

GROWTH AND CHARACTERIZATION OF THIOUREA ZINC SULPHATE (TZS) SINGLE CRYSTAL FOR NLO APPLICATION

Submitted in partial fulfillment of the requirements for the award of

Master of Science degree in Physics

By

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DEPARTMENT OF PHYSICS

SCHOOL OF SCIENCE AND HUMANITIES

SATHYABAMA

**INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

**Accredited with “A” grade by NAAC | 12B Status by
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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of T. Jemima (41590006) who carried out the project entitled "GROWTH AND CHARACTERIZATION OF THIOUREA ZINC SULPHATE (TZS) SINGLE CRYSTAL FOR NLO APPLICATION" under my supervision from November 2022 to May 2023.

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ABSTRACT

The developing field of nonlinear optics, which is at the cutting edge of science and technology, is crucial to the development of photonics. Nonlinear optical (NLO) processes have applications in crucial processes like frequency conversion and optical switching, and photonics, which uses photons for information and image processing, is dubbed the technology of the twenty-first century. There is a huge need for single crystals of device quality since these processes call for materials with second-order NLO effects. The earliest materials to be used for these purposes were inorganic ones. Additional research on organic NLO materials has since developed excellent materials with very desirable properties. Many of the applications require materials with substantial second-order nonlinearities, short transparency cut-off wavelengths, and robust physicochemical performances. Due to the efficiency of harmonic production and sum and difference frequency generation in creating new frequencies from existing lasers, there has been a great deal of work done in recent years to find suitable materials for these procedures. These materials must have high nonlinearity and be transparent to both the laser frequency and the newly generated frequency. These substances should have the following qualities: (i) optical damage resistance; (ii) excellent mechanical hardness; (iii) good thermal and chemical stability; (iv) ability to be grown to usable size; and (v) adequate phase-matching properties. Nearly all of the aforementioned characteristics are found in the thiourea family of crystals, which makes them promising NLO materials. The majority of thiourea's chemical analogs have outstanding NLO properties. Particularly, the materials selected for this work have been recognized as promising nonlinear optical materials. There are five chapters in the project report. An overview of the theoretical side of nonlinear optics is provided in the first chapter. The numerous crystal growth techniques, in particular the growth from solution method, and the most recent state-of-the-art NLO material creation are also provided.

The goal of the current work is to create a newer kind of NLO crystals. The promising NLO materials are found to be crystals from the thiourea family. In light of this, efforts were undertaken to grow and examine the properties of Thiourea Zinc Sulphate (TZS) crystals. The growth and characterization of thiourea zinc sulfate are the topics of the fourth chapter. By employing a slow solvent evaporation process over the course of 35 days, optically excellent single crystals of TZS with size

0.5×0.5×0.5cm³ were produced. The crystals generated in the current work have been characterized using Powder-XRD, Fourier Transform Infrared (FTIR), UV-visible spectroscopy, and thermal analyses. The findings of the current study are discussed in detail.

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LIST OF ABBREVIATIONS AND SYMBOLS

nm - nanometre

μm -----micrometre

Å - Angstrom

θ ----- Theta

α -----Alpha

β -----Beta

γ -----Gamma

g-----Gram

a, b, c Unit cell parameters

λ - Wavelength

ϵ_0 -----Permittivity of free space

ϵ_r -----Dielectric constant

TZS – Thiourea Zinc Sulphate

KDP ---Potassium Dihydrogen Phosphate

KTP ----Potassium Titanyl Phosphate

FT-IR--Fourier Transform Infrared

NLO ---Nonlinear optics

SHG Second Harmonic Generation

UV -----Ultraviolet

XRD---X-Ray Diffraction

CHAPTER 1

INTRODUCTION TO NONLINEAR OPTICS AND CRYSTAL GROWTH TECHNIQUES

1.1 INTRODUCTION:

A period developed in which the study of nonlinear optics has attracted enormous interest. This period began with the invention of the laser in 1960 and Franken's initial observation of the second harmonic generation in 1961. Since then, several publications addressing the theory, creation, and uses of nonlinear optical molecules and materials have surfaced. The ability to accelerate information processes like photonic switching and optical computing, which have potential applications in communication and information technologies, is a significant benefit of using photonics instead of electronics.

1.1.1 Phenomena of Nonlinear Optics

Intense electromagnetic fields interact with materials to produce modified fields that are different from the original field in phase, frequency, or amplitude. This process is known as nonlinear optics (NLO) (Firdous Anwar 1988). A nonlinear optical process known as second harmonic generation (SHG) transforms an optical wave input into an output wave with twice the input frequency. Within a nonlinear medium—typically a crystal—the process takes place. For instance, a Nd:YAG (yttrium-aluminum-garnet) laser operating at 1064 nm is frequently employed in this frequency doubling process to generate green light (532 nm). Because crystalline solids lack a center of symmetry, light that is incident on them produces light at the second and higher harmonics of the incident frequency. Second harmonic generation (SHG) is an important nonlinear characteristic of non-centrosymmetric crystals, and both the phenomenon and the materials in which it occurs are the focus of extensive research [01].

In nonlinear optics, light of one wavelength is converted to light of a different wavelength. When considering the electrons in a nonlinear crystal, it is easiest to see how new wavelengths of light might be created. A nonlinear crystal's bound electrons are held to the lattice point by a potential well that

functions as a spring (Figure 1.1). An electron is pulled back by the spring with a force proportionate to the displacement if an external force pushes it out of its equilibrium position. The electron's deviation from its equilibrium position causes the spring's restoring force to grow linearly. The electrons are pulled away from their equilibrium location by a force created by the electric field in a light wave that is travelling through the crystal. The electrons in a typical optical material fluctuate about their equilibrium position at this electronic field's frequency. These electrons in the crystal "generate" light at the frequency of the original light wave because, according to the fundamental law of physics, an oscillating charge will radiate at its frequency of oscillation.

There are various ways in which the nonlinear material differs from the linear material. A nonlinear substance is one in which the electrons are held together by incredibly brief springs. The electrons can be pulled by the material's electric field to the point where they reach the ends of their springs if the light travelling through the material is powerful enough. The restoring force then deviates from its linear relationship with the displacement and turns non-linear. Instead of being drawn back smoothly, the electrons are jerked back forcefully, and they oscillate at frequencies other than the driving frequency of the light wave. These electrons emit light at the brand-new frequencies, which results in the brand-new wavelength of light. Energy conservation dictates the precise values of the new wavelengths. It is necessary for the energy of the new photons produced by the nonlinear interaction to match the energy of the photon that was consumed. The second harmonic generating process's photons.

1.1.2 Nonlinear optics explained in theory

Nonlinear effects can be explained by looking at how a light beam moves through a solid. Electric dipoles are formed by the atoms' nuclei and related electrons in solids. These dipoles fluctuate as a result of the electromagnetic radiation's interaction with them, and in accordance with the fundamental principles of electromagnetism, the oscillating dipoles become sources of electromagnetic radiation.

The dipoles produce radiation at the same frequency as the incident radiation if the vibration's amplitude is minimal. The relationship between the incident

radiation intensity and vibration amplitude become nonlinear as incident radiation intensity rises, leading to the development of harmonics in the radiation frequency generated by the oscillating dipoles. As the incidence intensity increases, frequency doubling, second harmonic generation, and even higher-order frequency effects happen.

The induced polarization is a nonlinear function of the applied field in a nonlinear material. A crystal made up of molecules with asymmetric charge distributions and positioned in the crystal in such a way as to retain a polar orientation is a medium that exhibits SHG.

The induced polarization is linearly proportional to the electric field at very low levels.

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E}$$

Where,

χ is the linear susceptibility of the material,

$\mathbf{E}$ is the electric field vector,

ϵ_0 is the permittivity of free space.

High fields cause the susceptibility to become field-dependent and the polarization to become field-independent. In order to express this nonlinear reaction, the induced polarization is written as a power series in the field.

$$\mathbf{P} = \epsilon_0 \chi^{(1)} \mathbf{E} + \epsilon_0 \chi^{(2)} \mathbf{E} \cdot \mathbf{E} + \epsilon_0 \chi^{(3)} \mathbf{E} \cdot \mathbf{E} \cdot \mathbf{E} + \dots$$

Since the sum of two or more oscillating fields produces oscillation at a variety of frequencies in nonlinear terms, the aforementioned equation can be represented as follows in terms of frequency:

$$\mathbf{P}(-\omega_0) = \epsilon_0 \chi^{(1)}(-\omega_0; \omega_1) \cdot \mathbf{E}(\omega_0) + \epsilon_0 \chi^{(2)}(-\omega_0; \omega_1, \omega_2) \cdot \mathbf{E}_{\omega_1} \cdot \mathbf{E}_{\omega_2} +$$

$$\epsilon_0 \chi^{(3)}(-\omega_0; \omega_1, \omega_2, \omega_3) \cdot \mathbf{E}_{\omega_1} \cdot \mathbf{E}_{\omega_2} \cdot \mathbf{E}_{\omega_3} + \dots$$

Where χ is the medium's nonlinear susceptibility. The linear term $\chi^{(1)}$ is in charge of the linear optical characteristics of a material, including its refractive index, dispersion, birefringence, and absorption. In noncentrosymmetric materials,

second harmonic generation is described by the quadratic expression $\chi^{(2)}$. The cubic term $\chi^{(3)}$ is in charge of optical instability, stimulated Raman scattering, third harmonic production, and phase conjugation. The fundamental frequency can therefore be multiplied to produce second, third, and even higher harmonics by the induced polarization. $\chi^{(2)} = 0$ if the molecule or crystal is centrosymmetric. Equation 1.3 states that the polarization caused by the first nonlinear term is projected to be $+E^2$ if a field $+E$ is applied to the molecule (or medium), but if the medium is centrosymmetric the polarization should be $-E^2$. In centrosymmetric media, this paradox can only be reconciled if $\chi^{(2)} = 0$.

In centrosymmetric media, $\chi^{(3)}$ is the first non-zero nonlinear term because, according to the same reasoning used for the next higher-order term, $+E$ produces polarization $+E^3$ and $-E$ produces $-E^3$. The two input wavelengths for the second harmonic generation are the same, or $2\omega_1 = \omega_2$ or $(\lambda_1 = 2 \lambda_2)$.

This results in the creation of a polarized wave with the second harmonic frequency of $2\omega_1$. The medium's phase velocity and wavelength are what determine the refractive index, or n_1 . The electromagnetic wave receives energy from the polarized wave with a frequency of ω_2 .

