



Sudan University of Science and Technology



College of Graduate Studies

Synthesis and Characterization of Zinc (II) Oxide Using Different Alkoxides

تخليق وتشخيص اوكسيد الزنك (II) باستخدام الكوكسيديات مختلفة

A Thesis Submitted in Partial Fulfillment for the Requirement of the Degree
of M.Sc. in Chemistry

By:

Nada Seidahmed Abdallah
B.Sc. (HONORS) in Chemistry

Supervisor: Dr. Mohamed Sulieman Ali Altoum

May-2017

الاستفتاح

بسم الله الرحمن الرحيم

قال تعالى:

(وقل رب زدني علما)

(طه:114)

صدق الله العظيم

Dedication

To:

**My father
My mother
My brothers and sisters**

Acknowledgement

All praise is due to allah the most gracious the most merciful for giving me health and patience to accomplish this work. I would like to express my deep thanks to my supervisor dr. Mohamed Sulieman Ali Altoum for his continuous encouragement and support also i extend my thanks to everyone helped me in completing this project.

Abstract

In this study zinc oxide was prepared by sol-gel method from zinc alkoxide, zinc alkoxide was obtained using sodium alkoxides and zinc chloride, the shape, structure and concentration of the obtained products were characterized by infra-red spectroscopy (ir), x-ray powder diffraction (xrd). the ir-spectra of zinc oxide and alkoxides were agreed well to their literature review, also the x-ray diffraction of zinc oxide showed the characteristic peaks of the oxide, the percentage of zinc in oxide was 79%.

مستخلص البحث

في هذه الدراسة تم تحضير اوكسيد الزنك (II) بطريقه صول-جل من الكوكسيد الزنك, الكوكسيد الزنك تم تحضيره من الكوكسيد الصوديوم وكلوريد الزنك , الشكل والتركيز للمركبات الناتجه تم تشخيصها باستخدام جهاز الاشعه تحت الحمراء , وجهاز الاشعه السينيه التفريقيه. طيف الاشعه تحت الحمراء لاوكسيد والكوكسيد الزنك يتطابق مع الدراسات السابقه. كما ان الاشعه السينيه التفريقيه لاوكسيد الزنك وضحت القمم المميزه لهذا الاوكسيد , والنسبه المئويه للزنك في الاوكسيد 79%.

Tables of Contents

Title	Pages No
الاستفتاح	I
Dediction	II
Acknowledgement	III
Abstract	IV
المستخلص	V
Table Of Contents	VI-VIII
List Of Figures	IX
Chapter One-Introduction	
1.1alkoxide	1
1.1.1. Structural Properties of Alkoxides	2
1.1.2. Uses of Alkoxides	3
1.1.2.1 Catalysis	3
1.1.3. Synthesis of Simple Metal Alkoxides	4
1.1.3.1. Synthesis from the Metal And Alcohol	4
1.1.3.2. Synthesis from the Metal Halide and Alcohol	5
1.1.3.3. Synthesis from the Metal Hydroxide or Oxide, and Alcohol	5
1.1.3.4. Synthesis by Alcohol Exchange Reactions	6
1.1.3.5. Transesterification Reactions for Alkoxide Synthesis	6
1.1.3.6. Synthesis From the Metal Dialkylamide and Alcohol	6
1.1.3.7. Miscellaneous Methods	6
1.1.4. Reactions of Alkoxides	6
1.2.Zinc Alkoxide	7
1.2.1. Synthesis of Zinc Alkoxide	7
1.2.2. Properties of Zinc Alkoxide	8
1.3. Oxides	8
1.3.1. Reactivity	8
1.3.1.1acidic Oxides	9
1.3.1.2. Basic Oxides	9
1.3.1.3.Amphoteric Oxides	10
1.3.1.4. Neutral Oxides	11
1.3.1.5. Compound Oxides	11
1.3.2. Preparation of Oxides	12
1.3.2.1. By Direct Heating of An Element with Oxygen	12

1.3.2.2. By Reaction of Oxygen with Compounds at Higher Temperatures	12
1.3.2.3. By Thermal Decomposition of Certain Compounds Like Hydroxides, Carbonates, and Nitrates	12
1.4 .Zinc Oxide	13
1.4.1.Properties	13
1.4.1.1. Physical Properties.	13
1.4.1.2. Chemical Properties	14
1.4.1.3. Crystal Structures	14
1.4.1.4. Toxicology	16
1.4.1.5.Bulk Zinc Oxide	16
1.4.2. Synthesis of Zinc Oxide	17
1.4.2.1. Industrial Production Methods	17
1.4.2.1.1.Pyrometallurgical Synthesis	17
1.4.2.1.1.1. Direct or American Process.	17
1.4.2.1.1.2. Indirect or French Process.	18
1.4.2.1.1.3. Wet Process.	19
1.4.2.1.1.4. The Spray Pyrolysis Process.	20
1.4.2.1.2.Hydrometallurgical Synthesis	20
1.4.2.2.Small-Scale Production Routes	21
1.4.2.2.1.Precipitation of Zn(OH) ₂ or ZnO From Aqueous Solutions of Zinc Salts	21
1.4.2.2.2.Solvent Extraction and Pyrolysis of Zinc Nitrate	21
1.4.2.2.3.Gas-Phase Synthesis	21
1.5. Applications of Zinc Oxide	22
1.5.1. Rubber	23
1.5.2.Ceramics and Concrete	24
1.5.3. Plastics and Linoleum	24
1.5.4.Pigments and Coatings	25
1.5.5.Foods and Food-Packaging Materials	25
1.5.6.Sulfur Removal	25
1.5.7.Pharmaceutical Industry and Cosmetics	25
1.6 Literature Review	26
1.7. The Aim of The Study	29
Chapter Two -Materials And Methods	

2.1. Chemicals	30
2.2. Instruments and Equipment's	31
2.4. Preparation Procedure	31
2.4.1. Preparation of Soduim Ethoxide	31
2.4.2. Preparation of Zinc Alkoxides Using (Ethanol, 2-Pr Butanol).	32
2.4.3.Preparation of Zinc(II) Oxide	32
2.5. Determination of Concentration of Zinc (II).	32
2.6. Characterization of The Zinc (Ii) Alkoxide and Zinc (II) Oxide	32
2.6.1.Fourier Transform Infrared Spectroscopy (Ft-Ir)	32
2.6.2. X-Ray Diffraction Analysis	33
2.7. Percent Zinc of Zinc Compound	33
Chapter Three- Result And Discussion	
3.1. Characterization of Zinc Oxide	34
3.1.1. X-Ray Diffraction Analysis	34
3.1.2. FT-IR Spectroscopy	35
3.2. Conclusion	38
References	39

List of Figures

Title	Pages no
Figure1.1 Alcohol Which has been Replaced by Metal	1
Figure1.2. Stick and Ball Representation of ZnO Crystal Structures	15
Figure1.3. Schematic Representation of A Wurtzitic ZnO Structure	16
Figure 1.4 Worldwide Consumption of Zinc Oxide.	22
Figure1.5. Application of ZnO	23
Figure3.1 XRD Diffraction Pattern Of ZnO	35
Figure3.2 IR Spectra of Methoxide	35
Figure 3.3 IR Spectra of Isopropoxide	36
Figure 3.4 IR Spectra of Tert Butoxide	36
Figure3.5 IR Spectra of Zinc Oxide after Calcination	37

1. Introduction

1.1 Alkoxide

An alkoxide is the conjugate base of an organic group bonded to a negatively charged oxygen atom. They can be written as RO⁻, Which R is the organic substituent, and When R is not bulky good nucleophiles and good ligands. So Alkoxides products of replacement of atoms H in hydroxyl group of the molecule of alcohol on atom of a chemical element.

Metal alkoxides, represented by a general formula M (OR) _x (M = a metal of valency x; R=alkyl or aryl group) are salt like compounds containing the alkoxide ion, RO⁻.

The alkoxide ion RO⁻ seems to have originated from the parent compound, alcohol ROH, in which the hydroxylic hydrogen has been replaced by a metal M. Thus metal alkoxides are basically formed by reactions of alcohols with metals.

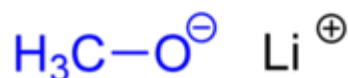
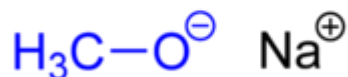
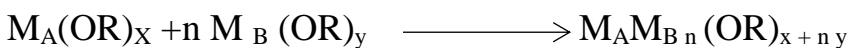


Figure 1.1 alcohol which has been replaced by metal

When a molecule of alkoxide contains only one metal the alkoxide is called homometal alkoxide whereas one containing two or more different metals is called heterometal alkoxide.

Heterometallic alkoxides are alkoxides containing two or more different kinds of metal-ions connected through oxygens of the alkoxo-ligands[1]. They are mostly prepared through one of two common routes:

a. Mixing different alkoxides in solution



For the same combination of metals and ligands, especially when both of the alkoxides are insoluble and the reaction is slow, the salt elimination reaction is preferred.

b. Mixing a metal chloride with a heterometallic alkoxide containing an alkali metalion.



Alkoxides can be categorized into three main groups on the basis of the parent alcohol structure. These are:-

- a) Normal alkoxide, RCH₂O-
- b) Secondary alkoxide, R₂CHO-
- e) Tertiary alkoxide, R₃CO-

Metal alkoxides have been formed from various types of metals, the alkali metals; alkaline earth metals, the main-group metals; transition metals; Lanthanides; and actinides' These alkoxides contain M-O- C bonds" in their molecules which are polarised in the direction due to the highly electronegative character of oxygen. The degree of polarization depends upon the electronegativity of the central metal M and the structure of the alky I or aryl group R[2]. Metal alkoxides are known to be excellent starting materials for production of metal oxides which are vital in electronics and ceramics industries for fabrication of electronics glassy and ceramics materials. Their suitability resides in the ease of removal of the organic groups in the molecules. These organic groups are easily removed in the form of volatile non-reactive products. Furthermore, because the metal is normally strongly bonded to oxygen of the alkoxide group, the metal alkoxide contains more than enough oxygen to satisfy the metals requirement in forming the oxide.

Metal alkoxides are strongly caustic and are rapidly decomposed by the humidity of air or moisture of the skin, necessitating careful handling and storage. alkoxides must be stored under cool, dry conditions, preferably under an inert atmosphere. The health hazards are dependent on the toxicity of the metal and on the oxides and alcohols formed on hydrolysis or decomposition [3].

1.1.1. Structural Properties of Alkoxides

Alkoxides have physical properties that vary according to the nature of the metal and alkoxy group. They range from non-volatile, insoluble solids (e.g. copper and zinc dialkoxides) to volatile, soluble solids (e.g. titanium and zirconium tetra alkoxides). This great variation in physical properties is due to the differing molecular complexities observed in alkoxide chemistry:

those forming large polymeric frameworks are insoluble and non-volatile whilst those forming small oligomers are generally volatile and soluble.

The formation of oligomers or larger polymeric frameworks is due to alkoxide groups bridging two or more metal centres and the tendency of metals to increase their coordination number[4]. The extent of oligomerisation is affected by:

(a) The Alkoxy Group: For a given metal the more bulky the alkoxy group, the lower the degree of association. This steric effect is demonstrated by the insoluble, non-volatile, polymeric nature of aluminium methoxide compared to the volatile, soluble, tetrameric nature of aluminium iso-propoxide.

