Chapter 2: Growth

2.1.Introduction

Advances in the techniques of growing and assessing ever more perfect crystals of wide range of materials lie at roots of today's advance technology. In the earlier stages of progress of crystals science in general, the production of synthetic crystals made a tremendous impact on the traditional branches, the mechanical treatment of materials, precision instrument making, and the jewellery industry. Later it considerably influenced the development of such vital branches of science and industry as radiotechnics and electronics, semiconductor and quantum electronics, optics, including nonlinear optics, acoustics etc. The search for crystals with valuable physical properties, study of their structure, and development of new techniques for their synthesis constitute one of basic lines of contemporary science endeavour.

The investigation of the structure, growth and properties of crystals should be regarded as a single problem. These three intimately connected aspects of modern crystallography complement each other. The study, not only of the ideal atomic structure, but also of the real defect structure of crystal make it possible to conduct a purposeful search for new crystals with useful properties and to improve technology of their synthesis by various techniques for controlling their composition and real structure. The theories dealing with crystals are based on their atomic structure as well as on the theoretical and experimental findings of elementary and macroscopic processes involved in crystal growth.

It is widely accepted fact that semiconductor and optoelectronics are two major fundamental hardware technology groups supporting the information technology. The fast development in the field of optoelectronics has stimulated the search for highly new nonlinear optical crystals for efficient signal processing. New non-linear optical (NLO) frequency conversion materials can have a significant impact on laser technology[1] optical communication[2] and optical data storage technology. [3]

A new approach to high performance, optical quality organic based NLO materials is to consider compounds generally known as "semiorganics", in which a polarizable organic molecule is stoichiometrically bonded within an inorganic host forming either an organic/inorganic salt or an organic ligand/metal ion complex. They are categorized as Type I and Type II semiorganics respectively. Examples of both types have been known for many years, and a few have recently become subject of investigation for their NLO properties. Recent results for synthesis and optical studies of these crystals suggest that a number of these relatively transparent semiorganic compounds have significant second and /or third order NLO responses and often display favorable crystal growth morphologies. Semiorganics share advantages of both inorganics and organics, which include extended transparency (down to UV), high optical nonlinearity, amenable crystal growth, good mechanical hardness and chemical inertness. Another remarkable advantage of this class is the high resistance to laser induced damage.

In the field of crystal growth there are two groups of researchers: -

1. Those who study how crystals grow and

2. Those who grow crystals

A great deal of efforts and money are being continuously spent for producing single crystal materials for exploiting possibility of novel structures and properties which can be put to serve both scientific and technological advances. Still crystal growers and theoreticians find great difficulty in integrating theoretical concepts with actual growth techniques and as a result, crystal growth remains by and large an art, an art of manipulating the theoretical prescription and the practical physical facts with a sole aim to obtain crystals of desired size, perfection and properties.

A successful crystal growth process involves the control of phase change and is categorized in following manner:

1) Solid growth: S→S process involving solid –solid phase transition
2) Melt growth: L→S process involving liquid-solid phase transition.
3) Vapour growth: V→S process involving vapour-solid phase transition.

Crystal growth, as a science, is therefore mostly concerned with the chemistry and physics of heat and mass transport in the relevant phase transitions. Transport concepts are largely built upon equilibrium considerations, i.e. on thermodynamics and phase equilibrium concepts. Crystal growth can be called in a wide sense, the science and technology of controlling phase transitions that lead to (single crystalline) solids.

Thus depending on various phase transitions there are various methods of crystal growth.

1) Crystal growth from solid state.
2) Crystal growth from vapour phase which include
    i) Sublimation
    ii) Vapour transport

        iii) Gas phase reaction

3) Crystal growth from aqueous solution
4) Gel method
5) Hydrothermal growth
6) High temperature solution growth
7) Melt growth

The commonest and cheap way to grow crystals is by separation from aqueous solution, provided the material has a considerable solubility in water at normal conditions. Most of the semiorganic or organometallic crystals are grown by this method.

2.2. Aqueous Solution Method

Recrystallization from aqueous solutions as a method of purification has been practiced for last thousand years. The study of kinetics of crystals growth from solution also has a long history and the method has been used on a large scale for about five decades.

The expression "solution" is most commonly used to describe the liquid, which is the result of dissolving a quantity of a given substance in a pure liquid. The pure liquid is usually, water, though in some rare special case, liquids like alcohol, acetic acid, petroleum, carbon disulphide, ether, benzene, carbon tetrachloride, turpentine, etc. may be used. It is usually convenient to think of the bulk liquid as the "solvent", of the dissolving substance - solid or liquid- as the "solute", and of the result as "solution". At a specified temperature and pressure the saturation concentration of the solute a solvent will dissolve is called the "solubility" of the solute in the solvent. Tables of solubility of many materials can be referred from" Hand book of chemistry and Physics, (Chemical Rubber publishing Co., Cleveland, Ohio) and also from excellent volumes by Comey and Hahn, Dictionary of Chemical Solubilities" (the Macmillan Co., 1921).

Solutions are usually described in terms of the concentrations of substances present in them. The only way to get the solution hold more solid is to raise the temperature until, at a given higher degree; another saturation value will be reached. It can be observed that the saturation of a given solvent by a solid (the solute) cannot be represented by a single value, but by a series of values, which can be plotted on a curve with the temperature as ordinate, and the concentrations of solute as abscissae. For every given solvent, such a succession of points can be plotted for every substance soluble in it; the curves are often referred to as "solubility" curves or curves of "saturation", Typical solubility diagram is shown in Figure 2.1. [4]

The whole concentration –temperature field is separated by the saturated -solution line (solubility curve) into two regions: 1) unsaturated and 2) supersaturated solutions. Saturated solutions are those mixtures, which can retain their equilibrium indefinitely in contact with solid phase with respect to which they are saturated. With increasing the temperature the solubility of most substances increases i.e. the temperature coefficient is positive.

The region of supersaturated solutions can be divided into two subregions:

-Metastable (stable) and

-Labile (unstable) regions.

The terms "metastable" and "labile" appear to be first put forward by Ostwald.[5]

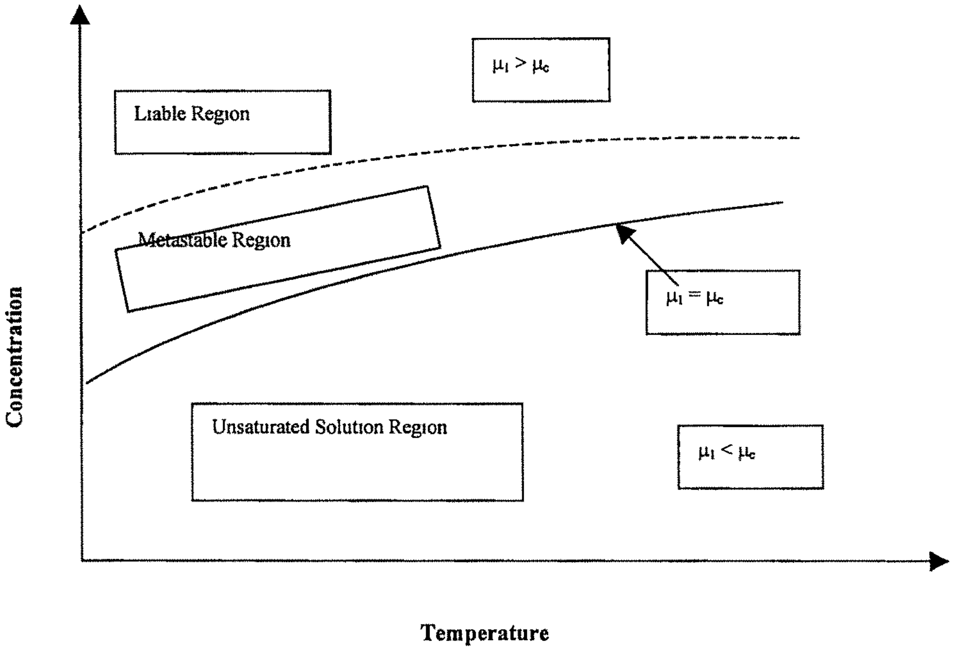


Figure 2.1 Typical solubility curve

The width of the metastable subregion depends on the concentration of chemical, colloidal, and mechanical impurities. Single crystals grow only in the metastable subregion near the solubility curve.

To understand why super saturated solutions are divided in to metastable and labile states, one must first understand the terms chemical potential, driving force etc. The chemical nature and structure of a crystallization medium governs the habit of crystal and its perfection within the limits of a possible crystal structure. Here the author does not consider the solid and the gaseous crystallization media and solely concentrates on the liquids. A very important characteristic of the state of crystallization medium is the degree of its deviation from the equilibrium. This deviation is the **driving force** in crystallization, and is governed, as in other physicochemical processes, by the difference between the free energies of the system in the initial and final states. The process proceeds in the direction, which result in a decrease of the free energy of the system. The free energy of a mole of a substance is known as the **chemical potential** μ. For a dissolved substance in a solution in which the interaction between the particles of the solute is unimportant, μ is given as

$$\mu = \mu_o + RT \, \mathrm{In} C,$$

Where μ_o the chemical potential of the substance when its concentration in the solution is equal to unity, R is then Universal gas constant, T is the absolute temperature, in K and C is the concentration of the solute in the solution.

If the solution is saturated at a concentration C_o and is in equilibrium with a crystal, the chemical potential of the solute is equal to the chemical potential of the crystal. However, if some characteristics of the system (temperature, pressure, or concentration) are altered, the chemical potentials of the crystal and of the solute change as well. The specific relationship, for example, between the temperature and chemical potential of each component of the system, is responsible for the difference between the chemical potentials of a substance in the crystalline state and in solution. This difference is defined as follows:

$$\Delta\mu = (\mu_o + RT\,\mathrm{In}C) - (\mu_o + RT\,\mathrm{In}\,C_o) = RT\,\mathrm{In}C/C_o$$

In practice, when it is not necessary to compare the rates and other features of crystal growth under different conditions, it is usual to employ simpler expressions to estimate the driving force (supersaturation) of the crystallization process. There are many ways of defining the supersaturation but their common feature is that this quantity is not expressed in terms of energy. A quantity used very frequently is the relative supersaturation

$$\Delta\, C/C_o = (C-C_o)/C_o.$$

Near the surface the crystal has an excess of energy above the value of the energy in the interior and this excess is known as the surface energy. The greater the difference between the nature of the bonds in each of two phases in contact, the weaker are the bonds between the particles at the phase contact boundary. Consequently, the greater the difference between the nature of the bonds in the two phase, the larger is the surface energy, and conversely. Therefore to form a boundary separating a crystal from its ambient medium, one must perform work – the work of formation of a nucleus of a new phase. Even in unsaturated solutions, fluctuations of the concentration give rise to regions extending over several ions or molecules, in which the particle position are the same as in the corresponding crystal phase. In a supersaturated metastable solution, the number of such regions and their dimensions are much larger. However, these regions are unstable and they disperse under the action of fluctuations of opposite sign. Such nuclei are called subcritical. If the supersaturation is increased still further so that the labile solution region is reached, nuclei of supercritical dimensions may be forced as a result of any fluctuations. Such a nuclei do not disperse again and new particles are captured by them. Thus, supercritical nuclei grow in size.