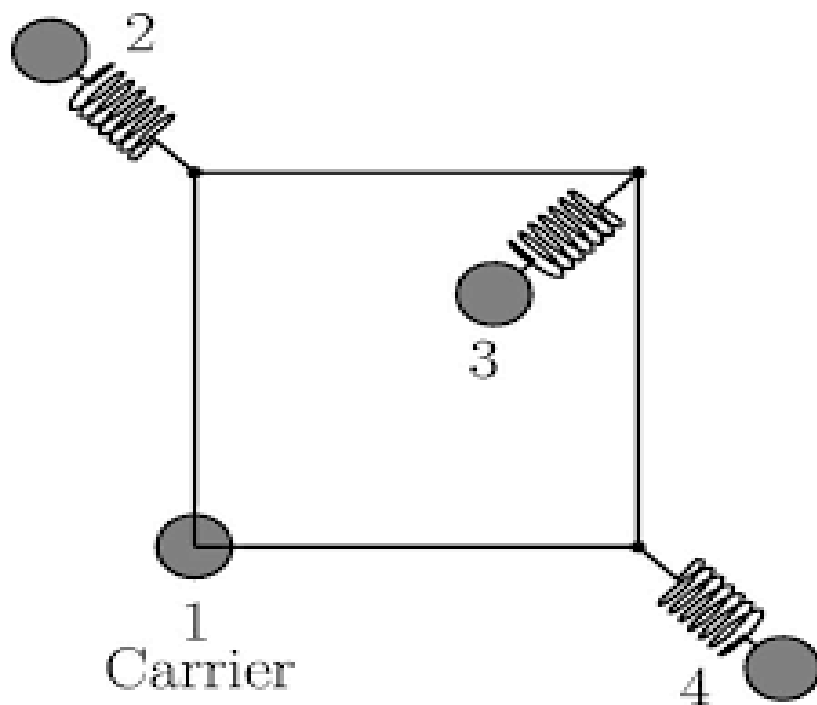


Fig.1.1 Schematic representation of the Einstein molecule, in which particle 1 is fixed and acts as the carrier of the lattice. The movement of all the remaining particles is given relative to the position of particle 1.

Nonlinear optics (NLO) field added in the research as well as in the industry before five decades by the Frenken et al for the discovery of the second harmonic generation in which it was first used in the development of the first operating laser and frequency doubling phenomena. A nonlinear optical (NLO) material plays a significant role in information technology, industrial applications in applied aspects of nonlinear optics. The continuous studies of NLO materials provide a new way of development of optical communication system with high performance for use as components in optical devices [02].

In 1961, Franken and his co-workers study the experiment in which light was made to traverse a quartz crystal and observed ultraviolet light at twice the frequency of a ruby laser light. If the refractive index of a crystal is modulated by frequency of an alternating applied field, then beam passing through the crystal is phase modulated which gives the bands at combination frequency and this create a different frequency of the crystal by the altering the parameters of the crystal by the phase modulation [02]. Nonlinear optics is the study of produced modified electromagnetic field by the interaction of intense electromagnetic fields with materials which gives the resultant field which is different from the input field in phase, frequency and amplitude. Basically, phenomena of nonlinear optical (NLO) are 'nonlinear' in the sense of that they occur when the response of a material system to an applied optical field in nonlinear manner. Second harmonic generation of the materials occurs due to the atomic response in which it is depend on the strength of the applied optical field.

Nonlinear optical (NLO) frequency conversion materials have most important factor in optical communication and optical storage technology. Ferroelectric and antiferroelectric materials are used in electro optical devices, calculators, laser equipment due to their important characteristics [3-4]. Now a day, there is a demand on developing new ferroelectric and antiferroelectric materials in order to increasing an efficiency of the devices. The development of the new materials can be divided in to three categories such as

- Growth of single crystals of promising NLO materials
- Improving the characteristics of NLO crystals
- Discovery of new NLO materials

There for continuous research is going on the antiferroelectric and ferroelectric materials by changing the concentration of materials gives information of phases as well as phase transition due to their change in properties [5-7]. Various research and investigation have been done on the crystal growth and its properties of the Potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP), potassium niobate, potassium thiourea phosphate (KTP) and lithium niobate. From the last 10 year, the interest in the crystal growth, growth rate, size of the crystal and its application in the field of industry increases using the new technique for the pure as well as doped crystals [8-20].

1.2 CRYSTAL GROWTH

Without crystals, the fields of electronics, photonics, and fiber optic The unsung heroes of modern technology are crystals. Communications—which rely on substances/crystals like crystallized films for the microelectronics and computer industries, as well as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, electro-optic, acoustic-optic, and photosensitive materials. It is possible to study crystal growth from the perspectives of physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, etc. There has been an increase in interest in crystal formation procedures over the past few decades, especially considering the rising demand for materials for technological applications [26][27][28]. Single crystals are three-dimensional periodic atomic arrays with repeated distances.

Due to the great advantages of single crystals, the preparation of single crystals is unquestionably more difficult than that of poly-crystalline material [29]. The influence of grain boundaries obscures or complicates many physical aspects of solids, which is why single crystals are grown. The main benefits are the lack of

borders between individual grains, anisotropy, and homogenous composition, all of which are present in polycrystalline materials by necessity. The most recent developments in the aforementioned domains show how single crystals have had a significant impact on modern technology. Therefore, high-quality single crystals are required for the device to operate at its peak performance. Due to the significance of single crystals for both theoretical and practical research, the growth of single crystals and their characterization for device manufacture have gained significant momentum.

1.2.1 CRYSTAL GROWTH TECHNIQUES

A crystal can grow using a simple, low-cost method or a complicated, expensive one, and it might take minutes, hours, days, or even months to crystallize. When crystallization ingredients are transported in the solid, liquid, or vapor phases, single crystals can be created. This allows crystal growth to be divided into the following three categories:

- (i) Solid-to-solid phase transition during solid growth
- (ii) Liquid Growth - Transition from the Liquid to Solid phase
- (iii) Vapour Growth - Transition from the Vapour to Solid phase

Crystal growth methods are divided into four categories based on the phase transition process: solid growth, vapor growth, melt growth, and solution growth[30]. The solid growth of crystals results in the transformation of a polycrystalline piece of material into a single crystal by causing the grain boundaries to be swept through and pushed out of the crystal [31]. Several authors [32] [33] [34] have gone into great detail about the aforementioned techniques. Reviews and publications by Faktor and Garrett (1974) on vapor growth, Brice (1973) on melt, Henisch (1970) on gel growth, Buckley (1951) on solution growth, and Elwell and Scheel (1975) on high-temperature solution growth detail the many approaches used in each category.

An effective process is one that yields crystals fit for use while using the least number of resources. A better growth method selection is crucial as it indicates

potential impurity and other defect concentrations. The optimal way to grow a specific material will rely on its properties. Melt and solution growth are both considered forms of liquid growth in the categories indicated above. Nearly 80% of single crystals are believed to form from melt, compared to only 2% by hydrothermal methods, 5% from vapour, 5% from low temperature solution, 5% from high temperature solution, and 3% from the solid.

In contrast to earlier research, it appears that crystal growers' most important duty now is to learn the fundamentals of the relationship between crystal qualities and growing circumstances that are identified as specific factors. The design of crystal growth systems and control of growth parameters are influenced by this fundamental knowledge of atom deposition onto a suitable substrate surface, crystal growth, the generation of faults in the atomic structure during growth and subsequent cooling to room temperature, and crystal defect structure. Although the underlying principles are fairly straightforward, the intricate interactions at play, as well as the uniqueness of the various materials, systems, and growth processes, have prevented experimentally verifiable predictions from scientific principles from being fully realized; good crystal growth is still largely an art. Crystal growth has therefore long been associated with alchemy. The Art and Science of Growing Crystal [35], one of the first textbooks on crystal formation, expresses this point quite well. Recent developments have simplified growth systems and transformed the crystal growth process from an art to a science, technique, and field, with the reduction of growth temperature, elimination of reactant transport variables, use of better-controlled energy sources to promote specific reactions, and increased development and application of appropriate diagnostic techniques.

1.2.2 Classifying Crystallization Processes

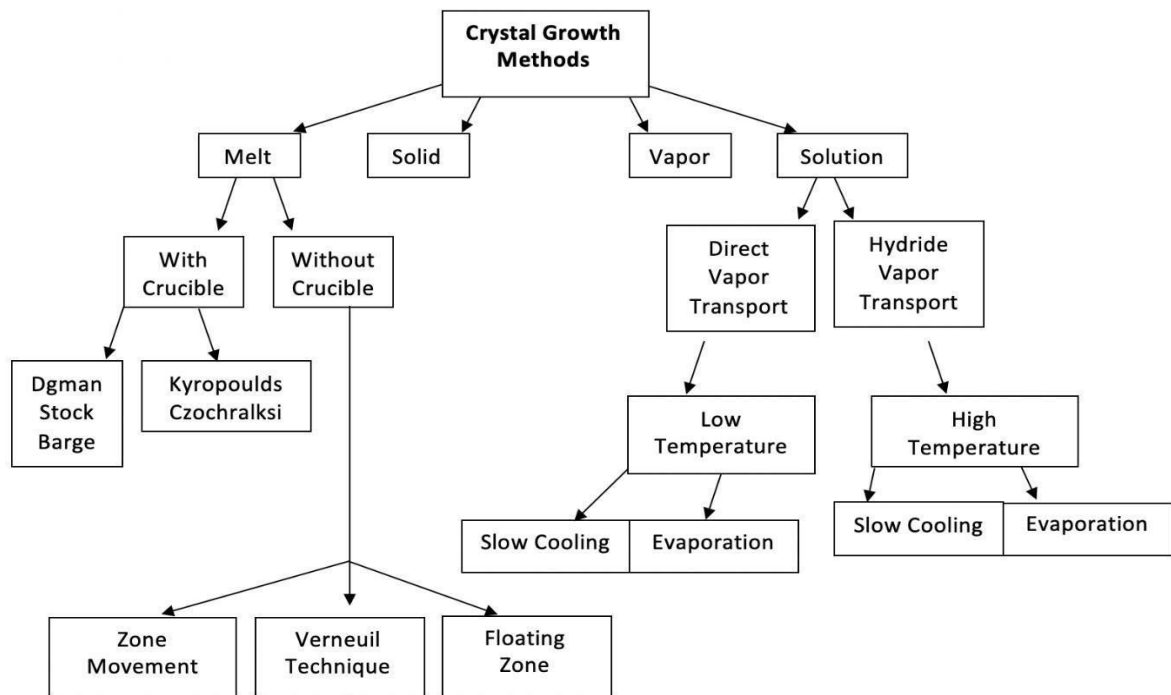


Figure 1.2 Process of crystal growth

1.2.2.1 MELTING TO GROW

Any material can be grown as a single crystal from the melt as long as it melts uniformly, without breaking down at the melting point, and without going through any phase changes between the melting point and room temperature. The strategies below are used based on the thermal properties.

- Bridgman technique
- Czochralski technique
- Kyropoulos technique
- Zone melting technique
- Verneuil technique

1.2.2.1(i) Bridgman–Stockbarger Technique

Percy Williams Bridgman of Harvard University and Donald C. Stockbarger

of MIT (1895–1952) are the namesakes of the Bridgman–Stockbarger technique. Both processes, which are primarily used to solidify single crystal ingots (boules), can also be used to solidify polycrystalline ingots.

Using these techniques, polycrystalline material is heated above its melting point and then slowly cooled from one end of its container, which houses a seed crystal. Along the length of the container, a single crystal that shares the same crystallographic orientation as the seed material gradually grows on the seed. Either a horizontal or vertical geometry can be used to carry out the process. Certain semiconductor crystals, such as gallium arsenide, for which the Czochralski process is more challenging, are frequently produced using the Bridgman method.

The Stock Barger technique needs moving the boat across a temperature gradient in order to produce the desired single crystal. Polycrystalline ingots can be created from a feedstock made up of rods, chunks, or any other irregularly shaped components after they have been melted and allowed to resolidify when seed crystals are not used as stated above. The ingots that were created as a result had microstructures that are typical of the aligned grain metals and alloys that solidify in a particular direction.