(b) The Metal: The oxidation state of the metal determines the number of alkoxy groups present per metal which in turn affects the bridging: those of low oxidation state requiring more bridges to achieve a given coordination number than those of higher oxidation state. The size of the metal may also affect the degree of bridging as the larger the size of the metal atom, the more easily it can accommodate bulky alkoxy groups and therefore the more easily it can increase its coordination number. This effect is seen in the molecular complexities of titanium and zirconium alkoxides: for a given substituent the molecular complexity is higher for the zirconium alkoxide[5,6].

1.1.2. Uses of Alkoxides

Despite the fact that alkoxides are moisture-sensitive and thus require special handling techniques they have many industrial applications alkoxides are generally used in one or other of the following areas

- i) Catalysis
- ii) Metal oxide preparation
- iii) Glasses and ceramics

1.1.2.1. Catalysis:

The alkoxides are mainly used as catalysts or intermediates in a variety of reactions.

The catalytic behaviour of aluminium alkoxides was realised many years ago when it was observed that the ethoxide reduced aldehydes and ketones to the corresponding esters[7].

ii) Metal oxides

Alkoxides, through their ease of hydrolysis, provide a valuable route to high purity, high surface area and metal oxides.

The metal alkoxides are purified by vacuum distillation and the oxides are obtained by hydrolysis or Chemical Vapour Deposition. The alkoxides used are those whose metal oxides have catalytic activity in industrial processes[8].

iii) Glasses and ceramics

Using alkoxide is ideally suited to the preparation of small quantities of high purity materials.

Different alkoxides are blended to the required composition and then hydrolysed to produce the precursor which sinters in low temperature ranges (300-600°C) to give uniform glasses.

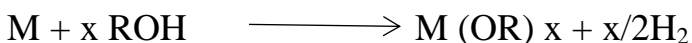
Metal alkoxides, M-OR, are excellent as precursors for metal oxides and especially for ceramics where a high elemental homogeneity is necessary [9].

1.1.3. Synthesis of Simple Metal Alkoxides

- 1) Synthesis from the metal and alcohol directly,
- 2) Synthesis from metal halide and alcohol,
- 3) Synthesis from metal hydroxide and alcohol,
- 4) Synthesis from metal oxide and alcohol,
- 5) Alcohol exchange reactions,
- 6) Transesterification reactions,
- 7) Synthesis from the metal dialkylamide and alcohol
- 8) Various other 'miscellaneous methods.

1.1.3.1. Synthesis from the Metal and Alcohol

This is the simplest method of alkoxide synthesis and involves the direct reaction of a metal with an alcohol with the evolution of hydrogen gas.



Where the metal M is one from Group I this reaction tends to be highly exothermic. The rate of the reaction depends both on the metal and on the alcohol. The rate increases with increasing electropositively of the metal and decreases with the length and branching of the alcohol. As the branching of the alkyl chain increases the acidity of the hydroxyl hydrogen decreases, due to the +I inductive effect (electron releasing effect), producing a parallel decrease in reaction rate. Reactions with tertiary alcohols can take more than several hours to go towards completion. Pure alkoxides of the alkali metals can be prepared by dissolving the metal in alcohol at reflux temperature under an inert atmosphere[10].

1.1.3.2. Synthesis from the Metal Halide and Alcohol

From the metal halide and an alcohol. This reaction appears to occur completely only for halides of electronegative elements where the hydrogen halide produced is continuously removed.



The hydrogen halide produced can be removed by refluxing or by passing an inert gas through the reaction mixture[10].

1.1.3.3. Synthesis from the Metal Hydroxide or Oxide, and Alcohol

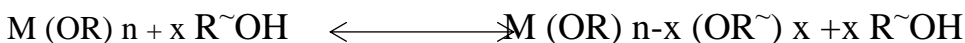
Hydroxides and oxides of several elements will react with alcohols to form alkoxides and water.



The continuous removal of water is essential to obtain good yields of the alkoxide products. This can be done by using various organic solvents which form azeotropes with water (benzene, toluene, xylene) and which can be fractionated out or separated using Dean-Stark apparatus. Although the method has fairly wide applicability there are limitations due to the boiling points of the alcohol and solvent and the acidity and steric properties of the alcohol.

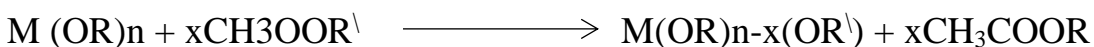
1.1.3.4. Synthesis by Alcohol Exchange Reactions

Alkoxides react with all hydroxy compounds, to some extent, to give Products where some or all of their alkoxy groups have been exchanged [11].



1.1.3.5. Transesterification Reactions for Alkoxide Synthesis

Treatment of a metal alkoxide with an ester leads to the formation of a new alkoxide and a volatile ester is produced. The method requires the product ester to be more volatile than the reagent ester [12].



1.1.3.6. Synthesis from the Metal Dialkylamide And Alcohol

This route involves the reaction of a metal dialkylamide with alcohol. Metal alkoxide and volatile dialkylamine, which can easily be removed by fractionation are produced in the reaction.



1.1.3.7. Miscellaneous Methods

There are several other methods for synthesising metal alkoxides but these are of limited applicability. They include oxidation, reduction, the use of metal alkyls and alkyl metal hydrides.

1.1.4. Reactions of Alkoxides

Metal alkoxides are generally very reactive species and the following section gives a summary of their more important reactions [13,2].

(a)Hydrolysis

Metal alkoxides are rapidly hydrolysed leading to the formation of hydroxides or hydrated oxides. e.g.



(b) Alcohol Exchange Reactions

Exchange of the alkoxy group of an alkoxide for a different alkoxy group is useful in the preparation of metal alkoxides and as such has been discussed in the section above.

(c) Reaction with Organic Acids

Organic acids react with metal alkoxides to form metal carboxylates.

(d) Meerwein-Ponndorf-Verley Reaction

The reduction of ketones by alcohols is catalysed by metal alkoxides of which aluminium alkoxides are the best. The reaction can be driven to completion by the removal of the volatile ketone formed (often acetone).

(E) Thermal Decomposition of Alkoxides

Metal alkoxides decompose on heating to the metal oxides, hydroxides or to the metal itself with the evolution of organic species. The mode of decomposition depends not only on the alkoxide but on the conditions of the pyrolysis.

(f) Other Reactions

There are many more reactions of alkoxides: some react with hydrogen halides to form metal halides or mixed alkoxy-halides; some react with esters to form new alkoxides (see transesterification above); some react with glycols to form glycolates which are often less moisture sensitive than alkoxides; some react with thiols to form thiolates.

1.2. Zinc Alkoxide

Zinc metal does not appear to react with alcohols even in the presence of catalysts like iodine, mercuric chloride and anhydrous aluminium chloride [14].

1.2.1. Synthesis of Zinc Alkoxide

a) Preparation of zinc alkoxide by the reaction of zinc chloride with lithium alkoxide

b) Preparation of zinc alkoxide by alcoholysis reaction

1.2.2. Properties of Zinc Alkoxide

These alkoxides are non-volatile and insoluble in alcohols and other organic solvents [14].

1.3. Oxides

Oxides are chemical compounds with one or more oxygen atoms combined with another element (e.g. Li_2O).

Oxide minerals are grouped into classes on the basis of the number of different types of sites they possess. Thus simple oxides are generally those with only a single cation site; they tend to have formulas like XO_2 , XO , or X_2O_3 . Multiple oxides usually contain two or more different sites, usually one with 6-coordination and one with 4-coordination; their compositions are usually expressed as XY_2O_4 .

1.3.1. Reactivity

Oxides can be reacted by acids or bases those reacted only by acids are basic oxides; those reacted only by bases are acidic oxides. Oxides that react with both acids and bases are amphoteric. Metals tend to form basic oxides, non-metals tend to form acidic oxides, and amphoteric oxides are formed by elements near the boundary between metals and non-metals (metalloids). This reactivity is the basis of many practical processes such, as the extraction of some metals from their ores in the process called hydrometallurgy.

Some oxides can react directly with water to form an acidic, basic, or amphoteric solution. An amphoteric solution is a substance that can chemically react as either acid or base. However, it is also possible for an oxide to be neither acidic nor basic. There are different properties which help distinguish between the three types of oxides. The term anhydride ("without water") refers to compounds that assimilate H_2O to form either an acid or a base upon the addition of water.

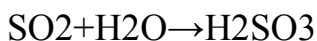
Oxides are binary compounds of oxygen with another element, e.g., CO_2 , SO_2 , CaO , CO , ZnO , BaO_2 , H_2O , etc. These are termed as oxides because

here, oxygen is in combination with only one element. Based on their acid-base characteristics oxides are classified as acidic or basic. An oxide that combines with water to give an acid is termed as an acidic oxide. The oxide that gives a base in water is known as a basic oxide.

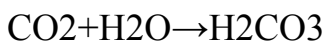
1.3.1.1 acidic Oxides

Acidic oxides are the oxides of non-metals (groups 14-17). These acid anhydrides or acidic oxides form acids with water:

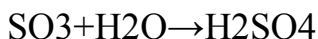
- Sulfurous Acid



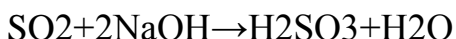
- Carbonic Acid



- Sulfuric Acid

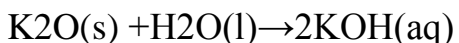


Acidic oxides are, therefore, known as acid anhydrides, e.g., sulfur dioxide is sulfurous anhydride; sulfur trioxide is sulfuric anhydride. When these oxides combine with bases, they produce salts, e.g

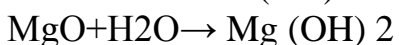
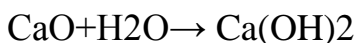


1.3.1.2. Basic Oxides

Generally Group 1 and Group 2 elements form bases called base anhydrides or basic oxides e.g.

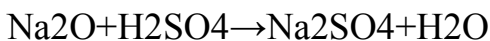
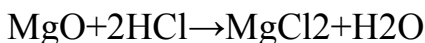


Basic oxides are the oxides of metals. If soluble in water they react with water to produce hydroxides (alkalies) e.g,



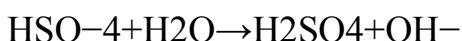
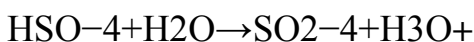


These metallic oxides are therefore, known as basic anhydrides. They react with acids to produce salts, e.g.,

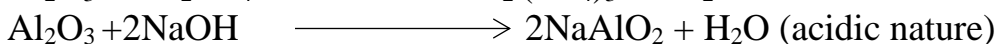
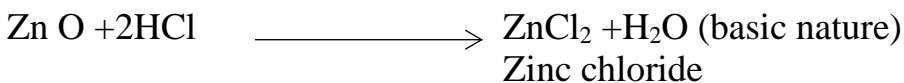
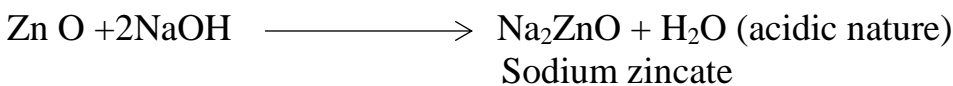


1.3.1.3. Amphoteric oxides

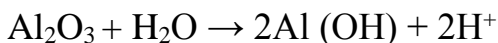
An amphoteric solution is a substance that can chemically react as either acid or base. For example, when HSO_4^- reacts with water it can make hydroxide or hydronium ions.



