high surface area, which allows for the adsorption of a greater number of dye molecules, thereby generating more current. Additionally, porosity plays a vital role as it offers an increased surface area and can accommodate a larger quantity of dye molecules **[7, 8]**. The material used in the photo anode should possess a high electrical conductivity to efficiently transfer the electrons excited by the dye through the film to the conducting plate. Additionally, a high refractive index is desirable in the material, as it enables the incident light to remain within the material for a longer duration, increasing the likelihood of its absorption by the dye. For the generation of a large number of electrons, it's important that the material has a high optical absorption coefficient, enabling it to absorb a significant number of photons. Other than TiO_2, materials such as ZnO, CeO_2, CdS, ZrO_2, and CuO also exhibit these properties.

The transport mechanism of electrons in a dye-sensitized solar cell involves the absorption of photons by dye molecules, injection of electrons into the semiconductor material, their movement through the semiconductor, collection at the electrode, flow through the external circuit, and regeneration of the dye molecules by a redox mediator. This process allows for the conversion of sunlight into usable electrical energy.

In Dye Sensitized Solar Cells (DSSCs), the issue of interfacial charge recombination presents a significant challenge, leading to the loss of electrons that are generated by light exposure and consequently, a loss in efficiency **[9].**

The recombination is schematically represented in Figure 1. A dashed arrow illustrates two potential recombination pathways: (i) the recombination of the injected electron with the oxidized dye molecule, and (ii) the recombination of the injected electron with the tri-iodide present in the electrolyte.

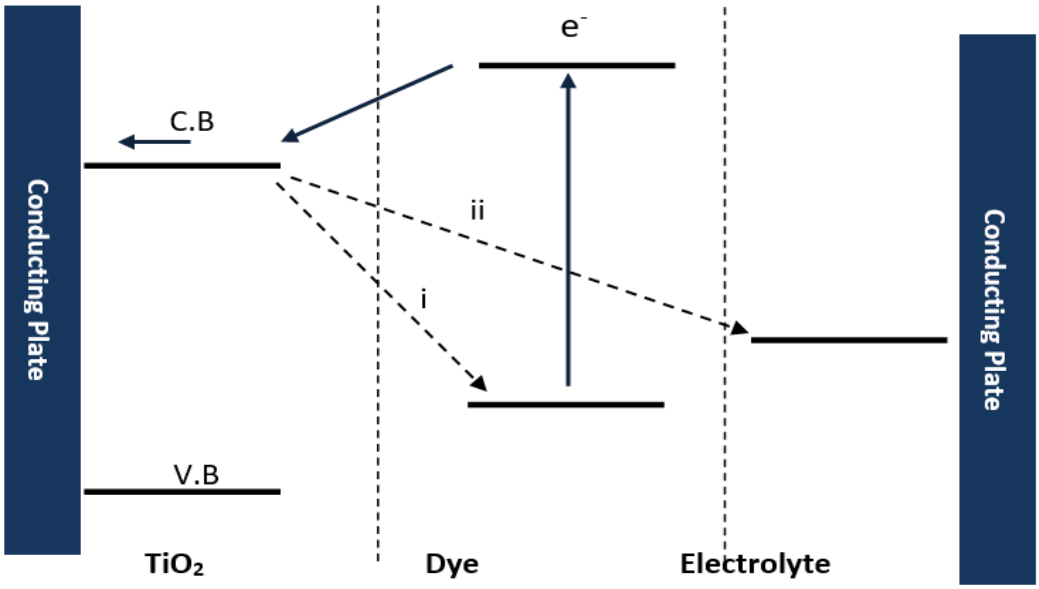


Figure 1: Recombination process in DSSC.

1.2 About The Work

There are numerous parameters which affect the efficiency of DSSCs, with the photo anode playing an important role in enhancing overall efficiency.

This study primarily aims to improve the performance of the photo anode material in Dye Sensitized Solar Cells (DSSCs) and thereby enhancing the power conversion efficiency. This effort involves reducing the recombination rate by incorporating a layer of material along with the existing layer of TiO_2, which acts as a barrier for recombination between the photoelectrode and the dye.

Hence, the work comprises the development of a photo-anode with optimized characteristics for use in Dye Sensitized Solar Cells (DSSCs) using a cascade of layers. To achieve this, various layers of materials, in different combinations, were applied onto a conducting glass substrate.