The material is melted using the Bridgman method in a vertical cylindrical container with a tapered conical bottom. The container is gradually lowered from the furnace's hot zone into its cold zone. For these processes, the rates of movement range from roughly 1 to 30 mm/hr. Crystallization starts at the tip and typically progresses via growth from the initial nucleus created. For materials that break down before melting, this approach cannot be employed. Low melting point materials are best suited for this method.

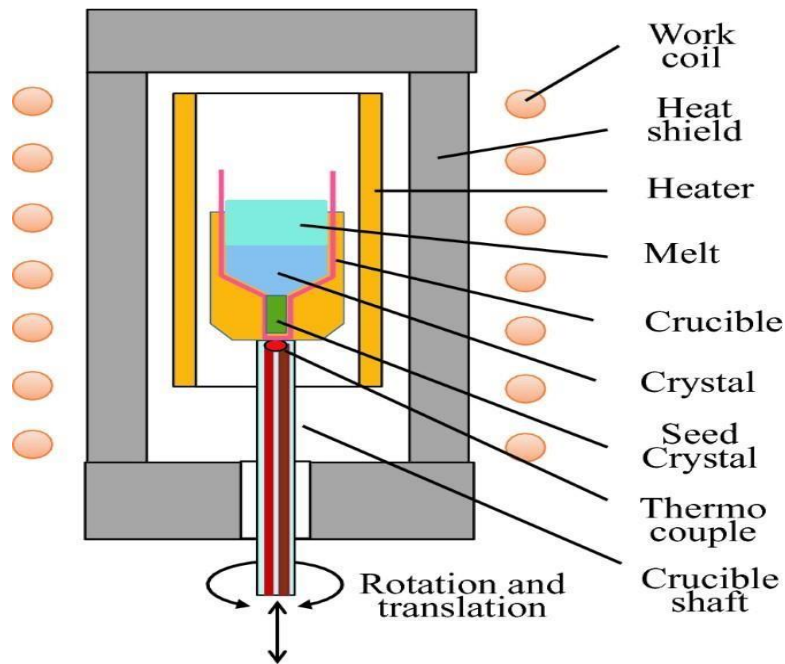


Fig.1.3. Vertical Bridgman growth method

1.2.2.1(ii) Czochralski Process

The Czochralski method of crystal development is used to produce single crystals of salts, metals, such as palladium, platinum, silver, and gold, semiconductors (such as silicon, germanium, and gallium arsenide), and synthetic gemstones. The procedure is named after Polish scientist Jan Czochralski, who developed it in 1916 while analyzing the rates at which various metals crystallized. The creation of massive cylindrical silicon ingots or boules could be the most significant application. This process can also be used to grow other semiconductors, such as gallium arsenide, although in this instance, different Bridgman-Stockbarger techniques can be used to achieve lower defect concentrations.

In the Czochralski process, the material to be produced is melted using induction or resistance heating in a suitable non-reacting container under a controlled atmosphere. The material is melted by regulating the furnace's temperature. To touch the molten charge, a seed crystal is lowered. By using an appropriate water-cooling system, the molten charge in contact with the seed will solidify when the temperature of the seed is kept far lower than the temperature of the melt. The seed is then pulled while the seed rod and crucible are rotating simultaneously in order to produce flawless single crystals. Encapsulated liquid

Growing single crystals of materials with constituents that yield high vapour pressure at the melting point is achievable because to the Czochralski process, also known as LEC. III-V compound semiconductors are grown using this improved Czochralski process method.

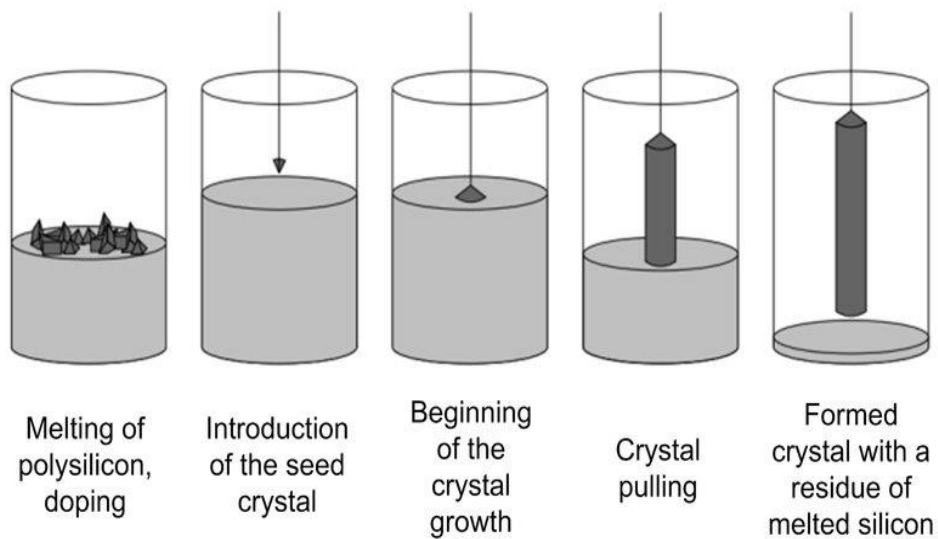


Fig.1.3.1.Czochralski process

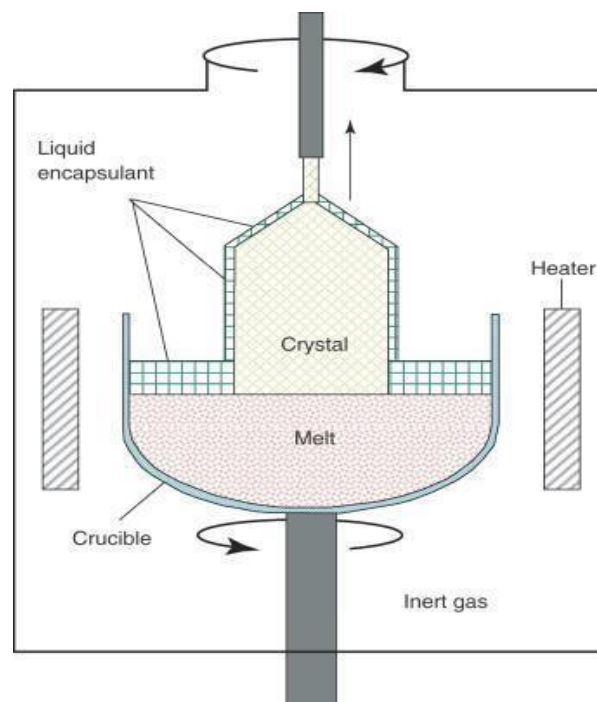


Fig.1.3.2. Diagram of the Czochralski crystal extraction mechanism

1.2.2.1(iii) Kyropoulos Technique

A bigger diameter of the crystal is generated using the Kyropoulos method. Similar to the Czochralski process, the seed is brought into contact with the melt in this case and is not lifted significantly during growth, allowing for the melting of a portion of the seed and the development of a short, narrow neck. Following this, growth continues while the power input into the melt is reduced. The seed's vertical motion is then stopped. Growing alkali halides to create optical components is the main application of this technique.

Comparing the Kyropoulos method to other melt methods, there are significant benefits:

- when the crystal is growing without being constrained by the crucible's walls, as is the case with the Kyropoulos method and the Czochralski method;
- is a very efficient technology that makes it possible to generate bulk optical grade crystals weighing several tens of kilogrammes;
- The produced crystals have a high chemical purity of 99.996% due of the effective evaporation of contaminants from the melt caused by the high vacuum in the growth chamber.

It is possible to create crystals with low dislocation density because single crystals are grown directly in the melt by a smooth temperature reduction at tiny temperature gradients.



Fig.1.3.3. Kyropoulos method

1.2.2.1(iv) Micro Pulling Down

The micro-pulling-down (-PD) technique, which is used to form crystals, relies on the continuous passage of melted material via one or more tiny channels carved out of the bottom of a crucible. On a liquid/solid interface beneath the crucible, the melt's solidification progresses continuously. Both the melt and the crystal are dragged down with a constant (but typically differing) velocity in a steady state. This method is used to generate crystals of many various sorts, such as $\text{Y}_3\text{Al}_5\text{O}_{12}$, Si, Si-Ge, $\text{LiNbO}_3\text{-Al}_2\text{O}_3$, Y_2O_3 , Sc_2O_3 , LiF, CaF_2 , BaF_2 , etc. [36] [37].

1.2.2.1(v) Zone Melting Technique

The feed material is used in the zone melting procedure in the form of a sintered rod with the seed fastened to one end. Surface tension between the seed and the feed keeps a small molten zone in place. Inching closer to the feed, the zone is. Over the seed, one crystal is produced. Materials with high surface tension are used in this process. The ease of the process, the capacity to generate a wide range of organic and inorganic materials of extremely high purity, and the ability to manufacture dislocation-free crystal with a low defect density are the primary factors influencing the impact of zone refining on the current electronic industry. To produce crystals of higher quality, vertical normal freezing causes the solid-melt interface to migrate from the cold bottom to the hot top. Growing single crystals of materials with volatile components, such as GaAs, using this technique is more practical.

Float-zone pulling

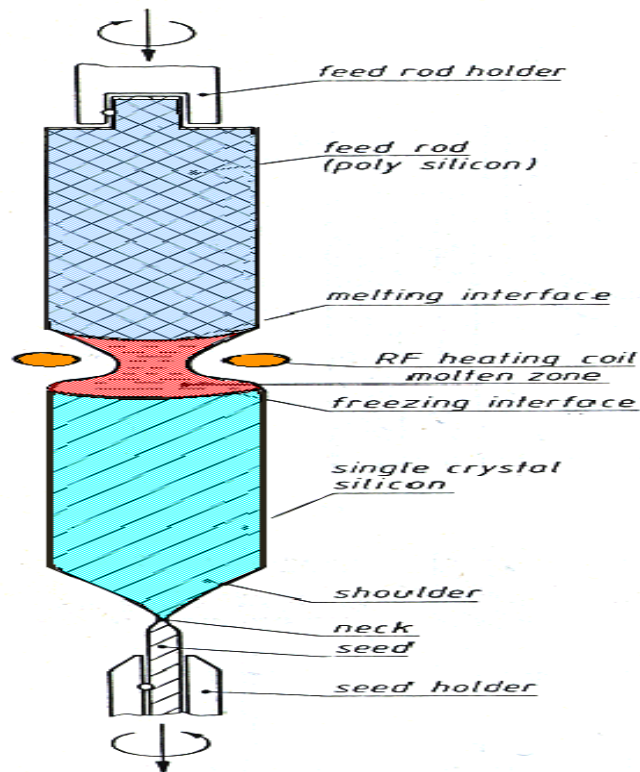


Fig.1.3.4. Float zone crystal growth

1.2.2.1(vi) Laser-Heated Pedestal Growth

When compared to other contemporary methods for growing crystals from the melt (liquid/solid phase transition), laser-heated pedestal growth (LHPG) has emerged as one of the most potent for materials research [38] [39]. LHPG can be thought of as a small-scale floating zone where the heat source is replaced by a potent CO₂ or YAG laser. The key benefits of this method are its high pulling rates, which are 60 times higher than those of the traditional Czochralski method, and its capacity to develop materials with extremely high melting temperatures [40][41][42]. LHPG is also a crucible-free method, which enables the growth of single crystals with great purity and minimal strain.