The differences and similarities between various crystal growth methods can be analysed on the base of following features:

1) Methods of applying the Driving Force (the difference of the chemical potential):

The chemical potential is a function of temperature, pressure and concentration. Also it is affected by the application of external fields, whether gravitational or electrical.[6] All these parameters are related in different ways to the chemical potential of the medium and the crystal. Therefore, to establish and maintain the necessary constancy of the driving force one needs an apparatus of great complexity.

2) Phase state and number of components in a medium:

A medium may be gaseous, liquid, or solid. The number of components may be one or many. These aspects are common to all methods and fundamental in the growth of crystals under hydrothermal conditions, from molten solutions, from solutions at low temperature, etc.

3) Dependence of the Driving Force on time:

Here there are two possibilities,

a) The chemical potential varies from point to point in the crystallization medium but the nature of the potential distribution does not vary with time i.e. Steady-State- growth conditions.
b) The chemical potential varies from point to point and with time. i.e. Non –Steady- growth conditions.

The difference between these two cases is of basic importance. Under steady state conditions, one can prepare crystals continuously. Moreover, steady- state conditions give the best chance of obtaining very uniform crystals, whereas the variation of any parameter (temperature, concentration, etc.) alters the crystallization process and reduces its uniformity.

The author concentrates only on the Non-Steady growth conditions and explains it further.

2.2.1. Crystallization Under Non-Steady State Conditions:

Crystallization under non- steady sate conditions can be obtain by two methods

1) Crystallization by cooling of solutions and
2) Crystallization by solvent evaporation.

2.2.2. Crystallization by cooling of solutions:

In this method the supersaturation is produced by a change in temperature usually throughout the whole crystalliser.

The solubility of most substances increases with temperature and therefore it is almost always necessary to cool solutions. There are, however, rare cases of substances whose solubility is small. Therefore this method cannot be used for such kind of materials as $Li_2SO_4.H_2O$.

This method consists of the crystallization process is carried out in a way that the point on the curve of the temperature dependence of the composition moves into the metastable solution region in the direction of lower solubility. Since the volume of the crystalliser is finite and the amount of substance placed in it is limited, one cannot achieve simultaneously a constant temperature and a constant supersaturation. Therefore the supersaturation requires a systematic cooling. As discussed earlier, any change in any crystallization parameter (such as temperature) unavoidable affects the crystallization process and gives rise to inhomogneneties of the morphological structure and also possibly composition of a crystal as well. This is the main disadvantage of the cooling method.

2.2.3. Crystallization by Solvent Evaporation:

The solubility curve reported by V. Venkataramanan for Zinc (tris) thiourea sulphate (ZTS), suggests that the variation of solubility with temperature is quite low, hence this proves to be a serious handicap in growing crystals by slow cooling and hence solvent evaporation is a better technique to grow ZTS crystals.[7] However, ZTS crystals have been grown by slow cooling by P.M.Ushasree *et.al* [8]

In solvent evaporation method, an excess of a given solute is established by utilising the difference between the rates of evaporation of the solvent and the solute. In contrast to the cooling method, in which the total mass of the system remains constant, in the solvent evaporation method, the solution loses particles, which are weakly bound to other components, and, therefore, the volume of the solution decreases. In almost all the cases, the vapour pressure of the solvent above the solution is higher than the vapour pressure of the solute and, therefore, the solvent evaporates more rapidly and the solution becomes supersaturated.

Usually, it is sufficient to allow the vapour formed above the solution to escape freely into the atmosphere. If this results in a considerable loss of the solute or if the solvent is toxic, it is necessary to confine, in some way, the solvent vapour to a closed volume. To achieve this, the crystallization vessel (a beaker or a flask) containing the solution is covered with a filter paper. The crystal-seed is suspended into the solution with the help of a thin nylin thread through the filter paper. The vessel is then placed inside a desiccator (Fig.2.2).

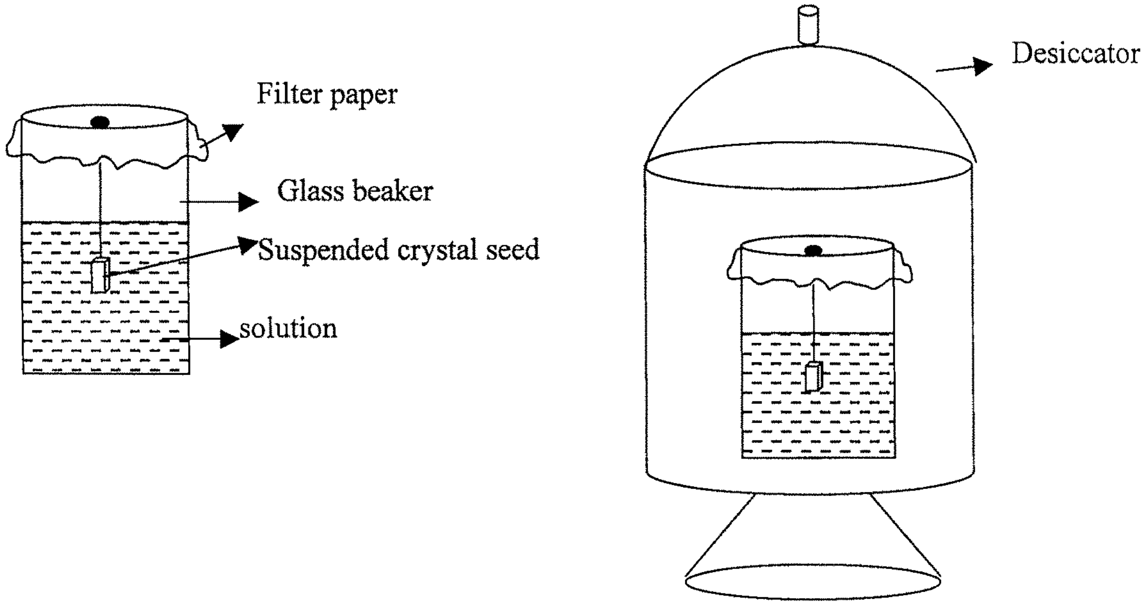


Figure 2.2 Schematic diagram of Crystallization by Solvent Evaporation

When crystals are grown by this method, all the available solute is in the solution. As the amount of solvent decreases and the solute precipitates, the concentration of all those impurities whose segregation coefficient in this system is less then unity increases. When the amount of the solvent is reduced to half its original value, the concentration of such impurities in the solution is practically doubled and, if the segregation coefficient remains constant, the concentration of these impurities in a growing crystal also doubles. Therefore it is necessary to use specially purified solutes and solvents.

Another important factor, which affects the uniformity of crystals, is the supersaturation. The change in the supersaturation in this method depends primarily on the rate of evaporation of the solvent. The rate of evaporation of a unit mass of the solvent depends, other conditions being equal, on the surface area S of the liquid in a crystalliser. The resultant excess of the solute is distributed in the solution whose volume is V. The rate of increase of the supersaturation in the absence of a seed is proportional to S/V. If one uses a cylindrical container, the supersaturation changes little if the liquid column in the cylinder is high but it changes very rapidly when the amount of the liquid is small. The dependence of the rate of loss of the solvent on the height of the liquid column is elementary:

$$S/V = \pi r^2/\pi r^2 h = 1/h,$$

where h is the height of the liquid in the cylinder. Thus, evaporation of the same volume of the solvent at the beginning and end of a run produces very different changes in the supersaturation; the change is greater when the amount of liquid is less. Therefore, it is best to carry out a crystallization run in such a way that the change of the level of the solution is small compared with the height of the liquid column.

The physio-chemical factors that affect the crystal growth are listed below and explained in brief as how they affect the crystal growth.

1) Concentration Currents
2) Temperature
3) Viscosity
4) Growth Pressure
5) pH of the solution

Following precautions must be taken during the growth of crystals from solutions by slow cooling method:

- The crystalliser should be placed in a thermostat at a constant temperature or in a place practically of transient temperature fluctuations
- The glassware used for the growth purpose should be thoroughly cleaned with distilled water.
- The chemicals used should be of high purity.
- The solution must be isolated from a dusty atmosphere.
- For a lower supersaturating requirement, the number of sheets of filter paper covering the crystalliser should be increased or the area of the aperture in the cover may be reduced.
- Precautions should be taken to avoid even slight shocks being transmitted to the solution during crystallization, which would then, presumably, be in a labile state.

2.3. Growth of ZTS from aqueous solution

The growth of Zinc (tris) thiourea sulphate crystals can be explained in three parts,

1. The crystals grown using 99% pure chemicals of Zinc Sulphate and Thiourea
2. ZTS crystals grown at higher temperature
3. ZTS crystals grown using highly pure 99.999% Zinc Sulphate Heptahydrate and Thiourea.

1) For crystal growth, aqueous solutions of molecular proportions of thiourea and zinc sulphate in the molar ratio of 3:1 were reacted under continuous stirring at room temperature (27°C) according to following reaction

$$ZnSO_4 + 3CS(NH_2)_2 \rightarrow Zn[CS(NH_2)_2]_3SO_4$$

The ZTS compound so obtained was dissolved to saturation in distilled water at room temperature and the solution was left in evaporation dish to seed crystallites by free evaporation. The seed crystallites are usually of platelet shape, transparent and so apparently quite perfect. Carefully selected moderate sized crystal seeds were used for the seeded growth of bulk crystals. The average dislocation density for the crystal so obtained was 74 % 10^4 cm^{-2} using formic acid as the dislocation etchant (discussed later in the chapter).

2) In the case of growth at higher temperature, viz. 53°C, a thermostatted oven was used to incubate the solution, which was supersaturated at the same temperature. For both

higher temperature growths, the seed crystallites with [001] held horizontal were lowered into the growth solutions at thermal equilibrium with the respective solutions.

Apparently the growth rate at 53°C was observed to be higher than at room temperature, however, profuse spurious nucleation could not be avoided in 53°C growth, while in the room temperature conditions these were to a tolerable extent. The biggest crystals obtained in any case (1 & 2) were about 15x 7x 5 mm^2.

2) To control the evaporation rate and thus obtain better quality crystals, the growth was carried by using various shapes of glass beakers and conical flask and also higher purity chemicals. To achieve this, thiourea and zinc sulphate heptahydrate of analar grade (99.999%) were taken in the molar ratio 3:1 and were dissolved in a ultrapure-distilled water and were reacted under continuous stirring at constant room temperature (22°C) according to following reaction

$$ZnSO_4.\,7H_2O + 3[CS\,(NH_2)_2] \rightarrow Zn[CS(NH_2)_2]_3.SO_4$$

Figure 2.3 shows the molecular representation of the ZTS crystal. The growth by slow evaporation in conical flask yielded highly transparent crystals at room temperature by while those grown in beaker led to stray crystals.