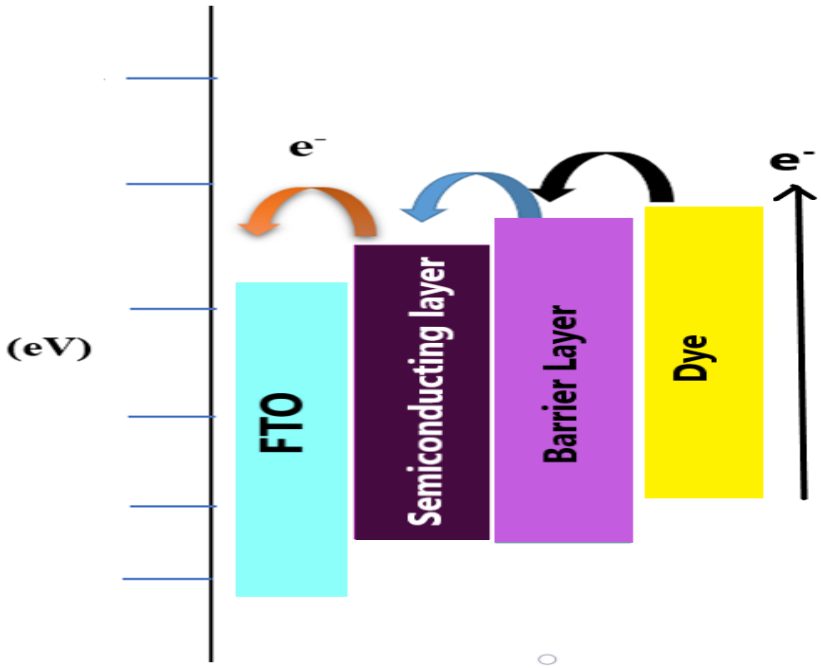


Figure 2: Proposed electron transport mechanism in DSSC.

The selection and deposition of these materials were guided by their respective Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) band level values. The mechanism underlying this approach is depicted in Figure 2.

Based on the same approach, a study was undertaken using a composite of TiO_2 -ZrO_2 and Europium doped composite of TiO_2 -ZrO_2 for study a photoanode material and its comparison with only TiO_2 as photoanode material.

The objective of the work was to develop a Dye Sensitized Solar Cell using low-cost materials and processes, while attempting to enhance the efficiency by reducing the limiting factors.

A low-cost option was chosen for the dye by using a plant-based alternative. The simple Doctor Blade Technique was used to deposit the layers. The limiting factor of recombination was attempted to be reduced.

The work was carried out in the following steps:

- **Synthesis and Characterization of all materials (metal oxides) to be used as electrode or barrier layer (ZnO,TiO_2, CeO_2, CdS, ZrO_2, CuO)**
- **Investigation the structural, optical, and electron transport properties of the materials.**
- **Deposition of the ZnO electrode layer and subsequent Barrier layers on the ZnO electrode with varying thickness for optimization.**
- **Fabrication of the Dye Sensitized Solar Cell, measurement of photovoltaic performance and analysis of results.**

Following is a brief discussion on the materials used for the study along with their properties.

1.3 Zinc Oxide (ZnO)

Zinc Oxide is an inorganic compound which is also known as Calamine or Zinc White. It is naturally found as a mineral Zincite **[10].** ZnO is a wide-band gap semiconductor. Zinc oxide (ZnO) is a white powder in its pure form, but its colour can be influenced by impurities when found in nature. The rare mineral zincite is one such natural occurrence of Zinc Oxide, and it often contains impurities, such as Manganese and other elements. These impurities can impart various colours to the mineral, ranging from yellow to red.

The presence of Manganese, in particular, is known to contribute to the yellow to red hues observed in Zincite. The colour of minerals can be affected by the presence of trace elements or impurities in their crystal lattice structures. In the case of Zincite, the specific impurities determine the coloration of the mineral. Despite its natural variations in colour, when Zinc Oxide is synthesized in a controlled environment, it typically