Single-crystal fibers (SCF) made by LHPG are an excellent replacement for bulk crystals in many devices, particularly those that use high melting point materials [43][44]. This is due to the geometric shape of the crystals (the technique can produce small diameters), as well as the low production cost. To replace bulk crystals in technological applications, single-crystal fibers must, however, have

optical and structural properties that are equal to or better than those of bulk crystals. This can be accomplished by meticulously managing the growing environment [45][46].

Only two laser beams focused over the source material were used for laser-heated crystal growth up until the year 1980 [47]. The process became unstable as a result of the significant radial thermal gradient created by this state in the molten zone. Even though the growing process was enhanced, increasing the number of beams to four did not fix the issue [48]. Fejer (1982) added a unique optical component known as a reflexion, which is composed of an inner cone surrounding by a wider coaxial cone portion, both of which have reflecting surfaces. This modification to the laser-heated crystal growth method was the most significant. The laser beam's cylindrical shape is changed by this optical component into a hollow cylinder surface with a bigger diameter [49]. Radial thermal gradients are decreased thanks to the radial distribution of the laser energy made possible by this optical component over the molten zone. When compared to conventional crystal growth techniques (10-100°C/cm), the axial temperature gradient in this method can reach a very high value of 10,000 °C/cm.

The LHPG technique's fast convection speed in the liquid phase as a result of Marangoni convection is another intriguing aspect [50].

1.2.2.1(vii) Verneuil Process

In 1902, the French chemist Auguste Verneuil invented the Verneuil process, also known as flame fusion, which became the first commercially effective technique for creating synthetic gemstones. Corundum in the ruby and sapphire kinds, as well as the diamond imitator's rutile and strontium titanate, are typically made from it. The basic idea behind the procedure is to melt a finely powdered substance using an oxyhydrogen flame, and then form the molten droplets into a boule. Obtaining a starting material that is extremely pure, at least 99.9995% pure is one of the most important factors in crystallizing an artificial gemstone successfully. In a Verneuil furnace, this initial material is finely pulverized and put in a container with a bottom aperture through which the powder can escape when the container is vibrated. As the powder is released, oxygen is

injected into the furnace and followed the powder down a short tube. A bigger tube, into which hydrogen is injected, contains this smaller tube. With a flame that has a core temperature of at least 2000 °C (3,600 °F) at the point where the little tube joins the bigger one, combustion takes place.

Small droplets of melted powder fall onto an earthen support rod that is positioned below as the powder passes through the flame. On the rod, the droplets progressively coalesce into a sinter cone, the tip of which is close enough to the core to maintain a liquid state. The eventual formation of the seed crystal occurs at that tip. The support is gradually pushed downward, allowing the base of the boule to crystallize while its cap is always liquid. As additional droplets fall onto the tip, a single crystal, known as a boule, begins to form. The boule has a tapered cylinder shape, with a diameter that initially widens away from the base before settling into a more-or-less constant size. Very long cylindrical boules can be produced by continuously adding powder and removing the support. To release internal pressure after being taken out of the furnace and given time to cool, the boule is divided along its vertical axis. If this is not done, the crystal will be more likely to fracture when the stalk is broken because of a vertical parting plane.

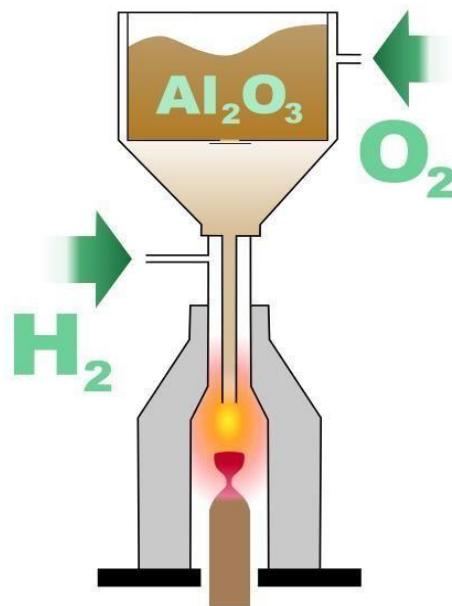


Fig.1.3.7. Verneuil Process

1.4 BASED ON SOLUTION GROWTH

Bulky crystal production is a common application of this technique. It can take weeks, months, or even years for crystals to develop via low-temperature solution growth. The qualities listed below are excellent for a good solvent.

1. Good solubility for the given solute.
2. Good temperature co-efficient of solute solubility.
3. Less viscosity.
4. Less volatility.
5. Less corrosion or non-toxicity.
6. Small vapour pressure.
7. Cost advantage.

1.4.1 The four major types of solution growths are

1. Low temperature growth (35°C to 100°C)
2. High temperature growth(or) Flux growth (about 1200°C)
3. Hydro thermal growth
4. Gel growth

1.4.1.1 *Low Temperature Growth*

- Slow cooling method.
- Slow evaporation method.
- Temperature gradient method.

The solvents used in this process include water, ethyl alcohol, acetone, carbon tetra chloride, etc.; in some cases, mixed solvents are also used to reduce solubility or to change the viscosity. Because the temperature must be maintained under control throughout the process, the entire growth chamber must be balanced in a temperature-controlled room or thermostat. Solvent evaporation, slow cooling of the

solution, solvent/non-solvent diffusion, vapor diffusion, sublimation, and other variations on these themes are examples of commonly used processes. The quantity of the sample may determine the approach to use.

1.4.1.1(i) Slow Cooling Method

In a crystallized and thermally sealed container, a saturated solution is poured that is above room temperature. Large single crystals form when a crystal seed is suspended in the solution and the crystallizer is kept in a water thermostat whose temperature is lowered in accordance with a predetermined plan. The necessity of using a range of temperatures is where disadvantages originate. The range of possibilities is typically limited to how much solute is still present in the solutions after the run. There is a requirement for huge quantities of solutions to offset this effect.

1.4.1.1(ii) Slow Evaporation Method

Slow cooling and slow evaporation techniques are comparable in terms of the apparatus. The slow evaporation approach allows for evaporation while maintaining the saturated solution at a specific temperature. It is acceptable to permit evaporation into the atmosphere if the solvent is non-toxic, such as water. A temperature stabilization of around 0.05°C and a rate of evaporation of a few mm³/h are typical growing conditions. The advantage of the evaporation method is that crystals only grow at a specific temperature. The growth rate is still significantly impacted by the temperature control system's shortcomings, though. For materials with very low-temperature coefficients of solubility, this approach works well. However because more impurities are able to fit into the crystal faces as the crystal grows larger, the crystals are often less pure than those made using the slow cooling process. High local supersaturation and the production of undesirable nuclei are caused by the solvent evaporating from the solution's surface. Small crystals are also created from the substance left behind after evaporation on the vessel walls close to the liquid's surface. These microscopic crystals dissolve into the solution and prevent crystal formation. The inability to adjust the rate of evaporation is another drawback. The quality of the crystal could

be impacted by a varying rate of evaporation. Despite all of these drawbacks, this is a straightforward and practical method for producing big single crystals.

1.4.1.1(iii) Temperature Gradient Method

In this process, the materials are moved from a warm area where the source material for the crystal is present to a cool area where the solution is supersaturated. The growth rate is more affected by a smaller temperature difference between the crystal and the source. The method's key benefits are that

1. Crystal grows at fixed temperature.
2. Insensitive to temperature fluctuations as long as the source and the crystal's growth experience the same change.
3. Economy of solvent and source

1.4.2 High Temperature Solution Growth (or) Flux Growth

Only at temperatures above room temperature are the solvents under consideration usually effective. Low temperature solution growth is based on the same principles. With this technique, crystals are formed under high pressure from a molten salt solvent. Flux is a term used to describe high-temperature molten salt solution. In order to create a saturated solution, the flux-containing crucible must be kept at a temperature just above that of the material being crystallized.

1.4.3 Hydrothermal Growth

High temperature and high pressure are both implied by the term "hydrothermal." Although materials like calcite and quartz are thought to be insoluble in water, they are soluble under high pressure and temperature. The hydrothermal method is a high-temperature, high-pressure crystal formation technique. There are often high pressures (hundreds or thousands of atmospheres) and temperatures between 400° C and 600° C.

Most of the time, growth is done in steel autoclaves with gold or silver interiors. Low-pressure, medium-pressure, and high-pressure autoclaves are the

three categories into which they are divided. A temperature differential between the nutrient and growth zones creates the concentration gradient necessary to induce growth. Only a few crystals of high quality and large dimensions are grown using this technique due to the practical difficulties associated with the requirement for high pressure. The best example of industrial hydrothermal crystallization is quartz. The frequent integration of OH ions into the crystal, which renders them inappropriate for many applications, is one significant drawback of this method.

1.5 CRYSTAL GROWTH BY GEL TECHNIQUE

The availability of crystalline materials of high quality and without defects is essential for the advancement of current solid-state technology. Different gel techniques have been used to grow a sizable number of crystals. Each crystal growth technique has its own potentialities and limitations. Crystal growth is still a very challenging task requiring a lot of knowledge and talent, despite the advancements in condensed matter physics technology. In this context, the gel method has become a practical approach for growing crystals with advanced applications in the disciplines of optics, acoustic optics, optoelectronics, and electronics.

There are intrinsic limitations to each method used to generate single crystals from melt, vapor, and solution. When crystal development occurs at a high temperature, the crystals' lattice is disrupted by strong thermal vibration. Due to the increase in solubility of one of the components involved in the development at high temperatures, the likelihood of impurities contaminating the lattice is enhanced. In the developing matrix, flaws and lattice stresses are typically absorbed. For obtaining high-quality single crystals in this situation, the gel method is thought to have promise.

German scientist Robert Edward Liesegang made the initial discovery of the periodic precipitation phenomena in 1896. When a few drops of a silver nitrate solution were added to gelatine gel that had been impregnated with potassium dichromate, he made his first observation of it. We noticed periodic precipitations of infinite rings. At the end of the nineteenth century, the German chemist Ostwald

provided a thorough description of the phenomenon's mechanism. These results prompted numerous researchers to focus their research on colloids in order to study this specific behavior.

Fisher and Siemen proposed the use of gel as a substrate for crystal formation in 1926. However, crystal growers did not show much interest in it, and it remained unfinished until 1962. The hunt for novel intelligent materials was sparked by the rapid advancements in semiconducting materials throughout the second half of this century. The rising interest in crystal development prompted researchers to focus on the less well-known gel approach once they realized its potential and advantage in producing flawless crystals devoid of flaws. The method became very popular due to the pioneering work of Henish H.K. (1970), who gave an authentic and narrative record of this method. Following him, a number of investigators has used this elegant and relatively easy method for growing perfect or defectless crystals. Currently, this method has been used to grow not only the inorganic crystals but also to grow organic crystals.

1.5.1 The Structure and Properties of Gel

A highly viscous, two-part, liquid-rich, semisolid solution with small holes is what is meant by the term "gel." The unfettered movement of electrolytes through these tiny holes might support nucleation. The gel medium functions as a "Smart" material, which means it is sensitive to even the smallest alterations in the environment. Between organic and inorganic gels, there is a general division. Hydrogel is what is created when water replaces the liquid. There are several different kinds of gels used in crystal formation research, including agar-agar gel, clay gel, soap fluid, polyacrylamide, hydroxide in water, stearates, and hydrosilica gel (sodium metasilicate). Due to its wide availability and superior performance in growing a variety of crystal compounds, sodium metasilicate-based silica gel (SMS) is frequently used. When choosing a gel, one must take into account the type of electrolytes that will be used [51]. In some situations, organic gels are preferred.

