GROWTH AND CHARACTERIZATION OF BIS THIOUREA ZINC CHLORIDE

Submitted in partial fulfilment of the requirements for the award of

Master of Science Degree in Physics

By

K. SARANYA

(41590018)

DEPARTMENT OF PHYSICS

SCHOOL OF SCIENCE AND HUMANITIES

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited with "A" grade by NAAC I 12B Status by
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JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI - 600 119.

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BONAFIDE CERTIFICATE

This is to certify that this project report is the bonafide work of **K. SARANYA (REG NO 41590018)** who carried out the project entitled **"GROWTH AND CHARACTERIZATION OF BIS-THIOUREA ZINC CHLORIDE**" under our supervision from August 2022 to May 2023.

INTERNAL GUIDE

Dr .K. PARASURAMAN

HEAD OF THE DEPARTMENT

Dr.S. RAVICHANDRAN

Submitted for Viva voce Examination held on 9.5.2023 2023

INTERNAL EXAMINER

EXTERNAL EXAMINER

Dr. D. DINESH KUMAR

Associate Professor (Research)

DECLARATION

I **K.SARANYA (Reg.No.41590018)** hereby declare that the project report entitled **"GROWTH AND CHARACTERIZATION OF BIS THIOUREA ZINC CHLORIDE"** done by me under the guidance of **Dr.K.PARASURAMAN** (Internal) submitted in partial fulfilment of the requirements for the award of Master of Science Degree in Physics.

Date: 09-05-2023

Place: Chennai **Signature of the candidate**

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ABBREVIATION

E	Electric Field vector
C	Capacitance
D	Electric field displacement vector
ε_0	Permittivity of free space
ε_r	Dielectric constant
$\chi^{(1)}$	Linear susceptibility
$\chi^{(2)}$	Nonlinear susceptibility
μV	Micro volt
n	Work hardening coefficient
Hv	Vickers hardness number
P	Polarization
nm	Nanometer
μm	Micrometer
μ_0	Permeability of free space
Å	Angstrom
Θ	Theta
Δ	Delta
α	Alpha
β	Beta
ω	Omega
a, b, c	Unit cell parameter
λ	Wavelength
NLO	Nonlinear optics
SHG	Second Harmonic Generation
UV	Ultra violet
XRD	X-Ray Diffraction

ABSTRACT

The single crystal of Bis thiourea zinc chloride (BTZC), an efficient semi organic nonlinear optical (NLO) material was grown successfully by slow evaporation method. Single crystal X-ray diffraction study reveals that BTZC crystallizes into orthorhombic system with the space group Pn2la. The optical transmission spectrum shows that BTZC has highly transparent in the entire visible region for large photon absorption. Vickers micro hardness measurement was performed to know the mechanical strength of the crystal. Dielectric constant and dielectric loss were calculated by varying frequency at different temperatures. The SHG efficiency of the crystal is also examined by Kurtz's powder test using Nd: YAG Laser.

CHAPTER – I

INTRODUCTION

1.1. INTRODUCTION TO NLO MATERIAL

The demand for non-linear optical crystals with superior perfection is rising day by day due to quantum jump in the design of non-linear optical materials and investigations into them have become most indispensable and efficacious disciplines in the field of Materials Science and Engineering. Consequently, there have been extensive efforts to develop new kinds of non-linear optical crystals for number of applications such as second harmonic generation, frequency mixing and electro-optic modulation etc. Non-linear optical (NLO) organ metallic complexes are given much attention due to their ability to combine the flexibility of organic materials with the thermal stability and mechanical strength of inorganic material[1-3]. Nonlinear optics is the study of how intense light interacts with matter. The optical response of a material usually scales linearly with the amplitude of the electric field. At high powers, however, the material properties can change more rapidly.

This leads to nonlinear effects including self-focusing, solutions and high-harmonic generation. It deals with the interaction of electromagnetic field of light with NLO material results in the generation of electromagnetic fields. Optical communications, Optical computing and image analysis have been developed by NLO process to perform frequency conversion, light modulation, optical switching, image processing. Current research is concentrated on the growth of organic semi-organic bulk single crystal having second orders NLO properties. The semi organic crystal possesses positive aspects of both organic and inorganic material hence it is important to synthesis and growth of the novel semi organic NLO crystals[4].

Nonlinear optical (NLO) materials are at the core of many optical electronic warfare (EW) systems and other next-generation defences technologies because they can be used to shift the wavelength and frequency of laser light, enabling

operation in parts of the electromagnetic spectrum (EMS) that would normally be inaccessible.

Fig.1.1 Types of NLO material

Nonlinear optics (NLO) is the branch of science deals with the study of interaction of intense electromagnetic field with materials and this leads to different nonlinear optical phenomena such as frequency conversion, dispersion, parametric amplification etc., Second harmonic generation (SHG) is a nonlinear optical process that results in the conversion of an input optical wave into an output wave of twice the input frequency.Nonlinear optical (NLO) materials play a major role in information technology and industrial applications.The understanding of the nonlinear polarization mechanisms and their relation to the structural characteristics of the materials are important to synthesize new NLO materials. In the recent years there has been a growing interest in nonlinear optical materials due to their effective usage in the field of electro-optical devices, data storage technology and optical signal processing. However, semi-organic single crystals are attracting great attention in the field of nonlinear optics because of their high optical nonlinearity, chemical flexibility of ions, thermal stability and excellent transmittance in the UV–visible region[5] .

Nonlinear optical (NLO) materials are essential for the development of advanced modern technologies ranging from telecommunication, signal processing, data storage, super resolution lithography, and microscopy to higher harmonic and terahertz (THz) generation. In particular, NLO materials with well-

defined architectures on the (sub) wavelength length scales are regarded as key materials for the development of the next generation integrated photonic circuits. One of the most widely studied and applied second-order NLO effects is second harmonic generation (SHG), in which two photons of incident light combine and generate a photon with doubled frequency and energy.

Nonlinear optics allows us to change the color of a light beam, to change its shape in space and time, and to create the shortest events ever made by humans. Nonlinear optical phenomena are the basis of many components of optical communications systems, optical sensing, and materials research. Nonlinear optics play a major role in many of the optical applications such as optical signal processing, optical computers, ultrafast switches, ultra-short pulsed lasers, sensors, laser amplifiers, and many others. Most NLO materials used for military and intelligence purposes are optical crystals. In these crystals, the electric field associated with light can interact with the crystal's internal structure – also known as its lattice – in non-linear (unexpected) ways.

In recent years, many researchers have tried to find varieties of NLO crystals for laser applications. Inorganic crystals are widely used in these applications because of their high melting point, high mechanical stability and high degree of chemical inertness. The optical nonlinearity of inorganic crystals is generally lower than that of the optical device demand. Organic compounds are often formed by weak Vander Wall's, hydrogen bonds and possess a high degree of delocalization. A major drawback of organic NLO crystals is the difficulty in growing large size, good optical quality and higher mechanical stability single crystals[6-8]. NLO properties of semi-organic materials are currently under intense investigation, triggered by potential applications in NLO due to their incorporated advantages of both organic and inorganic crystals. Most NLO materials used for military and intelligence purposes are optical crystals.

In these crystals, the electric field associated with light can interact with the crystals internal structure and also known as its lattice in non-linear ways. This nonlinear response usually only occurs under very intense irradiation, like that from a laser, can be used to achieve frequency-converting processes that can shift the laser's wavelength into the spectral range needed for a particular use or application. For efficient frequency conversion, a crystal must:

- Be non-centrosymmetric (have a non-zero nonlinearity)
- Have a nonlinear d-coefficient large enough to generate tunable wavelengths over a broad range
- Be highly transparent at the required input and output wavelengths
- Be able to match different phases.

1.2 INTRODUCTION TO SECOND HARMONIC GENERATIONS (SHG)

Second harmonic generation (SHG), also called frequency doubling, is a nonlinear optical process, in which photons interacting with a nonlinear material are effectively 'combined' to form new photons having twice the frequency of initial photons.

We mainly introduce the SHG behavior the second-order nonlinear substability of a medium characterizes its tendency to cause SHG. Second-harmonic generation, like other even-order nonlinear optical phenomena, is not allowed in media with inversion symmetry (in the leading electric dipole contribution). However, effects such as the Bloch – seigher shift (oscillation), found when two-level systems are driven at Rabi frequencies comparable to their transition frequencies, will give rise to second harmonic generation in Centro-symmetric systems.

In addition, in non-Centrosymmetric crystals belonging to crystallographic point group 432, if SBN nano crystal/PC composites. The SHG is not possible and under Klein man's condition SHG in 422 and 622 point groups should vanish although some exceptions exist.