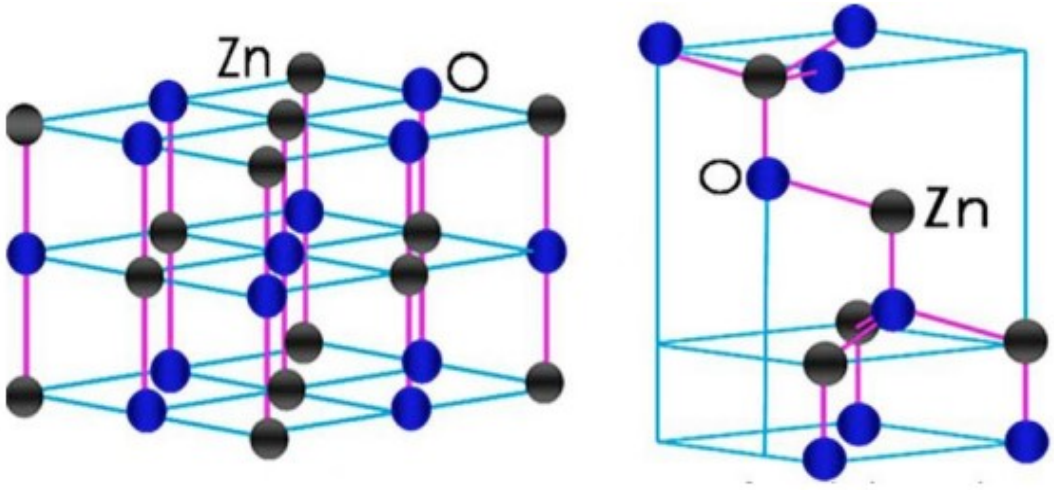
remains a white powder. Nanostructured ZnO possesses a good chemical stability, low toxicity, intrinsic hydrophilicity, and high electron mobility **[11-14]**.

1.3.1 Crystal Structure of ZnO

Zinc Oxide (ZnO) can crystallize in two main structural forms: hexagonal Wurtzite and cubic Zincblende. The Wurtzite structure is the most stable at ambient conditions, making it the predominant form of zinc oxide encountered in nature and under normal circumstances. In the hexagonal Wurtzite structure, both the Zinc and oxide ions are arranged in a tetrahedral coordination, which is a characteristic geometry for Zn (II) ions in ZnO crystals. The tetrahedral coordination refers to the spatial arrangement of four atoms or ions forming a tetrahedron **[15]**. Under certain conditions, such as when ZnO is grown on substrates with a cubic lattice structure, the Zincblende form can be stabilized. In the cubic Zincblende structure, Zinc and oxide ions are also tetrahedrally coordinated.

Understanding the crystal structures and phase transitions of materials like ZnO is crucial for various applications, including in the fields of materials science and semiconductor technology.

ZnO structure is composed of two interconnecting sub lattices of Zn^{+2} ions surrounded by tetrahedral O^{-2} ions and vice versa. At room temperature, ZnO exhibits a direct band gap of 3.37 eV **[16,17].**



(a) Wurtzite (b) Zinc Blend

Figure 3: Unit cell of (a) Wurtzite ZnO, (b) Zinc Blend.

Table 1: Physical Properties of ZnO**.**

Bandgap (eV)	Refractive Index	Density (gm/cm^3)
3.3	2.004	5.606

Zinc oxide (ZnO) is a versatile material used in a wide range of applications across various industries due to its unique set of properties, including its chemical stability, electronic, and optical characteristics.

ZnO is used in the production of semiconductors for transistors, diodes, and other electronic components. Its wide band gap makes it suitable for light-emitting diodes (LEDs) and laser diodes, particularly for UV light emission. ZnO is also utilized in the manufacturing of varistors, which are voltage-dependent resistors used to protect circuits against high voltage spikes **[18]**.

ZnO's transparency and ability to conduct electricity make it an excellent candidate for use in solar cells, particularly in the form of thin-film transistors and transparent conducting oxides (TCOs) that form part of the cell's electrode structure **[19]**.

1.4 Titanium Dioxide (TiO_2)

Titanium dioxide (TiO_2) is a semiconductor that has a large band gap. TiO_2, a naturally occurring mineral, is known for its chemical inertness, low cost, and simple synthesis technique. It has three unique crystalline forms: anatase, rutile, and brookite. Anatase and Rutile phases are widely used in different applications due to their ease of synthesis **[20]**. In recent years, it has been discovered that Brookite demonstrates good photocatalytic characteristics **[21]**.

The bandgap of Anatase TiO_2 is 3.2 eV, while Rutile TiO_2 has a bandgap of 3.0 eV. Brookite TiO_2 have bandgap ranges from 3.0 eV to 3.2 eV **[22]**. The Rutile form of TiO_2 is known for its thermodynamic stability, while the Anatase and Brookite phases are metastable. The latter two can readily transform into the Rutile phase when subjected to heat **[23]**. Rutile TiO_2, known for its high refractive index, is extensively utilized in white pigments. In terms of optical properties, Rutile TiO_2 is optically positive, while

Anatase TiO_2 is optically negative. Detailed physical parameters can be found in Table 2.