1.5.2 Crystallization Process in Gel Medium

According to the crystallization process, the experimental gel diffusion technique is divided into three categories:

1. Growth by chemical reaction
2. Growth by chemical reduction
3. Complex de-complexion method
4. Solubility reduction method

1.5.2.1 The Chemical Reaction Method

This is one of the common techniques for producing plenty of crystals. The chemical reaction of the growth-related components serves as the foundation for the reaction method. It is particularly well suited for producing crystals that are insoluble or only partially soluble as well as those that are thermally unstable. In a chemical reaction, there are two different ways that growth might occur either by the reaction of one component with another, or through the reaction of one component soaked in the gel media. With this technique, the crystals develop within the gel. The reactants combine as a result of ion diffusion through tiny holes, making the process extremely regulated. The response can be described as $AX + BY \rightarrow AY + BX$.

In the case of hydrosilica gel, this procedure is rather simple and is carried out by combining an aqueous solution of the molecule, let's say "AXE," with a solution of sodium metasilicate. The second component, the feed solution, can be carefully poured on top of the aged and firmly set gel. The process depicted in the figure shows how AXE gets surrounded by a gel in the shape of a solid. AX is slowly poured into the gel, then BY is poured on top of the hardened gel. The crystals are generated in the gel itself through controlled diffusion in the gel media. Double gel approaches, one of which is the neutral gel technique, must be utilized to better regulate diffusion. The crystals display a great degree of precision since the neutral gel medium is where the chemical reaction takes place.

The U-tube method is advantageous because it prevents a component's reactivity with the gel, much like the neutral gel technique does. The gel, which was earlier set by a neutral acid component, is in this instance given the opportunity to diffuse both interacting molecules into it. Each of the methods has advantages and disadvantages of its own [29].

1.5.2.2 The Chemical Reduction Method

This is an extremely effective method that is only appropriate for generating metallic crystals from gel media. This process has been used to generate crystals of copper, nickel, lead, selenium, and other elements. A properly titrated gel with CuSO_4 impregnated in it is taken in a test tube to grow the copper crystals. A reducing agent, such as hydroxylamine hydrochloride or hypophosphoric acid, is added from the top as an outside reactant after the gel has been properly set. The required copper crystal in the gel is produced by the chemical reduction of the CuSO_4 .

1.5.2.3 Complex- Decomplexion Method

This technique is appropriate for materials whose solubility increases nonlinearly with the concentration of the other soluble material when the two are present. In order for the material to resurface as crystals, the concentration of the mixed solution must be lowered during diffusion. Cuprous halides and silver iodide are two crystals that can be produced through decomplexing.

Solubility Reduction Method

Materials that are extremely soluble in water can be used with this procedure. In this process, the water content is decreased using a water-absorbing substance like alcohol to achieve supersaturation. Some significant water-soluble crystals, including KDP, ADP, etc., have been grown using this technique.

1.5.3 GROWTH FROM VAPOR

1.5.3.1 Chemical Vapor Deposition

High-purity, high-performance solid materials are created using the chemical technique known as chemical vapor deposition (CVD). The method is frequently applied in the semiconductor sector to create thin sheets. A typical CVD method involves exposing the wafer (substrate) to one or more volatile precursors, which then react and/or breakdown on the substrate surface to create the desired

deposit. The removal of volatile by-products, which occur often, is accomplished via gas flow through the reaction chamber.

Materials such as silicon, carbon fibre, carbon nano fibres, filaments, silicon-germanium, tungsten, silicon carbide, silicon nitride, silicon oxynitride, titanium nitride, and various dielectrics are commonly deposited in monocrystalline, polycrystalline, amorphous, and epitaxial forms using the CVD process in micro fabrication processes.

1.5.3.2 Physical Vapor Deposition

Physical vapor deposition (PVD) is a type of vacuum deposition and is a general term used to describe any of a number of processes to deposit thin films by the condensation of a material's vaporized form onto different surfaces. Unlike chemical vapor deposition, which includes a chemical reaction at the surface to be coated, the coating method uses only physical processes such high-temperature vacuum evaporation or plasma sputter bombardment. Pulsed

1.5.3.3 Pulsed Laser Deposition

A high-intensity pulsed laser beam is directed inside a vacuum chamber to impact a target of the material that is to be deposited in the process known as pulsed laser deposition (PLD), which is a thin film deposition method. A thin layer of this substance is formed on a substrate (such as a silicon wafer facing the target) when it is vaporized from the target (in a plasma plume). This procedure can take place in an extremely high vacuum or in the presence of a background gas, like oxygen, which is frequently employed while depositing oxides to completely oxygenate the formed coatings.

While the setup is relatively straightforward compared to many other deposition methods, the physical processes governing film growth and laser-target interaction are quite intricate. The energy from the laser pulse is transformed into electronic excitation, thermal, chemical, and mechanical energy when it is absorbed by the target, leading to exfoliation, evaporation, and plasma production. Before depositing on the normally heated substrate, the ejected species expand into the surrounding vacuum in the form of a plume that contains a variety of energetic

species, including atoms, molecules, electrons, ions, clusters, particulates, and molten globules.

1.5.3.4 Sputter Deposition

Sputtering, or ejecting, material from a "target," or source, which then deposits onto a "substrate," such as a silicon wafer, is a physical vapor deposition (PVD) process of forming thin layers. Sputtering is the process of reemitting the deposited material that has been bombarded with ions or atoms during the deposition process. Typically, up to tens of eV (100,000 K), sputtered atoms that are expelled from the target have a wide energy distribution. The sputtered ions can ballistically fly from the target in straight lines and crash energetically on the substrates or vacuum chamber (resulting in resputtering) because normally only a small percentage of the ejected particles (order of one percent) are ionised. In contrast, at greater gas pressures, the ions move diffusively and clash with the gas atoms that serve as a moderator. They eventually reach the substrates or the vacuum chamber wall and condense after taking a random walk. By adjusting the background gas pressure, one can access the complete spectrum from high-energy ballistic impact to low-energy thermalized motion. Commonly, inert gases like argon serve as the sputtering gas. For effective momentum transfer, the sputtering gas' atomic weight should be close to that of the target, hence neon is used for sputtering light elements while krypton or xenon are used for heavy elements. Compounds can also be sputtered using reactive gases. Depending on the process settings, the compound may be produced on the substrate, in flight, or on the target surface. Sputter deposition is a complicated process, but the availability of numerous controllable parameters gives professionals a great deal of control over the growth and microstructure of the film.

1.6 TREND IN CRYSTAL GROWTH TECHNOLOGY

The foundation of contemporary technological advancement is crystals. The unsung heroes of contemporary technology are crystals. In 1999, the anticipated annual global production of crystals was about 20,000 tons. Out of that, semiconductor materials made up the lion's share, or roughly 60%, including silicon, gallium arsenide, indium phosphate, gallium phosphate, cadmium telluride, and its alloys. As observed in Figure 2.10, optical crystals, scintillation crystals,

and acoustic-optic crystals all had almost equal shares of 10%, whereas laser and nonlinear-optic crystals, as well as crystals for the jewelry and watch industries, only had shares of a few%.

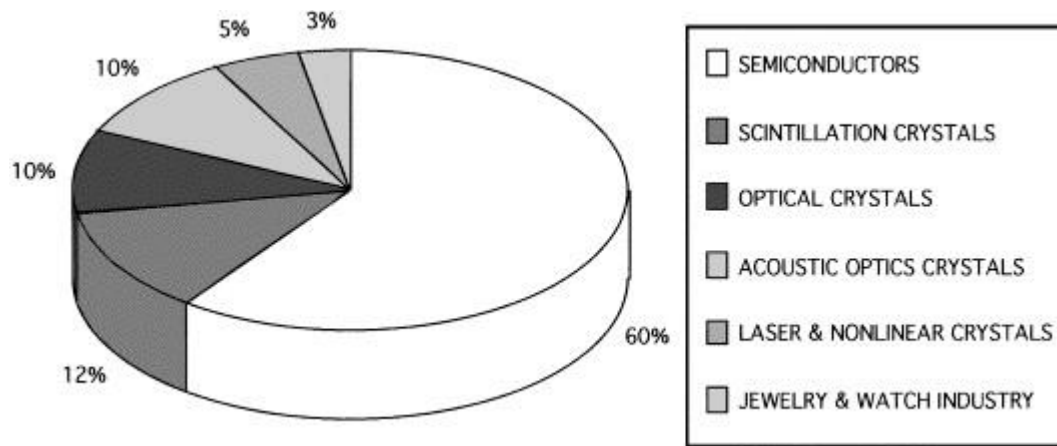


Fig.1.6 Estimated shares of world crystal production

However, with advancements in the fields of medicine, material science and engineering, biochemistry, pharmaceuticals, and nanotechnology over the past ten years, the demand for synthetic biomaterials has increased significantly. In addition, H. J. Scheel (2003) categorized crystal growth into five main categories:

1. Fundamental theoretical and experimental investigations on crystal formation.
2. Growing crystals in the lab to prepare study samples.
3. Single crystal manufacturing, characterization, and machining
4. Creation of metallic or dendritic crystals (such as for turbine blades).
5. Mass crystallization (of chemicals, sugar, and salt).

The three essential components of crystal growth—the theory of nucleation and growth, experimental crystal growth, and crystal characterization—have been thoroughly elucidated by Schieber (1966). The competitive nucleation in crystals, which is thoroughly explained by a number of authors [30][52][53][54], is described in a poem by L. I. Preston. Gilman (1963) accurately cited this in his book "The Arts and Science of Growing Crystals" as follows: "The Systematic creation of artificial crystals might be considered as a new agriculture that has begun flourishing. While it has many characteristics in common with traditional agriculture and is expected

to have an impact on society that is somewhat comparable, it differs from true agriculture in that its products are currently primarily inorganic. A nutrient phase (gas, liquid, or solid) is used to develop solid crystals in the new form of agriculture. Some employees mention repeating the harvest after a predetermined amount of time. The nutrient is frequently planted with little crystal to start the growth process.

Many successful attempts to describe the art and science of crystal growth have been made over the years, and a large number of review articles, monographs, symposium volumes, and handbooks have been published to present thorough reviews of the advancements made in this field. On topics including the principles of crystal development, various crystal growth techniques, their theories, characterisation, and applications, as well as comprehending the growth mechanism, there are numerous well-written books accessible. There are also books with stunning crystal pictures. Whereas, Stangl and Stang (1990) agreed with Gilman's (1963) theory by comparing the development of many beautiful crystals to the development of flowers in a garden. Several authors have gone into great detail about various crystal growth processes. Reviews and books by Faktor and Garrett (1974) on vapour growth, Brice (1973) on melt growth, Henisch (1988) on gel growth, Buckley (1951) on solution growth, and Elwell and Scheel (1975) on high temperature solution growth detail the many approaches used in each category. Mirkin and Moreno (2005) provide an overview of the developments in crystal formation techniques. A book titled "Handbook of Crystal Growth" was just released, and it covers the basics of crystal growth and defect formation, bulk growth from melt, solution, and vapour, epitaxial growth, crystallization from gels, modeling of growth processes and defects, and methods for defect characterization.

