CHAPTER III

THEORY

This chapter is the explanation about the theories that concerned with this work. The theories about titanium oxide, iron oxide and zinc oxide are shown in section 3.1,3.2 and 3.3 respectively. The theories about the crystal preparation are shown in section 3.4.

3.1 Titanium (Ti)

Titanium is the first member of Group IVB of the periodic table. It has four valence electrons. The titanium (IV) state is the most stable one and is well characterized with a wide variety of compounds. The lower valence state Ti (II) and Ti (III) exist, but the II state is very strongly reducing, the III state is reducing but resonable stable; in water. The only solid compounds are unstable polymerized solids and it rapidly decomposes in water. Titanium metal is used in high-performance situations where a high strength / weight ratio is needed. It is also resistant to corrosion in harsh environments.

3.1.1 Titanium (IV) oxide (TiO$_2$)

Titanium (IV) oxide occurs naturally in three crystalline forms: anatase, which tends to be more stable at low temperature, brookite, which is usually found only in minerals, and rutile, which tends to be more stable at high temperatures and thus is sometimes found in igneous rock. These crystals are substantially pure titanium (IV) oxide but usually contain small amounts of impurities e.g., iron, chromium or vanadium, which darken them.

Although anatase and rutile are both tetragonal, they are not isomorphous. Anatase occurs usually in near-regular octahedra, and rutile forms slender prismatic crystals, which are frequently twinned. Rutile is the thermally stable form and is one of the two most important ores of titanium.

The three allotropic forms of titanium (IV) oxide have been prepared artificially but only rutile, the thermally stable form, has been obtained in the form of transparent large single crystal. The transformation from anatase to rutile is accomponied by the evolution of ca. 12.6 kJ/mol (3.01 kcal/mol), but the rate of transformation is greatly affected by temperature and by the presence of other substances which may either catalyze of inhibit the reaction. The lowest temperature at which conversion of anatase to rutile takes pace at a measurable rate is ca. 700°C, but this is not a transition temperature. The change is not reversible; ΔG for the change from anatase to rutile is always negative.

Brookite has been produced by heating amorphous titanium (IV) oxide, prepared from an alkly titanates of sodium titanate with sodium or potassium hydroxide in an autoclave at 200 to 600°C for several days. The important commercial forms of titanium (IV) oxide are anatase and rutile, and these can readily be distinguished by X-ray diffraction spectrometry.

Since both anatase and rutile are tetragonal, they are both anisotropic, and their physical properties, e.g. refractive index, vary according to the direction relative to the crystal axes. In most applications of these substances, the distinction between crystallographic direction is lost because of the random orientation of large numbers of small particles, and it is mean value of the property that is significant.

Measurement of physical properties, in which the crystallographic directions are taken into account, may be made of both natural and synthetic rutile, natural anatase crystals, and natural brookite crystals. Measurement of the refractive index of titanium (IV) oxide must be made by using a crystal that is suitably orientated with respect to the crystallographic axis as a prism in a spectrometer. Crystals of suitable size of all three modifications occur naturally and have been studied. However, rutile is the only form that can be obtained in large artificial crystals from melts. The refractive index of rutile is 2.75. The dielectric constant of rutile varies with direction in the crystal and with any variation from the stoichiometric formula, TiO_2; an average value for rutile in powder form is 114. The dielectric constant of anatase powder is 48.

Titanium (IV) oxide is thermally stable (mp 1855°C) and very resistant to chemical attack. When it is heated strongly under vacuum, there is a slight loss of oxygen corresponding to a change in composition to $TiO_{1.97}$. The product is dark blue but reverts to the original white color when it is heated in air.

Hydrogen and carbon monoxide reduce it only partially at high temperatures, yielding lower oxides or mixtures of carbide and lower oxides. At ca. 2000°C and under vacuum, carbon reduces it to titanium carbide. Reduction by metal, e.g., Na, K, Ca, and Mg, is not complete. Chlorination is only possible if a reducing agent is present; the position of equilibrium in the system is

$$TiO_2 + 2Cl_2 \rightleftharpoons TiCl_4 + O_2$$
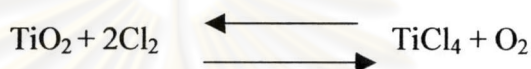
The reactivity of titanium (IV) oxide towards acids is very dependant on the temperature to which it has been heated. For example, titanium (IV) oxide that has been prepared by precipitation from a titanium (IV) solution and gently heated to remove water is soluble in concentrated hydrochloric acid. If the titanium (IV) oxide is heated to ca. 900°C, then its solubility in acids is considerably reduced. It is slowly dissolved by hot concentrate sulfuric acid, the rate of salvation being increased by the addition of ammonium sulfate, which raises the boiling point of the acid. The only other acid in which it is soluble is hydrofluoric acid, which is used extensively in the analysis of titanium (IV) oxide for trace elements. Aqueous alkalies have virtually no effect, but molten sodium and potassium hydroxides, carbonates, and borates dissolve titanium (IV) oxide readily. An equimolar molten mixture of sodium carbonate and sodium borate is particularly effective as is molten potassium pyrosulfate.