Table 2: 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

1.4.1 Crystal Structure of TiO_2

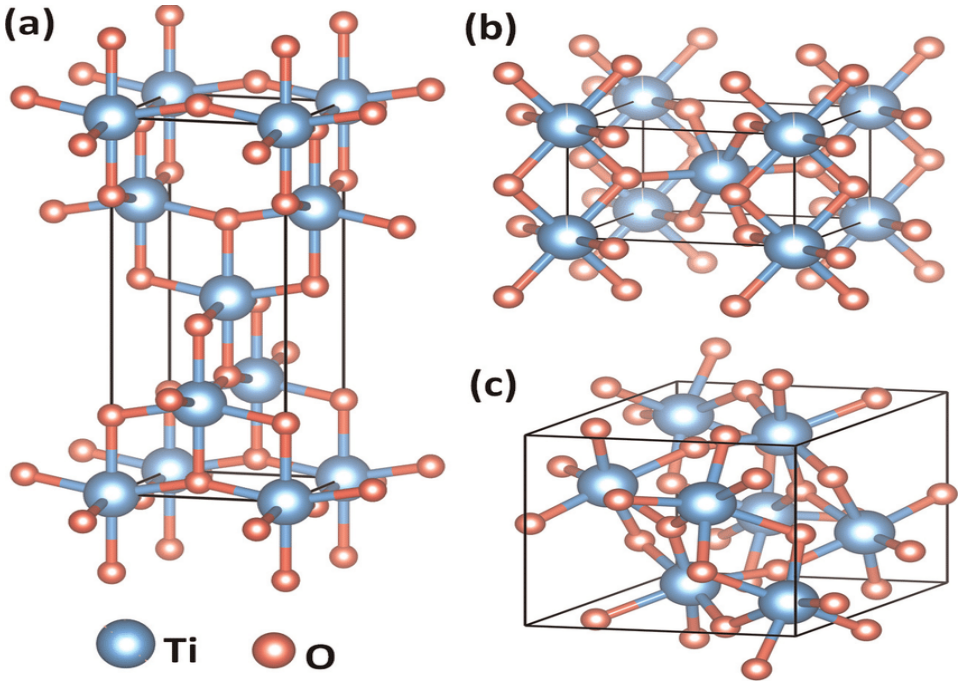


Figure 4: Unit cells of TiO_2(a) Anatase, (b) Rutile, (c) Brookite.

Rutile and Anatase both have a tetragonal crystal structure, consisting of chains of deformed TiO_2 octahedra. The Rutile phase, which is the most stable, has a unit cell containing two TiO_2 units. In this structure, Titanium cations are coordinated by six oxygen atoms, forming an octahedral arrangement. This includes two apical bonds with a length of 1.976 Å and four equatorial bonds each measuring 1.946 Å **[24]**. In the

structure of TiO_2, oxygen anions are coordinated by three titanium cations, forming a plane through two equatorial, and one apical bond. Each unit cell of the Anatase phase comprises four TiO_2 units, whereas the Brookite phase's unit cell contains eight TiO_2 units. The distance between Titanium atoms shorter in Rutile phase as compare to that in Anatase, leading to differences in mass density; Anatase is 9% less dense in comparison with Rutile.

In the coatings industry, titanium dioxide (TiO_2) is an extremely important inorganic white pigment. This prominence is owing to its superior refractive index, exceptional brightness, and high opacity. Among its forms, rutile TiO_2 is particularly favoured for its enhanced light scattering efficiency, along with its stability and durability. Additionally, TiO_2 is employed in the creation of refractive optical coatings for dielectric mirrors **[25].**

When exposed under UV light, titanium dioxide functions as a photocatalyst. Rutile is not that much active as the anatase phase for photocatalyst. In the photocatalytic process electrons in TiO_2 absorb UV radiation energy and makes transition from the valance band to the conduction band. This result into electron-hole pair formation. Usually, these free radicals react again with oxygen, water molecules, or other contaminants, and adsorbed on the surface of TiO_2 where they break down **[26].**

For many years, titanium dioxide (TiO_2) has been a key ingredient in cosmetics and sunscreens, serving as a protective agent against UV radiation. As a material with a wide band gap, TiO_2 is effective in absorbing UV rays. Sunscreen formulations typically combine both organic and inorganic UV filters, and TiO_2-based materials are particularly useful for UVB protection, often substituting organic UV filters. Moreover, TiO_2-based UV absorbers have the added benefit of providing a whitening effect upon application to the skin **[27]**.