SHG was firstly demonstrated by Franken and his colleagues in 1961 (Franken et al., 1961). In recent years, ferroelectric NLO powders with unexpected high efficiencies for frequency conversion and random lasers have attracted considerable attention (Wiersma and Cavalier, 2001**;** Skipetrov, 2004). By embedding NLO nano crystal in a transparent, deformable matrix, the fabrication of novel NLO device seems possible (Wing, 1997; Tsai et al., 2004; Lisinski et al., 2006).

In biological and medical science, the effect of second-harmonic generation is used for high-resolution optical microscopy. Because of the non-zero second-harmonic

coefficient, only non-centrosymmetric structures are capable of emitting SHG light[9-11].

1.2.1 SECOND HARMONIC GENERATION (SHG)

Second harmonic generation (SHG, also called frequency doubling) is a nonlinear optical process in which two photons with the same frequency interact with a non linear material, are “combined”, and generate a new photon with twice the energy of the initial photons that conserves the coherence of the excitation. It is a special case of the sum-frequency generation (2 photons), and more generally of harmonic generation.

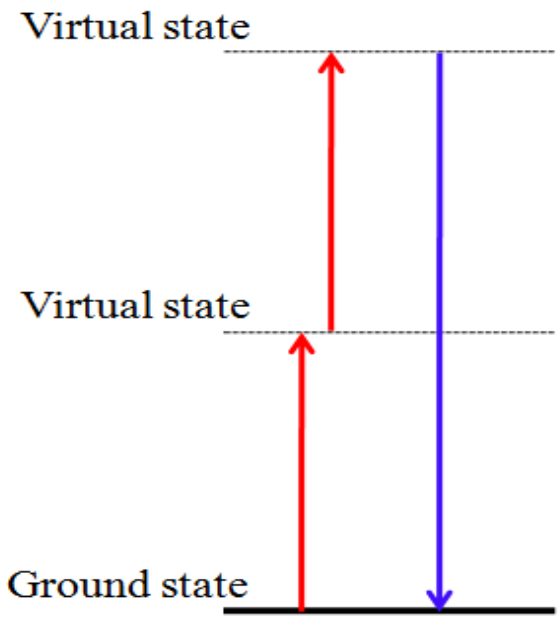

Fig.1.2 Energy level scheme of SHG process

Second Harmonic Generation (SHG) is a coherent optical process of radiation of dipoles in the material, dependent on the second term of the expansion of polarization. The dipoles are oscillated with the applied electric field of frequency w, and it radiates electric field of 2w as well as 1w. So the near infrared input light comes out as near UV light. In centrosymmetric materials, SHG

cannot be demonstrated, because of the inversion symmetries in polarisation and electric field. The only odd terms survive, thus the second order harmonics are not present. SHG can be useful in imaging biological materials. For example, the collagen fibres and peripheral nerves are good SHG generating materials. Since the SHG is a coherent process it, the molecules, or the dipoles are not excited in terms of the energy levels. Thus SHG doesn't, in principle photo damage the cells because there are no photo excitations. Also SHG is from the intrinsic property of the molecules and the input light, so external dyes are not necessary. The goal of this project, for now is to investigate the SHG signal quantitatively. Particularly, to explore angular, spatial, intensity dependence of SHG signals from βBaBO4 (BBO) crystal.

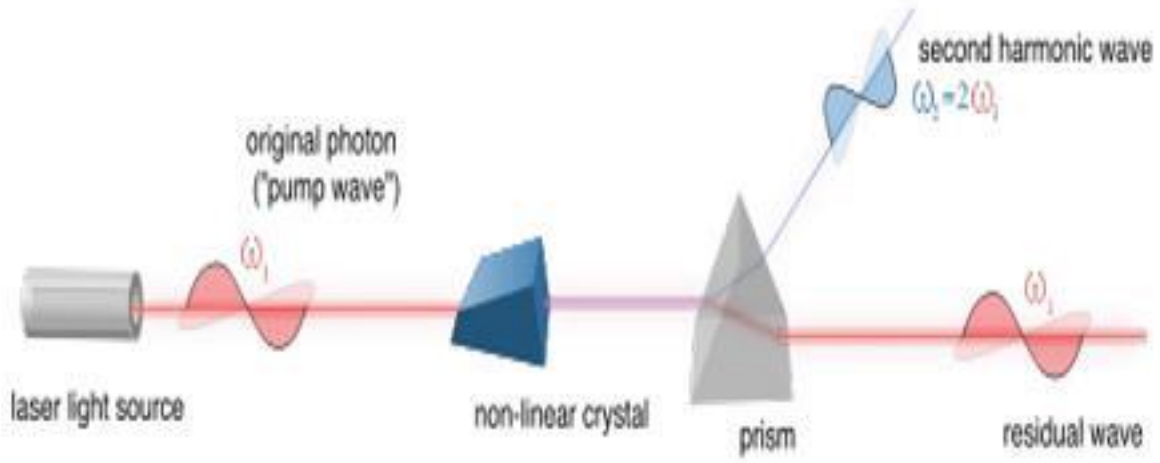

Fig 1.3 Second harmonic generations

In some cases, almost 100% of the light energy can be converted to second harmonic frequency. These cases typically involve intense pulsed laser beams passing through large crystals, and careful alignment to obtain phase matching. In other cases, like second harmonic imaging microscopy, only a tiny fraction of the light energy is converted to the second harmonic but this light can nevertheless be detected with the help of optical fibres. Generating the second harmonic, often called frequency doubling, is also a process in radio communication; it was developed early in the twenty century, and has been used with frequencies in the megahertz range. It is a special case of frequency multiplication.

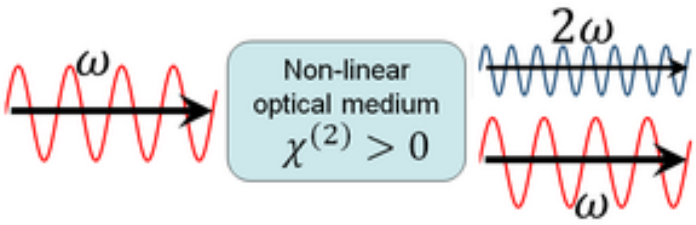

Fig 1.4 Non- linear optical medium

1.3 INTRODUCTION OF CRYSTAL GROWTH

Crystal growth is the process by which a solid crystalline material is formed from a fundamental process in materials science and plays an important role in the production of many everyday items, such as semiconductor, solar cells and pharmaceuticals. During crystal growth, atoms or molecules are arranged in a specific pattern, known as a crystal lattice, which repeats in all direction. The growth process can occur through a variety of mechanisms, such as nucleation and growth from a solution, deposition from a solution, deposition from a vapour, or solid-state diffusion. Controlling crystal growth is important for achieving desired material properties, such as crystal size, purity, and orientation. It is a complex process that is influenced by many factories, including temperature, pressure concentration and the presence of impurities. Understanding the mechanisms of crystal growth is crucial for developing new materials with desired properties and for optimizing existing production processes.

1.3.1 IMPORTANCES OF CRYSTAL

Crystals are important for a variety of reasons, both practical and scientific. Here is some of the key importance of crystals:

- **MATERIALS SCIENCE:** Crystals play an important role in materials science as they are the building blocks of many materials such as metals, semiconductors, ceramics and polymers. The properties of their materials depend on the arrangement of atoms or molecules in their crystal structures.
- **TECHNOLOGY:** Many technologies such as electronics, optoelectronics and photonics rely on the unique properties of crystals. For example, the use of

single crystals in semiconductors and transistors has revolutionized the field of electronics.

- **RESEARCH:** Crystals are also important in scientific research as they can be used to study the behaviour of atoms and molecules in solid states. This can provide insights into the fundamental properties of matter and help to develop new materials with unique properties.
- **HEALTH:** Crystals are used in medicine for a variety of purposes such as drug delivery, imaging and diagnosis. For example, X-ray crystallography is a powerful tool used to determine the three dimension structure of proteins, which is important for drug design.
- **AESTHETIC:** Crystals are also valued for their beauty and used in jewellery, decoration and art. Many people find crystals to aesthetically pleasing and believe that they have healing properties.

1.3.2 INDUSTRIAL USES OF CRYSTALS

Crystals have a wide range of industrial application due to their unique physical and chemical properties. Some common industrial of crystals are:

- **SEMICONDUCTORS:** Crystals are used in the production of semiconductors, which are used in electronic devices such as computers, Smartphone and television. Silicon is the most commonly used semiconductor material and its crystal structure plays a key role in determining its electronic properties.
- **OPTICS:** Crystals are used in the production of optical components such as lenses, mirrors and prisms. Certain crystals have unique optical properties that make them useful for specific applications such as the use of sapphire in laser technology.
- **PHARMACEUTICALS:** Crystals are used in the pharmaceutical industry to produce drugs in a crystalline form, which can improve their stability, bioavailability and effectiveness, Crystal engineering techniques are used to optimize the crystal structure of drugs for specific applications.
- **CHEMICALS:** Crystals are used in the production of a variety of chemicals such as fertilizers, pigments and catalysts. For example, zeolites are crystalline materials with a porous structure that make them useful as catalysts in the chemical industry.