The ZTS crystals obtained at room temperature in conical flasks and using analar grade chemicals were optically transparent and free from visible inclusions. It was observed that sudden dryness in the room or slight vibrations led to growth of stray crystals. Hence during the growth process extreme care was taken to avoid any kind of vibration. Also the place was kept dust free. The conical flasks used were thoroughly cleaned with distilled water before using for the growth process. The conical flask

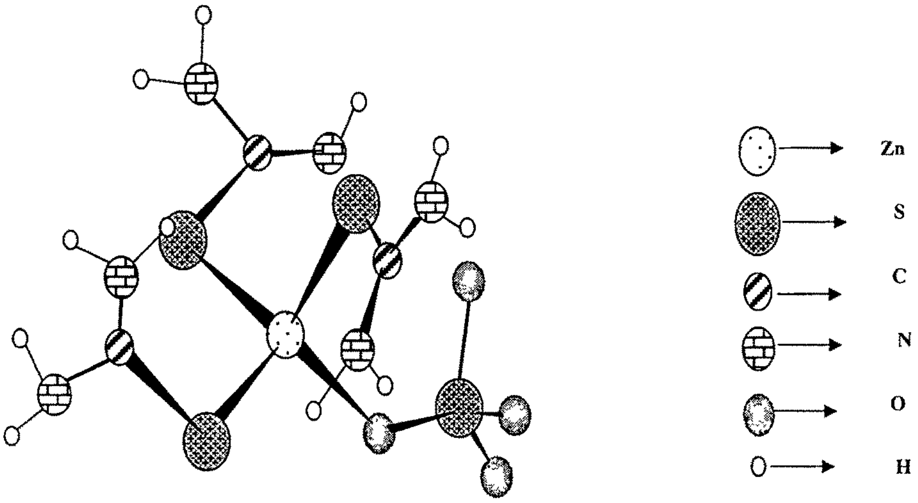


Figure 2.3 A projection of the ZTS molecule; three thiourea sulfur atoms and a sulfate ion oxygen atom are complexed to a Zn (+2) ion in a tetrahedral fashion. Ref. [11]

opening was covered with number of layers of filter paper to control the evaporation rate. The crystals so obtained were taken out from the conical flask after about three week's time. The crystals were then dried on a filter paper and with a cold blast of air and then preserved in a desiccator in small glass bottles. The average dislocation density of the crystals in this case was found to be about 19×10^4 cm^{-2}. The crystal size ranged up to 6 mm × 6 mm × 1.5 mm (along the [010], [001] and [100] axes, respectively).

2.4. Influence of solution pH on growth of ZTS crystals

For studying several direction-dependent properties e.g., second-harmonic generation (which is discussed in the following chapters), preferential growth along specific directions is often required. Growth of the crystal depends on one or more variable conditions present in or imposed on the crystallizing system. These variable conditions include the physicochemical properties like temperature, viscosity, surface tension, degree of supersaturation of the solution, concentration of impurities, pH and others. In the present study the authors investigate the effect of pH on the morphology and the growth rate of ZTS crystals. A previous study reports on the influence of pH on the growth morphology of ZTS crystals, with the pH value ranging from 3.15 to 6.54.[8, 9] The yet lower pH was suggested to be preferable for obtaining better crystals assuming uniform growth along all crystal direction to be signature of better quality of the crystal. In the present study the author has used solutions of pH, from 2.5 to 4.2. The investigation of effect of pH (2.5 to 4.2) on the optical absorption coefficient of ZTS is discussed in chapter 4.

2.4.1. Experimental section

ZTS crystals were grown by slow evaporation at room temperature. For the growth process, puratronic grade chemicals were used. The aqueous solutions of heptahydrate Zinc sulphate and thiourea were prepared in distilled water in the molecular ratio of 1:3. These solutions were reacted at room temperature with continuous stirring. The ZTS compound so obtained was used to prepare the growth solution. This solution was then transferred to four conical beakers in equal amounts. The pH of the solution in each of these was varied, the values being: 2.5, 2.8, 3.6 and 4.2. The pH of the solution was measured with a Hanna Instruments pHep3 microprocessor pH Tester with a resolution of 0.1pH. The electrode was calibrated using standard buffer before and after each experiment. The seed crystal in each case was initially weighed before transferring it to the solutions. The crystals were weighed by a Mettler Toledo AT 261 Delta Range microbalance, having a least count 0.01 mg. After 13 days, several crystals with dimensions up to a few millimeters were obtained in each pH solution, which were used to study the influence of pH on the crystal growth. Figure 2.4 shows the ZTS crystals from different pH solutions. One crystal from each pH solution was weighed and used as a seed crystal for further growth to determine the mass rate of growth per unit mass.

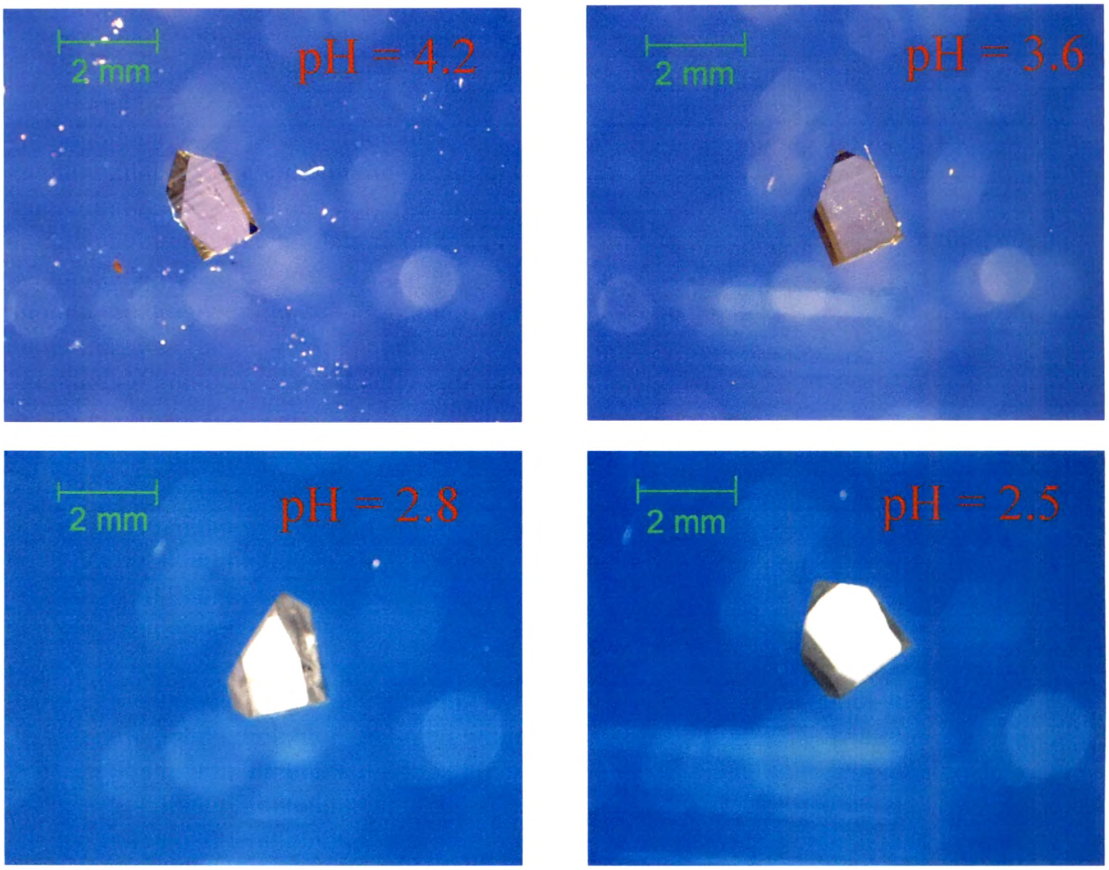


Figure 2.4 ZTS crystals from different pH solutions.

The ratio of length along the c-axis to that along the a-axis and the ratio of length along c-axis to that along the b-axis of the crystals were measured using the Mitutoyo model CD-6"BS Digimatic caliper.

2.4.2. Results and Discussion of pH studies

The pH of the solution from which ZTS crystals are grown appears to have a strong influence on the properties of the resulting single crystals. In Figure 2.5 the mass-rate of growth per unit mass is plotted as a function of the pH. The rate of growth per unit mass decreases with increasing pH. Thus by varying the pH value one can control the growth rate of a crystal. In the present study the crystals grown from a solution with pH 3.6 were measured to have the lowest growth rate per unit mass. The growth rate was measured to be the highest for crystals grown from a solution with pH 2.5. Visual examination indicates that the pH 3.6 crystals appear highly transparent as compared to the crystals grown from a solution with pH 2.5. Thus the lower growth rate at the pH of 3.6 favours growth of better quality crystals.

The results of this study indicate that pH of the growth solution also affects the relative growth of the single crystal along different crystallographic directions. Figure 2.6 is a plot of the relative growth along different crystal directions as a function of pH. In figure 2.6 (A) the c/b ratio, which is the ratio of crystal length along the c-axis ([001] direction) to the length of the crystal along the b-axis ([010] direction), is plotted as a function of the pH. Figure 2.6(B) is a plot of the c/a ratio, which is the ratio of crystal length along the c-axis to the length of the crystal along the a-axis ([100] direction), as a function of the growth solution pH. Figure 2.6(A) suggests that the growth along c- axis