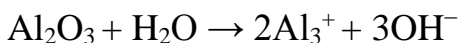
Amphoteric oxides are metallic oxides, which show both basic as well as acidic properties. When they react with an acid, they produce salt and water, showing basic properties. While reacting with alkalies they form salt and water showing acidic properties, e.g.,



Amphoteric oxides have both acidic and basic properties. A common example of an amphoteric oxide is aluminum oxide. In general, amphoteric oxides form with metalloids, Example with acidic properties:



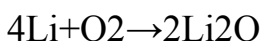
Example with basic properties:



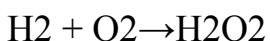
1.3.1.4. Neutral Oxides

These are the oxides, which show neither basic nor acidic properties, that is, they do not form salts when reacted with acids or bases, e.g., carbon monoxide (CO); nitrous oxide (N₂O); nitric oxide (NO), etc., are neutral oxides.

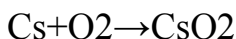
Oxides: Group 1 metals react rapidly with oxygen to produce several different ionic oxides, usually in the form of M₂O. With the oxygen exhibiting an oxidation number of -2.



Peroxides: Often Lithium and Sodium reacts with excess oxygen to produce the peroxide, M₂O₂. with the oxidation number of the oxygen equal to -1.



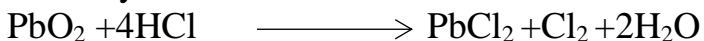
Superoxides: Often Potassium, Rubidium, and Cesium react with excess oxygen to produce the superoxide, MO₂. With the oxidation number of the oxygen equal to -1/2.



Peroxide is a metallic oxide which gives hydrogen peroxide by the action of dilute acids. They contain more oxygen than the corresponding basic oxide, e.g., sodium, calcium and barium peroxides.



Dioxides like PbO₂ and MnO₂ also contain higher percentage of oxygen like peroxides and have similar molecular formulae. These oxides, however, do not give hydrogen peroxide by action with dilute acids. Dioxides on reaction with concentrated HCl yield Cl₂ and on reacting with concentrated H₂SO₄ yield O₂.



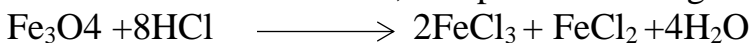
1.3.1.5. Compound Oxides

Compound oxides are metallic oxides that behave as if they are made up of two oxides, one that has a lower oxidation and one with a higher oxidation of the same metal, e.g.,

Red lead: $\text{Pb}_3\text{O}_4 = \text{PbO}_2 + 2\text{PbO}$

Ferro-ferric oxide: $\text{Fe}_3\text{O}_4 = \text{Fe}_2\text{O}_3 + \text{FeO}$

On treatment with an acid, compound oxides give a mixture of salts.

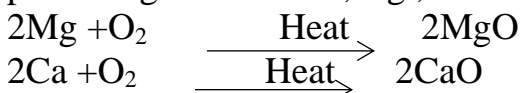


Ferro-ferric oxide \longrightarrow ferric chloride + ferrous chloride

1.3.2. Preparation of Oxides

1.3.2.1. By Direct Heating of an Element with Oxygen

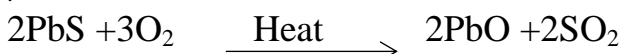
Many metals and non-metals burn rapidly when heated in oxygen or air, producing their oxides, e.g.,



1.3.2.2. By Reaction of Oxygen with Compounds at Higher Temperatures

At higher temperatures, oxygen also reacts with many compounds forming oxides, e.g.,

- Sulphides are usually oxidized when heated with oxygen



- When heated with oxygen, compounds containing carbon and hydrogen are oxidized.



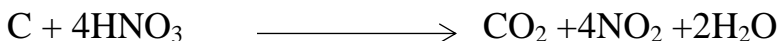
1.3.2.3. By Thermal Decomposition of Certain Compounds like Hydroxides, Carbonates, and Nitrates



1.3.2.4. By oxidation of some metals with nitric acid



1.3.2.5. By oxidation of some non-metals with nitric acid



1.4. Zinc Oxide

Zinc oxide, with its unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photostability, is a multifunctional material. In materials science, zinc oxide is classified as a semiconductor in group II-VI, whose covalence is on the boundary between ionic and covalent semiconductors. A broad energy band (3.37 eV), high bond energy (60 meV) and high thermal and mechanical stability at room temperature make it attractive for potential use in electronics, optoelectronics and laser technology. The piezo- and pyroelectric properties of ZnO mean that it can be used as a sensor, converter, energy generator and photocatalyst in hydrogen production. Because of its hardness, rigidity and piezoelectric constant it is an important material in the ceramics industry, while its low toxicity, biocompatibility and biodegradability make it a material of interest for biomedicine and in pro-ecological systems.

The variety of structures of nanometric zinc oxide means that ZnO can be classified among new materials with potential applications in many fields of nanotechnology. Zinc oxide can occur in one- (1D), two- (2D), and three-dimensional (3D) structures. One-dimensional structures make up the largest group, including nanorods, -needles, -helixes, -springs and -rings -ribbons, -tubes -belts, -wires and -combs. Zinc oxide can be obtained in 2D structures, such as nanoplate/nanosheet and nanopellets. Examples of 3D structures of zinc oxide include flower, dandelion, snowflakes, coniferous urchin-like, etc. ZnO provides one of the greatest assortments of varied particle structures among all known materials [15].

1.4.1. Properties

1.4.1.1. Physical Properties.

Zinc oxide is a fine white powder that turns yellow when heated above 300 °C. It absorbs UV light at wavelengths below 366 nm. Traces of monovalent or trivalent elements introduced into the crystal lattice impart semiconducting properties [16]. The elementary particles of ZnO obtained by the thermal method may be granular or nodular (0.1–5 µm) or acicular (needle-shaped). Some physical Properties are given below:

Density	5.65–5.68 g/cm ³
Refractive index	1.95–2.1

<i>mp</i>	1975 °C
Heat capacity	
25 °C	40.26 J mol ⁻¹ K ⁻¹
100 °C	44.37 J mol ⁻¹ K ⁻¹
1000 °C	54.95 J mol ⁻¹ K ⁻¹
Thermal conductivity	25.2 W m ⁻¹ K ⁻¹
Crystal structure	hexagonal, wurtzite
Mohs hardness	4–4.5

1.4.1.2. Chemical Properties

Zinc oxide is amphoteric; it reacts with organic and inorganic acids, and also dissolves in alkalis and ammonia solution to form zincates. It combines readily with acidic gases (e.g., CO₂, SO₂, and H₂S). It reacts at high temperatures with other oxides to form compounds such as zinc ferrites[17].

1.4.1.3. Crystal Structures

Most of the group-II-VI binary compound semiconductors crystallize in either cubic zinc-blende or hexagonal wurtzite structure where each anion is surrounded by four cations at the corners of a tetrahedron, and vice versa. This tetrahedral coordination is typical of *sp*³ covalent bonding, but these materials also have a substantial ionic character. ZnO is a II-VI compound semiconductor whose ionicity resides at the borderline between covalent and ionic semiconductor. The crystal structures shared by ZnO are wurtzite (*B*₄), zinc blende (*B*₃), and rocksalt (*B*₁), as schematically shown in Fig. 1. At ambient conditions, the thermodynamically stable phase is wurtzite. The zinc-blende ZnO structure can be stabilized only by growth on cubic substrates, and the rocksalt NaCl structure may be obtained at relatively high pressures[18,19].

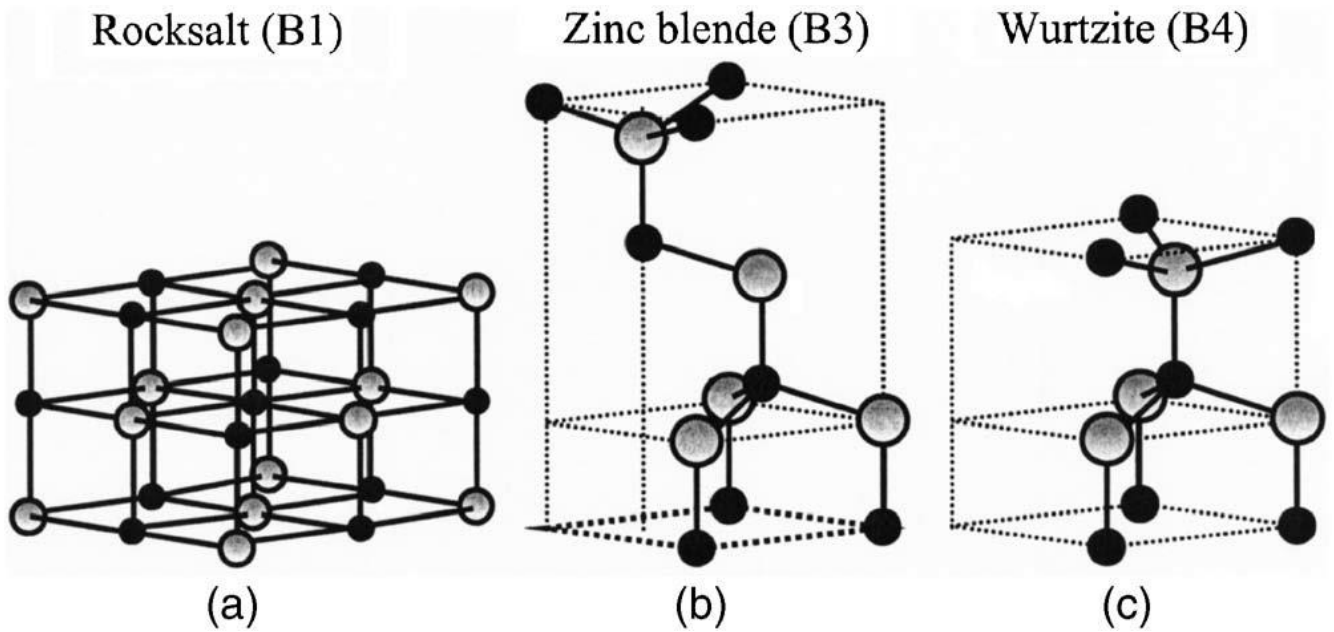


Figure 1.2. Stick and ball representation of ZnO crystal structures: (a) cubic Rocksalt (*B1*), (b) cubic zinc blende (*B3*), and (c) hexagonal wurtzite (*B4*). The shaded gray and black spheres denote Zn and O atoms, respectively.