3.1.2 Titanium (IV) oxide uses

Titanium (IV) oxide has been know to be an excellent catalyst support in industrial processes, e.g., as a support in a commercial vanadium (V) oxide catalyst for selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with ammonia and the selective oxidation of hydrocarbons. Using a TiO_2 support having a large surface area to disperse a catalyst material effectively and to increase the number of active sites in the catalyst.

Titanium (IV) oxide is used increasingly as a catalyst, either as an active agent of an inert support. The catalytic oxidation of o-xylene to phthalic anhydride using a mixture of titanium (IV) oxide and vanadium pentoxide as catalyst on an inert support is a well-established commercial process. The same agents have also been used for the reduction of nitrogen oxides in exhaust gases from internal combustion engines.

Numerous other reactions, which as yet are only of academic interest, have been studied in which titanium (IV) oxide is used as a catalyst These include the oxidation of hydrogen sulfide to sulfur dioxide, the dehydration of alcohols, ammonoxidation, methylation isomerization, and alkylation.

Titanium (IV) oxide impregnated with precious metal (e.g., platinum, rhodium, or ruthenium) or nickel is used in the Fishcher-Tropsch synthesis for the production of hydrocarbons from carbon monoxide and hydrogen. Titania is also used as a good catalyst for photocatalytic reaction. Such as photocatalytic water purification using titania-based semiconductor catalysts because of the high effectiveness if the catalyst against various organic pollutants such as chlorinated organic substrates, dyes, pesticides, and endocrine disrupters.

Besides catalytic applications, it also has many applications such as the production of components for electronic equipment. Its high dielectric constant and high resistance make it ideal for use in the miniaturization of capacitors. These are made by pressing high purity rutile into the desired shape and then heating the pressure until the particles sinter at ca.1400 to 1450°C. Additions of materials, e.g., clay, assist in producing the mold and reduce the firing temperature. These additions must be kept small to avoid adverse effect on the electrical properties of the product.

Synthetic gems have been produced from rutile and strontium titanate. The high refractive index of these materials results in gems of high brilliance. The stones also provide a fine display of colors because of their high dispersion, which is superior to that of diamond; however, they are not very hard.

Furthermore titanium (IV) oxide is used as pigment, filler, membrane and anti-reflection coating.

3.2 Iron (Fe)

The highest state of iron is VI and the main ones are II and III. The III state is only slightly oxidizing while the III state is more stable. By comparison with the II and III states of other transition elements, the iron (II) and (III) states lie much closer together in stability, and this accord with the well-known properties of ferrous and ferric solutions which are readily interconverted by the use of only mild oxidizing or reducing agents.

Iron is the most abundant of the fairly heavy elements in the earth's crust and is used on the largest scale of any metal. Its production in the blast furnace is well-known, and basically involves the reduction of the oxide by carbon. The resulting metal contains a small proportion of carbon, and various types of iron and steel result from varying carbon contents, and from other metal additions. In particular , the form of iron exist at difference temperatures, the carbide phase is Fe_3C , called cementite. Thus a steel cooled slowly from above 720°C and containing about 1%C, consists of layer alpha-iron interleaved with cementite to give the steel call pearlite, a soft malleable material. Alternatively rapid cooling of the same mixture prevents separation of the layers a martensite is formed which is hard but brittle. Iron is reactive in air and the process of rusting involves the formation of a coat of hydrate oxide on the surface in moist air. Iron combine at moderate temperatures with most non-metals and readily dissolves in dilute acids to give iron (II) in solution except with oxidizing acids which yield iron (II) solution very strongly oxidizing agents, such as dichomate, concentrated nitric acid, produce a passive form of the metal, probably by forming a coherent surface film of oxide.

3.2.1 Iron (III) oxide (Fe_2O_3)

Iron forms three oxides, FeO, Fe_2O_3 and Fe_3O_4 which all commonly occur in non-stoichiometric forms. Indeed, FeO is thermodynamically unstable with respect to the structures with a deficiency of iron. The three oxide show a number of structures, some based on a cubic close packed array of oxide ions.