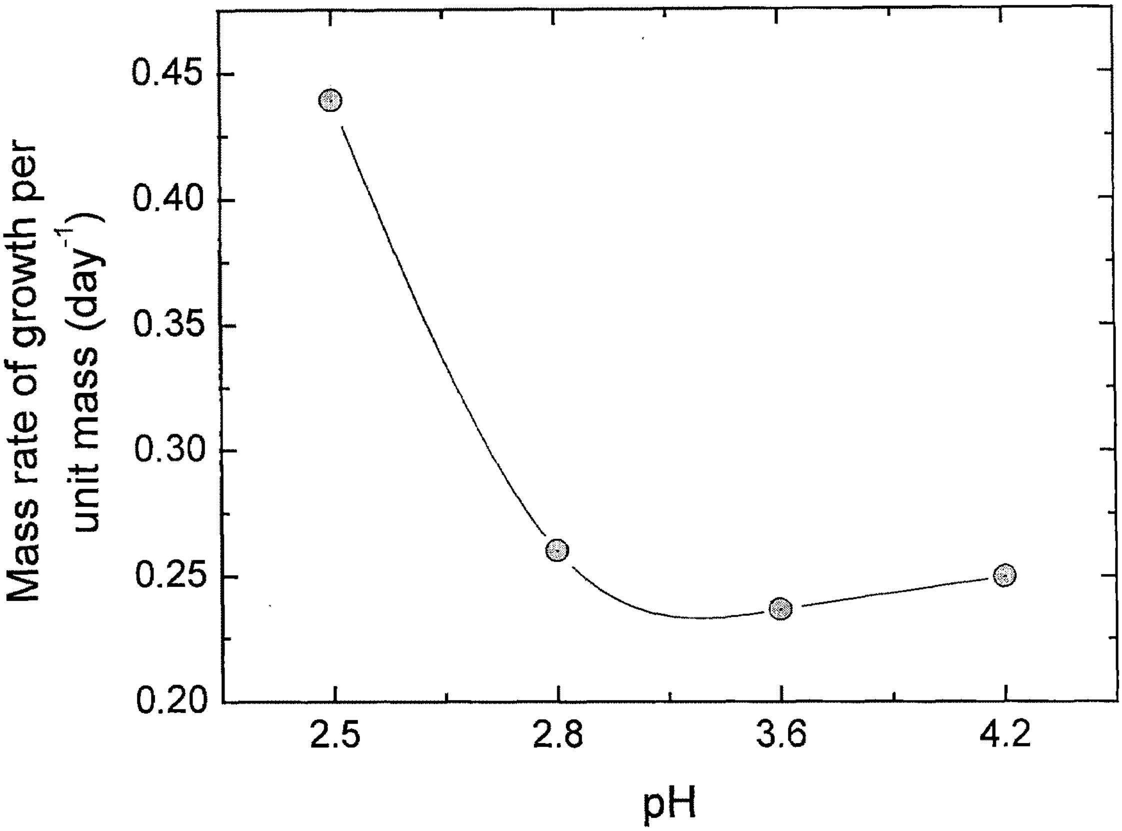


Figure 2.5. Variation of mass-rate of growth per unit mass with pH.

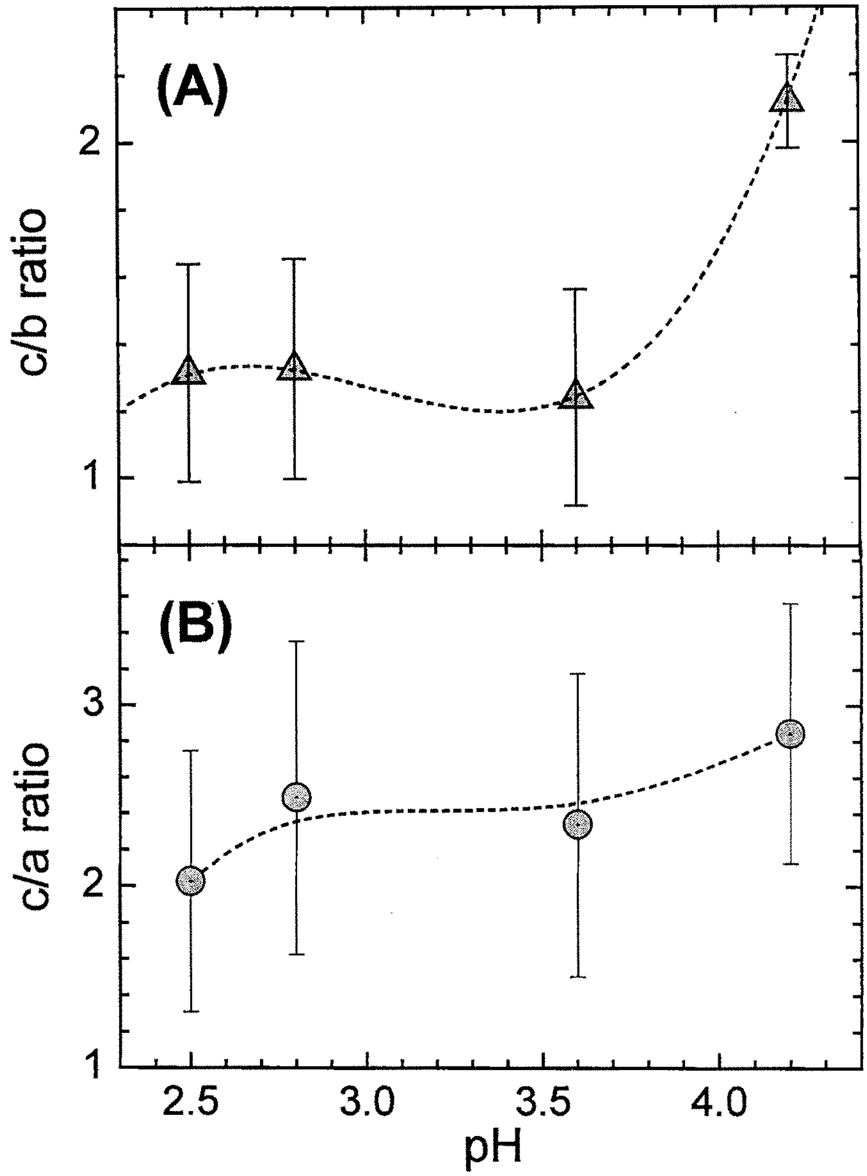


Fig. 2.6 The c/b (A) and the c/a (B) ratios are plotted as a function of the growth solution pH.

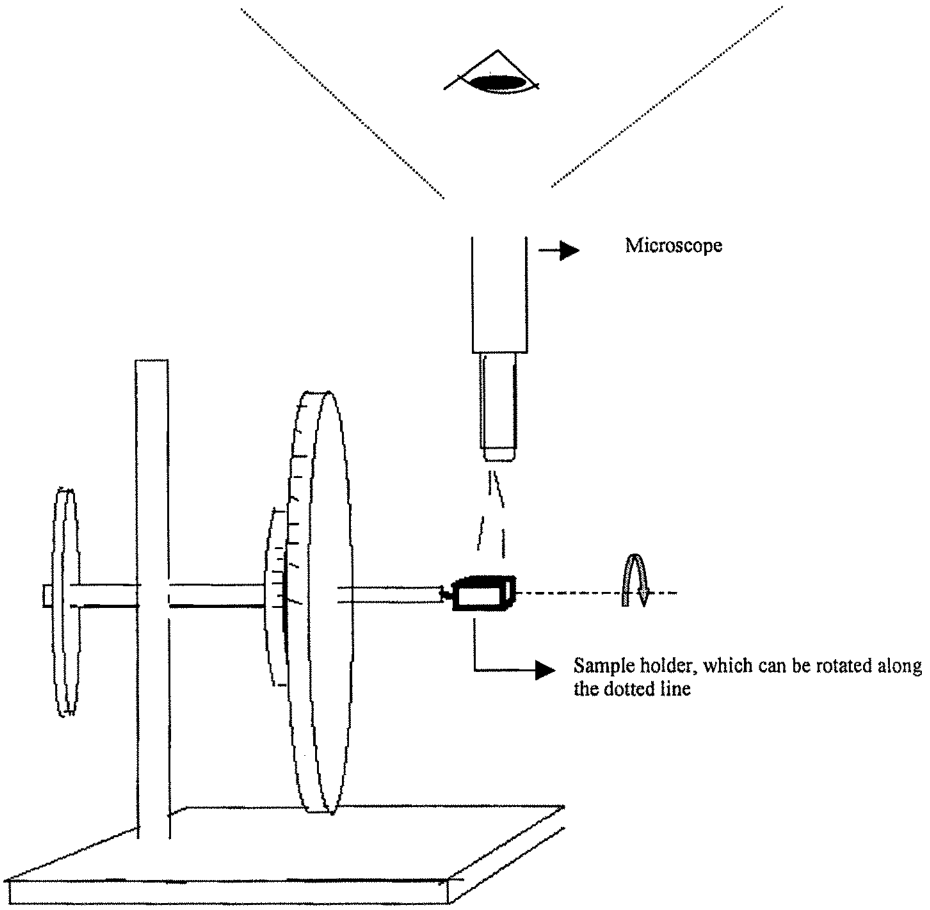
is more for pH 4.2 as compared to that along the b axis. However the changes in the c/a ratio with change in the pH are not statistically significant. A likely explanation is that the sulphate ion, which is oriented along the c-axis of the ZTS crystal and plays a major role in crystal packing and growth, makes the growth along the c-direction susceptible to the solution pH.[10, 11]

2.5. Characterization of ZTS crystals

2.5.1. Experimental Techniques

Optical microscopy is one of the simplest of crystal characterization techniques. A crystal is observed under an optical microscope to access its external structure, surface features and general qualities such as transparency. This tool is also used for the etching and dislocation studies to observe etch-pits formed on the surface of the crystal by the etchant. Microscopes used in this study include a simple table microscope, Vickers projection microscope and the Carl Zeiss –JENA table microscope. An optical goniometer was used to measure the interplanar angles of the crystal. A schematic diagram of the optical goniometer is shown in Figure 2.7.

X- ray diffraction techniques offer one of the most direct ways to characterize the structure of a crystal. It has been used in the present study to confirm the orientation of the crystal employing Laue pattern obtained with the X-ray beam perpendicular to the (100) plane of the ZTS crystal. The X-ray generator used was Phillips No. 1009 with tungsten target tube operated at 35kV and 20 mA. The X-ray photographic film and the crystal were separated by 2.5 cm. The discussion of the Laue pattern is presented later in this chapter.



Optical Goniometer

Figure. 2.7 Schematic Diagram of the Optical Goniometer

Crystallographic problems involving the angles between lines or planes may often be quickly solved by projecting these elements onto a sphere. Standard stereograms for (100) plane and [100] direction of ZTS crystals were constructed on the basis of the reported crystallographic data.

Chemical etching is the simplest tool to detect dislocations in a crystal and it has been used in the present case also. The etching results are detailed later in this chapter.

2.1.1. Characterization, results and discussion

It was observed that the crystals so obtained were generally of platy habit with the prominent face identified as (100) plane. The morphologies of almost all the crystals were identical. The crystals were observed to be non-hygroscopic. Figure 2.8 is the schematic diagram of the typical crystals grown, showing major planes present on the crystals.