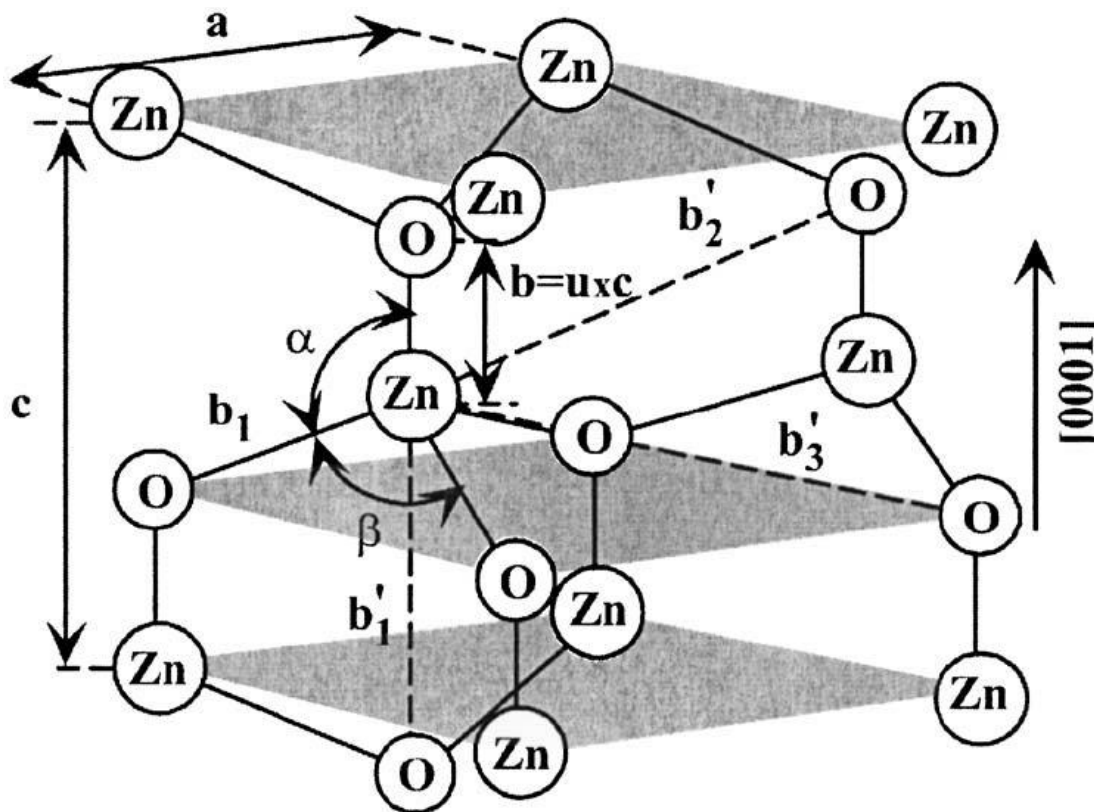


Figure 1.3. Schematic representation of a wurtzite ZnO structure

1.4.1.4. Toxicology

Zinc oxide is generally categorized as a non-toxic material. Zinc oxide does not cause skin and eye irritation and there is no evidence of carcinogenicity, genotoxicity and reproduction toxicity in humans. However, the powder can be hazardous by inhalation or ingestion because it causes a condition known as zinc fever or zinc ague. The symptoms of this syndrome are chills, fever, cough, and tightness in the chest. Therefore appropriate safety precautions should be observed when preparing, packaging, transporting and handling ZnO [20].

1.4.1.5. Bulk zinc oxide

As mentioned earlier, most of the bulk ZnO in the world is produced by either the “French” or “American” processes. The specific surface area varies between 1 and 10 m² g⁻¹ depending on process used. Such grades of ZnO are not considered as “active” due to their low specific surface area.

Highly crystalline particles are formed during the high-temperature manufacturing process [20].

1.4.2. Synthesis of Zinc Oxide

The synthetic processes for ZnO may be divided into two groups: low cost bulk industrial methods and high cost laboratory methods.

About 1–2% of zinc oxide is produced by the wet process, 10–20% by the direct process, and the remainder by the indirect process.

In the early days, the raw materials were mainly zinc ores or concentrates for the direct process, or metal from zinc producers for the indirect process. Nowadays, zinc oxide manufacturers mainly use residues and secondary zinc. This fact, combined with the demand for chemical purity imposed by the users, means that processes have had to be modified and a number of purification techniques are used [20].

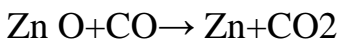
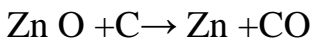
1.4.2.1. Industrial Production Methods

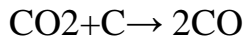
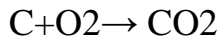
Industrially, most ZnO is produced by pyrometallurgical methods (e.g. the indirect process, the direct process, or spray pyrolysis) or by hydrometallurgical methods. Zinc oxide can also be produced as a by-product of some chemical reactions such as in the production of sodium dithionite. Generally, the selection of the production process is based on the zinc-containing raw material to be consumed. Each process produces grades of ZnO with relatively different properties and hence different applications [20].

1.4.2.1.1. Pyrometallurgical Synthesis

1.4.2.1.1.1 Direct or American Process.

The direct process is noted for its simplicity, low cost, and excellent thermal efficiency. It consists of an initial high-temperature reduction (1000–1200 °C) of a zinc-containing material (as oxide), the reducing agent being coal. Reduction takes place according to Boudouard's equations:





The zinc vapor and the CO gas are then oxidized to zinc oxide and carbon dioxide above the reaction bed or at the furnace exit. Various zinc containing materials are used, e.g., zinc concentrates, metallization residues, byproduct zinc hydroxide, and above all zinc dross from casting furnaces or galvanizing. The dross must first be treated to remove chloride and lead by heating at ca. 1000 °C in rotary kilns. Only rotary kilns are now used for the direct process; the use of static furnaces has been discontinued. The zinc content of raw materials is between 60 and 75 %. There are two types of rotary kiln:

1) One type is a long (ca. 30 m), fairly narrow (2.5 m diameter) kiln, heated by gas or oil. The raw material (a mixture of zinc-containing material and coal) is charged continuously either countercurrent or cocurrent to the combustion gases. The residues, which still contain some zinc and unburned coal, leave the furnace continuously at the end opposite to the feed end. The excess coal is sieved out and recycled. The combustion gases, containing zinc vapor, ZnO, and CO, pass into a chamber where oxidation is completed and large particles of impurities settle out. The gases are then cooled in a heat exchanger or by dilution with air. The zinc oxide is collected in bag filters.

2) The second type of rotary kiln is shorter (5 m) and has a larger diameter (ca. 3 m). Charging is continuous, but the dezincified residues are removed batchwise. In both cases, operating conditions are controlled to obtain a high yield and to give the required particle shape and size. Provided no contamination is introduced, chemical purity is determined solely by the composition of the raw materials used [21,22].

1.4.2.1.1.2. Indirect or French Process.

The zinc is boiled, and the resulting vapor is oxidized by combustion in air under defined conditions. The crystallographic and physical properties of the ZnO can be controlled by adjustment of the combustion conditions (e.g., flame turbulence and air excess). The chemical composition of the ZnO is solely a function of the composition of the zinc vapor. Many types of furnace are available to produce vapor of the required purity from various raw materials and obtain a high yield of zinc. Pure zinc (super high grade, SHG; high grade, HG) or, to an increasing extent, metal residues (e.g., scrap

zinc, die casting dross, or galvanizer's dross) are used as raw materials. Various liquid- or vapor-phase separation techniques are used for separating Cd, Pb, Fe, and Al from zinc metal before it is oxidized.

1) Muffle Furnaces or Retorts of Graphite or Silicon Carbide. The metal is fed into the furnace either batchwise as a solid or continuously as a liquid. The heat of vaporization is supplied by heating the outside of the retort with a burner. The nonvolatile residues (iron and lead in the case of dross from smelting) accumulate in the retort and must be removed at intervals. This is facilitated by tipping the retorts.

2) Fractional Distillation. The vapor, containing Cd, Pb, Fe, Al, and Cu, can be purified by fractional distillation in columns (New Jersey Zinc Co.) with silicon carbide plates. Oxidation takes place at the exit of the column.

3) Furnaces with Two Separate Chambers. The metallic raw material, which can be in large pieces, is fed into the first chamber where it melts. This is connected to the second, electrically heated chamber where distillation takes place in the absence of air.

The nonmetallic residues are removed at the surface of the melting chamber. Impurities, such as Fe, Al, and some of the Pb, accumulate in the distillation chamber and are periodically removed in the liquid state. The last traces of lead are then removed by fractional distillation.

4) Smelting Process in a Rotary Kiln. Indirect zinc oxide is also made by smelting in a rotary kiln, starting from the same raw materials. Melting, distillation, and part of the oxidation all take place in the same zone, allowing utilization of a large part of the heat of combustion of the zinc. By controlling the temperature and partial pressures of carbon dioxide and oxygen, the impurity content (Pb) can be limited and the shape and size of the ZnO particles can be adjusted, though to a lesser extent than in the other processes[23,24].

1.4.2.1.1.3. Wet Process.

Zinc oxide is also produced industrially from purified solutions of zinc sulfate or chloride by precipitating the basic carbonate, which is then washed, filtered, and finally calcined. This method produces a grade of zinc oxide with a high specific surface area. Products of this type are also obtained from waste hydroxides which are purified by a chemical route[25].

1.4.2.1.1.4. The Spray Pyrolysis Process.

In this process a solution of thermally-decomposable zinc-bearing salt is atomized and then thermally decomposed to ZnO in a spray pyrolysis tower, or similar apparatus. A high specific surface area is attainable, often $>12 \text{ m}^2 \text{ g}^{-1}$. Material produced by this method is homogenous with uniform particle shape and narrow size distribution and controlled purity. Suitable precursors are aqueous solutions of a zinc salt such as zinc acetate, formate, carboxylate, nitrate or sulfate. Organic salts of zinc may be preferred to inorganic salts because of their lower decomposition temperatures [25].

1.4.2.1.2. Hydrometallurgical Synthesis

Hydrometallurgical processes currently dominate the production of zinc metal but are not as popular for the production of ZnO. One reason is that the ZnO they produce is often less pure and may contain a significant amount of water; another is that the particle morphology may be irregular and porous, unlike the equiaxed or blocky crystalline form of the pyrometallurgical grades. On the other hand, hydrometallurgical grades of ZnO are cheaper to produce and may have a high specific surface area and chemical reactivity, which may be desirable in some applications. The term 'active zinc oxide' is widely used to denote ZnO with very high specific surface area and chemical reactivity. Many of the industrial hydrometallurgical processes for zinc or ZnO production use a significant proportion of zinc-containing wastes such as the zinc ash from hot-dip galvanizing plants as input materials due to their availability and relatively lower prices. In these processes, zinc-containing compounds are precipitated from aqueous solution, separated and then converted to ZnO by calcination. Direct precipitation of ZnO from aqueous solution at elevated temperatures is also possible. Zinc oxide produced via wet chemical processes can be categorized into three main groups: (1) ZnO produced as a by-product of the production of sodium dithionate, (2) ZnO made by the reaction of a zinc salt such as zinc sulfate and a base such as ammonium or sodium hydroxide, followed by calcination or drying of the $\text{Zn}(\text{OH})_2$ or ZnO produced, and (3) ZnO produced by a two-step reaction of zinc salts and carbon-containing bases such as sodium carbonate, ammonium bicarbonate or urea followed by calcination or alkaline treatment of the resultant basic zinc carbonate [26].

1.4.2.2. Small-Scale Production Routes

There are a large number of techniques available for the production of ZnO in small quantities or in a laboratory context. Some of these are mentioned below.