CHAPTER 2

LITERATURE SURVEY

Sl. No	TITLE	JOURNAL DETAILS	AUTHOR	ABSTRACT
1	Growth & Characterization of ZINC (Tris) Thiourea Sulphate (ZTS) Single Crystals	International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056 Volume: 03 Issue: 04 April-2016	Hiral Baraniya, Anand Panchal	In the present study of Single crystals of pure zinc tris-thiourea sulfate (ZTS) were grown by the slow evaporation solution growth method at a constant temperature (~360C). The qualitative analysis is study from the Fourier transform infrared spectroscopy.
2	Growth of zinc thiourea sulfate (ZTS) single crystals: a potential semiorganic NLO material	Journal of Crystal Growth Volume 197, Issues 1-2, 1 February 1999, Pages 216-220	P.M. Ushasree, R. Jayavel, C. Subramanian, P. Ramasamy	The growth of zinc thiourea sulfate (ZTS) <u>single crystals</u> has been investigated. The crystals were grown from aqueous solution by slow cooling technique. The influence of pH on both the morphology and growth rate of ZTS crystals has been studied. Powder X-ray diffraction and single-crystal X-ray diffraction studies confirm the crystal structure and <u>single crystallinity</u> respectively.

				The presence of sulfur-to-zinc bonds in the complex has been revealed by Fourier transform infrared analysis.,
3	Synthesis, Growth And Characterization Of Bis Thiourea Sodium Zinc Sulphate Single Crystals-A Semi Organic Nlo Material	International Journal of Chemistry and Materials Research 2015 Vol. 3, No. 4, 91-99.	K. Uma R. Manimekalai G. Pasupathi	The slow evaporation of the solvent technique is used to grow transparent nonlinear optical (NLO) single crystals of bis thiourea sodium zinc sulphate (BTSZS). The grown crystal is characterized by single crystal X-ray diffraction analysis to confirm the crystallization of the synthesized materials and to determine its unit cell parameters. The crystalline nature and purity of the grown crystals are confirmed by powder Xray diffraction pattern. The FT-IR and FT-Raman spectra are recorded to identify the functional groups present in BTSZS crystals. The UV-VIS-NIR transmission spectrum of BTSZS crystals are recorded in the wavelength range 190 - 1100 nm to determine the lower cut-off wavelength, percentage of the transmittance and the optical constants such as bandgap,

				refractive index, extinction coefficient, reflectance etc., Fluorescence study confirms the green emission of BTSZS which indicates the grown crystal is well suited for NLO applications.
4	Crystal Growth, Morphology, Spectral and Optical Studies of Tris (thiourea) Zinc Sulphate - Nonlinear Optical Material	Indian Journal of Science and Technology, Vol 8(S7), 165-170, April 2015	R. Muraleedharan J. Ramajothi and M. Basheer Ahamed	The Nonlinear Optical(NLO) material Tris (thiourea) zinc sulphate (ZTS) was grown by slow evaporation method. The unit cell parameter and morphology were determined by single crystal XRD. The molecular structure of ZTS was identified by FTIR analysis. The optical properties of ZTS were determined by UV-Vis spectral studies. The photoluminescence spectrum of ZTS shows the strong emission in ultraviolet region at 360 nm. The thermal behaviors were identified by TG/DTA analyzes and the melting point is 240°C. The hardness of the material is measured by micro hardness test. The SHG efficiency was confirmed by powder technique.

CHAPTER 3

AIM AND SCOPE OF THE PRESENT INVESTIGATION

3.1 AIM OF THE PRESENT WORK

The unacknowledged cornerstones of contemporary technology are crystals. Without crystals, the electronic, photonic, and fiber optic industries would not exist. These industries rely on materials/crystals like semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid-state lasers, non-linear optics, piezoelectric, electro-optic, acoustic-optic, photosensitive, refractory of various grades, and crystalline films for micro. Growing interest in crystal formation techniques has been observed over the past few decades, particularly in light of the rising need for materials for technological applications [26]. Due to the significance of crystals in contemporary technology, single-crystal formation has been the focus of extensive research in solid-state physics and materials science. Numerous superb crystals have been developed as a result of significant advancements in crystal growth methods to suit the expanding demands of the laser, optical communication, and data storage industries. Laser, optical communication, and optical data storage technologies are all greatly impacted by nonlinear optical (NLO) materials for frequency conversion. Since second harmonic generation was first discovered in quartz crystal by Franken and colleagues in 1961, research has been actively looking for new and effective nonlinear optical materials.

The advancement of laser technology and new nonlinear optical materials of both organic and inorganic types have led to numerous notable successes in the field of nonlinear optics in recent years. In general, organic crystals may exhibit optical nonlinearity that is superior to that of their inorganic counterpart. The molecular structure of organic crystals, where molecules are held together by weak van der Waals interactions that tend to retain their individuality to a great extent, determines their nonlinear property. The ideal organic substance for nonlinear applications has been determined to be thiourea.

The current work's objectives are to grow high-quality nonlinear optical single crystal from thiourea and to examine various physicochemical aspects. One technique for crystal development that is quite popular in the creation of many technologically significant crystals is the growth of crystals from aqueous solutions. The single crystals have thus been grown at room temperature using the slow evaporation solution growth approach.

3.2 SCOPE OF THE WORK

In order to process materials and operate lasers, it is crucial to find and construct high-efficiency nonlinear optical (NLO) crystals for the visible and ultraviolet (UV) spectrum. In nonlinear optical applications, organic nonlinear optical crystals made using thiourea have been found as viable replacements for KDP. In terms of NLO materials, thiourea zinc sulphate (TZS) crystals appear promising. In light of this, efforts are undertaken to grow and investigate the spectral, optical, and thermal properties of single crystals of thiourea zinc sulphate (TZS).

The goal of the current study is

1. To grow single crystals of bulk size
2. To determine the crystal structure by using Powder-XRD analysis.
3. To find the functional groups of the compound by using FT-IR spectral analysis.
4. Characterising the grown crystals using UV-Vis and Kurtz powder NLO test to find the optical properties.
5. Estimating the thermal stability of the formed crystals using TG/DTA analyses.

CHAPTER 4

EXPERIMENTAL TECHNIQUES

4.1 INTRODUCTION

A thorough description of the substance's physical and chemical characteristics is referred to as a characterization of that material. Today, a crystal can be characterized using a variety of precise measurement techniques. These comprise spectrum analysis, thermal research, structural characterization, magnetic research, and measures of optoelectrical property. UV and IR procedures are the two most commonly used fundamental spectral approaches. Common thermal analyses include TG and DTA. The most effective and powerful tool for structural characterization is X-ray crystallography. Different analytical methods are employed for electric, magnetic, and optical measurements depending on the intended usage. This study uses photoluminescence, fluorescence, laser damage threshold tests, single crystal and powder XRD, FTIR, TG and DTA, UV-vis analysis, dielectric measurement, microhardness studies, as well as SHG and THG to characterize and evaluate the properties of the generated crystals. In this chapter, the crucial characterization approaches used in this work's instrumentation and operating process are discussed.

4.2 X-RAY DIFFRACTION METHODS

The most effective and well-known method for ascertaining the atomic structure of crystal and molecule structures is X-ray diffraction (XRD). Facilities for measuring both low and high temperatures are available, and the findings are frequently precise and without ambiguity. The two types of XRD techniques are single and powder.

4.2.1 POWDER XRD

The powdered sample of the grown crystal is ground using an agate mortar and it is spread in a sample holder. It is allowed to rotate with respect to the impinging X-ray beam. The diffracted X-ray photons are recorded by a scintillation counter, which is connected to an electronic counting system and is synchronized with a strip chart recorder, a rate meter, a timer, a goniometer, and a pulse height analyzer. A typical powder X-ray diffractometer consists of three basic elements: an X-ray tube,

a sample holder, and an X-ray detector. Copper is the most common target material for powder X-ray diffraction, with Cu K α radiation = 1.5418 Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies Bragg's equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or a computer monitor. Peak positions occur where the X-ray beam has been diffracted by the crystal lattice and the unique set of d-spacings derived from the X-ray pattern can be used to fingerprint the crystalline material. In a powder X-ray diffractometer, the sample in powder form rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ . For typical powder patterns, data is collected at 2θ from $\sim 5^\circ$ to 80° angles that are present in the X-ray scan. A fully computerized advance Bruker AXS D8 powder X-ray diffractometer (Fig.4.2.1) has been employed for the X-ray powder diffraction studies and this is a versatile, sensitive and high resolution X-ray diffractometer



Fig.4.2.1 X-Ray diffraction

4.2 FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

The study of infrared light's interactions with matter and the vibrational spectra of molecules is known as infrared spectroscopy. Infrared radiation absorption is primarily limited to molecular species for which there are negligible energy differences between different vibrational and rotational states. Absorption of energy occurs when the incident radiation's frequency and the molecules' vibrational frequency match. The absorbed energy is released when the molecules move back and forth between the excited and ground states, creating distinct peaks in the IR spectrum. This sample's molecules' states are shown by the absorption bands. The routine quantitative determination of several species, including water, carbon dioxide, sulfur, low-molecular-weight hydrocarbons, amine nitrogen, and many other simple compounds of importance in business and agriculture, is done in the near-infrared range. Inorganic and metal-organic species' structures have been determined using the far-infrared region based on absorption measurements. In order to detect the functional groups of both organic and inorganic substances, the Fourier Transform Infrared (FTIR) approach is most helpful. It can be used to analyze gases, liquids, and solids. The FTIR spectroscopic approach, which offers greater resolution, whole wavelength coverage, and improved accuracy in frequency and intensity measurements, is based on the Michelson Interferometer concept and uses a sensitive infrared detector and a digital minicomputer. Potassium bromide (KBr) can be used to grind solid materials into an incredibly fine powder. This powder is then compacted into a thin pellet that can be examined.



Fig 4.2.2 FT/IR 6600 FT-IR SPECTROMETER

4.3 UV-VISIBLE RADIATION

Materials for solar energy conversion, electronics, lasers, and detectors, as well as transparent or partially transparent optical components, can all be characterized by UV-vis spectroscopy. The visible and nearby near ultraviolet regions of light are typically used in UV-visible spectroscopy. A fraction of the electromagnetic radiation in the visible and ultraviolet spectrum is typically absorbed by the substance. The wavelength of the radiation and the composition of the chemical both affect how much radiation is absorbed. When electrons in lower-energy orbitals are excited into higher-energy orbitals, the radiation is absorbed as a result of the radiation beam's energy being subtracted. A deuterium (D2) lamp for ultraviolet light and a tungsten (W) lamp for visible light are the two light sources used by the UV-visible spectrophotometer. The light beam strikes a diffraction grating after passing through a slit and hitting a mirror. One can choose a certain wavelength by rotating the grating. Higher levels of diffraction that are not desired are removed using a filter. Before being split in two by a second mirror, the light beam passes through a second mirror. While the other beam travels through the sample cuvette, one of the beams is permitted to pass through a reference cuvette. The spectra of a compound represent a group of wavelengths or frequencies, continuously varying over a small region of the electromagnetic spectrum versus either transmission percentage (%T) or absorbance (A). In this work, UV-visible transmittance spectra of the grown crystals were recorded using a Perkin Elmer Lambda 35 (Fig.4.3) spectrophotometer in the range 190- 1100 nm covering the near-infrared region.[24]. Other linear optical constants, such as the absorption coefficient, reflectance, refractive index, extinction coefficient, and optical conductivity, were determined from the transmittance values of the formed crystals. The optical band gap of the samples was assessed using Tauc's plots.