The interplanar angles of the habit faces were measured with an optical goniometer and were indexed using the calculated angles or the (100) standard stereogram prepared on the basis of the reported crystallographic data (Fig. 2.9). It was found that the prominent habit faces were (100), (010), (001) and (012), the first three being the major ones. Among these, the (100) plane was the largest, giving a platelet shape appearance to the crystals. A typical crystal measuring approximately 5mm x 5.5mm x 3mm is shown in the photograph Figure 2.10. The calculated and measured values of interplanar angles were found to be in agreement within $\pm 1^{0}$. The (100)

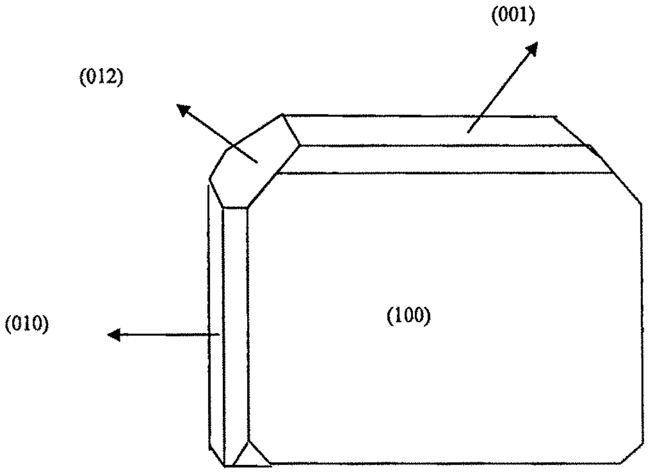


Figure 2.8 Diagrammatic representation of the ZTS crystal. Ref. [11]

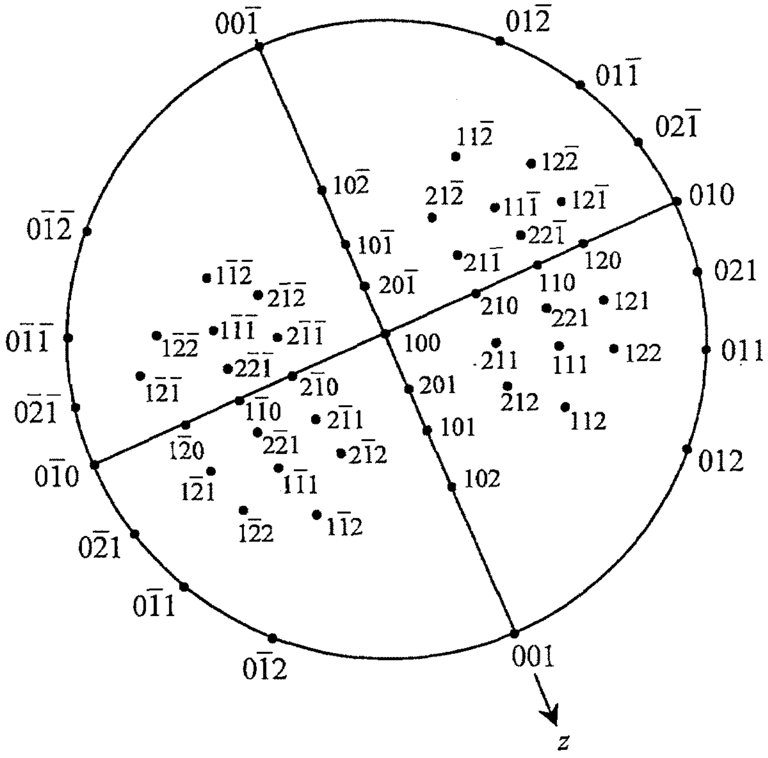


Figure 2.9 (100) stereogram of planes for ZTS

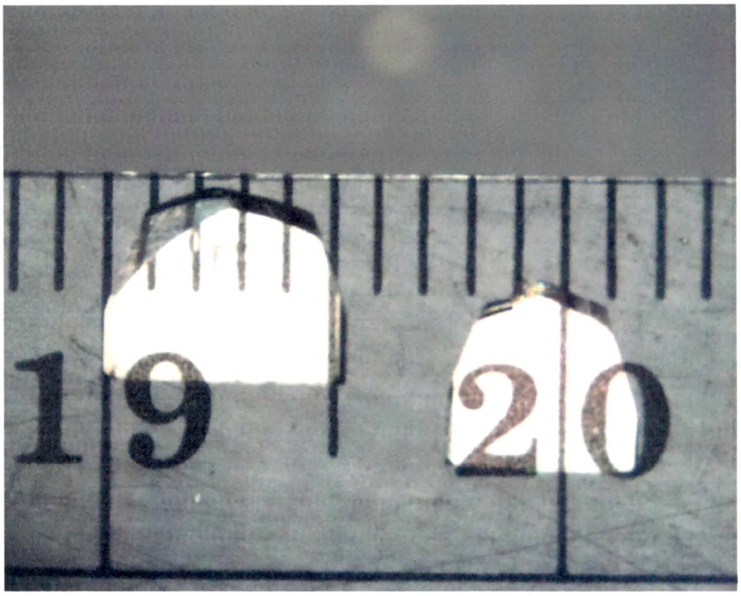


Figure 2.10 ZTS crystals grown from analar grade chemicals

standard stereogram constructed on the basis of the lattice parameters of the crystal is as shown below in Figure 2.9. An X-ray transmission Laue pattern obtained with X-ray beam perpendicular to the (100) plane of the crystal is shown in Figure 2.11. It can be seen in figure the Laue pattern exhibits mirror line centrally in the plane of photograph, which confirms the mm2 point group of the ZTS crystal. A slight misoreintation in mounting of the crystal may be the cause of the deviation observed in the exact symmetrical locations of the Laue spots. The well-defined nature of the spots implies good perfection of the crystal.

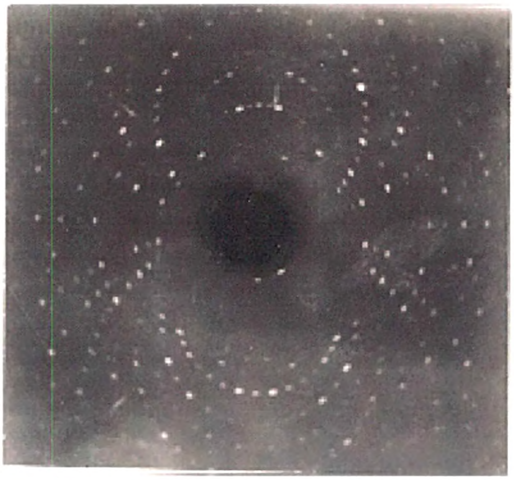


Figure 2.11 Laue Pattern for ZTS crystal

2.6. Etching

2.6.1. Introduction to defects and etching

When a real crystal is formed many factors prevent the formation of a perfectly regular lattice of particles. Thus, departures from the ideal structures, known as defects, appear in a real crystal. Knowledge of the nature and distribution of defects in crystals is necessary because they (1) have deleterious effects on the performance of the crystal device, (2) affect plasticity and crystal strength, electronic and ionic conductivity, and diffusion properties, and above all, (3) play an important role in crystal growth itself. Single crystals for optical applications, especially, should be of the lowest possible defect concentration. Defect and impurity distribution (inhomogeneities) within the single crystal can affect many optical properties, for example a crystal with high concentration of defect will no doubt yield damage threshold well below the values expected of a good laser device. Impurities are expected to affect both the optical absorption and laser damage threshold.

A real crystal is formed as a result of two opposing tendencies:

1) A tendency to achieve an ordered distribution of particles so as to obtain a maximum compensation of chemical bonds;
2) A tendency to mixing and disorder due to their thermal motion of particles.

These tendencies depend on the actual conditions (the chemical nature of the medium, temperature, etc.) under which crystals are grown. It follows that crystals of different degrees of perfection can be obtained.

Defects in a real crystal may be divided into chemical impurities, non-stoichiometry and lattice defects.

When the deviation from the periodic arrangement of the lattice is localized to the vicinity of only a few atoms it is called as a point defect. Interstitials, vacancies, substitutions and antisites are the examples of point defects. However, if the defect extends across large number of atomic sites in the crystal, it is called a lattice imperfection or lattice defect. Lattice defects can be classified as

- Surface or Plane defects
- Volume defects
- Line defects

Grain boundaries, twin boundaries, stacking fault, domain boundaries, etc., are examples of plane defects. Inclusions, precipitates and point-defect clusters are common examples of volume defect. The line defects, known as dislocations, occur in two idealized types, namely, Edge and Screw dislocations. In the field of semiconductor and opto-electronic materials, these defects are particularly pronounced and bear adverse effects on the material properties. These effects are reflected in the yield and performance of devices fabricated from such materials.[12]

Although, the concept of the dislocation was proposed independently by Taylor, Orowan and Polanyi in 1934, the idea lay relatively undeveloped until the end of World War II. There followed a period of approximately 10 years in which the theory of dislocation behavior was developed extensively and applied to practically every aspect of plastic deformation. [13, 14, 15] The theory explained many physical and mechanical phenomena in crystalline materials. Plastic deformation corresponds to the motion of large number of dislocations. The process by which plastic deformation is produced by dislocation motion is termed as "Slip"; the crystallographic plane along which the dislocation line traverses is the slip plane. Macroscopic plastic deformation simply corresponds to permanent deformation that results from the movement of dislocation in response to an applied shear stress. The slip plane together with the slip direction establishes the "slip system".

Virtually all-crystalline materials contain some dislocation that were introduced during crystallization, as a consequence of thermal and mechanical stresses that attend the crystallization process to more or less extents. The dislocation density in a material is expressed as the total dislocation length per unit volume or, equivalently, the number of dislocation that intersect a unit area of a random section. In the next chapter the author discusses in detail the role of dislocation motion / slip in the material response to the hardness indentation and the accompanying plastic deformation.

There have been developed a variety of techniques for observing and studying dislocations in a real crystals. They have provided experimental verifications for most of the concepts of dislocations theory. Principly, all the experimental techniques for detecting dislocations utilize the strain field around a dislocation to increase its effective size. These experimental techniques can be roughly classified into two categories, those involving chemical reactions with the dislocations, and those utilizing the physical change at the site of a dislocation.[16,17] The chemical method includes etch-pit techniques and precipitation techniques. Methods based on the physical structure at a dislocation site include the transmission electron microscopy, X- ray diffraction technique, etc.

Etching is a powerful and relatively simple tool to study the dislocations, their density and distribution. The terms preferential and non-preferential etching are often used to designate the presence and absence of crystallographic orientation effects, respectively. Etching is the result of variation in surface reaction or dissolution rates, brought about by crystallographic orientation, imperfection and chemical composition. It involves spontaneous chemical reaction between the crystal surface and chemical reactant.

Earlier results on the studies of the relationship between spiral growth terraces and screw dislocation imply a connection between etchpits and dislocation. Horn was first to establish that the dissolution of a crystal occurs preferentially at the site of emergence of screw dislocation.[18] The presence of edge dislocation had not been observed on any material; later on it was Vogel observed the presence of edge dislocations in the etched germanium crystals.[19] This discovery of Vogel evoked the interest of many workers and, in the following years, numbers of etching reagents for various materials were found. The list of defect etchants for almost all sorts of materials are given by Johnson[20], Faust[21], Wanekois [22], Holmes [23], Amelinckx [17], Gatos and Lavine [30] Robinson [24] and Kanne and Larrabee.[25] Etch study on LiF by Gilman and Johnson [26] is one of the elegant and pioneering works in the field. Their extensive study on LiF crystals explains the etching phenomenon with respect to various aspects including the distinction between grown in and new dislocations and the movement of dislocation under the action of applied stress. Cabrere and Lavine were the first to give a theoretical explanation of etching process.[27] Scharwachter proposed a concept of dislocation core energy and derived that the dislocation core energy and strain energy both are responsible for the formation of etch pits at dislocation sites.[28] Gatos and Lavine explained the formation of etch pits on the diamond type structure on the basis of the chemical bonding of the atoms along the dislocation lines.[30] A new approach to the problem was made by Frank, which is being called the kinematics theory of growth and dissolution.[29]

The overall etching process may be electrochemically controlled, or diffusion controlled or controlled by the combination of both. The electrochemical concepts involved in chemical etching are discussed by Gatos and Lavine[30] and Gatos[31]. Etching processes are generally very complex and their detailed mechanisms are not quantitatively understood. Although a number of generalizations and guidelines have been formulated over the years, etching techniques are still based on qualitative or empirical approaches. Developing an etchant or an etching procedure for a specific material or purpose is most usually a "trial and error" process.