It will be seen that the structures of the cubic forms of all these oxides are related. If the cubic array of oxide ions is taken, then all the structures result from different dispositions of ferrous and ferric ions in the octahedral and tetrahedral sites.

The basic structural unit of iron oxide is an octahedral in which the Fe atom is surrounded by 6 O+OH ions in either hexagonal (α forms) or cubic (γ forms) close packing. Tetrahedrally coordinated Fe sheets are also present in magnetite and maghemite. The various forms differ mainly in their arrangement of the octahedra. In goethite (α form, isostructural with diapore) the Fe-O-OH octahedra form infinite double bands linked by O-H-O bonds 2.65 Å in length with the H atoms displaced slightly from the O-O axis. In contrast, the Fe-O-OH octahedra of lepidocrocite (γ form, isostructural with boehmite) are arranged in complex layers, linked by O-H-O bonds producing a more open strcture than that of goethite. The Fe-O octahedra in hematite form an infinite, three-dimensional network (corundum structure)

Magnetite and maghemite have an inverse spinel structure containing 32 O and 24 Fe sites per unit cell of which 8 are coordinated tetrahedrally and 16 octahedrally. In magnetite all 24 sites are occupied, the divalent Fe generally being confined to the octahedral site. Infully oxidized maghemite (γ Fe_2O_3) produced from magnetite, the number of Fe sites per 32 O is reduced to 21 1/3. If the oxidation is carefully carried out, the resultant Fe site vacancies may be ordered, giving rise to a tetragonal modification of the original cubic structure of magnetite which causes superlattice lines in X-ray diffraction pattern. Table 3.1 provides three forms of iron oxide.

Table 3.1 The iron oxide

FeO (black)	Prepared by thermal decomposition of ferrous oxalate at a high temperature , followed by rapid quenching to prevent disproportionation to $Fe+Fe_3O_4$
Fe_2O_3 (brown)	Occurs naturally. Otherwise by ignition of hydrated ferric oxide, precipitated from a ferric solution by ammonia.
Fe_3O_4 (black)	Occurs naturally as magnetic. It is the ultimate product of strong ignition in air of the other two oxides.

3.2.2 Iron (III) oxide uses

Iron oxide is a technologically important magnetic material that has a wide range of applications such as in information storage, in magnetic recording, ferrite magnets as ferrite cores, ferrite wave absorbers because of their applicability at high frequency, low price and high resistance to corrosion. Furthermore iron oxide is used as catalyst for oxidation or dehydrogenation reactions as single oxides promoted by alkalies or as mixed oxide. Typical example are dehydrogenation of ethyl benzene, water gas shift reaction (Fe_2O_3-Cr_2O_3), ammoxidation of propylene (Fe_2O_3-Sb_2O_5) and dehydrogenation of methanol (Fe_2O_3-MoO_3)

3.3 Zinc (Zn)

Zinc is a lustrous, blue-white metal, which can be formed into virtually any shape by the common metal-forming techniques such as rolling, drawing, extruding, etc. The hexagonal close-packed crystal structure governs the behavior of zinc during fabrication.

Zinc is in Group IIB of the periodic table and exhibits a valence of +2 in all its compounds. Being high on the electromotive series, Zinc form quite stable compounds and, as such, resemble magnesium. Bonding in zinc compounds tend to be covalent, as in the sulfide and oxide. With strongly electropositive elements, e.g., chlorine, the bond is more ionic. The coordination number is usually four, to a lesser degree six, and in some cases five. In compounds such as the oxide, borate, and silicate, the covalent bonds with oxygen are very stable.

3.3.1 Zinc (II) oxide (ZnO)

Zinc oxide is being coordinated with four oxide ions. The crystal structure of zinc oxide is likely to stabilize defects, e.g., zinc excess or deficiency and inclusion of foreign ions. Zinc oxide produces H_2 and CO_2 from formic acid. This selectivity indicates that zinc oxide is a solid base. The acidity and basicity increase when zinc oxide is mixed with other oxides.

Zinc oxide, as an amphoteric material, reacts with acids to form zinc salts and with strong alkalies to form zincates. Zinc oxide reacts with carbon dioxide in moist air to form oxycarbonate. Acidic gases, e.g., hydrogen sulfide, sulfur dioxide, and chlorine, react with zinc oxide, and carbon monoxide or hydrogen reduce it to metal.

3.3.2 Zinc (II) oxide uses

Zinc oxide is intensively used in a variety of applications, it has been found to have diversified applications in electronic devices such as gas sensors, transducers, as the main component in varistors, which are used in surge suppressors for circuit overvoltage protection, dielectric, piezoelectric, pyroelectric, semiconductors. Moreover, zinc oxide ceramics containing several metal oxides, such as Cr_2O_3, Bi_2O_3, Sb_2O_3, Co_3O_4, MnO_2 etc., show highly nonlinear current-voltage characteristics which enables them to be used as protection devices against voltage surges and voltage transients.