Fig.4.3. Perkin Elmer lambda 35 UV-visible spectrophotometer

4.4 THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS (TG/DTA)

Thermogravimetric and Differential Thermal Analysis (TG/DTA) was used to measure any weight changes and energy changes connected to thermally induced transitions quantitatively. For transitions involving dehydration or breakdown, TG can directly record weight loss as a function of temperature. As the temperature rose, a constant weight reading of the sample was kept. In an atmosphere of inert nitrogen, a sample is placed in a crucible or shallow dish and heated there between 30 and 1000°C at a heating rate of 20°C/min. DTA measures the temperature differential between a sample and a thermally inert reference material as a function of temperature (often the sample temperature). Whenever the sample goes through a transition, energy is released or absorbed by the sample, which causes a corresponding change in the sample's temperature relative to the reference. A sample is frequently subjected to both DTA and TG tests at the same time [25]. Using the Perkin Elmer lambda 35 and Diamond TG/DTA thermal analyzer, the thermal characterization of the produced crystals was performed.



Fig.4.4Perkin Elmer STA 6000 Thermal analyser

CHAPTER 5

RESULT AND DISSCUTION

5.1 INTRODUCTION:

Non-linear optical (NLO) materials have a considerable impact on laser development, optical correspondence, optical capacity development, and electro optic adjustment. New classes of nonlinear optical materials that are suitable for frequency conversion in the UV to near IR spectral region must continue to be created. High nonlinear optical qualities are used to create high-performance electro-optic switching components for optical information processing and telecommunication. Significant interest has been shown in materials that can produce second harmonic blue-green light utilizing laser diodes. Due to their significant optical non-linearity, low cut-off wavelength, rapid response time, and high thresholds for laser power, organic NLO materials are potential candidates for frequency mixing, electro-optic modulation, optical parametric oscillation, optical biostability, etc.[21][56]. Because they fall somewhere between inorganic crystals and polymers, organic single crystals are utilized as model systems to explore the effects of ion impact.

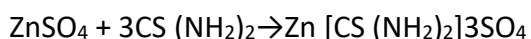
Many ideas, including surface energy theory, diffusion theory, surface adsorption theory, and others, have been put out to explain the kinetics and mechanisms involved in the development of crystals. Early in the 19th century, the first crystal formation theory was put out. The development of crystal growth theories has increased our understanding of the phenomenon of crystal growth.[22].When compared to inorganic NLO materials, organic materials can often meet these requirements, but they also have some drawbacks, such as poor chemical and mechanical stability, red shifting of the cut-off wavelength, weak laser damage thresholds, and poor phase matching properties.[23] The development of semi-organic crystals has recently gained prominence as a way to improve the characteristics and get around these disadvantages. Finding and growing novel optical crystals with good crystalline nature has emerged as an intriguing branch in crystal growth in order to satisfy the growing need for new

material with strong optical properties. In this course, extensive examination led to the discovery of additional stage coordinate inorganic materials such ZTS crystals.

5.2 EXPERIMENTAL PROCEDURE

5.2.1 CRYSTAL GROWTH

The single crystal of TZS was grown from aqueous solution by slow solvent evaporation method. The starting material was synthesized by dissolving suitable amounts of Thiourea and Zinc sulfate (AR grade) in deionized water taken in the molar ratio of 1:1. The expected chemical reaction that takes place in the deionized water is as follows:



The prepared solution was stirred well for nearly 6 hours using a magnetic stirrer to obtain the homogeneous mixture. The solution was slowly heated to dryness below an optimum temperature of 60°C to avoid any possible decomposition of the compound. The material was then purified further by successive recrystallization processes. The synthesized dried salt of TZS was again thoroughly dissolved in deionized water at room temperature to get a clear saturated solution. This was then filtered twice using Whatman filter papers to remove unwanted impurities. The filtered solution of TZS was kept in a crystallizing vessel, covered with a perforated sheet, and placed in a dust-free atmosphere. The crystal was allowed to grow in the crystallizing vessel by slow solvent evaporation of the solvent. A good quality single crystal of optimum size was attained in a period of 30 days at room temperature. The image of the as-grown crystal of TZS is shown in Fig. 5.2.1.

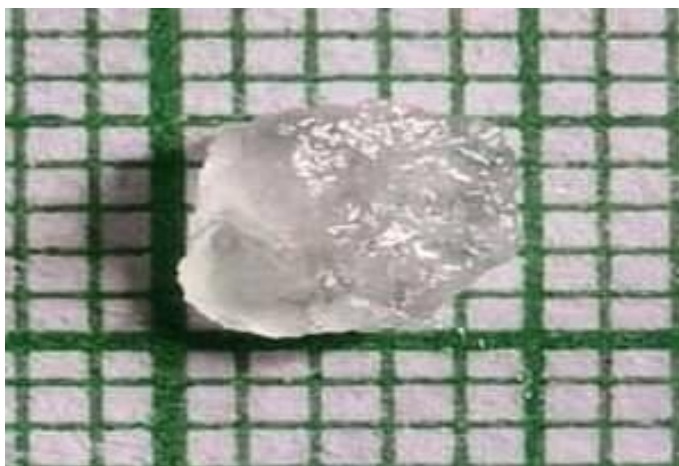


Fig.5.2.1 As grown crystal of thiourea zinc sulphate (TZS)

5.2.2 FTIR ANALYSIS

Using a BRUKER IFS 66V FT-IR spectrometer, the FT-IR range was recorded between 3500 cm^{-1} and 550 cm^{-1} . The FT-IR Spectra of TZS exhibit essentially identical FT-IR spectra. The Alkyl halide is confirmed by the peak at 451 cm^{-1} . At 444 cm^{-1} for TZS, the distinctive ingestion for the -NH collection in the aromatic ring is visible. The expansive intake of about 430 cm^{-1} shows how closely C=O extending and O-H extending are related. The FT-IR spectra of TZS affirms the auxiliary viewpoints. Doping of metal particles into the crystal lattices does not demonstrate any centrality change in assimilation design. A portion of the assimilations demonstrates a stamped contrast in rate transmittance. The rate change of transmittance particularly, at 1197 cm^{-1} and 1023 cm^{-1} is important. It is induced that the metal particle shapes powerless linkages in the interstices of the related crystal. The TZS crystals' FTIR spectra are displayed in Fig.5.2.2. The asymmetric NH between 3400 cm^{-1} and 3100 cm^{-1} , symmetric bands of thiourea have created a large envelope. The band at 1617 cm^{-1} is responsible for NH_2 deformation. While the IR band for the C=S group's symmetric and asymmetric stretching vibrations in pure thiourea is typically at 740 and 1417 cm^{-1} , respectively, in TZS, these vibrations are displaced to lower values of 730 cm^{-1} and 1413 cm^{-1} . The development of metal sulfur bonds results in the shifting of C=S bonding to lower values and the non-shifting of NH_2 vibrations. As a result, using all the information on thiourea that is currently accessible, we have

determined the distinctive IR bands for the several molecular perspectives found in TZS. Due to overtones and combination bands, peaks between 1700 and 2700 cm^{-1} were produced.

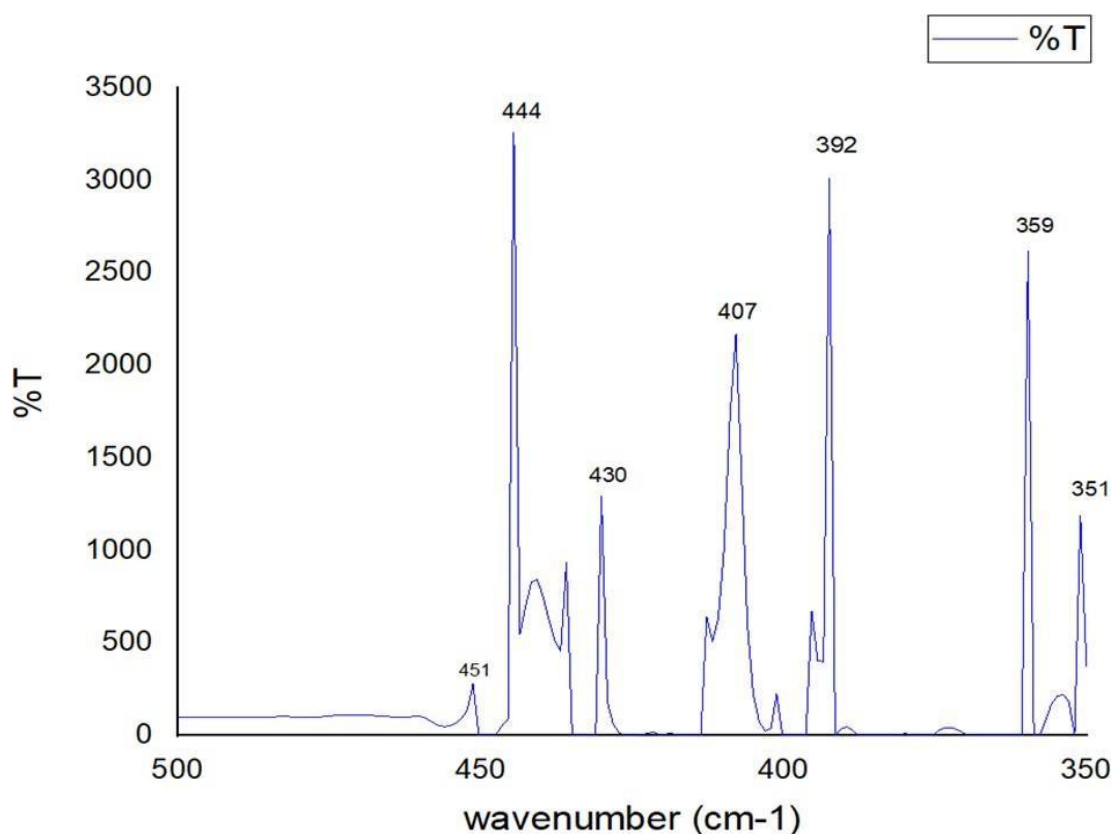


Fig. 5.2.2 FTIR SPECTRA OF TZS

5.2.3 XRD ANALYSIS

The x-ray diffraction examination was performed utilizing the powder sample of TZS in order to confirm the crystalline nature of the produced crystals as well as to establish the unit cell characteristics. The sample was scanned at a rate of 1 scan per minute over the range of 20 to 80 scans. The X-ray diffraction pattern of the powdered TZS sample is displayed in Fig. 5.2.3. Using the PROSZKI software program, the unit cell dimensions were estimated from the powder x-ray diffraction pattern. According to XRD analysis, the TZS crystallized in an orthorhombic crystal structure.