- **ENERGY:** Crystals are used in the production of solar cell, which convert sunlight into electricity. Certain crystal such as silicon and cadmium telluride has the unique properties required to efficiently convert solar energy into electricity.

Overall, crystals have a wide range of industrial applications, from electronics to pharmaceuticals to energy production. The unique physical and chemical properties of crystals make them versatile materials for a variety of industrial processes.

1.3 .3 VARIOUS METHODS OF CRYSTAL GROWTH

There are several methods for crystal growth each of which is suited to different types of materials and application. Here are the most common methods:

- **SOLUTION GROWTH**: In solution growth crystals are grown from a solution by controlling the temperature, pressure and concentration of the solvent and solute. This method is commonly used for growing single crystals of inorganic salt and organic compounds.

- **VAPOUR DEPOSITION**: Vapour deposition involves depositing a vaporized material onto a substrate, where it condenses into a crystal. This method is used for growing thin films of materials such as metals, semiconductors and ceramics.
- **BRIDGMAN-STOCKBARGER METHODS:** The Bridgman-stockbarger method involves slowly cooling a melt of the material to be grown, which creates a gradient of temperature and concentration. This method is used for growing large single crystals of oxides.
- **CZOCHRALSKI METHODS**: The czochralski method involves melting the material in a crucible and then slowly pulling a seed crystal through the melt, which causes the crystal to grow on the end of the seed. This method is used for growing large, high-quality single crystals of semiconductors such as silicon.
- **HYDROTHERMAL SYNTHESIS:** Hydrothermal synthesis involves growing crystals from a superheated water solution under high pressure. This method is commonly used for growing crystal of minerals and synthetic materials.
- **FLAME FUSION METHODS:** In flame fusion method, a powdered material is melted in a flame and then rapidly cooled to form a crystal. This method is

commonly used for growing synthetic gemstones such as ruby and sapphire.

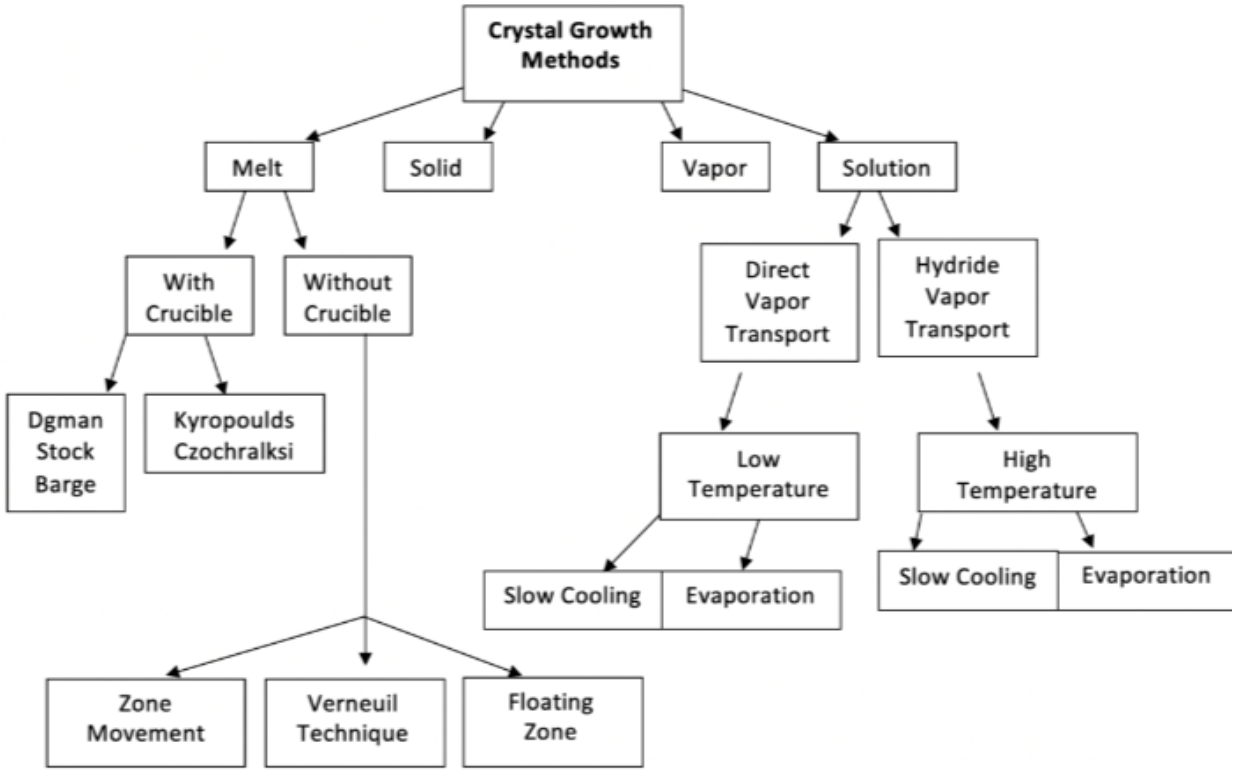

Fig. 1.5 Crystal Growth Methods

1.4 SLOW EVAPORATION METHOD:

The slow evaporation method is a common technique used to grow crystals from a solution. It involves dissolving a solid solute in a solvent to create a supersaturated solution, which is then allowed to slowly evaporate under controlled conditions. As the solvent evaporates, the solute evaporates the solute concentration in the solution increases until it reaches a point where crystals start to form.

The process of slow evaporation typically involves the following steps:

- **Preparation of the solution:** The solute is dissolved in a suitable solvent to create a supersaturated solution. The solubility of the solute in the solute in the solvent must be carefully controlled to achieve the desired level of supersaturation.

- **Selection of the container:** The contain used to hole the solution must be clean, smooth and free from any impurities that could interfere with crystal growth
- **Controlled evaporation:** The container is left open to the air and the solvent is allowed to slowly evaporate under controlled conditions. This can be achieved by covering the container with a lid that has small holes or using desiccators to regulate the humidity and temperature of the environment surrounding the solution.
- **Crystal growth:** As the solvent evaporates, the solute concentration in the solution increases, reaching a point where crystal start to form. The crystal will continue to grow until the solute concentration in the remaining solution falls below the saturation point.
- **Harvesting the crystals:** Once the crystals have reached the desired size, they can be harvested by carefully removing them from the solution using a spatula or a filter paper.

The slow evaporation method is often used to grow small to medium sized crystal of various compounds, including salt, organic compounds and proteins. The size and morphology of the crystals depend on factors such as the solute concentration; the solvent used the rate of evaporation and the environment condition during crystal growth. Carefully control of these parameters is essential to achieve high quality crystals with uniform size and shape.

The evaporation of the solvent causes the molecules of the soluble compound to separate out as crystals due to the higher concentration exceeding the chemical compound's solubility. This is the most popular method of crystallization, especially when working with common compounds such as inorganic salts and sucrose.

Solvent-evaporation synthesis produces crystals by slowly increasing the concentration of the mother liquor. Crystals can slowly grow as the solution becomes saturated by either cooling of the solution or by evaporation of excess solvent.

Method of crystalline – There are three types of growth slow cooling method, slow evaporation method, temperature gradient method. Prepare a solution of the compound in a suitable solvent filter the solution through a clean glass fir into a clean vessel and cover but not tightly gently put the container in a quiet, out of

the way place and allow the solvent to evaporate slowly. This method works best when there is sample material to allow for at least a few mile liters of solvent. The next method being slow cooling (from high temperature to Room Temperature or Low temperature, slowly). The compound can be dissolved in a single solvent or mixture of two solvents and left for Slow Evaporation. It can be done either under atmospheric conditions or under inert atmosphere.

Evaporation is also used to concentrate liquid foods such as noodles and make condensed milk, the product of a process that removes water from milk. Similarly, pharmaceutical companies use evaporators to remove excess moisture from drugs, thus improving product stability.

The general disadvantages are:

- Generally, only purifies one component.
- Yield is limited by phase equilibria.
- Process kinetics are more complex and less well-understood than some alternatives; obtaining detailed kinetic parameters involves complex experimental procedures.
- One disadvantage of evaporation to dryness is that any soluble impurity present will be deposited together with the required solid. Evaporation to dryness is also not suitable for all substances as many substances decompose when heated strongly.
- Evaporation method is only used for separating homogeneous mixtures when solid is dissolved completely in liquid. It is not useful for separating heterogeneous mixtures. They can be separation.