TiO_2 is most commonly used in dye-sensitized solar cells. Third-generation solar cells, known as dye-sensitized solar cells (DSSCs), were developed in 1991 by Dr. Brian O'Regan and Professor Michael Graetzel **[28]**. The working principle of DSSC's operation is photosynthesis. Chapter 2 provides information on dye-sensitized solar cells.

1.5 Cerium Dioxide (CeO_2)

The oxide cerium is derived from the rare earth element cerium. Its chemical formula is CeO_2, and it is a powder that is somewhat yellow-white. CeO_2 is significant for its wide range of uses in many industries because of its distinct physical and chemical properties **[29].**

It's used as a catalyst and a polishing agent, and its gaining interest in the realm of renewable energy, particularly in photovoltaic technologies like DSSCs, for its potential in enhancing the efficiency and stability of these devices.

The ability of Cerium Oxide to switch between Ce(IV) and Ce(III) oxidation states is vital for its role as a catalyst and oxygen buffer. This redox flexibility allows it to participate in oxidation-reduction reactions, making it useful in applications such as catalytic converters for automotive exhaust systems, where it helps in reducing harmful emissions.

1.5.1 Crystal Structure of CeO_2

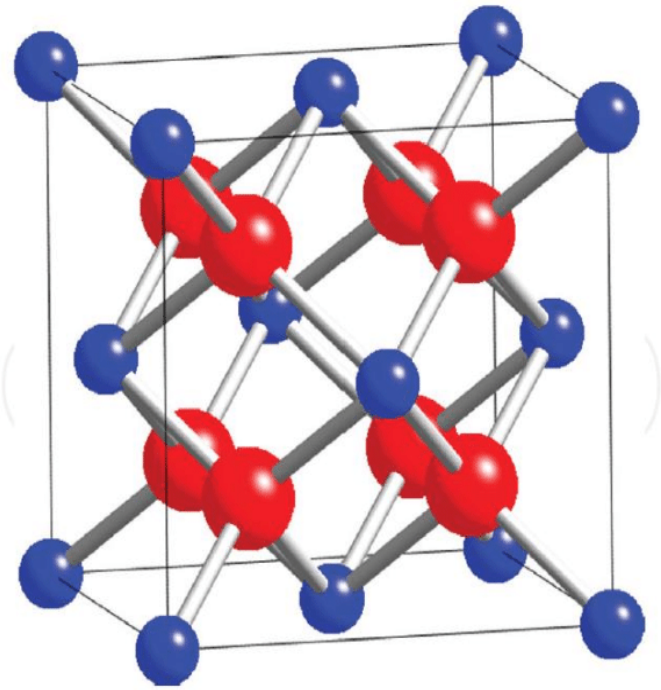


Figure 5: The pure CeO_2 crystal structure. Ce^{4+} and $O^{2-}$are shown in blue and red spheres respectively **[30]**.

This crystal structure is the basis for many of Cerium Oxide's properties. In a cubic fluorite structure, oxygen atoms are arranged in a face-centred cubic lattice with cerium ions filling all the cubic sites. This structure is particularly stable and can accommodate a high degree of oxygen vacancy without collapsing, which is crucial for its catalytic activity.

Cerium oxide (CeO2), commonly known as Ceria, has a wide range of applications across various industries due to its unique chemical and physical properties.

In the field of electronics and optics, cerium oxide is used as a polishing agent for glass, due to its effectiveness in removing surface imperfections at the microscopic level. It's commonly used for polishing high-precision lenses, mirrors, and other optical components, as well as in the semiconductor industry for planarizing silicon wafers **[31]**.

Due to its high oxygen ion conductivity, cerium oxide is used in solid oxide fuel cells (SOFCs) and as a material for electrolytes in other types of fuel cells. It is also being explored for use in battery technologies, especially in the development of lithium-ion batteries **[32]**.

CeO_2 can be utilized as an electron transport layer in DSSCs. Its high electron mobility and stability help in the efficient transport of electrons from the dye molecule back to the anode, reducing recombination losses and improving the cell's efficiency **[33]**.

1.6 Cadmium Sulfide (CdS)

Solid yellow cadmium sulphide (CdS) is an inorganic substance. It is a semiconductor with a wide range of uses, mostly in electronics, photonics, and solar cells. It typically takes the form of crystals or a bright yellow powder. One of the reasons CdS can be useful in many optical applications due to its significant absorption ability in the visible portion of the electromagnetic spectrum. Some basic properties of cadmium sulphide are listed below **[34]**.