On the contrary, zinc oxide powders with ultrafine particles are applicable to various materials such as nonlinear optical materials, medicine (ointments) pigments,

solar cells, and catalyst, which is zinc oxide-titania reveals high activity for hydration of ethylene. A mixed oxide catalyst consisting of zinc oxide and iron oxide is a good basic catalyst for the methylation by methanol of phenol to 2,6-xylenol.

These various applications of zinc oxide are due to the specific chemical, surface and microstructural properties of zinc oxide.

3.4 Various preparation method

3.4.1 Precipitation Method

Precipitation method involves the growth of crystals from a solvent of different composition to the crystal. This is achieved by bringing the solution into supersaturation, either by changing the temperature, the salt concentration, the pH or by exploiting the slow release of some hydrolysis products in a water solution. The solvent may be one of the constituents of the desired crystals, e.g., crystallization of salt hydrate crystals using water as the solvent or the solvent may be entirely separate liquid element or compound in which the crystals of interest are partially soluble, e.g., SiO_2 and various high melting silicates may be precipitated from low melting borate or halide melts. In these cases, the solvent melts are sometimes referred to as fluxed since the effectively reduce the melting point of the crystals by a considerable amount.

A variety of particle sizes and shapes can be produced, depending on the reaction conditions. Moreover, the particles can be agglomerates of much finer primary particles.

3.4.2 Sol-Gel Method

To prepare a solid using the sol-gel method, a sol is first prepared from a suitable reactants in a suitable liquid. Sol preparation can either be simply the dispersal of an insoluble solid or addition of a precursor which reacts with the solvent to form a colloid product. A typical example of the first is the dispersal of oxides or hydroxides in water with the pH adjusted so that the solid particles remain in

suspension rather than precipitate out. A typical example of the second method is the addition of metal alkoxides to water. The alkoxides are hydrolyzed giving the oxide as a colloidal product. The sol is then either treated or simply left to form a gel. To obtain a final product, the gel is heated. The heating serves several purposes-it removes the solvent, it decomposes anions such as alkoxides or carbonates to give oxides, it allows rearrangement of the structure of the solid and it allows crystallization to occur.

3.4.3 Hydrothermal Method

Hydrothermal methods utilize water under pressure and at temperature above its normal boiling point as a means of speeding up the reactions between solids. The water performs two roles. The water-as solids or vapor-serves as the pressure transmitting medium. In addition, some or all of the reactants are partially soluble in the water under pressure and these enables reactions to take place in, or with the aid of, liquid and/or vapor phase. Under these conditions, reactions may occur that, in the absence of water, would occur only at much higher temperatures. The method is therefore particularly suited for the synthesis of phases that are unstable at higher temperature. It is also a useful technique for growth of single crystals, by arranging for a suitable temperature gradient to be present in the reaction vessel, dissolution of the starting material may occur at the hot end and reprecipitation at the cooler end.

Since hydrothermal reactions must be carried out in closed vessels. The pressure-temperature reactions of water at constant volume are important. The critical temperature of water is 374°C. Below 374°C, two fluid phases, liquid and vapor, can coexist. Above 374°C only one fluid phase, supercritical water ever exists. At pressure below staturated steam curve liquid water is absent and the vapor phase is not saturated with respect to steam.

The design of hydrothermal equipment is basically a tube, usually of steel, closed at one end. The other end has a screw cap with a gasket of soft copper to provide a seal. Alternatively, the bomb may be connected directly to an independent pressure source, such as a hydraulic ram; this is known as the 'cold seal' method.

The reaction mixture and an appropriate amount of water are placed inside the bomb which is then sealed and placed inside an oven at the required temperature.

The applications of the hydrothermal method is:

3.4.3.1 Synthesis of new phases: calcium silicate hydrate

Hydrothermal methods have been used successfully for the synthesis of many materials. A good example is the family of calcium silicate hydrates, many of which are important components of set cement and concrete. Typically, lime, CaO and quartz, SiO_2 are heated with water at temperature in the range 150 to 500°C and pressure of 0.1 to 2 kbar. Each calcium silicate hydrate has, for its synthesis, optimum prefered conditions of composition of starting mix, temperature, pressure and time. For example xonolite, $Ca_6Si_6O_{17}(OH)_2$, may be prepared by heating equimolar mixtures of CaO and SiO_2 at saturated steam pressure in the range 150 to 350°C