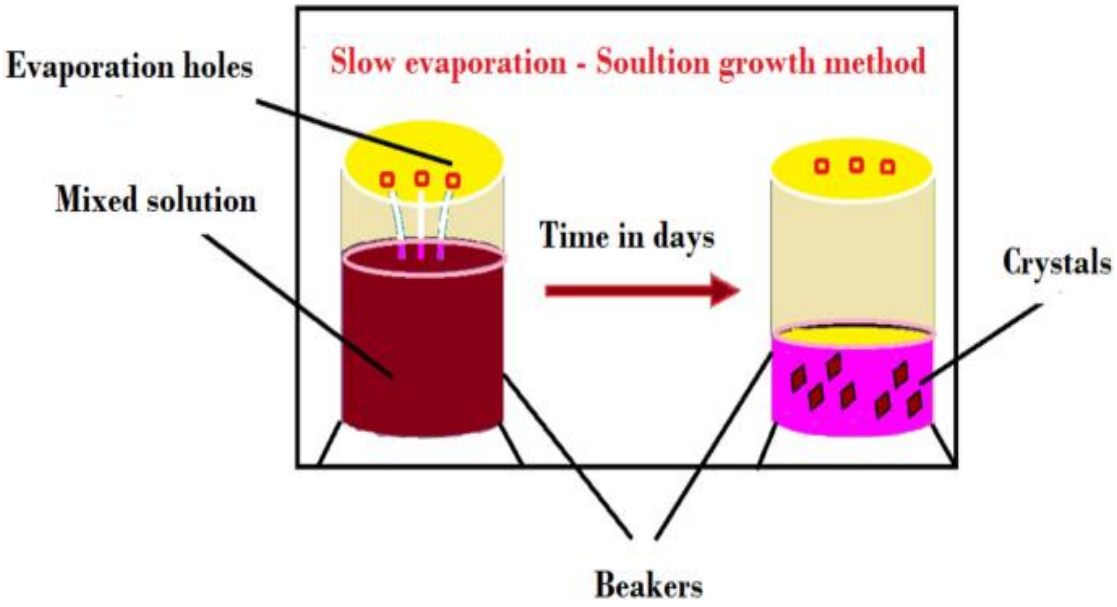

Fig.1.6 Slow Evaporation Method

CHAPTER II

EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

2.1 XRD ANALYSIS

X-Ray diffraction (XRD) replies on the dual wave /particle nature of X-rays to obtain information about the structure of crystalline materials. A primary use of the technique is the identification and characterization of compounds based on their diffraction pattern.

2.1.1 PRINCIPLE

Consider two parallel monochromatic X-ray beams with the wavelength falling on the successive planes of the crystal at an angle; Constructive interference of the reflected rays from two successive planes occurs; only the path difference between the two rays fulfils the interplanar distance.

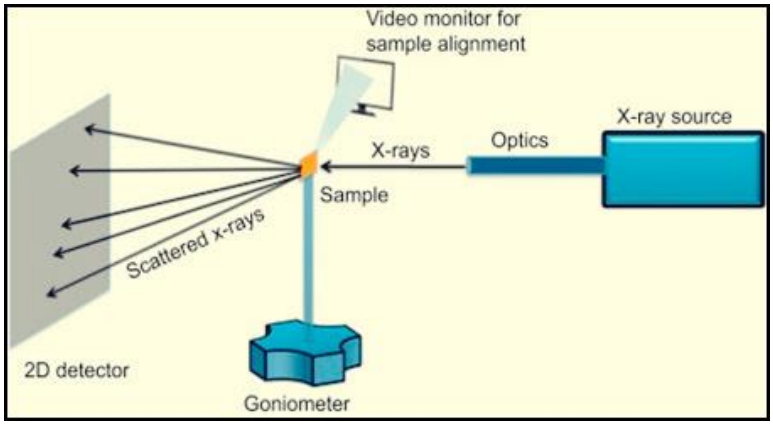

Fig 2.1 Experimental arrangement of XRD analysis

2.1.2 WORKING

The domain effect that occurs when an incident beam of monochromatic X-ray interacts with a target material is scattering of those X-ray from atom within the target material. In material with regular structure, the scattered X-rays undergo constructive and destructive interference. This is the process of diffraction. The diffraction of the X-rays by crystals is described by Bragg's Law, n (ƛ) = 2d sin (Ɵ). The direction of possible diffractions depends on the size and shape of the unit cell

of the material. The intensities of the diffracted waves depend on the kind and arrangements of atoms in the crystal structure. However, most materials are not the single crystals, but are composed of many tiny crystallites in all possible orientations called polycrystalline aggregate. When a powder with random oriented crystalline is placed in an X-ray beam, the beam will see all possible interatomic planes. If the experimental angle is systematically changed, all possible diffraction peaks from the crystal will be detected.

Fig.2.2 Instrumental setup of BRUKER KAPPA APEX 2 CCD diffractometer

2.1.3 WORKING

Single crystal X-ray diffraction is an analytical technique in which X-rays are employed to determine the actual arrangement of atoms within a crystalline specimen. Single crystal structure of compounds, which can be grown as single crystals. In the present study, the single crystal X-ray diffraction analysis was performed using BRUKER kappa 2.CCD single crystal X-ray diffractometer. A single crystal is mounted on a thin glass fiber fixed on the goniometric head. The unit cell dimensions and orientation matrix are determined using multiple reflections and then the intensity data of a given set reflections are collected automatically by the

compute[12]. The instrumental setup of BRUKER kappa Apex 2CCD diffractometer is shown in fig .2.2.

2.1.4 CALCULATION OF CRYSTAL SIZE

The crystal structure is found using **BRAGG'S LAW** in order to find its length, distance etc.

According to Bragg Equation: $n\lambda = 2d \sin\theta$ – (1)

According to the equation of Bragg's Law:

The equation explains why the faces of crystals reflect X-ray beams at particular angles of incidence (ɵ, λ).

The variable d indicates the distance between the atomic layers, and the variable. The variable d indicates the distance between the atomic layers, and the variable λ specifies the wavelength of the incident X-ray beam and n as an integer**.**

2.1.5 APPLICATION FOR SINGLE CRYSTAL XRD

- Single crystal X-ray diffraction is most commonly used for precise determination of a unit cell, including cell dimensions and positions of atoms within the lattice.
- Differentiation between crystalline and amorphous materials.
- Determination of electron distribution within the atoms and throughout the unit cell.
- Measurement of strain and small grain size.
- Determination of the orientation of single crystals.

2.2 ULTRAVIOLET –VISIBLE SPECTROSCOPY (UV –VISIBLE)

UV-Vis spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference or blank sample. This property is influenced by the sample composition, potentially providing information on what is in the sample and at what concentration.

UV detector employs a deuterium discharge lamp as a light source, with the wavelength of its light ranging from 190 to 380 nm. If components are to be detected

at wavelength longer than this, a UV-VIS detector is used, which employs an additional tungsten lamp.

2.2.1 PRINCPLE

Measuring in UV /visible region covers the wavelength of 200nm to 800nm. The absorption of UV or visible radiation by a molecule leads to transitions among the electronic energy levels of the molecule. It is ideal for characterizing the optical and electronic properties of various materials such as: films, powders, solids and liquids.

Infrared region of the electromagnetic spectrum utilizes wavelength from about 700-1000nm.The transitions measured in this region are generally related to overtone and combination band.

Fig 2.3 5E Varian Cary UV -Vis spectrophotometer

2.2.2 WORKING

The experimental arrangement of **Varian Cary 5E UV –VIS-IR spectrophotometer is shown in fig 2.3. UV -VIS –IR** when incident light strikes matter it can be absorbed, reflected, or transmitted. The absorbance of radiation in the UV-Vis range causes atomic excitation, which refers to the transition of molecules from a low-energy ground state to an excited state[13].

Light is focused into the entrance slit of the monochromatic from the source. Monochromatic uses dispersing elements, namely optical grating to separate the light by wavelength. The light is passed into a charged coupled device (CCD), which

is made up of individual tiny detectors; hence the intensity of light at each wavelength will be measured. CCD is read-off to a computer and the result obtained is a spectrum, which shows the intensity of each wavelength of light.

2.2.3 APPLICATION FOR UV VIS SPECTROSCOPY

- UV- Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of diverse analytic or sample.
- Qualitative and quantitative analysis
- Forensic toxicology.
- Detection of impurities from organic mixture.
- Molecular weight determination.

2.3 MICRO HARDNESS TEST – VICKERS HARDNESS

2.3.1 INTRODUCTION

Micro hardness Testing is a method of determining a material's hardness or resistance to penetration when test samples are very small or thin, or when small regions in a composite sample or plating are to be measured. It can provide precise and detailed information about surface features of materials that have a fine microstructure, are multi-phase, non-homogeneous or prone to cracking. The micro hardness test can measure surface to core hardness on carburized or case-hardened parts (case depths), as well as surface conditions such as grinding burns, carburization or decarburization. It is based on the principle of creating an indentation on the surface of the material using a diamond indenter, and then measuring the size of the indentation. The Vickers hardness test is widely used in industry and research because it can provide accurate and reproducible results.