2.6.2. Chemical Etching:

The chemical etching of crystals surface involves the following reaction sequence:

The reactant/s (a) approach the surface

(b) interact with the surface, and

(c) react chemically

The products (d) disengage themselves from surface and

(e) move away from the surface.

When a chemical reagent selectively reveals the surface micorstructure, including defects, the process is referred to as selective etching. If the revelation of dislocation is of prime concern, the term "dislocation etching" is frequently used.

The process of dissolution of a crystal surface is affected by number of factors such as:

(1) Crystallographic orientation of the surface

(2) Impurity concentration on the surface

(3) Crystal defects present in the crystal surface

(4) Surface damage and cleanliness.

(5) Chemical composition of the etching reagent selected.

(6) Temperature of the etching

(7) The length of time, for the specimen is etched

The etching reagent should possess the following characteristics:

1) It should be of such a composition that it gives all round results and reveal greatest number and variety of structural characteristics, defects and irregularities present. At the same time, it should be able to distinguish its effects from those produced by other etchants that can attack only definite type of defects. Thus, this selective etching should enable one to study only specific defects.
2) The reagent should be simple in composition and stable so that its concentration will not change appreciably upon standing or during use at the working temperature.
3) The reagent should have constant characteristics at a particular temperature so that the conditions of etching can be easily reproduced.

The rate at which the etching reagent attacks the specimen depends upon the temperature at which etching takes place. The precise influence of temperature, however, varies according to the composition and previous history of the specimen. It is, therefore desirable to carry out etching experiments only at definite temperature, for reproducibility.

Time of etching is an important factor contributing to successful etching and the attendant appearance of the structure, making their detailed study possible with the help of optical techniques. For example, if the time of etching is short compared to that appropriate for a particular crystal, the etched structure will not be completely developed nor will there be sufficient details revealed to permit accurate interpretation of the etched area. However, too long a time of etching is just as unsatisfactory, owing to details of the surface structure being thereby obscured to varying degrees and frequently some parts being completely obliterated. The etching time to be used depends upon the conditions of the specimen and the temperature of the reagent.

The etchants, while acting on the specimen should not form products which would precipitates on the surface of the specimen, but must have such a composition that reaction products are immediately dissolved-chemically or physically -in the solution. The products must possess closer affinity with the etchant than with the specimen.

Etch pits formed during etching do not necessarily correspond to dislocation precipitates or impurity inclusions, point defect. Clusters created during irradiation or quenching and fission tracks may also lead to the formation of etch pits. Chemical etching thus is widely accepted technique for analyzing the degree of imperfection of a crystal.

Usually etchants are developed by trial and error method and proper composition of the etchant is selected which produces pits having well defined crystallographic morphology. However, many times, the etchpits produced may not be at the sites of dislocations. Care has to be taken while establishing the reagent as dislocation etchant. The reliability of an etchant as a dislocation etchant is usually judged by the following tests:

1) Etch pits associated with individual dislocation reappear upon repeated polishing and etching, since the dislocation line cannot terminate a within the crystal.

2) When a cleavage is possible for a crystal, the two cleaved surface should show the appearance of etch pit pattern as mutual mirror image.

3) Whenever possible the etch pit density calculation should show a reasonable agreement with the theoretical estimation.

4) The comparison of measured distances between pits on a lineage line to those calculated from the X-ray orientation differences across the boundary also helps in judging the reliability of an etchant.

Although etching is used for the quantitative determination of dislocation densities, not all dislocation intersecting the surface lead necessarily to the formation of etch pits. Hence the one-to-one correspondences between etch pits and dislocations have not been conclusively established. Therefore it is accepted fact that etch pits should not be attributed to dislocation with further confirmation.

Many workers have studied the kinetics of etching process to understand the basic problems of etching mechanisms. They have tried to know the probable types of reaction occurring at the crystal surface and have calculated apparent activation energies associated with the etching process.

The energy, which must be supplied to the reacting substances to make them capable of chemical transformation into the products, is called the activation energy. Abramson and King have suggested that the general limit for the diffusion controlled reactions is 10 Kcal/mole or less.[32] Between 10 to 20 Kcal/mole for the adsorption or deabsorption steps, and for surface reactivity controlled reactions greater than 25 Kcal/mole. In order to determine the activation energy associated with the etching processes, the method adopted by Faust and others[33] has been utilized by the author. Thin platelets were used, in order to minimize the effects on side areas with respect to those on main face area. Surface areas were determined and weight loss by a sensitive microbalance to the nearest micrograms. The chemical used as an etchant was of A. R. quality and distilled water was used throughout the study for washing the glassware. The etching was carried out in at constant temperature and etch rates were measured at different temperatures. In each run the reaction at the solid liquid interface did not change the temperature of the solution more than 1°C. The etched platelets were dipped in xylene to stop the reaction and then further dried on a filter paper and further with a cold blast of air. The apparent activation energy was determined by using the Arhenious equation:

$$k = A.e^{-ERT}$$

where K = the etch rate, A = a constant, E = the apparent activation energy, R = the gas constant, and T = absolute temperature.

A graph of log$K$ versus $1/T$ was plotted and from the slope of the graph, apparent activation energy was determined.

2.6.3. Dislocation-Etching on ZTS crystals: Experiments, results and discussion

Previous studies on etching on ZTS crystals report a dislocation etchant, namely methanol, for the (100) plane of ZTS.[7] Figure 2.12 shows the etch pits due to methanol as an etchant for 20 seconds of etching time, on (100) planes of the crystal. In addition, it could be applicable on the (010) and (001) planes also as shown in Figure 2.13 (a) and 2.13(b). Actually it yields better-defined geometry of pits on (010) and (001) than on (100). Note worthily, the fourth side of the rectangular shape of pits on (100) was observed to be characteristically undeveloped or absent. This may be associated with the two-fold symmetry nonexistent along the a-axis; whereas the symmetry plane normal to the observation plane is manifest in the geometry of the pits. However, the action of methanol was observed to be too fast, frequently tending to make the etch pits overlap.

Various other organic solvents like xylene, propionic acid, benzoic acid, acetic acid and formic acid were tried out and among these, the action of formic acid was found to be more suitable than that of methnol.[34] It can be applied up to 10 seconds of etching time. Figure 2.14 shows, in particular, the etch-pits produced on (100). The geometry of the pits in this case is non-symmetric as in the case of methanol etch pits, but is more contrastive on the general surface, implying a higher longitudinal dissolution rate resulting in pit constitutive planes more inclined to the surface. Various etching experiments were carried out before establishing the etchant as a dislocation etchant. Two cleaved counter-parts of the crystal were identically etched in the etchant and the resulting pattern on the two surfaces showed nearly one-to-one correspondence of the

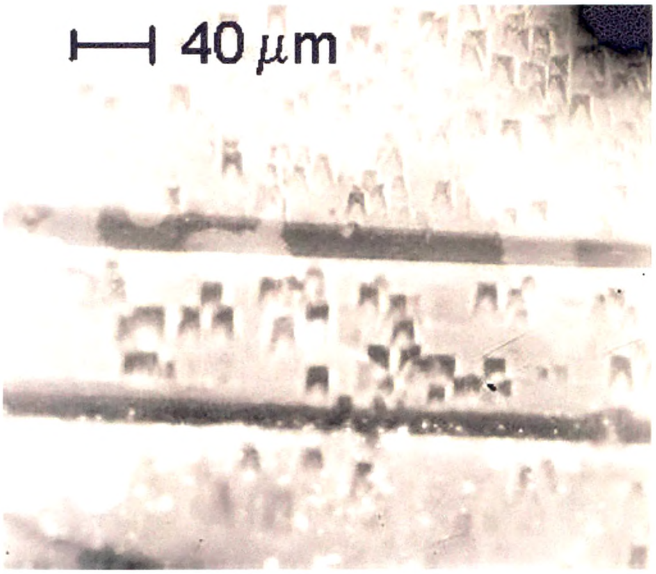


Figure 2.12 etch pits due to methanol as an etchant on (100) plane of ZTS

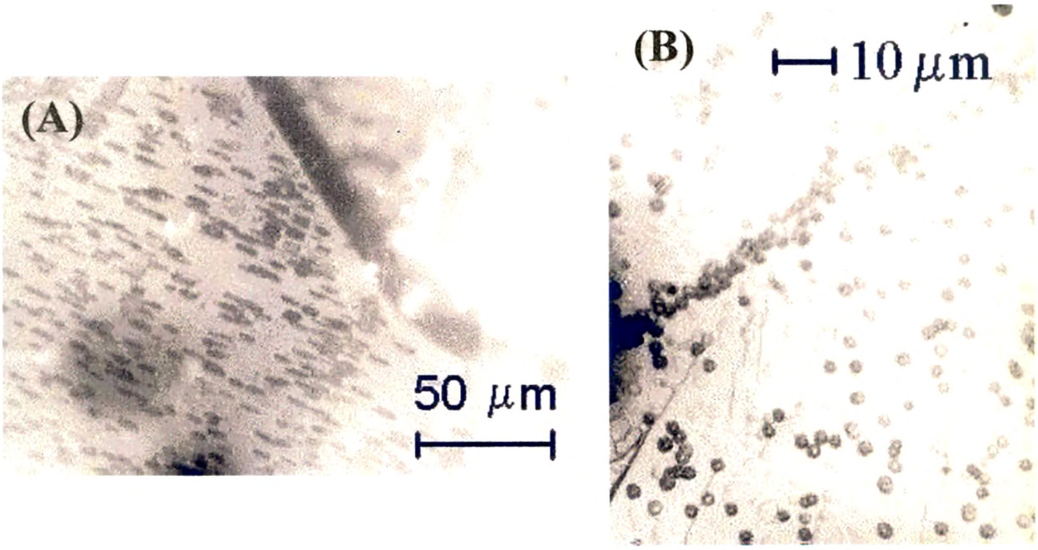


Figure 2.13 (A) Etchpits on (001) plane of ZTS and (B) Etchpits on (010) plane of ZTS, due to methanol as an etchant

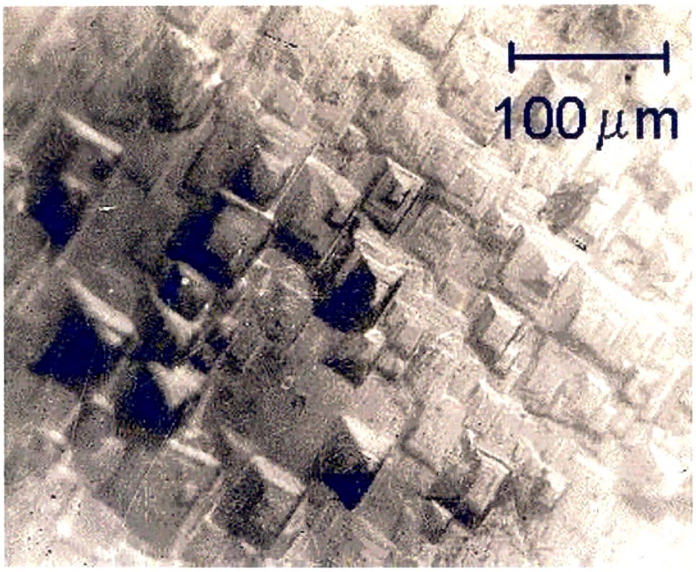


Figure 2.14 Etch-pits on (100) plane of ZTS due to Formic acid as an etchant.