1.4.2.2.1. Precipitation of Zn (OH)₂ or ZnO from Aqueous Solutions of Zinc Salts

A typical one-step process for this type of wet-chemical process is based on Reaction:



However specific surface area of the grades produced by Reaction is generally limited to <30 m² g⁻¹ which, while higher than that of ZnO produced by the pyrometallurgical processes, is still not as high as that of 'active' ZnO[27].

1.4.2.2.2. Solvent Extraction and Pyrolysis of Zinc Nitrate

A method to produce ZnO has been patented that includes an organic solvent extraction stage to extract zinc out of zincontaining materials selectively, stripping of the organic phase with nitric acid to produce zinc nitrate and finally decomposition of the Zn(NO₃)₂ at a temperature above 200 °C to produce pure ZnO, An important aspect of this process is that the nitric acid is then regenerated by aqueous scrubbing of the gases produced by decomposition[28].

1.4.2.2.3. Gas-Phase Synthesis

Gas phase synthesis is generally conducted in a closed chamber. The synthesis is performed within a temperature range of 500–1500 °C. Some common techniques include vapor phase transport (VPT) including vapor–solid (VS) and vapor–liquid–solid (VLS) growth, CVD, physical vapor deposition, MOCVD, thermal oxidation of pure Zn and condensation, microwave assisted thermal decomposition, seeded vapor phase (SVP)

method, hydride or chloride vapor phase deposition (HVPE) . ZnO nanorods can also be formed by an arc-discharge technique [29, 30].

1.5. Applications of Zinc Oxide

Because of its diverse properties, both chemical and physical, zinc oxide is widely used in many areas. It plays an important role in a very wide range of applications, ranging from tyres to ceramics, from pharmaceuticals to agriculture, and from paints to chemicals. Figure 4 shows worldwide consumption of zinc oxide by region.

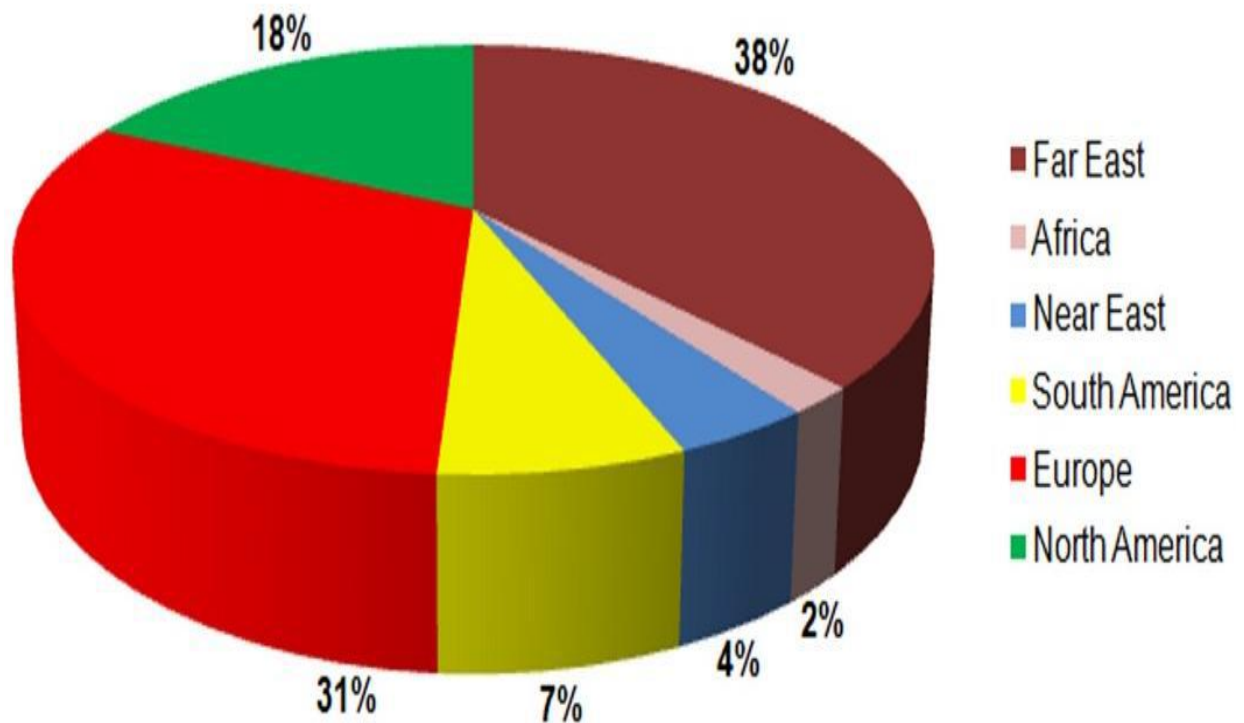


Figure 1.4. Worldwide consumption of zinc oxide.

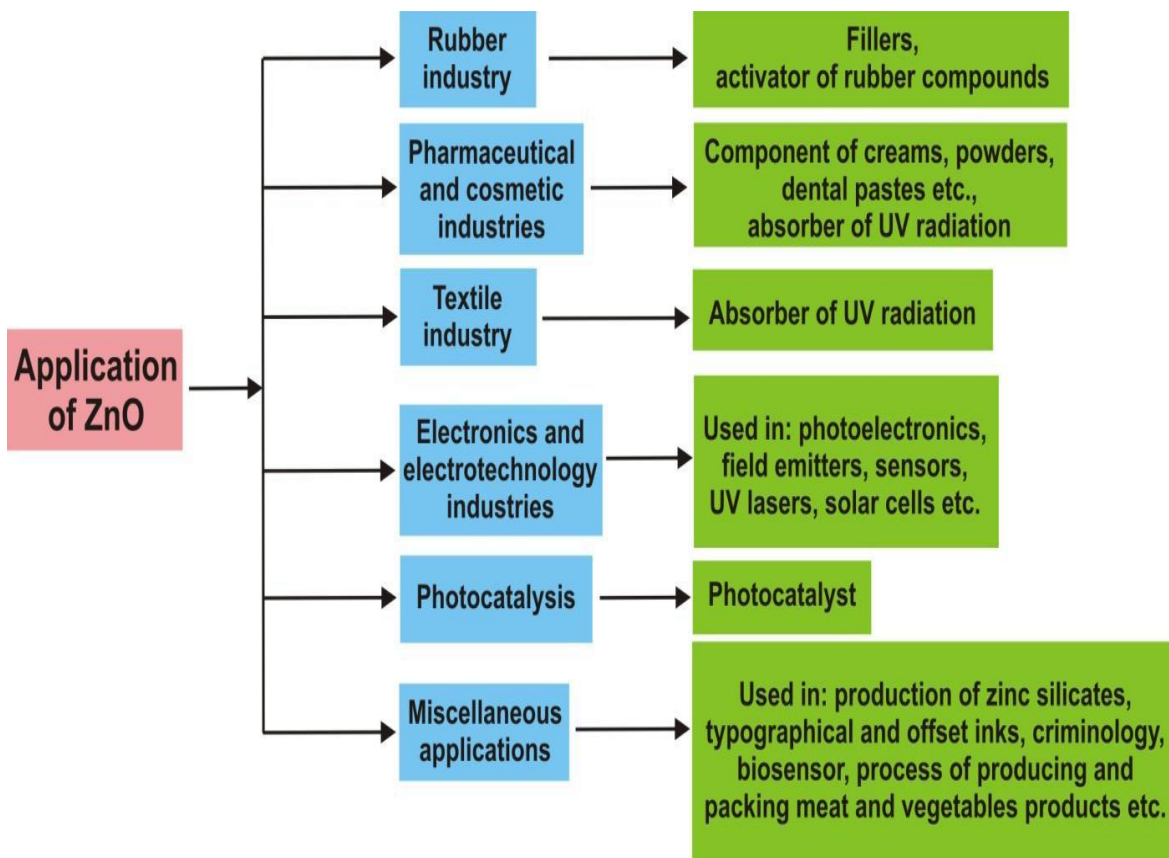


Figure 1.5. Schematic representation all the application of ZnO mentioned in the text.

1.5.1. Rubber

The major application of ZnO (more than half of the total use) is currently in the rubber industry where it is used as a vulcanizing activator (a substance applied in small doses to increase the effectiveness of the vulcanization accelerator). Early un-accelerated vulcanization processes used ~8 parts per hundred rubbers (phr) of activator and required temperatures above the sulfur melting point for several hours. Organic accelerators allowed the amount of sulfur and vulcanization times to be significantly reduced but a significant breakthrough in the vulcanization process involved activators such as ZnO. Zinc oxide is also used as a curing or cross-linking agent for halogen-containing elastomers such as neoprene or polysulfides. The addition of ZnO also considerably improves the thermal conductivity of rubber, which is crucial to dissipate the heat produced by deformation under load or cyclic stress. There is also evidence that the inclusion of ZnO in rubber compounds improves the abrasion resistance. It has also been found

that ZnO improves the heat resistance of the vulcanizates. ZnO additions also contribute to the processing of uncured rubber by decreasing the shrinkage of molded products and improving the cleanliness of the molds. Finally, the presence of ZnO appears to increase the bonding between rubber and metallic inserts, such as steel wire [31, 32].

1.5.2. Ceramics and Concrete

The second largest application of ZnO is in ceramics in particular the tile industry. Both the French or American process ZnO is suitable. The relatively high heat capacity, thermal conductivity and high temperature stability of ZnO coupled with a comparatively low coefficient of expansion are desirable properties in the production of ceramics. Zinc oxide in concrete provides longer processing time and improves its resistance against water. In the manufacture of Portland cement, ZnO can be used in the raw material mixture for the production of cement clinker Its addition in small amounts to Portland cement retards the setting and hardening effectively and improves the whiteness and final strength, Zinc oxide may also be used in quick-setting phosphate cements[33,34].

1.5.3. Plastics and Linoleum

Zinc compounds can provide a variety of properties in the plastics field. Heat resistance and mechanical strength are imparted to acrylic composites by Zinc Oxide. Zinc Oxide contributes to the formation and cure of epoxide resin. Addition of Zinc Oxide to epoxy resins cured with aliphatic polyamines imparts higher tensile strength and water resistance. Zinc Oxide imparts fire-resistant properties to nylon fibers and moldings. Zinc Oxide is also useful in the preparation of nylon polymers and in increasing their resistance. The formation of polyesters in the presence of Zinc Oxide imparts higher viscosity and other improvements. ZnO reacts with unsaturated polyesters to form higher viscosity and a thixotropic body. The dyeability of polyester fibers is improved by Zinc Oxide. Zinc Oxide mixtures stabilize polyethylene against aging and ultraviolet radiation. Zinc Oxide increases the transparency of poly(chlorofluoroethylene) molding resin. Polyolefin's are improved in color, tensile strength, and vulcanization properties by addition of Zinc Oxide. Thermal stabilization of PVC is effected by Zinc Oxide. Antistatic, fungistatic and emulsion stability are additional properties imparted to vinyl polymers by Zinc Oxide [35].

Applications in development for Zinc Oxide-stabilized polypropylene and high-density polyethylene include safety helmets, stadium seating, insulation, pallets, bags, fiber and filament, agricultural and recreational equipment [36].