2.3.2 PRINCIPLE

The micro hardness test can measure surface to core hardness on carburized or case hardened parts(case depths),as well as surface conditions such as grinding burns, carburization or decarburization[14]. It is based on the principle of creating an indentation on the surface of the material using a diamond indenter, and then measuring the size of the indentation. The Vickers hardness test is widely used in industry and research because it can provide accurate and reproducible results.

2.3.3 EXPERIMENTAL SETUP OF VICKERS HARDNESS TEST

The experimental setup for the Vickers hardness test typically involves the following steps:

- **Sample preparation**: The sample material is prepared by cutting and polishing it to a flat surface with a smooth finish. The surface must be free from any debris or contaminants that could affect the hardness measurements.
- **Mounting:** The sample is then mounted onto a sample holder or stage, which allows it to be securely held in place during the test.
- **Calibration:** The Vickers indenter is calibrated to ensure that it is accurately measuring the indentation size. This is typically done by using a standard reference material with a known hardness value.
- **Indentation:** The Vickers indenter is placed on the surface of the sample, and a load is applied for a set period of time. The load typically ranges from a few grams to several kilograms, depending on the material being tested.
- **Measurement:** The size of the indentation is measured using a microscope, which can be either manual or automated. The indentation size is typically measured in micrometers or millimetres.
- **Calculation**: The Vickers hardness number (HV) is calculated using the formula $HV = 1.8544\ P/d^2$, where P is the applied load in kilograms and d is the average diagonal length of the indentation in millimetres.
- **Data analysis:** The results of the Vickers hardness test can be used to compare the hardness of different materials or to factors such as heat treatment or deformation.

Overall the Vickers hardness test is a versatile and widely used method for measuring the hardness of materials, and its experimental setup is relatively straight forward and well- established. The experimental setup for Vickers hardness test is shown in fig 2.4

Fig.2.4 Experimental setup of Vickers hardness test

2.3.4 APPLICATIONS FOR VICKERS MICRO HARDNESS

- To determine hardness in materials in the micro hardness test load range.
- The Vickers method can be used with any and all test specimens, from soft to hard[15].
- There is only one type of indenter, which can be used for all Vickers methods.

2.4 DIELECTRIC - MEASUREMENTS

Dielectric, insulating material or a very poor conductor of electric current, when dielectrics are placed in an electric field, practically no current flows in them because, unlike metals, they have no loosely bound, or free, electrons that may drift through the material. Instead, electric polarization occurs. The positive charges within the dielectric are displaced minutely in the direction of the electric field, and the negative charges are displaced minutely in the direction opposite to the electric field.

This slight separation of charge, or polarization, reduces the electric field within the dielectric. The presence of dielectric material affects other electrical phenomena. The force between two electric charges in a dielectric medium is less

than it would be in a vacuum, while the quantity of energy stored in an electric field per unit volume of a dielectric medium is greater [16].

2.4.1 PRINCIPLE

In which it consists of two types' dielectric constant and dielectric loss. One of the useful methods of characterization of electrical response is dielectric studies. A study on the dielectric properties of solids gives an electric field distribution within solid. The frequency dependence of these properties gives great insight into the materials applications. The range of measurement depends upon the properties and the material of interest. From the study of dielectric constant as a function of frequency, temperature…etc., the different polarization mechanisms in solids such as atomic such as atomic polarization of the dipoles, space –charge polarization etc. can be understood.

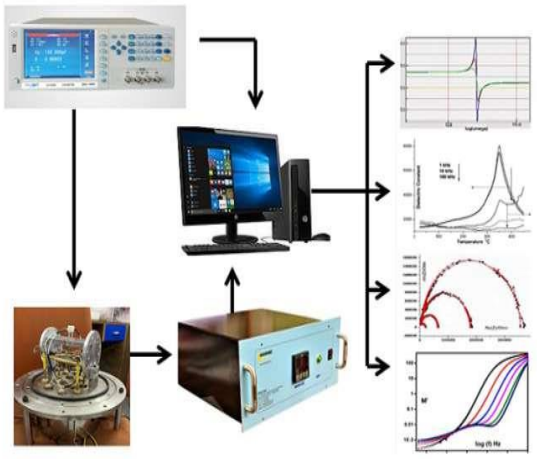

Fig.2.5 Experimental setup dielectrics

2.4.2 WORKING

The suitably cut and polished samples (with known dimensions) of grown crystals subjected to dielectric studies by using **HIOKI 3532-50 HITESTER LCR meter (fig2.6)** with a conventional four terminal sample holder for investigations involving temperature variations and a conventional two terminal sample holder

(westpal) for only ambient conditions. The sample are prepared and mounted between copper platforms and electrodes. In order to ensure good electrical contact, the crystal faces are coated with the silver paint. The capacitance and the electrode having the sample as a dielectric medium are measured. The measurements are made at frequencies ranges from 50HZ to 5MHZ at different temperature [17].

Fig 2.6 HIOKI 3532-50 HITESTER LCR meter

2.4.3 APPLICATION FOR DIELECTRICS

- Based on various properties like insulation, temperature dependency, permittivity, and dielectric strength, dielectric materials are used for various industrial materials for manufacturing of electrical devices.
- Dielectric materials can hold an electrostatic charge while dissipating minimal energy in the form of heat.
- Their application lies in power cables, capacitors and more.

2.5 NLO TEST – KURTZ POWDER SHG METHOD

2.5.1 INTRODUCTION

Recent interest is focused on to find the materials which have suitable nonlinear optical properties for use as the active media in efficient second harmonic generators, tunable parametric oscillators and broadband electro-optic modulators. Kurtz and perry (1968) proposed a powder SHG method for comprehensive analysis of the second order nonlinearity. Employing this technique, Kurtz (1968) surveyed a very large number of compounds[18].

2.5.2 EXPERIMENTAL SETUP

Nonlinear optical (NLO) materials play a major role in nonlinear optics and in particular they have a great impact on information technology and industrial applications. The non linear optical property of the single crystals can be tested by passing the output of Nd: YAG Quanta ray laser, where two photons of the same frequency are converted into a single photon with twice the frequency. The experimental setup for SHG typically involves the following components:

- **Laser:** A high - power laser is used as the light source. Typically, a pulsed laser is used, since it provides higher peak powers and shorter pulse durations, which increases the efficiency of SHG.
- **Nonlinear crystal:** A nonlinear crystal is used as the medium for SHG. The crystal must have a non Centro symmetric structure, which allows the generation of a second harmonic wave. The crystal should also have a high nonlinear coefficient to ensure efficient conversion of the incident light into the second harmonic wave. Popular nonlinear crystals for SHG include potassium dehydrogenate phosphate (KDP).
- **Optics:** A series of lenses and mirrors are used to focus and direct the laser beam onto the nonlinear crystal. The optics is carefully aligned to ensure that the laser beam is properly focused and that the polarization of the incident beam is properly aligned with the crystal axis.
- **Filters:** Filters are used to remove any residual fundamental wavelength light from the output beam. This is important because residual fundamental light can interfere with the detection of the second harmonic signal.

- **Detector:** A photo detector is used to measure the second harmonic signal. The detector must be sensitive to the second harmonic wavelength and have a high signal-to-noise ratio to detect the weak second harmonic signal.

  Overall, the experimental setup for SHG is a complex and delicate process that requires careful alignment of laser, crystal and optics to ensure efficient conversion of the incident light into the second harmonic wave. The experimental setup is shown in fig.2.7

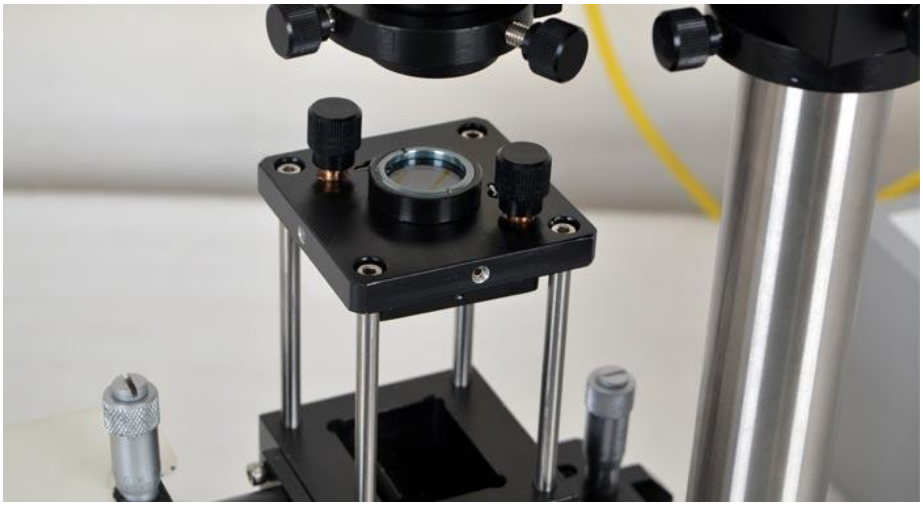

Fig 2.7 NLO-Test Second Harmonic Generation (SHG)