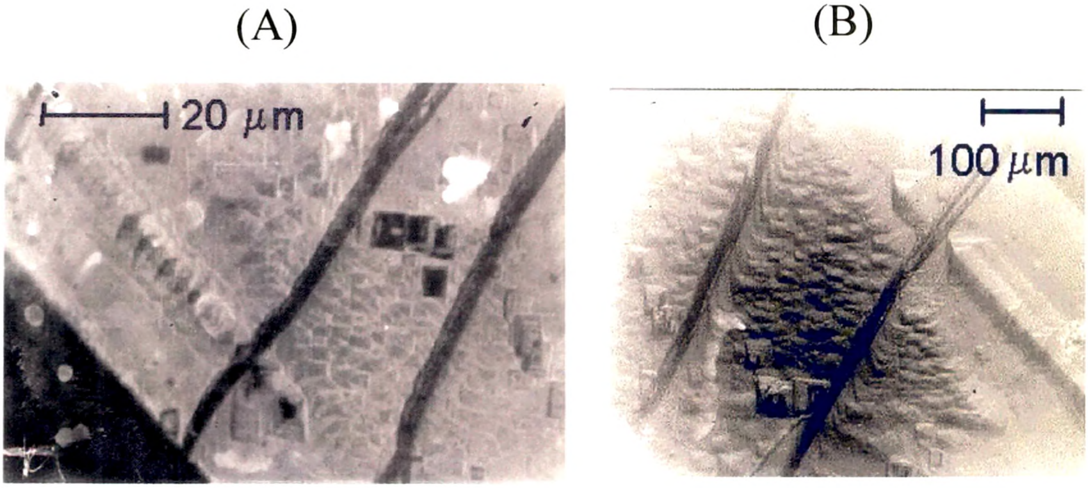


Figure 2.15 (A) and (B) An etch pit row on (100) cleavage plane of ZTS.

etch-pits. Figure 2.15 (A) and (B) is a photograph of a cleaved surface (100), etched in formic acid. One can clearly see in this figure the etch pits matching in number and position suggesting these to be at the sites of dislocations. Figure 2.15 shows a row of etch pits seen near one of the crystallographic edge of the (100) surface. The crystal edge in question is along [021], implying the etch pit row alignment along this direction.

The occurrence of the row itself signifies an unintentional deformation, which might have been produced by the action of cleavage or mechanical handling of the specimen. The etch pits aligned along a crystallographic direction are known to have their origin in the slip mechanism of plastic deformation giving rise to close row of dislocations. Hence, in the present observation, a slip trace along [021] implies the slip plane (012) to be operative, as indicated by a stereographic analysis. The crystal plane (012) intersects the observation plane (100) along [012] direction. The stereograms of crystallographic planes and direction in ZTS crystal (Fig. 2.16) were used to infer this. The correspondence of the effective resolved shear stress (ERSS) this slip plane and the orientational variations of the hardness (discussed in chapter 3) further confirms this fact. The test of successive etching by formic acid on the (100) surface was also carried out, indicating persistence of dislocations into the bulk crystal. Besides etching and matching, other test like etch-pitting on the other morphological planes was also been verified. Figure 2.17 shows the etch pit on the (010) of ZTS. These facts confirm that formic acid is indeed a dislocation etchant for ZTS crystal. It is well known that one of the techniques to measure of the quality of the crystals is to calculate the dislocation density of the crystal. For this, the average number of etch pits produced on unit area of crystal surface was measured. Such measurements on a number of crystals obtained under particular growth conditions were

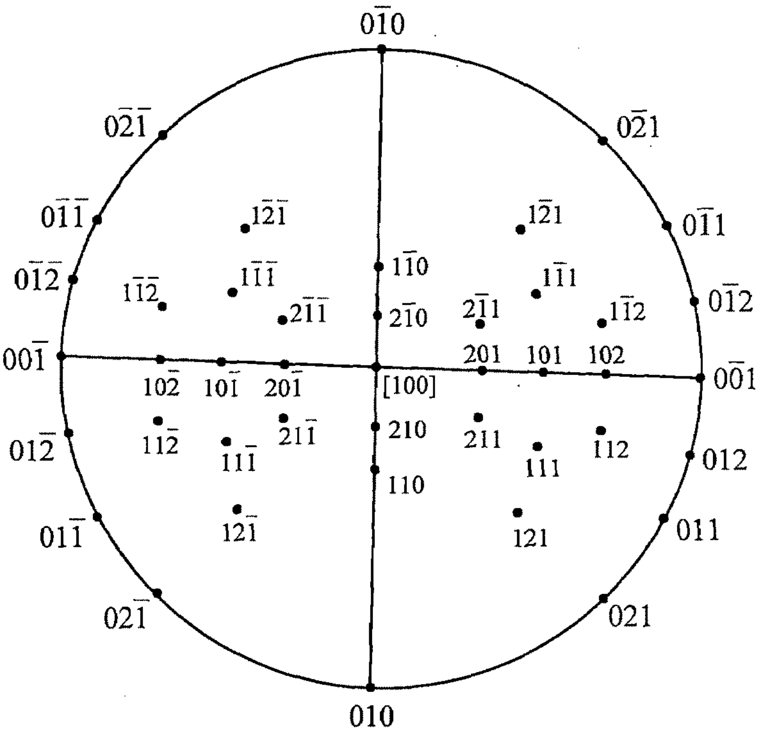


Figure 2.16 Stereogram for direction for ZTS crystal

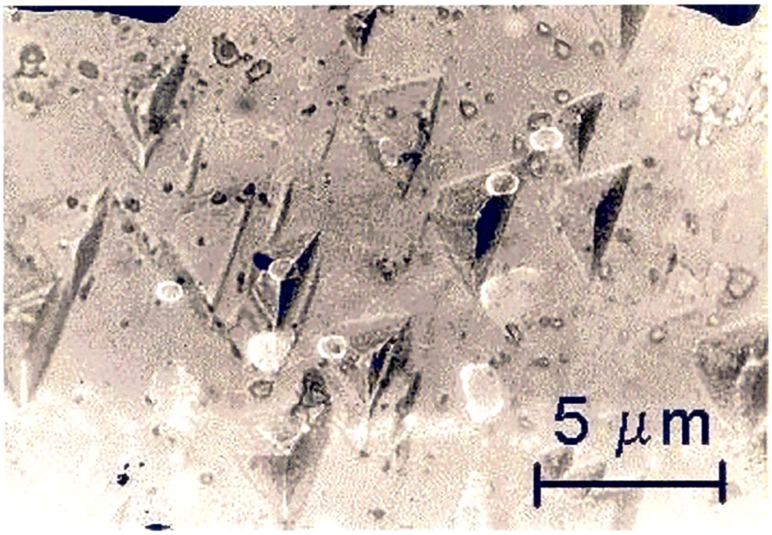


Figure 2.17 Etch-pits on (010) due to formic acid

averaged to assign the characterizing dislocation density. The dislocation density of ZTS crystals obtained by using $ZnSO_4$ (99%) and that using by heptahydrate $ZnSO_4$ (99.999%) have been mentioned earlier in this chapter.

This etchant was further used for assessing the crystal perfection of the crystals obtained from different pH solutions discussed earlier in this chapter. The dislocation density of crystals grown at each pH value was calculated using the etch-pit count method. Figure 2.18 is a plot of the measured dislocation density in ZTS crystals as a function of the growth solution pH. The value of dislocation density decreases with increasing pH. The dislocation density for the pH 2.8 crystals is the highest. Using the dislocation density as a measure of crystal quality suggested that the crystals grown from a solution of higher pH are desirable. However, pH values higher than 3.8 lead to crystals with increasing absorption coefficient (Chapter 4).

The activation energy of dislocation etching by formic acid was determined, as discussed below.

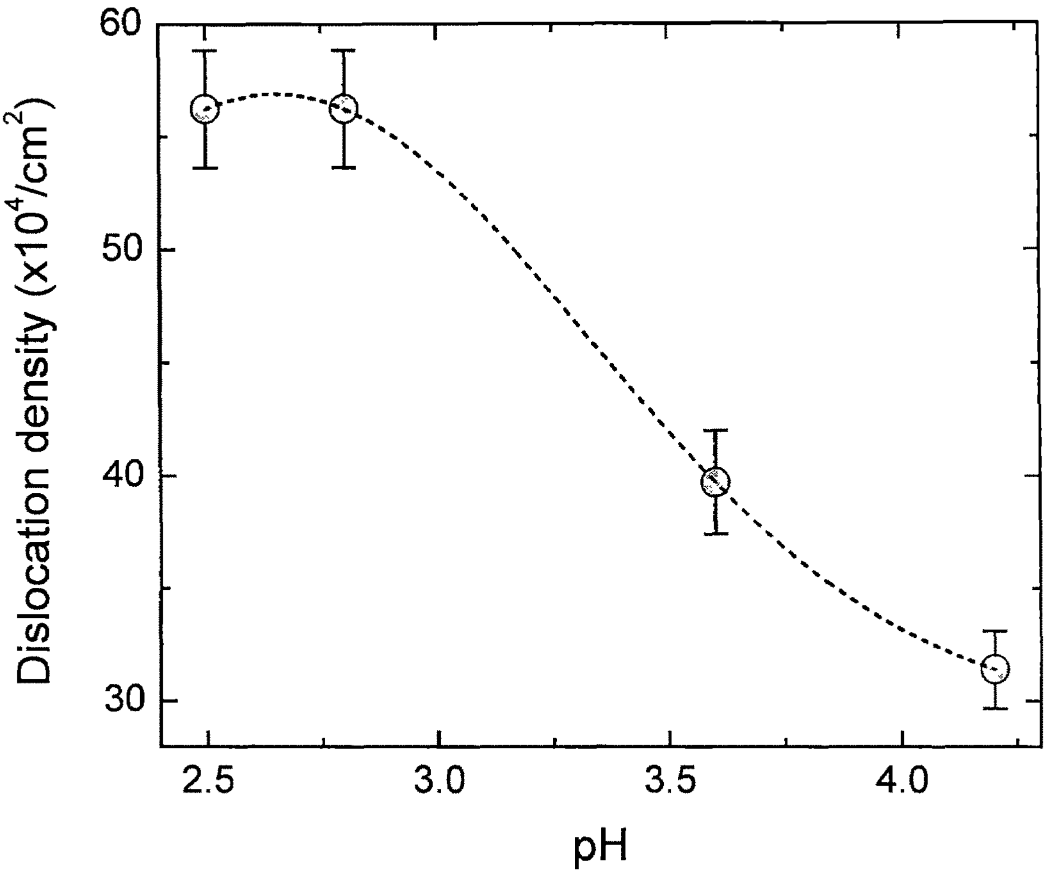


Figure 2.18 Dislocation density in ZTS crystals as a function of the growth solution pH.