Table 3: Physical properties of the CdS.

Property	Value
Physical state and appearance	Solid. (Solid powder.)
Molecular Weight	144.46 g/mole
Color	Yellow or brown
Melting Point	Sublimes. (980°C or 1796°F)
Specific Gravity	4.82 g/cm^3
Solubility	Insoluble in hot and cold water
Direct bandgap	2.42 eV

1.6.1 Crystal Structure of CdS

There are two naturally occurring forms of cadmium sulphide (CdS): Hawleyite and Greenockite. These two forms have different crystal structures. Whereas Hawleyite has the Sphalerite (Zinc blende) structure, Greenockite produces hexagonal crystals with the Wurtzite structure.

Greenockite structure (Wurtzite structure)

The mineral was named after the Scottish town of Greenock, where it was first discovered. Greenockite has a hexagonal crystal system. In the hexagonal system, Greenockite's unit cell is defined by these axes. The lattice structure of CdS in the Greenockite form can be described as a series of layers, with cadmium and sulfur atoms alternating in each layer. The atoms are arranged in such a way that each cadmium atom is surrounded by four sulfur atoms, forming a tetrahedron, and vice versa.

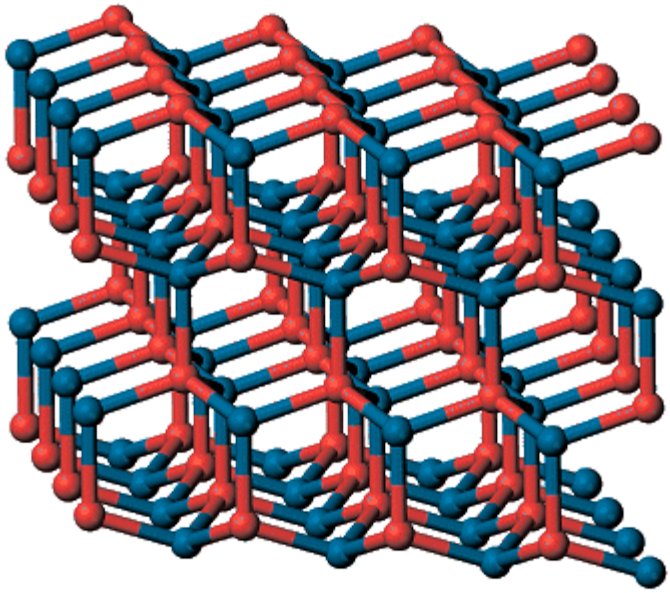


Figure 6: Greenockite (Hexagonal) structure (blue shows Cd atoms, orange shows S atoms) **[35]**.

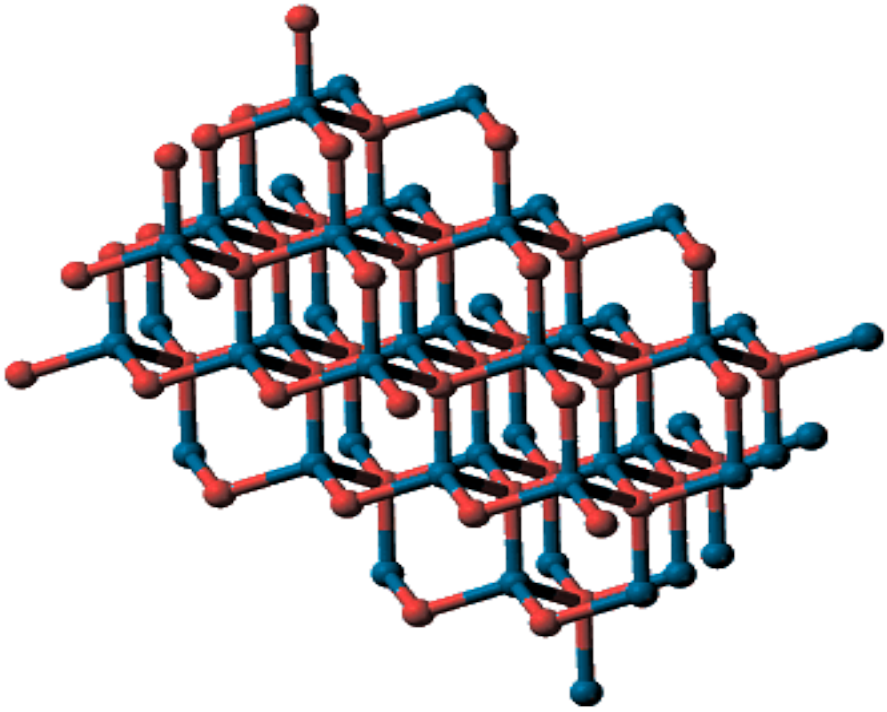


Figure 7: Hawleyite (cubic) (blue shows Cd atoms, orange shows S atoms) **[35]**.