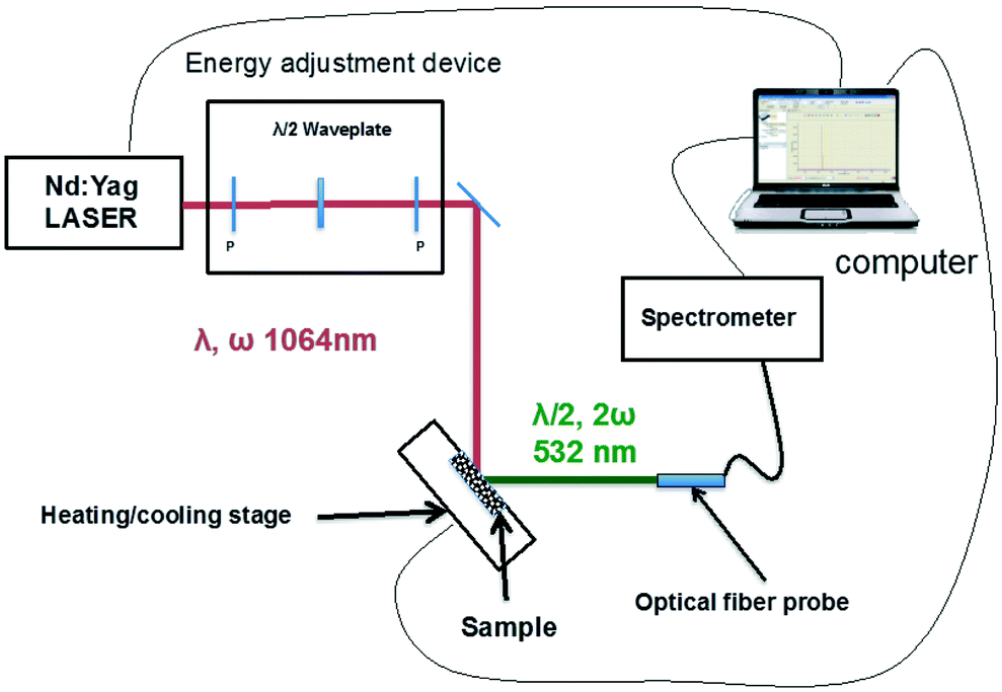

Fig.2.8 Schematic experimental setup for SHG efficiency measurement

2.5.3 APPLICATION FOR SHG METHOD

They are also excellent electro-optic crystals with high electro-optic coefficients, widely used as electro-optical modulators, such as Q-switches, pockets cells, etc.

CHAPTER III

AIM AND SCOPE

3.1 OBJECTIVE AND SCOPE

The ever increasing demand for highly efficient NLO crystals for visible and UV is extremely important for laser and material processing. In this content, the design and growth of single crystals suitable for such requirements, assumes centre stage. NLO crystals formed with thiourea have already been identified as potential candidates for NLO applications.

The present investigation deals with,

- Synthesizing the chosen materials for the growth of single crystals.
- Determining the solubility of the materials.
- Identifying the crystal structure by single crystal XRD analysis.
- Characterization of the grown crystals by UV-VIS-NIR, Vickers Micro hardness test, Dielectric studies and NLO.

The future scope of the work is also mention for further research. It is possible to grow bulk size crystals with improved optical quality by carefully adapting either the slow evaporation methods or by some innovations techniques with modified apparatus. Attempts can be made to identify suitable dopants which could provide better optical properties and enhance the NLO property of the crystals.

3.2 GROWTH AND CHARACTERIZATION OF BIS THIOUREA ZINC CHLORIDE

Recently, there is considerable interest in the synthesis of new materials with large second order optical non linerities because of their potential use in applications including telecommunications; optical computing, optical data storage, and optical information processing such applications require materials. Bisthiourea and zinc chloride (BTZC) is one of the semi organic crystals that have been put to practical uses. It has larger nonlinear optical coefficients, a high degree of relatively.

Among the various classes of semi organic nonlinear optical materials, metal complexes of thiourea have received potential interest, because they can be effectively used as the better alternatives for KDP crystals in frequency doubling

process and laser fusion experiments. As thiourea molecules possess a large value of dipole moment, they can form number of metal coordination compound like zinc thiourea chloride (ZTC), Bis -thiourea cadmium chloride (BTCC), zinc (tris) thiourea sulphate (ZTS), tris-thiourea copper chloride (TCC) etc.,. In this series, a NLO single crystal of Bis thiourea zinc chloride (BTZC) is found to be a good candidate for NLO applications[19-21].

3.3 EXPERIMENTAL PROCEDURE

3.3.1 Synthesis

The title compound (BTZC**)** was synthesized by mixing purified Bisthiourea and zinc chloride in de-ionized water in the stoichiometric ratio 2:1. The reaction of synthesis follows the equation,

$$ZnCl_2 + 2\,CS(NH_2)_2 \longrightarrow Zn(CS(NH_2)_2)_2Cl_2$$

- In the double-distilled water, salt is left to dissolve.
- After that, the salt is set to dissolve in a magnetic stirrer until it gets fully dissolved.
- Then the salt is filtered using filter paper, and the beaker top is covered with a butter sheet.
- The saturated sample is kept at room temperature until a seed crystal forms.
- The salt is kept again for the recrystallization process for a bulk crystal.

3.3.2 CRYSTAL GROWTH

The starting material was synthesized from Thiourea and zinc chloride salts at 2:1 molar ratio. The calculated amount of thiourea and zinc chloride salts were added to distilled water according to the solubility and finally the whole solution was mixed with continuous stirring for 3h using magnetic stirrer and to obtain a homogeneous mixture. The completely dissolved solution was filtered using Whitman filter paper to remove the suspended impurities and allowed to crystallize by slow evaporation method at room temperature for about 45 days. Finally a well defined single crystal was obtained. Photograph of grown crystal is shown in fig.3.1

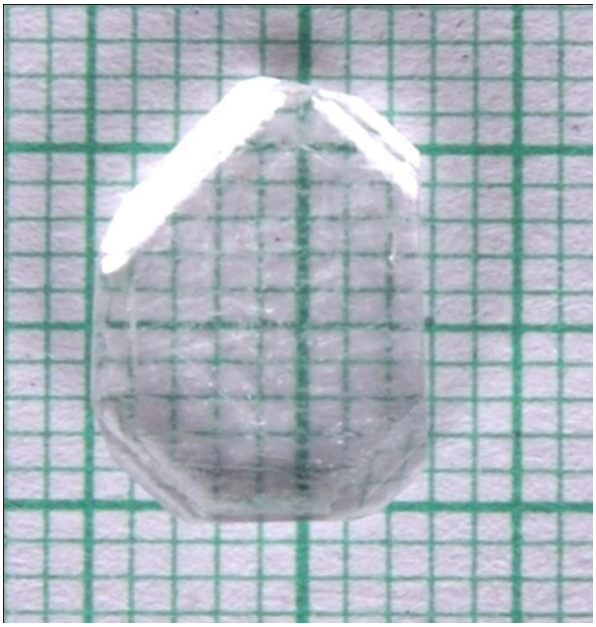

Fig. 3.1 Photograph of BTZC single crystal

CHAPTER IV

RESULT AND DISCUSSION

4.1. SINGLE CRYSTAL X-RAY DIFFRACTION

The grown BTZC crystal is subjected to single crystal X-ray diffraction studies using Bruker Kappa APEX-2 diffractometer with Mo Kα (λ=0.71073 Å) radiation to determine the cell parameters and crystal structure. The result of the study reveals that BTZC crystallizes into orthorhombic system with the space group $Pn2_1a$. The lattice parameters obtained in the present study a=5.706 Å, b=12.968 Å and c=12.762 Å are in good agreement with the reported values [22].The values of single crystal XRD is shown in the table (4.1)

Table 4.1 Crystallographic data of BTZC single crystal

BTZC	**Crystal Data**
Empirical formula	$Zn\ (CS\ (NH_2)_2)_2Cl_2$
Crystal system	orthorhombic system
Space group	$Pn2_1a$
Lattice Parameter	a=5.706 Å, b=12.968 Å and c=12.762 Å

4.2 OPTICAL TRANSMISSION SPECTRAL STUDIES

The optical transmission spectra of BTZC, single crystal was recorded in the region 200-2000 nm using the VARIAN CARRY 5E MODEL spectrometer covering the entire UV–vis and near infrared region. The recorded spectrum shown in Fig. 4.1, it is observed that the crystal possesses more than 75% transmission in the entire visible with the lower cut-off wavelength at 240 nm. This suggests that the material is quite suitable for SHG generation, UV tuneable Laser and optoelectronic applications. The good transmission of the crystal in the entire visible region is important for NLO devices [23].