1.5.4. Pigments and Coatings

ZnO remains an important white inorganic pigment in niche applications. Pigments made of ZnO are known as ‘zinc white’ or ‘Chinese white’ or ‘flowers of zinc’, with the term ‘zinc white’ now reserved for ZnO pigment produced by the French process. The pigment may be purchased in the dry form or as a paste in oil. An important property of white pigment is its low light absorbance together with high dispersion of radiation in the visible region (wavelengths of 400–800 nm). However, the scattering power depends on the particle size and also the wavelength of the incident beam. Therefore by controlling the particle size, it is possible to engineer the desired scattering power to some extent [37].

1.5.5. Foods and Food-Packaging Materials

Zinc Oxide and its derivatives contributing special fungi-static and chemical properties to the processing and packaging of various animal and vegetable products. In the packaging of meat, fish, corn and peas, for examples, Zinc Oxide has long been incorporated into the varnish linings of the metal containers to prevent formation of black Sulfides which discolor the food [38].

1.5.6. Sulfur Removal

Zinc Oxide is effective in removal of Sulfur and Sulfur compounds from a variety of fluids and gases, particularly industrial flue gases. Zinc is also effective in removal of H₂S from hydrocarbon gases and for desulfurization of H₂S and certain other sulfur-containing compounds[38].

1.5.7. Pharmaceutical Industry and Cosmetics

Zinc Oxide is mainly used in Zinc soap, ointment, dental inlays, food powders etc. Zinc Oxide forms an indispensable element of the production process of this industry [39].

The optical and biochemical properties of Zinc Oxide and its derivatives impart special features to a variety of cosmetic preparations for care of the hair and skin. In powders and creams it protects the skin by absorbing the ultraviolet sunburn rays; in burn ointments it aids healing. Simple salts of Zinc provide astringent and skin-conditioning properties to creams, while more complex salts furnish fungistatic properties which contribute to the effectiveness of deodorants, soaps, and antiodorants [40].

1.6 literature review

Zinc oxide powder has traditionally been used as a white pigment and as an additive to rubber [15, 41]. While it has largely been displaced as a pigment in paints, its usage in rubber remains very important. However, the myriad of other practical uses of ZnO are sometimes overlooked, and reviews in the recent scientific literature tend to emphasize high technology applications that do not yet have any commercial reality. Similarly, while some of the low-volume processes used to manufacture ZnO nanostructures have been well covered in the literature there has been far less reported on the tonnage chemical engineering processes by which most ZnO is actually made. The multiplicity of processes by which ZnO can be produced is a potential source of confusion, however, the process used has a large influence on the properties of the oxide, and hence on its suitability for various applications [15].

Preparation of Nano Zinc Oxide and its Application in Leather as a Retanning and Antibacterial Agent nano has been prepared by wet chemical method using zinc nitrate and sodium hydroxide precursors. Nano zinc oxide particles have been applied on goat skin during retanning, parallel to the control leather processing. Resulted leather has been subjected to determine the antibacterial activity by diffusion method using *Bacillus subtilis*, *Escherichia coli* & *Clostridium perfringens* species of bacteria. It has been observed that nano zinc oxide inhibits bacterial growth on leather without inserting bad effect on its quality [42].

Zinc oxide is an inexpensive material and is relatively abundant. It has high chemical and thermal stability, is non-toxic and is easy to re-prepare and therefore it is one of the most studied materials. ZnO has many useful properties such as high carrier mobility and transparency as well as a wide bandgap of 3.37 eV. ZnO occurs in nature as the mineral zincite and has the ionic and polar crystal structure of wurtzite. This structure is related to a

hexagonal close packed (HCP) structure with zinc atoms and oxygen atoms tetrahedrally four-coordinated [43].

Zinc methoxide and isopropoxide were prepared by the reaction of zinc chloride with the appropriate lithium alkoxide and a few other alkoxides, Zn(OR), (where R = Et, Buⁿ, Bu^t) have been synthesized by the alcoholysis of methoxide. All these alkoxides are non-volatile and insoluble in alcohols and other organic solvents. The non-formation of insoluble zinc ethoxide from zinc chloride by treating it, with lithium ethoxide was found to be due to its complexing tendency with lithium chloride, giving soluble products of the type Li_xZn(OEt)₂Cl_x. A few soluble double alkoxides of lithium and zinc have also been isolated [14].

Preparation and characterization of zinc oxide has been observed [44] using precipitation method and solid-state pyrolytic method, Nano zinc oxides was successfully prepared by precipitation and pyrolytic methods and their yield was high, Bulk density was greater than that of conventional zinc oxide, Surface area of prepared zinc oxides was greater than that of conventional zinc oxide, Zinc oxides prepared in the laboratory was highly pure. Zinc oxide has been characterized using Bulk density, Transmission Electron Microscopy (TEM) and X-ray powder diffraction (XRD).

Synthesis and application of zinc oxide has been observed using different methods and characterization [45]. The most important methods of preparation of ZnO divided into metallurgical and chemical methods. The mechanochemical process, controlled precipitation, sol-gel method, solvothermal and hydrothermal method, method using emulsion and microemulsion environment and other methods of obtaining zinc oxide were classified as chemical methods. The modification methods of ZnO were characterized. The modification with organic (carboxylic acid, silanes) and inorganic (metal oxides) compounds, and polymer matrices were mainly described. Finally, we present possible applications in various branches of industry: rubber, pharmaceutical, cosmetics, textile, electronic and electrotechnology, photocatalysis were introduced.

Structural and Optical Characterization of ZnO Nanoparticles has been Synthesized by Microemulsion Route in W/S ratio of 5 at room temperature. X-ray diffraction (XRD) pattern reveals wurtzite structure of ZnO

nanoparticles. Rod shape of ZnO nanoparticles of average particle size 10.0 to 12.0 nm were observed by transmission electron microscopy. FT-IR spectra confirmed the adsorption of surfactant molecules at the surface of ZnO nanoparticles and presence of Zn-O bonding. Thermal studies were carried out by the differential scanning calorimeter (DSC) techniques. In addition, UV-Visible spectra were employed to estimate the band gap energy of ZnO nanoparticles [46].

1.7. The Aim of the Study:

The objectives of the present study are:

- To prepare zinc (II) alkoxides using (ethanol, 2-propanol, tert-butanol) and characterize the formed metal complexes using IR spectrometer.
- To prepare zinc (II) oxides from zinc alkoxides and characterize the obtained oxides using IR, X-ray Diffraction (XRD) techniques.
- To determine the concentration of zinc (II) in the oxide.

2. Materials and Methods

2.1. Chemicals:

- Absolute ethanol $\text{CH}_3\text{CH}_2\text{OH}$ (HPLC-PLUS - Gradient , assay $\geq 99.8\%$ (GC) vapor density 1.59(vs air)
- Zinc (II) chloride Anhydrous ZnCl_2 (powder ,assay $\leq 99.995\%$ trace metals basis ,density 2.907g/ml at 25°C,M.Wt= 136.28 g/mol)
- 2-propanol $\text{C}_3\text{H}_8\text{O}$ (grade anhydrous, assay 99.5% M.Wt=60.1 g/mol, colorless , soluble in water completely ,density 0.785g/ml at 25 °C)
- Tert- butanol $\text{C}_4\text{H}_{10}\text{O}$ (grade anhydrous, assay $\leq 99.5\%$ M.Wt= 74.12 g/mol ,soluble in water miscible ,density 0.775g/ml at 25 °C)
- Sodium metal Na (sodium 25-35 wt % dispersion in paraffin).
- Ammonia/Ammonium Chloride Buffer Stock Solution, pH 10 (density 0.73 kg/m³ . M.Wt =17.031g/mol),(M.wt =53.489g/mol,colorless crystal,granular powder,odorless ,density1.53g/cm³).
- EDTA [ethylenediaminetetraacetic acid, $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$, $(\text{HOOCCH}_2)_2\text{N}-\text{CH}_2\text{CH}_2-\text{N}(\text{CH}_2\text{COOH})_2$. 292.244g/mol.
- Magnesium sulfate MgSO_4 (M.wt120.361g/mol, colorless

odorless, density 2.66g/cm³)

- Eriochrome Black T Indicator.

2.2. Instruments and Equipments:

- **Infra-Red Spectroscopy (IR):** JASCO, FT/IR-4100 LE Serial No. B18736106, protect: Class1, Made in Japan.
- **Water Bath:** Digital Water Bath, Daihan Labtech Co. L.T.D., Model; LWB-122 D, Serial No. 2014022849.
- **Sensitive Balance:** SHIMADZU, Electronic Balance, Type: AY120, NO. D432711233, Made in Japan.
- **X-ray Diffraction:** ADX-2700 X-ray Powder Diffraction Instrument

2.3. Glass wares:

All glass ware were Pyrex type.

2.4. Preparation Procedure

2.4.1. Preparation of Sodium Ethoxide:

The metal complex was prepared by mixing 1:1 molar ratios of sodium metal and absolute ethanol.

About 100 ml of alcohol was taken in the reaction vessel and stirred continuously using a magnetic stirrer. Solid sodium pieces weighing 500–1000 mg were added to the alcohol. The reaction was initially carried out at room temperature and then the temperature was gradually raised to near boiling point of the respective alcohol to dissolve as much sodium as possible and the addition of sodium was stopped when the solution was saturated. Stirring and heating were stopped and the saturated sodium alkoxide solution was allowed to cool naturally for about 16 h to facilitate the formation of sodium alkoxide crystals and completion of the

crystallization process. The crystalline sodium alkoxide was dried.

2.4.2. Preparation of Zinc Alkoxides using (Ethanol,2-Propanol,Tert-Butanol).

A solution of sodium alkoxide (2 moles) was added to a solution (or suspension) of zinc (II) chloride in the parent alcohol (ethanol,2-propanol,tert-butanol). This caused an immediate change in color with the formation of an insoluble product. Contents were stirred for 5-6 hours at room temperature (35°C). The insoluble product obtained was filtered out and washed with parent alcohol (ethanol, 2-propanol, tert-butanol).

2.4.3. Preparation of Zinc (II) Oxide:

1 gram of the sample was Weighed in a porcelain crucible and placed in an oven at a temperature above 600 C for an hour.

2.5. Determination of concentration of zinc (II).

0.29 grams of zinc (II) complex was dissolved in volumetric flask100mL with distilled water then 3ml of the solution was taken using pipette to conical flask, 10ml of EDTA (0.1M) was added, 3ml of buffer solutin PH(10) and 2drops of Eriochrome Black T Indicator (EBT) were added to the solution . the solution was titrated against magnesium(0.1M).

2.6. Characterization of the Zinc (II) Alkoxide and Zinc (II) Oxide:

2.6.1. Fourier Transform Infrared Spectroscopy (Ft-Ir):

2 mg of the zinc (II) alkoxide, zinc (II) oxide were triturated with 300 mg of dried potassium bromide. These quantities were usually sufficient to given a suitable intensity of spectrum when use a disc with diameter (10-15 mm). Carefully the mixture was grinded, spread uniformly in a suitable disc, and submitted to a pressure of about 800 MPa ($8 \text{ t}\cdot\text{cm}^{-2}$). For substances that were unstable under normal atmospheric conditions, the disc had been pressed in vacuum. Several factors might be caused the formation of faulty discs, such as insufficient or excessive grinding, humidity or other impurities in the dispersion medium or an insufficient reduction of particle size. A discwas rejected if visual examination had been show lack of uniform transparency or when transmittance at about 2000 cm^{-1} ($5 \mu\text{m}$) in the absence of a specific absorption band was less than 60 percent without compensation, unless otherwise prescribed.