Cadmium sulfide (CdS) is a versatile compound with several applications, particularly in the fields of electronics, optics, and photovoltaics. It's important to note

cadmium is a toxic heavy metal, and its compounds, including CdS, pose environmental and health risks if not handled and disposed of properly.

CdS is used in thin-film solar cells, often as a window layer. In these cells, it forms a heterojunction with another semiconductor, such as copper indium gallium selenide (CIGS) or cadmium telluride (CdTe). The band gap of CdS, which is about 2.4 eV, makes it suitable for absorbing visible light **[36]**.

Due to its band gap, CdS is used in optoelectronic devices like light-emitting diodes (LEDs), photodetectors, and lasers. Its ability to convert light into electrical signals and vice versa makes it suitable for these applications **[37-39]**.

1.7 Copper Oxide (II) (CuO)

An important inorganic substance having a wide range of uses in disciplines including chemistry, physics, and materials science is copper(II) oxide (CuO). The semiconductor CuO belongs to the transition metal oxide group and has a small bandgap, is a p type. It has monoclinic structure and other interesting characteristics including excellent stability, photovoltaic properties, super thermal conductivity, and antibacterial property. **[40]**.

CuO typically appears as a black powder or as black to brownish-black crystals. CuO is a semiconductor with a band gap of approximately 1.2 to 1.9 eV, which can vary based on the method of preparation and presence of impurities. CuO exhibits antiferromagnetic properties, meaning the magnetic moments of atoms or molecules usually align in opposite directions, leading to no net magnetic moment in the absence of an external magnetic field. CuO has a relatively high thermal stability and shows good thermal conductivity.

1.7.1 Crystal Structure of CuO

CuO is the chemical formula for copper (II) oxide, sometimes referred to as cupric oxide. It has a monoclinic crystal structure, a kind of crystal system with three unequally sized axes—two of which are perpendicular to one another and the third of which is inclined.

The Cu-O bonds in this structure are relatively short, which is indicative of strong ionic-covalent bonding. The unique arrangement of the Cu and O atoms in the CuO lattice leads to interesting physical properties, including anti-ferromagnetic behaviour and potential applications in materials science, such as in semiconductors, catalysts, and as a precursor for the synthesis of other copper-containing compounds.

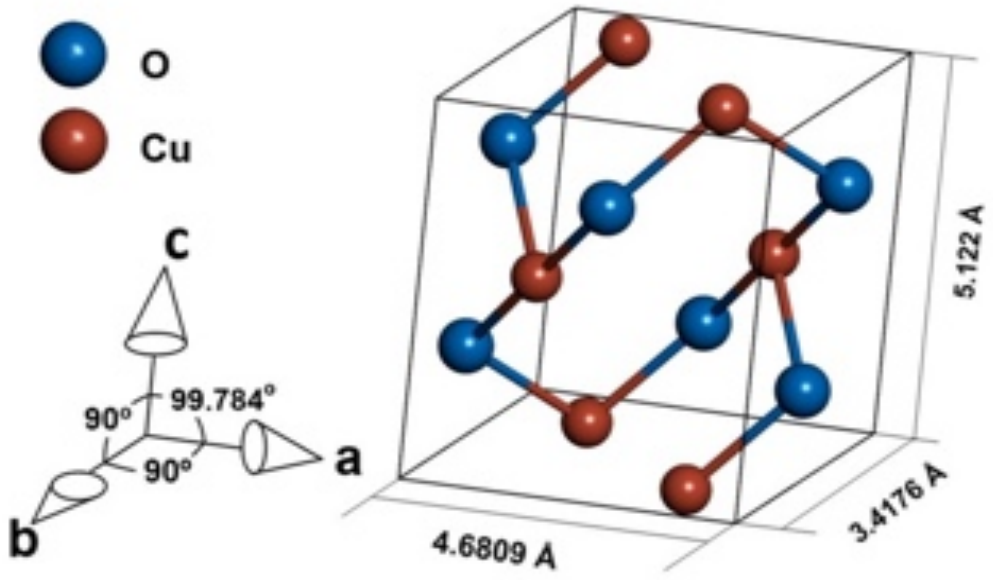


Figure 8: Crystal Structure of CuO **[41]**.