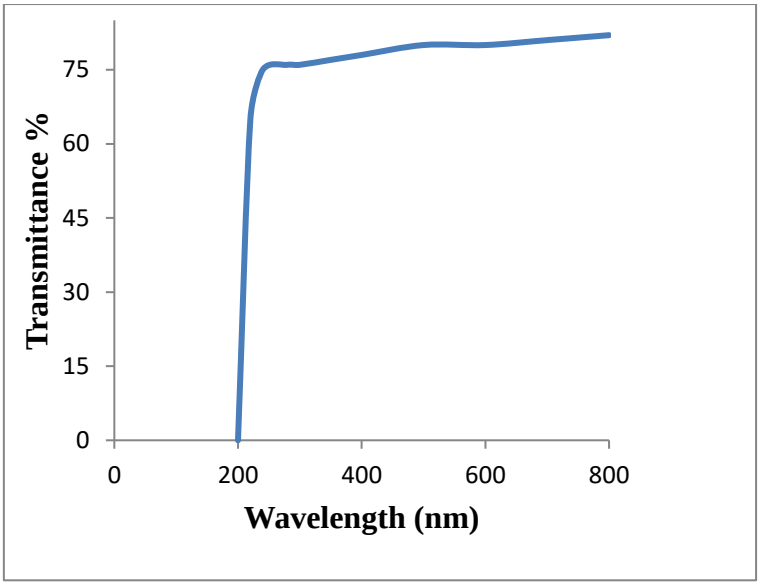

Fig. 4.1 Optical transmission spectrum of BTZC crystal

4.3. VICKERS MICRO HARDNESS TEST

The cut and well polished BTZC crystal was subjected to static indentation test at room temperature using Vickers's micro hardness tester. Indentations were made on the sample plane with the load ranging from 50 to 200 g, by keeping the time of indentation constant at (10s) for all trials. The distance between the consecutive indentations were kept more than five times the diagonal length of the indentation, to avoid surface effects. The Vickers's hardness number (Hv) for different loads were calculated [24] using the relation.

$$Hv = 1.8544 \frac{p}{d^2} kg/mm^2 \quad (1)$$

Where, P is the applied load in kilogram, and d is the diagonal length of indentation impression in millimetre and 1.854 is a constant of a geometrical factor for the diamond pyramid. The variation of micro hardness profile with applied load is shown in fig 4.2. From the profile it is observed that hardness increases with increasing load up to 105 g with maximum hardness number of 68 kg/mm^2.Further, the variation of load indicates that, above105 g the hardness number decreases with increasing load. The decrease in hardness number with increase load provides information about the formation of cracks due to release of internal stress generated by local indentation. From the results, it is also concluded that the crystal has

reverse indentation size effect due to increasing hardness number with respect load [25].

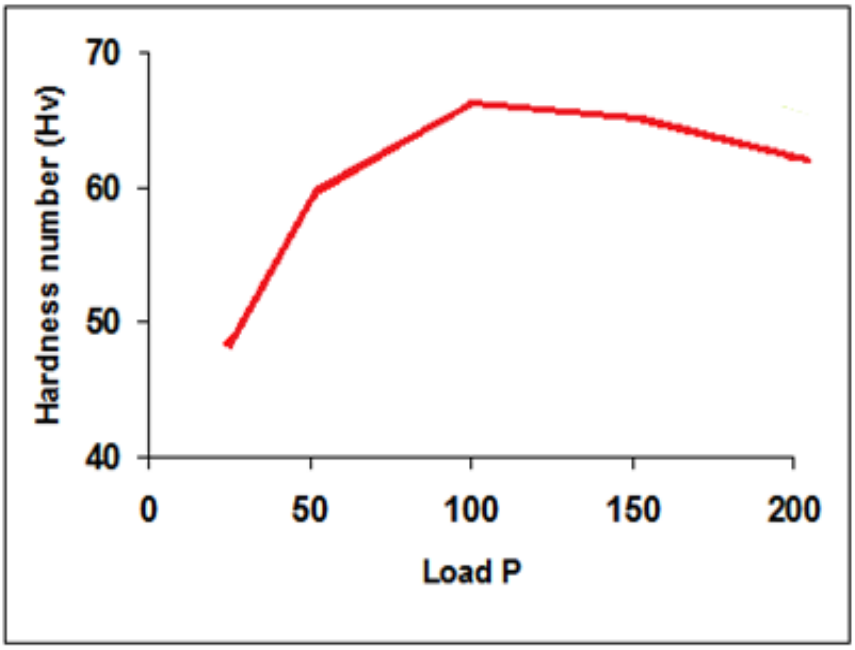

Fig .4.2 Plot of P versus Hv for BTZC crystal

4.4. DIELECTRIC STUDIES

The Dielectric measurements for BTZC single crystal is carried out using HIOKI 3532-50 LCR HITESTER in the frequency range 50 Hz to 5 MHz for different temperatures. The selected sample is cut using a diamond saw and polished using paraffin oil and fine-grade alumina powder to obtain a good surface finish. Silver paste is coated on both side of the sample to increase the ohmic contact. The dielectric constant ε is calculated using the relation

$$\varepsilon = \frac{cd}{A\varepsilon_0} \tag{2}$$

Where c is the capacitance, d is the thickness; *A* is the area of cross section and ε_0 is the absolute permittivity of the free space having the value 8.854×10^{-12} F/m. The dielectric loss ε' is also calculated using the relation,

$$\varepsilon' = \varepsilon \tan\delta \tag{3}$$

The variation of dielectric constant and dielectric loss with frequency are shown in Fig.4.3 and 4.4 respectively. It is observed from the profile that both the dielectric constant and dielectric loss decrease with increase in frequency at different temperature**.** In general, the dielectric study provides information regarding the dielectric constant arises from the contribution of different polarizations mechanism, namely electronic, ionic, atomic, space charge, etc., developed in the material subjected to the electric field variations. The large dielectric constant at low frequency indicates the present of space charge polarization [26] arising at the grain boundary interface. The low value of dielectric loss at high frequencies reveal the high optical quality of the crystal with lesser defects, and this parameter is of vital importance for nonlinear optical applications [27].

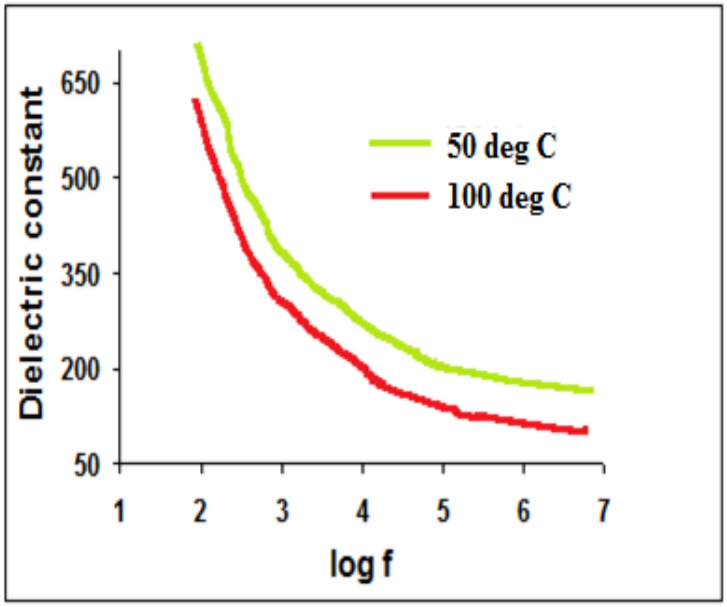

Fig. 4.3 Variation of dielectric constant with log F of BTZC crystal

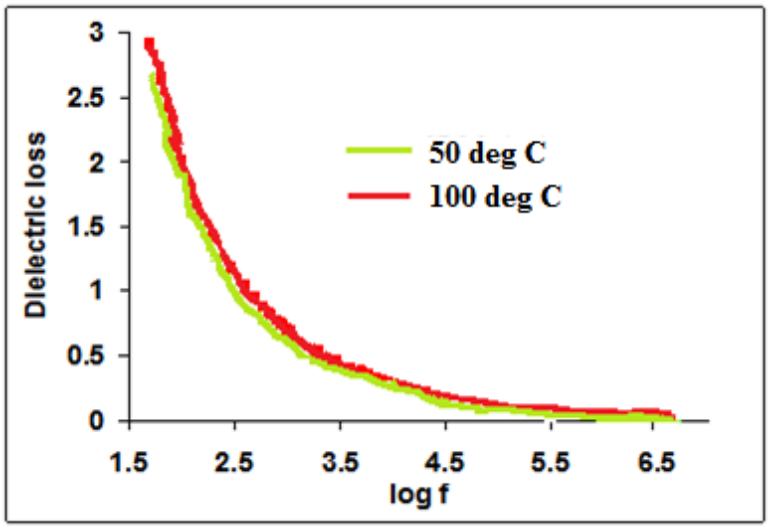

Fig. 4.4 Variation of dielectric Loss with log F of BTZC crystal

4.5 SECOND HARMONIC GENERATION (SHG) STUDY

The nonlinear optical (NLO) property of the grown crystal was confirmed by Kurtz and Perry powder test [28]. The BTZC single crystal was powdered with uniform particle size and this powder was packed densely between two transparent glass slides. KDP crystal was powdered to the identical size and was used as reference material in the SHG measurement. The Nd: YAG laser beam of 1064 nm wavelength, 8 ns pulse with 10HZ pulse rate was made to fall on the sample. The second harmonic generation in the crystal is confirmed with the emission green light as output. For the constant input energy of 1.9 mJ/pulse supplied for both crystals the output power is found to be 16.02 mV for BTZC and 9 mV for KDP respectively. Hence the SHG efficiency of grown crystal was found to be 1.78 times greater than that of KDP. The result suggests that BTZC crystal can be used effectively to optical and photonic device applications [29]. The second harmonic generation table is shown in table 4.2.