Samples have been prepared by the same procedure and the spectrum was recorded between $4000\text{-}400 \text{ cm}^{-1}$ ($2.5\text{-}15.4\mu\text{m}$) under the same operational

conditions. The transmission minima (absorption maxima) in the spectrum was obtained with the substance to be examined correspond in position and relative size to those in the spectrum obtained with the reference substance [47].

2.6.2. X-Ray Diffraction Analysis

Single crystals were finely ground between glass plates, and a thin layer of the resulting powder was dispersed with acetone on a glass slide. Powder diffraction patterns were obtained with a Philips-Norelco diffractometer using monochromatic high intensity $\text{CuK}\alpha_1$, radiation ($\lambda = 1.5405\text{\AA}$). For qualitative identification of the phases present, the patterns were taken from $12^\circ < 2\theta < 72^\circ$ with a scan rate of $1^\circ 2\theta/\text{min}$ and a chart speed of 30 in/hr. Cell parameters were determined by a least squares refinement of the reflections using a computer program which corrects for the systematic errors of the measurement[48].

2.7. Percent Zinc of Zinc Compound

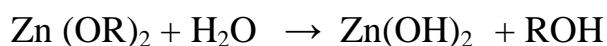
$$\% \text{Zinc} = \frac{\text{mass of zinc}}{\text{Mass of sample}} \times 100\%$$

This equation will allow determining the percent zinc in the sample.

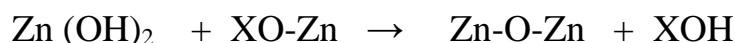
3.Results and Discussion

Zinc (II) alkoxides and zinc (II) oxide were synthesized and characterized. The percentage of yield of zinc (II) in zinc (II) oxide was found 79%. Sol- gel technology of oxide materials based on the growth of metal oxo polymers in a solvent, it involves inorganic step polymerization reactions through hydrolysis and condensation of metal alkoxide $Zn(OR)_2$...OR is an alkoxy group.

- first step hydroxylation upon the hydrolysis of alkoxy groups



- Second step polycondensation process leading to the formation of branched oligomers with a metal oxo based skeleton and reactive residual hydroxo and alkoxy groups using oxolation way is condensation in which a oxo -o- bridge is formed).



Where $X=H$, generally when hydrolysis ratio $h=H_2O/M \ll 2$ or $X=R$ when $h=H_2O/M > 2$.

3.1. Characterization of zinc oxide

3.1.1. X-ray diffraction analysis

Figure3.1 shows XRD diffraction pattern of ZnO .The peaks are indexed as 31(100), 34 (002), 36(101) and 64(103). All diffraction peaks of sample correspond to the characteristic hexagonal wurtzite structure of zinc oxide.

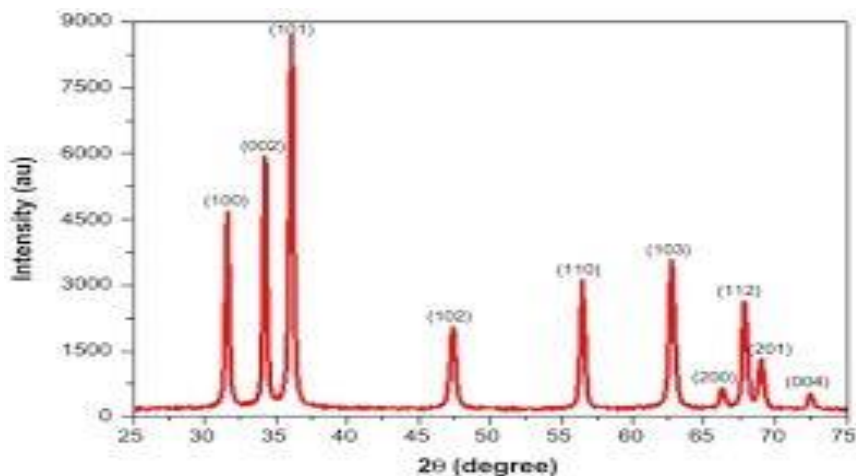


Figure3.1 XRD diffraction pattern of ZnO

3.1.2. FT-IR spectroscopy.

Figures(3.2 - 3.3 - 3.4) shows IR spectra of (methanol, isopropanol and tert butanol).The IR showed features around 3500-1600, 3000-1450 ,1050 and 500 Cm^{-1} . The features around 3500 Cm^{-1} and 1600 Cm^{-1} due to OH stretching and bending vibration . The features around 3000 Cm^{-1} -1450 Cm^{-1} due to CH stretching and bending vibration of alkoxide .The feature around 3500 Cm^{-1} due to ZnO . The features of zinc alkoxide shifted by the influence of the zinc oxide.



Figure3.2 IR spectra of methoxide

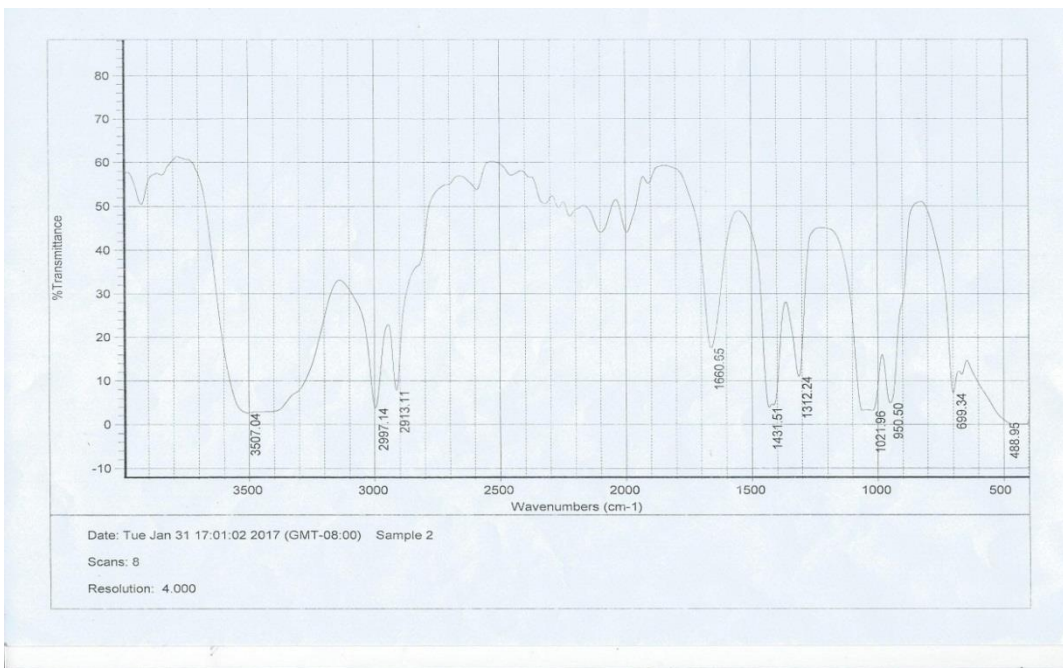


Figure 3.3 IR spectra of isopropoxide

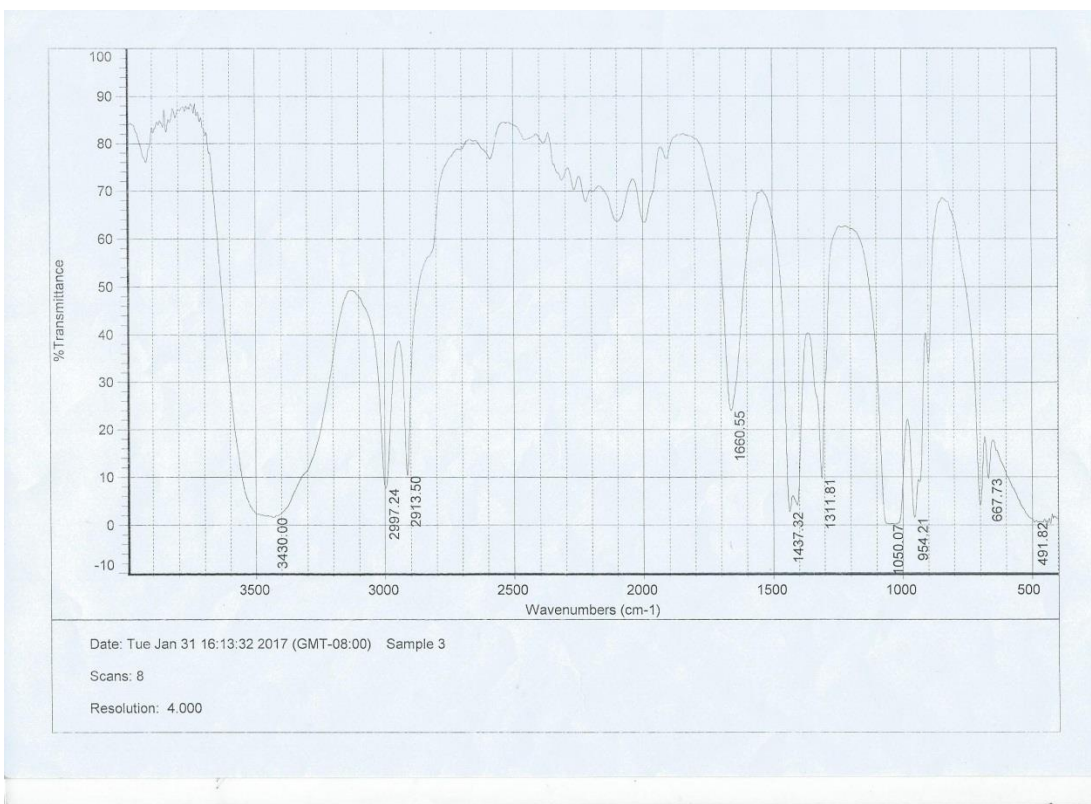


Figure 3.4 IR spectra of tert butoxide

Figure3.5 shows IR spectra of Zinc Oxide after calcination the main function groups of sample not changed .The peaks observed at 3496.86 Cm^{-1} and 1043.44 Cm^{-1} due to OH stretching and information respectively assigned to the water adsorption on the metal surface . the peaks at 161.44 Cm^{-1} and 723.14 Cm^{-1} are correspond to ZnO stretching and deformation vibration.