Copper(II) oxide (CuO) is a versatile material with a variety of applications across different fields due to its unique properties.

Application:

Due to its semiconducting properties, CuO finds applications in electronic devices. It is used in the production of semiconductor components such as diodes, transistors, and solar cells **[42]**.

CuO plays a crucial role in the fabrication of high-temperature superconductors, especially those based on the $YBa_2Cu_3O_{7}$-x compound, where layers of CuO are integral to the superconducting properties **[43]**.

CuO is used in battery electrodes. It has been explored for use in lithium-ion batteries due to its high specific capacity as a battery anode material **[44]**.

1.8 Zirconium Dioxide (ZrO_2)

Zirconium dioxide, often referred to as Zirconia (ZrO_2), is a highly durable refractory material. It is well recognized for its electrical and mechanical capabilities, ZrO_2 is extensively researched ceramic material **[45]**. ZrO_2 possesses excellent properties which include a high melting point, a significant refractive index, robust thermal and chemical stability, substantial fracture toughness, great density, and strong resistance to oxidation **[46].**

Zirconia exists in three distinct crystalline forms: Monoclinic, Tetragonal, and Cubic. At ambient temperature, it is typically in the Monoclinic phase, but as the temperature rises, it transitions to the Tetragonal and subsequently to the Cubic phase. The Cubic phase of ZrO_2 can be maintained at room temperature by adding different oxides, such as MgO, CaO, and Y_2O_3 **[47]**. While ZrO_2 is essentially an insulating material with a 6 eV band gap, it can exhibit semiconductor properties when prepared through the sol-gel method or when doped with transition metals **[48]**.

1.8.1 Crystal Structure of ZrO_2

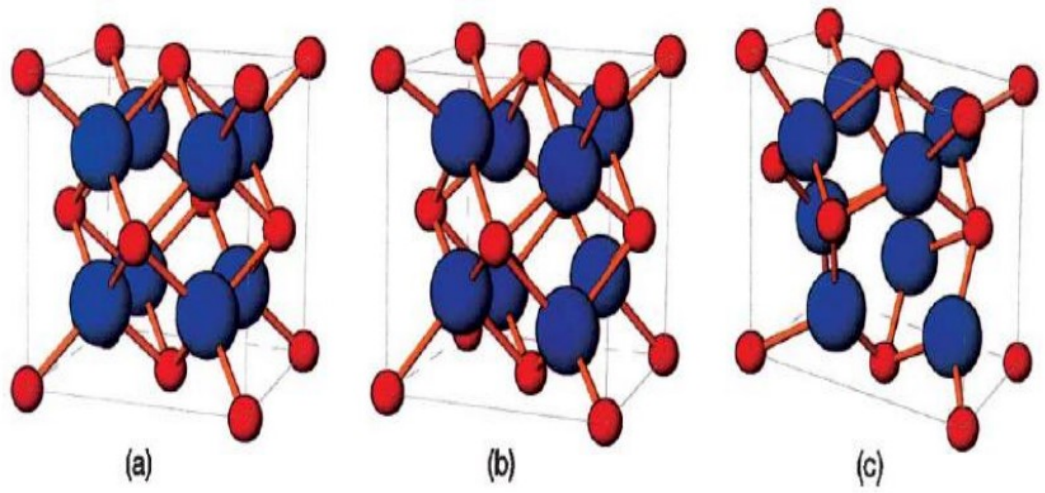


Figure 9: (a) Cubic ZrO_2, (b) Tetragonal ZrO_2, (c) Monoclinic ZrO_2.

Zirconium dioxide (ZrO_2) is found in three distinct crystalline forms: Monoclinic, Tetragonal, and Cubic. Among these, Monoclinic and Cubic represent stable phases, while the Tetragonal form is a metastable phase of ZrO_2. The various phases of ZrO_2 are depicted in Figure 9 **[49].**

Zirconia is known for its exceptional thermal, electrical, optical, and mechanical characteristics. These attributes make it an ideal material for a variety of applications, including refractory materials, insulation, catalysts, anti-corrosion coatings, oxygen sensors, fuel cell membranes, susceptors in high-temperature induction furnaces, and clinical uses.

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