3.4.3.2 Growth of Single crystals

For the growth of single crystals by hydrothermal methods it is often necessary to add mineralizer. A mineralizer is any compound added to the aqueous solution that speed up its crystallization. It usually operates by increasing the solubility of the solute through the formation of soluble species that would not usually be in the water. For instance, the solubility of quartz in water at 400°C and 2 kbar is too small to permit the recrystallization of quartz, in a temperature gradient, within a reasonable space of time. On addition of NaOH as a mineralizer, however, large quartz crystals may be readily grown. Using the following condition, crystals of kilogram size have been grown: quartz and 1.0 M NaOH solution are held at 400°C and 1.7 kbar: at this temperature some of the quartz dissolves. A temperature gradient is arranged to exist in the reaction vessel and at 360°C the solution is supersaturated with respect to quartz which precipitates onto a seed crystal.

In summary, therefore, quartz dissolves in the hottest part of the reaction vessel, is transported throughout the vessel via convection currents and is precipitated in cooler parts of the vessel where its solubility in water is lower. Quartz single

crystals are use in many devices in radar and sonar, as piezoelectric transducers, as monochromators in X-ray diffraction, etc. Annual world production of quartz single crystals, using hydrothermal and other methods, is currently a staggering 600 tons.

Using similar methods, many substances have been prepared as high quality single crystals, e.g. corundum (Al_2O_3) and ruby (Al_2O_3 doped with Cr^{3+})

3.4.4 Glycothermal Method

Glycothermal method has been developed for synthesis of metal oxide and binary metal oxide by using glycol solvents such as 1,4 butanediol as the reaction medium. The use of glycol instead of water in the hydrothermal method produced the different form of intermediate phase and the stability of such intermediate phase was not strong. Instability of the intermediate phase gives a large driving force to the formation of product under quite mild condition.

3.4.5 Solvothermal Method

Solvothermal method is the development of hydrothermal method which is like glycothermal method but using inert organic media such as toluene, benzene and/or others instead of glycol in glycothermal method.

3.5 Single Crystal

In crystalline solids the atoms or molecules are stacked in a regular manner, forming a three-dimensional pattern, which may be obtained by a three-dimensional repetition of a certain pattern unit called a unit cell. When the periodicity of the pattern extends throughout the certain piece of material, one speaks of a single crystal. A single crystal is formed by the growth of a crystal nucleus without secondary nucleation or impingement on other crystal.

3.5.1 Growth techniques

Among the most common methods of growing single crystals are those of P. Bridgeman and J. Czochralski. In the Bridgeman method the material is melted in a vertical cylindrical vessel, which tapers conically to a point at the bottom. The vessel then is lowered slowly into a cold zone. Crystallization begins in the tip and continues usually by growth from the first formed nucleus. In the Czochralski method a small single crystal (seed) is introduced into the surface of the melt and then drawn slowly upward into a cold zone. Single crystals of ultrahigh purity have been grown by zone melting. Single crystals are also often grown by bathing a seed with a supersaturated solution, the supersaturation being kept lower than necessary for sensible nucleation.

When grown from a melt, single crystals usually take the form of their container. Crystals grown from solution (gas, liquid, or solid) often have a well-defined form, which reflects the symmetry of the unit cell. For example, rock salt or ammonium chloride crystals often grow from solutions in the form of cubes with faces parallel to the 100 planes of the crystal, or in the form of octahedrons with faces parallel to the 111 planes. The growth form of crystals is usually dictated by kinetic factors and does not correspond necessarily to the equilibrium form.

3.5.2 Physical properties

Ideally, single crystals are free from internal boundaries. They give rise to a characteristic x-ray diffraction pattern. For example, the Laue pattern of a single crystal consists of a single characteristic set of sharp intensity maxima.

Many types of single crystal exhibit anisotropy, that is, a variation of some of their physical properties according to the direction along which they are measured. For example, the electrical resistivity of a randomly oriented aggregate of graphite crystallites is the same in all directions. The resistivity of a graphite single crystal is different, however, when measured along crystal axes. This anisotropy exist both for structure-sensitive properties, which are strongly affected by crystal imperfections (such as cleavage and crystal growth rate), and structure-insensitive properties, which are not affected by imperfections (such as elastic coefficients)

Anisotropy of a structure-insensitive property is described by a characteristic set of coefficients, which can be combined to give the macroscopic property along any particular direction in the crystal. The number of necessary coefficients can often be reduced substantially by consideration of the crystal symmetry, whether anisotropy, with respect to a given property, exists depends on crystal symmetry. The structure-insensitive properties of crystals (for example, strength and diffusion coefficients) seem governed by internal defects, often on an atomic scale.