2.6.4. Activation Energy of Dislocation Etching for ZTS crystals

For obtaining the activation energy of etching, ZTS platelets with sufficiently large area of (100) were used and for each platelet the surface area was calculated. The etching was carried out at different temperatures respectively by keeping the time of etching constant. The etch rates (rates of weight loss) were measured at different temperatures. The apparent activation energy was determined by using the Arhenious equation mentioned above.

In Figure 2.19 log of the etch rate *K* is plotted as a function of the inverse absolute temperature (*1/T*) and from the slope of the graph, the apparent activation energy was determined. This was calculated to be 8.787 Kcal/mole.[35] This value of the activation energy suggests that the reaction is diffusion controlled.[32]

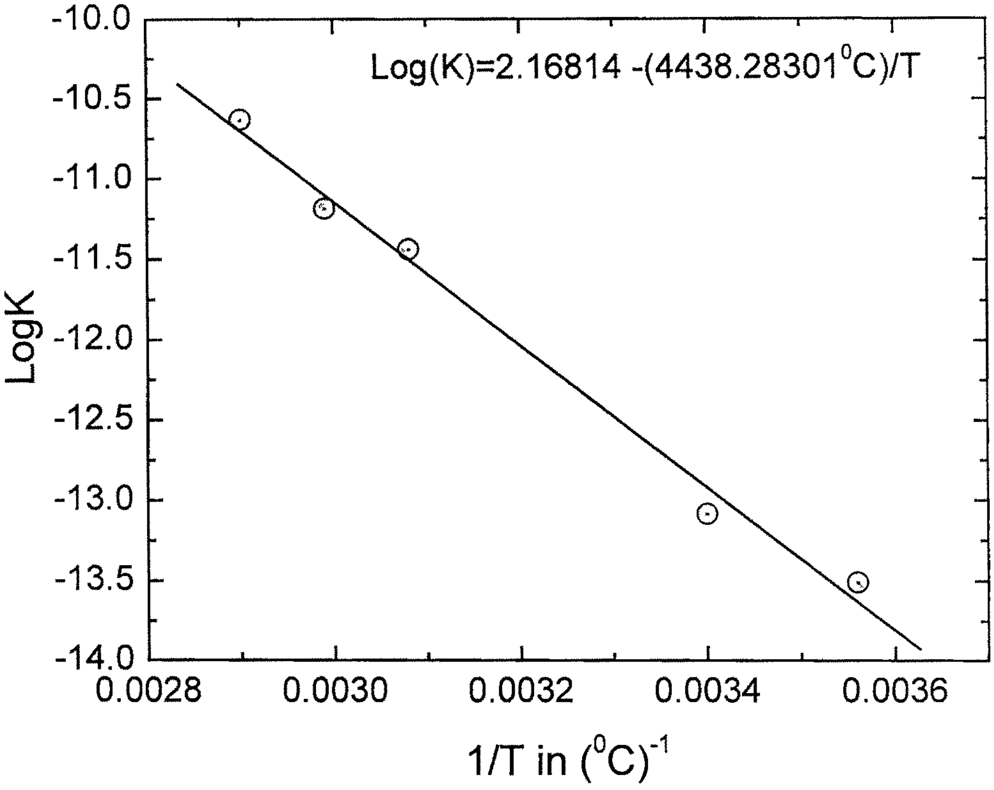


Figure 2.19. Plot of Log*K* versus *1/T*

2.7. Conclusions:

In summary, the Zinc (tris) thiourea sulphate crystals used in this work were grown using the solvent evaporation method. Some authors have reported a method of slow cooling for growth of ZTS crystal. However, this method was found unsatisfactory by the author. The solvent evaporation method yielded crystals of good quality and large size.

The purity of the chemicals used to synthesize the ZTS compound was a critical factor in determining the quality of the crystal. When chemical ingredients with 99.99+% purity were used the resulting crystals were found to be highly transparent as compared to those grown with 99 % purity. The constancy of the temperature during the solvent evaporation process was also an important in ensuring high quality of the crystal.

An important variable for crystal growth that was investigated was the pH of the growth solution. A detailed study of the influence of the growth solution pH on the quality of the solution-grown ZTS single crystals was conducted. Using the dislocation density as measures of crystal quality it was observed that the crystals grown from solutions with pH values in the 3.6 to3.8, yielding the lowest mass rate growth per unit mass, were of the best quality. This indicates that slower growth rate is desirable. Further the growth along the c-axis was found to increases with increasing pH.

A new etchant, formic acid was found to be more suitable than methanol, the earlier reported etchant. The fact that formic acid is a dislocation etchant was confirmed by etching the cleaved pairs and observing the one-to-one correspondence. The geometry of the pits in this case were observed to be non-symmetric as in the case of methanol etch pits, but they were more contrastive on the general surface, implying a higher longitudinal dissolution rate resulting in pit constitutive planes more inclined to the surface. The etching results have been used to interpret the slip system in the crystal. The activation energy of etching using Formic acid as an etchant was determined which suggested the reaction to be the diffusion-controlled type.

REFERENCES

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1. Belt, R. J. Gashurov, G. Liv, Y.S. Laser focus **10**, 110 (1985).
2. Clark, R. S.: Photonics spectra **22**, 135 (1988).
3. Gambino, R. J.: Bull. Mater. Res. Soc: **15**, 20 (1990).
4. "*Growing Crystals for Solution*" by Thomas G. Petrov and Evgenii B. Trevius and Aleksei P. Kasatkin, translated from Russian by Albin P. Tybulewicz, editor, Sovient Physics- Semiconductor, Consultants Bureau: Newyork (1969).
5. Wilh. Ostwald, Z.Physik. Chem., **34**, p. 493-503 (1900).
6. Landau, L. D., and Lifshitz, E. M., Course of Theoritical Physics: Vol. **5**, Statistical Physics, 2nd ed., Pergamon Press, Oxford (1968).
7. V. Venkataramanan *et al.*, J.Cryst. Growth **154**, p.92-97(1995).
8. P. M. Ushasree, R.Jayavel, C. Subramanian, P. Ramaswamy J. Cryst. Growth. **197**, 216-220 (1999).
9. Ushasree, P. M., Jayaval R., Ramasamy, Materials Chemistry and Physics, **61**(3), p. 270-274, (1999).
10. G. D. Andreeti, L. Cavalca, and A. Musatti, Acta Cryst. Sect. **B24**, 683-690 (1968),
11. H. O. Marcy, L. F. Warren, C. A. Ebber, S. P. Velsko, Appl. Optics, **31**, No.24, p.5051-5060 (1992).
12. Rozgonyi, G. A., Petroff, P. M. and Read, M. H. "*Stacking fault by preoxidation gettering of silicon wafers*", J. Elecrochem. Soc. **122**, p.1725-1729 (1975).
13. G.I.Taylor, Proc. R. Soc. London, vol. **145 A**, p. 362 (1934).

14. E. Orowan, Z. Phys. Vol. **89**, p. 605,614,634, (1934).

15. M. Polanyi, Z.Phys. Vol. **89**, p. 660, (1934).

16. P. B. Hirsch, Metall. Rev; Vol. **4** no.14, p.101-104. (1959).

17. S. Amelinekx, "*The Direct Observation of Dislocations, solid state phys*". Suppl. **6**, (1964)

18. Horn, I. H. Phil. Mag. **43**, p.1210 (1952).

19. Vogel, F. L., Pfann, W. G., Coreg, H. E. and Thomas, E. E., Phys. Rev. **90**, p.489. (1953).

20. John, W. G. Prog in Ceram. Sci 2, 1. (1962).

21. Faust, J. W. in "*Compounds Semiconductors*", Vol.**1** Ed. By Willardson, R. K. and Goering, H. L. (1962).

22. Warekois, E. P., Lavine, M. C., Mariano, A. N and Gatos, H. C. J. Appl. Phys. **33**, p.690 (1962).

23. Holmes, P.J. in "*Electro chemistry of Semiconductors*" Ed. by P. J. Holmes, Academic Press, P. (1962).

24. Robinson, W. H. in "*Techinques of Metals Research*" Vol. **II** Part 1, Ed. by R. F. Bunshah Interscience Publishers, p.291 (1968).

25. Kanne P. F. and Larrabee, G. B. "*Characterization of Semiconductor materials*" McGraw-Hill Book. Co. (1970).

26. Gilman, J. J. and Johnston, W. G. "*Dislocation and Mechanical Properties of crystals* ", Wiley Publishers, N. Y., p.116. (1957).

27. Cabrera, N. and Levine, M. M. Phil. Mag. **1**, 450 (1956).

28. Schaarwachter, W. Phys. Status Solidi, **12**, 375 (1965).

29. Frank, F. C. in "*Growth and Perfection of Crystals*" ed. by R. H. Doremus, B. W. Roberts, and D. Turnbull, Wiley New York, p. 411 (1958).
30. Gatos, H. C and Lavine, M. C. in "*In progress in semiconductors*" Vol. **9** Ed. By A. Gibson and r Burgess, Temple Press Books, Ltd; p.3 (1965).
31. Gatos, H. C. in "*Crystal Growth and Characterization*" Ed. By R. Uede and J. B. Mullin, North Holland Publishing company p. 301 (1975).
32. Abramson, M. B. and King, C. B., J.Am.Chem.Soc.**61**, 2290, (1939).
33. Faust, J. W. in "*Reactivity of solids*", Ed, by Mitchell, J. W; John Wiley and Sons, Inc, N. Y; p.337 (1969).
34. C. F.Desai and Sonal Gupte, Surface Review and Letters, Vol.**6**, No.1, p. 23-26 (1998)
35. S. S. Gupte and C. F. Desai, (in preparation for Publication).