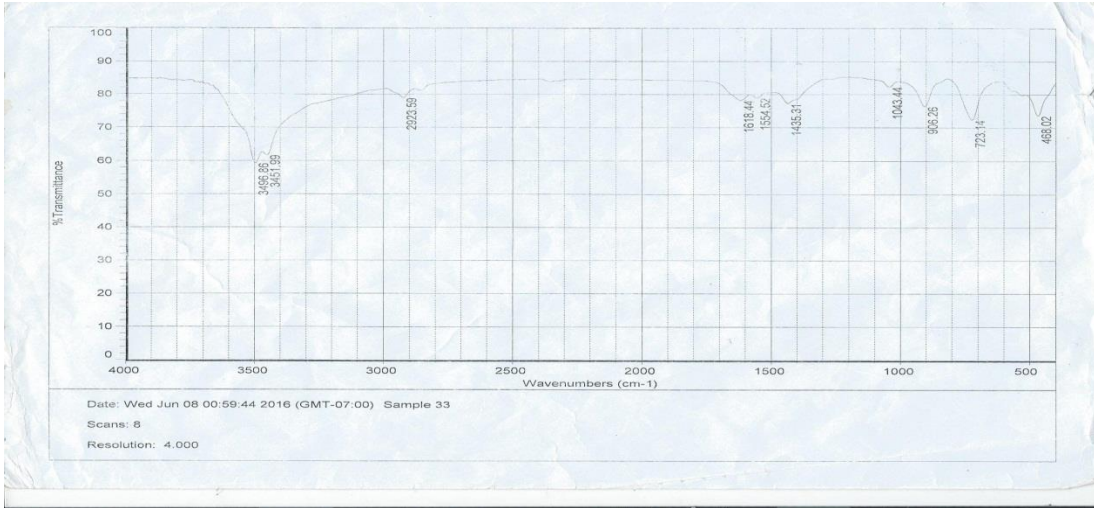


Figure3.5 IR spectra of Zinc Oxide after calcination

3.2. Conclusion

In the present study zinc oxides were prepared using sol-gel process. Firstly sodium alkoxides were prepared using different alcohols (ethanol,2-propanol,tert-butanol)react with sodium metal. Secondly zinc alkoxides were prepared using different sodium alkoxides(ethoxide,2-propoxide,tert-butoxide) react with zinc chloride then calcinated using high temprature(600) to obtain zinc oxide.

It can be concluded that the IR-spectra and X-ray diffraction of the obtained alkoxide and oxide were agreed well with the prepared compounds.

Referances

1. Bradley, D.C.,(1989). Metal alkoxides as precursors for electronic and ceramic materials. *Chemical Reviews*, **89**(6), pp.1317-1322.
2. Bradley, D., Mehrotra, R.C., Rothwell, I. and Singh, A.,(2001). *Alkoxo and aryloxo derivatives of metals*. Academic press.
3. Mazdiyasn, K.S., Lynch, C.T. and Smith, J.S., (1965). Preparation of Ultra-High-Purity Submicron Refractory Oxides. *Journal of the American Ceramic Society*, **48**(7), pp.372-375.SSS
4. Turova, N.Y., Kozunov, V.A., Yanovskii, A.I., Bokii, N.G., Struchkov, Y.T. and Tarnopol'skii, B.L., (1979). Physico-chemical and structural investigation of aluminium isopropoxide. *Journal of Inorganic and Nuclear Chemistry*, **41**(1), pp.5-11.
5. Brubaker, C.H. and Wicholas, M., (1965). Copper (II) alkoxides and alkoxide-halides. *Journal of Inorganic and Nuclear Chemistry*, **27**(1), pp.59-62.
6. Bradley, D.C., Mehrotra, R.C., Swanwick, J.D. and Wardlaw, W., (1953). Structural chemistry of the alkoxides. Part IV. Normal alkoxides of silicon, titanium, and zirconium. *Journal of the Chemical Society (Resumed)*, pp.2025-2030.
7. Habashi, F.,(2001). Zinc-the metal from the East. *CIM Bull*, **94**, pp.71-76.
8. McHale, J.M., Auroux, A., Perrotta, A.J. and Navrotsky, A., (1997). Surface energies and thermodynamic phase stability in nanocrystalline aluminas. *Science*, **277**(5327), pp.788-791.
9. Segal, D.L., (1984). Sol-gel processing: routes to oxide ceramics using colloidal dispersions of hydrous oxides and alkoxide intermediates. *Journal of Non-Crystalline Solids*, **63**(1-2), pp.183-191.
10. Mehrotra, R.C., (1988). Synthesis and reactions of metal alkoxides. *Journal of Non-Crystalline Solids*, **100**(1), pp.1-15.
11. Bradley, D., (1972). Metal alkoxides and dialkylamides. *Advances in inorganic chemistry and radiochemistry*, **15**, pp.259-322.
12. Schuchardt, U., Sercheli, R. and Vargas, R.M., (1998). Transesterification of vegetable oils: a review. *Journal of the Brazilian Chemical Society*, **9**(3), pp.199-210.
13. Mehrotra, R.C., 1983. Transition-metal alkoxides. *Advances in Inorganic Chemistry*, **26**, pp.269-335.
14. Mehrotra, R.C. and Aroda, M., (1969). Alkoxides and double alkoxides of zinc. *Zeitschrift für anorganische und allgemeine Chemie*, **370**(5-6), pp.300-309.

15. Wang, Z.L., (2008). Splendid one-dimensional nanostructures of zinc oxide: a new nanomaterial family for nanotechnology. *Acs Nano*, **2**(10), pp.1987-1992.
16. Hurt, J.C. and Phillips, C.J., (1970). Structural Role of Zinc Oxide in Glasses in the System Na₂O-ZnO-SiO₂. *Journal of the American Ceramic Society*, **53**(5), pp.269-273.
17. Brown, H.E., (1978). Zinc Oxide--Properties and Applications. *International Lead Zinc Research Organization, Inc., New York. 1978, 218.*
18. Liu, J., Huang, X., Duan, J., Ai, H. and Tu, P., 2005. A low-temperature synthesis of multiwhisker-based zinc oxide micron crystals. *Materials Letters*, **59**(28), pp.3710-3714.
19. Özgür, Ü., Alivov, Y.I., Liu, C., Teke, A., Reshchikov, M., Doğan, S., Avrutin, V.C.S.J., Cho, S.J. and Morkoc, H., 2005. A comprehensive review of ZnO materials and devices. *Journal of applied physics*, **98**(4), p.11.
20. Auer, G., Griebler, W.D. and Jahn, B., (2005). Industrial inorganic pigments. by G. Buxbaum and G. Pfaff, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, pp.129-130.
21. Wetherill, S., (1855). *Improvement in processes for making zinc-white.* U.S. Patent 13,806.
22. Wetherill, S., (1855). *Apparatus for collection of white oxide of zinc.* U.S. Patent 0,012,418.
23. Moezzi, A., McDonagh, A.M. and Cortie, M.B., (2012). Zinc oxide particles: Synthesis, properties and applications. *Chemical Engineering Journal*, **185**, pp.1-22.
24. Mahmud, S., Johar Abdullah, M., Putrus, G.A., Chong, J. and Karim Mohamad, A., 2006. Nanostructure of ZnO fabricated via French process and its correlation to electrical properties of semiconducting varistors. *Synthesis and Reactivity in Inorganic and Metal-Organic and Nano-Metal Chemistry*, **36**(2), pp.155-159.
25. Laundon, R.D., Elementis UK Limited, (1999). *Zinc oxide and a process of making it.* U.S. Patent 5,876,688.
26. Habashi, F.,(2001). Zinc-the metal from the East. *CIM Bull*, **94**, pp.71-76.
27. Moezzi, A., Cortie, M. and McDonagh, A., (2011). Aqueous pathways for the formation of zinc oxide nanoparticles. *Dalton Transactions*, **40**(18), pp.4871-4878.
28. Duyvesteyn, W.P., Bakker, T. and Lastra, M.R., Bhp Minerals International Inc., 1995. *Hydrometallurgical process for producing zinc oxide.* U.S. Patent 5,441,712.

29. Baruah, S. and Dutta, J.,(2009). Hydrothermal growth of ZnO nanostructures. *Science and Technology of Advanced Materials*, **10**(1), p.013001.
30. Look, D.C.,(2001). Recent advances in ZnO materials and devices. *Materials Science and Engineering: B*, **80**(1), pp.383-387.
31. Nieuwenhuizen, P.J.,(2001). Zinc accelerator complexes.: Versatile homogeneous catalysts in sulfur vulcanization. *Applied Catalysis A: General*, **207**(1), pp.55-68.
32. Hattori, R.S. and Goncalves, J.F.,(1992), June. The effects of metal oxides on thermal stabilization of EPDM insulation compounds. In *Electrical Insulation, Conference Record of the 1992 IEEE International Symposium on* (pp. 173-176). IEEE.
33. Perl, A.S., (1997). Zinc oxide. *American Ceramic Society bulletin*, **76**(6), pp.140-143.
34. Porter, F.C., (1991). *Zinc handbook: properties, processing, and use in design*. CRC Press.
35. Moezzi, A., McDonagh, A.M. and Cortie, M.B., (2012). Zinc oxide particles: Synthesis, properties and applications. *Chemical Engineering Journal*, **185**, pp.1-22.
36. Szerreiks, U. and Baum, M., Dlw Aktiengesellschaft, (2004). *Linoleum floor covering*. U.S. Patent 6,831,023.
37. Vassilev, S.V., Baxter, D., Andersen, L.K. and Vassileva, C.G., (2013). An overview of the composition and application of biomass ash.: Part 2. Potential utilisation, technological and ecological advantages and challenges. *Fuel*, **105**, pp.19-39.
38. Perl, A.S., (1997). Zinc oxide. *American Ceramic Society bulletin*, **76**(6), pp.140-143.
39. Venkatasubbu, G.D., Ramasamy, S., Ramakrishnan, V. and Kumar, J., 2011. Nanocrystalline hydroxyapatite and zinc-doped hydroxyapatite as carrier material for controlled delivery of ciprofloxacin. *3 Biotech*, **1**(3), pp.173-186.
40. Pirot, F., Millet, J., Kalia, Y.N. and Humbert, P., 1996. In vitro study of percutaneous absorption, cutaneous bioavailability and bioequivalence of zinc and copper from five topical formulations. *Skin Pharmacology and Physiology*, **9**(4), pp.259-269.
41. Moezzi, A., McDonagh, A., Dowd, A. and Cortie, M., (2012). Zinc hydroxyacetate and its transformation to nanocrystalline zinc oxide. *Inorganic chemistry*, **52**(1), pp.95-102.
42. Nawaz, H.R., Solangi, B.A., Zehra, B. and Nadeem, U., (2011). Preparation of nano zinc oxide and its application in leather as a retanning

- and antibacterial agent. *Canadian Journal on Scientific and Industrial Research*, **2**(4), pp.164-170.
43. Morkoç, H. and Özgür, Ü., (2009). Optical Properties. *Zinc Oxide: Fundamentals, Materials and Device Technology*, pp.131-244.
44. Heideman, R.G., Kooyman, R.P.H. and Greve, J., (1993). Performance of a highly sensitive optical waveguide Mach-Zehnder interferometer immunosensor. *Sensors and Actuators B: Chemical*, **10**(3), pp.209-217.
45. Kołodziejczak-Radzimska, A. and Jesionowski, T., (2014). Zinc oxide—from synthesis to application: a review. *Materials*, **7**(4), pp.2833-2881.
46. Kumar, H. and Rani, R., (2013). Structural and optical characterization of ZnO nanoparticles synthesized by microemulsion route. *International Letters of Chemistry, Physics and Astronomy*, **14**, pp.26-36.
47. Shah, P.B. and Patel, P.U., (2012). Q-absorbance ratio spectrophotometric method for the simultaneous estimation of cinnarizine and dimenhydrinate in their combined dosage form. *Journal of Pharmaceutical Science and Bio-Scientific Research*, **2**(2), pp.83-87.
48. Collins, B.T., Desisto, W., Kershaw, R., Dwight, K. and Wold, A., (1989). Preparation and characterization of Cu (II) oxide. *Journal of the Less Common Metals*, **156**(1-2), pp.341-346.