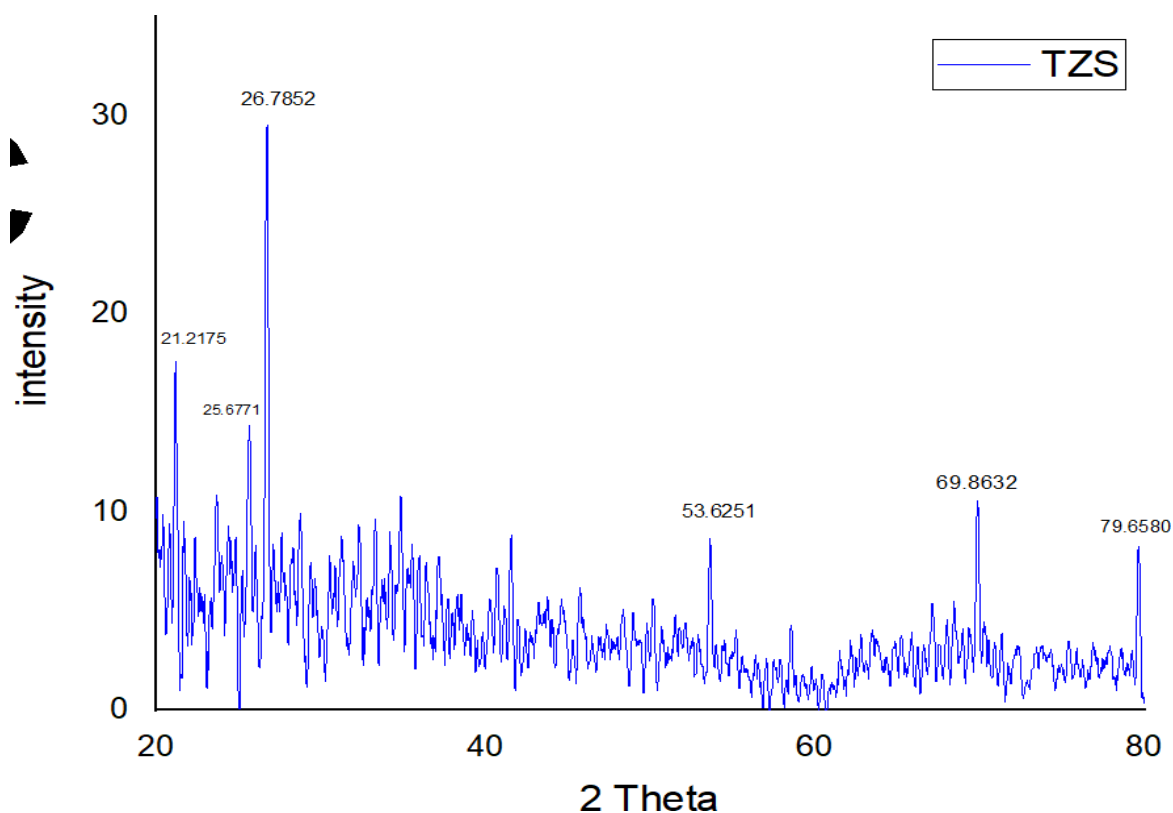


Fig. 5.2.3 powder XRD patterns of the crystal TZS

5.2.3 UV ANALYSIS

The optical absorbance spectrum of thiourea zinc sulphate (TZS) crystal was recorded using Perkin Elmer Lambda 35 spectrophotometer in the wavelength range of 200 to 800 nm. The UV-Visible spectrum of the single crystals of TZS is displayed in Fig. 5.2.4. The spectrum indicates low absorption in the entire visible and near-infrared region of the crystals. In other words, the optical transmittance of TZS between 200 to 800nm is nearly 100% and the lower cut-off wavelength is found at 233nm. This is a desirable property for NLO applications since wider optical transparency in these regions enhances the frequency conversion efficiency in the UV region [55].

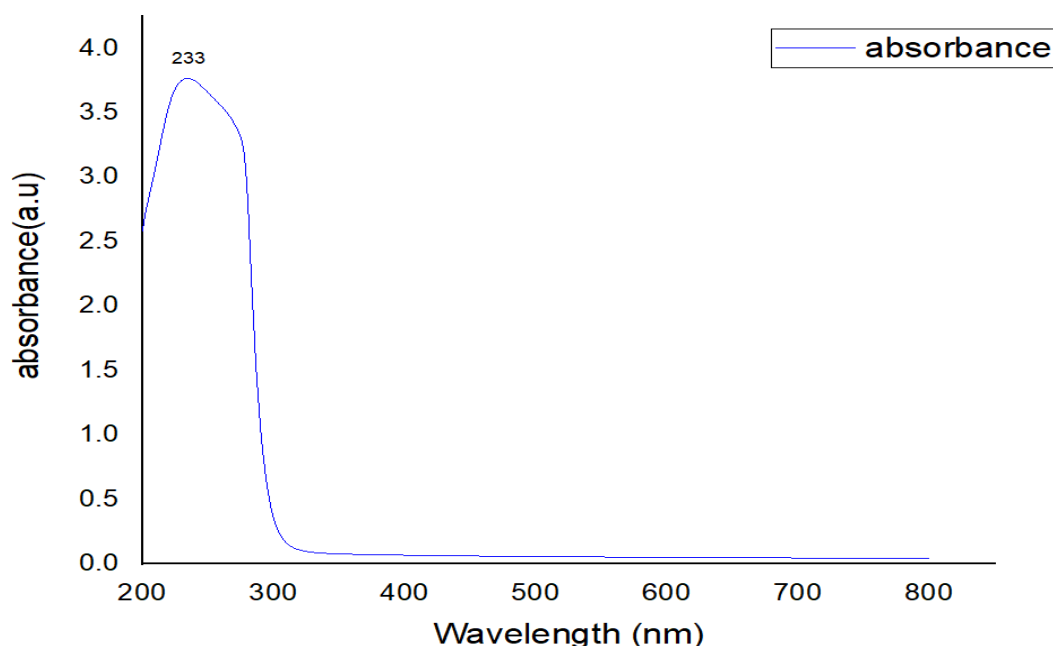


Fig 5.2.4 UV-visible spectrum of TZS

5.2.4. Thermogravimetric and differential thermal analysis (TGA/DTA)

The thermal behavior of the crystal was assessed by thermogravimetric analysis (TGA), and differential thermal analysis (DTA) using the instrument Perkin Elmer STA 6000 Thermal analyzer. The TGA/DTA measurements were carried out in a nitrogen atmosphere at a heating rate of 20°C per minute in the temperature range of 50°C to 800°C. The TGA curve shows three stages of weight loss from 50°C to 800°C. There is a small weight loss between 50–80°C in the curve which may be due to the release of water molecules from the substance. The second weight loss from 120–160°C may be due to the partial decomposition of the sample. The third stage of weight loss from 250–800°C may be due to the gradual decomposition of the entire substance. The DTA trace shows a broad endothermic peak observed around 400°C may be attributed to the decomposition of TZS.

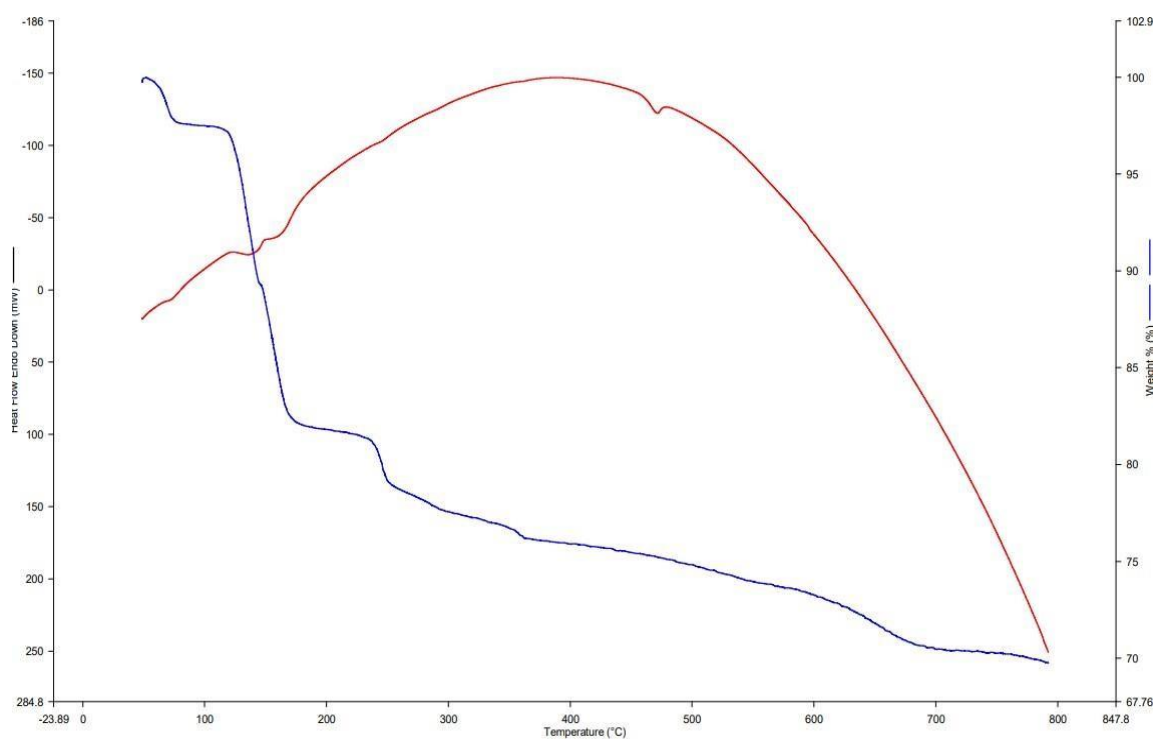


Fig. 5.2.5 Perkin Elmer STA 6000 Thermal analyser

5.3 CONCLUSION

In present work, Single crystals of Thiourea Zinc Sulphate (TZS) were grown slow evaporation technique in a period of 30 days. The grown TZS crystals were subjected to X-ray spectroscopy, UV-Vis spectroscopy, FTIR spectroscopy, and thermal studies. According to XRD analysis, the TZS crystallized in an orthorhombic crystal structure. According to UV spectroscopy, the optical transmittance of TZS is nearly 100% between 200 to 800nm with the lower cut-off wavelength of 233nm. This is a desirable property for NLO applications since wider optical transparency in these regions enhances the frequency conversion efficiency. The presence of various functional groups was determined using FTIR spectroscopy. From TGA-DTA analysis, we conclude that the TZS crystal is stable up to 120°C. According to the findings, the grown Thiourea Zinc Sulphate (TZS) crystals might be useful for nonlinear optical applications below this temperature.

CHAPTER 6

SUMMARY AND CONCLUSION

Due to their potential utility in sectors such as telecommunication, optical computing, optical data storage, and optical information processing, there has been a great deal of interest in the synthesis of novel materials with good second-order optical nonlinearities in recent years. The search for novel NLO materials is advancing quickly. Due to a quantum leap in the design of nonlinear optical materials, the need for nonlinear optical crystals with excellent perfection is growing daily, and research into them has emerged as one of the most important and effective disciplines in the world of materials science and engineering. As a result, significant efforts have been made to create new types of organic nonlinear optical crystals, which have a variety of uses including second harmonic generation, frequency mixing, electro-optic modulation, etc. The selection of the material is the most crucial element in ensuring that the aforementioned parameters are met because it depends on the laser settings as well as the physical characteristics of the crystal, such as transparency, damage threshold, conversion efficiency, and temperature stability.

Following the expansion of Thiourea Zinc Sulphate, the thiourea salts attracted a lot of interest as potential NLO materials. In the current study, efforts were made to manufacture nonlinear optical crystals of the thiourea in response to the steadily growing demand for nonlinear applications. The materials used for this study are potential nonlinear optical, specifically Thiourea Zinc Sulphate. In this study, the slow solvent evaporation method was used to grow the single crystals at room temperature. The crystals that had formed were characterized using techniques such as powdered XRD, FT-IR, UV-Visible, and TGA-DTA analyses.

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