Table 4.2 SHG signal output of BTZC compared with KDP

Input Power (mJ/pulse)	KDP (Mv)	BTZC (mv)
1.9	9	16.02

CHAPTER V

CONCLUSION

Slow evaporation technique has been employed for the growth of semi organic Bis thiourea zinc chloride (BTZC) single crystal. Single crystal XRD confirms that the crystal belongs to orthorhombic system with the space group Pn21a.UV-VIS spectrum shows that the crystal possesses high transparency in the entire visible and IR region. Microhardness measurement reveals that Vickers' hardness number increases as the load increases and then decreases for higher loads, satisfying reverse indentation size effect. The low dielectric constant and dielectric loss at high frequencies suggest that the sample possesses enhanced optical quality with lesser defects. Kurtz powder test shows that the SHG sufficiency of BTZC is nearly 1.78 times of standard KDP crystal. The detailed characterization and the nonlinear optical properties confirm that the grown crystal is suitable for the fabrication of various optoelectronic and photonic devices.

REFERENCES

1. N.B. Singh, T. Henningsen, E.P.A. Metz, R. Hamacher, E. Cumberledge, R.H. Hopkins, Solution growth of vanillin single crystals, Mater. Lett. 12 (1991) 270–275.
2. M.D. Aggarwal, J. Stephens, A.K. Batra, R.B. Lal,Bulk crystal growth and characterization of semiorganic non linear optical materials, J. Optoelectron. Adv. Mater. 5 (2003) 555–562.
3. R. Rajasekaran, P. Mohan Kumar, R. Jayavel, P. Ramasamy, Influcence of PH on the growth and characterization of non linear optical zinc thiorea choloride single crystals, J. Cryst. Growth 252 (2003) 317-327
4. X.J. Liu, Z.Y. Wang, D. Xu, X.Q. Wang, Y.Y. Song, W.T. Yu, W.F. Guo, Investgation of micro crystlaization of L-arginine trifluroacetate crystals, J. Alloys Compd. 441 (2007) 323–326.
5. T,Dhanapal,G.Amirthaganesan,Growth, spectral, thermal and dielectric studies on a new semiorganic material Di-N- methylanilinum tetra chlorocadmiate,optik,125(2014),238-242
6. S. Arjunan, A. Bhaskaran, R.MohanKumar, R. Mohan, R. Jayavel, Effect of rare earth dopants on the growth and structural,optical,electrical,and mechanical properties of L- arginine phosphate single crystals, J. Alloys Compd., 506 (2010) 784–787.
7. B. Milton Boaz, J. Mary Linet, Babu Varghese,M. Palanichamy, S. Jerome Das, Growth and characterization of a new nonlinear optical material: Potassium p-nitrophenolate dehydrate with new bonding properties J. Cryst.Growth 280 (2005) 448–454
8. P. Maadeswaranan, J.Chandrasekarana , Synthesis, growth and characterization of l-valine cadmium chloride monohydrate—A novel semiorganic nonlinear optical crystal, Optik 121 (2010) 26-30.
9. C. Justin Raj, S. Dinakaran, S. Krishnan, B. Milton Boaz, R. Robert, S. Jerome Das,studieson optical ,mechanical and transport properties of NLO active L-valine formate single crystal grown by modified SR method, Opt. Com. 281 (2008) 2285-2290

10. S.B. Monaco, L.E. Davis, S.P. Velsko, F.T. Wang, D. Eimerl, A.J. Zalkin,synthesis and characterization of L-arginine phosphate J. Cryst. Growth 85 (1987) 252-255.
11. G. Ramesh Kumar, S. Gokul Raj, R. Mohan, R. Jayavel, Influence of isoeletric pH on the growth linear and non linear optical and dielectric properities of L-threonine single crystals, Cryst. Growth Des. 6(2006) 1308-1310.
12. Bradley Ferguson, Xi-Cheng Zhang, Optical,photonic and opto electronic materials characterization and analytical techniques, Nat. Mater. 1 (2002) 26-33.
13. M.B. Johnston, L.M. Herz, et al. Low energy vibrational modes in phenylene studied time domain spectroscopy, Chem. Phys. Lett. 377 (2003) 256-262.
14. S.Dhanuskodi, J.Ramajothi ,Crystal growth,thermal and optical studies of L-histidine tetrafluroboate a semi organic NLO material, Cryst.Res.Technol.39 (2004) 592–597.
15. S.Dhanuskodi, K.Vasantha, P.A.AngeliMary,Structural and thermal characterization ofsemi organic NLO material L-alanine zinc chloride ,Spectrochim. Acta A66 (2007)637–642.
16. M.Anbuchezhiyan, S.Ponnusamy, C.Muthamizhchelvan, K.Sivakumar, , Crystal growth structural and characterization of semi organic NLO material β-alanine zinc chloride Mater, Res.Bull.45 (2010) 897-904
17. Redrothu Haumatharo,S.Kalainathan, Growth ,spectroscopic,dielectric and non linear optical studies of semiorganic non linear optical crystal –L-alanine lithium choloride, Spectrochim.Acta A86 (2012) 80-84
18. P.M. Ushashree, R. Muralidharan, R. Jayavel, P. Ramasamy, Growth of bis thiorea cadmium choloride single crystals-a potential NLO material of organo metallic complex, J. Cryst. Growth 218 (2000) 365-371
19. R. Uthrakumar , C. Vesta , C. Justin Raj , S. Krishnan , S. Jerome Das , Bulk crystal growth and characterization of non-linear optical bisthiourea zinc chloride single crystal by unidirectional growth method Current Applied Physics 10 (2010) 548–552
20. V. Venkataramanan, S. Maheswaran, J.N. Sherwood, H.L. Bhat, crystal growth and physical characterization of the semiorganic bis thiourea cadmium choloride, J. Cryst. Growth 179 (1997) 605-610.

21. M. Simon, K. Buse, R. Pankrath, E. Kratzig, Photoconductivity and phtoerfractive Sr_{06},Ba_{039} Nb_20_6 ce crystalsJ. Appl. Phys. 80 (1996) 251-258
22. B. Milton Boaz, S. Mary Navis Priya , J. Mary Linet ,P. Martin Deva Prasath, S. Jerome Das , Photoconductivity and dielectric studies on NLO active NPNa and NPLi single crystals Optical Materials 29 (2007) 827–832
23. K.Sugandhi, S.Dinakaran , M.Jose , R.Uthrakumar , A.JeyaRejendran , G.Bhagvannarayana, . Joseph , S.JeromeDas Crystalline perfection, spectroscopic investigations and transport properties of trisglycine zinc chloride NLO single crystal, Physica B 405 (2010) 3929–3935
24. L. Guru Prasad, R. Nagalakshmi, P. Muthusamy , V. Krishnakumar, Physicochemical properties of organic nonlinear optical crystal for frequency doubling: Glycine acetamide ,Materials Letters 63 (2009) 1255–1257..
25. Kanagasekaran T, Mythili P, Srinivasan P, Shailesh N, Sharma, Gopalakrishnan R. systhesis,crystal groth and characterization of organic material N-Broumousuccinimide for nlo applications ,Mater Lett 2008; 62:2486–2489.
26. B.W. Mott, Micro Indentation Hardness Testing, Butterworths, London (1956) p.9.
27. P. Mythili, T. Kanagasekaran, N. Shailesh, R. Sharma, Gopalakrishnan,Growth and characterization of sodium sulpanillate dehydrate crystals for NLO applications J. Cryst. Growth 306 (2007) 344-350.
28. P.C. Thomas, S. Aruna, J. Packiam Julius, A. Joseph Arul Pragasam, P. Sagayaraj, Growth and characterization of semiorganic NLO material of LAHClBr Cryst. Res. Technol. 41 (2006) 1231–1235.
29. S.K. Kurtz, T.T. Perry,A powder technique for the evaluation of non linear optical materials, J. Appl. Phys. 39 (1968) 3798-3813.