NON-LINEAR OPTICAL CHARACTERIZATION OF Zn²⁺ DOPED

L-GLYCINE BARIUM CHLORIDE SINGLE CRYSTAL

Project Report

Submitted to Mar Ivanios College (Autonomous) affiliated to the University of Kerala for the requirements of the degree of

B.Sc PHYSICS

DEPARTMENT OF PHYSICS

MAR IVANIOS COLLEGE (AUTONOMOUS)

THIRUVANANTHAPURAM

2021-24 BATCH

MAY 2024

HARIDEV S	**2210403**
AKARSH MOHAN	**2210423**
VISHNU B	**2210425**
DAVID DANN ISEC	**2210441**
NAVEEN MUHAMMED F	**2210443**

DECLARATION

We, Haridev S, Akarsh Mohan, Vishnu B, David Dann Isec and Naveen Muhammed F declare that this project work entitled "**Non-Linear Optical Characterization of Zn^{2+} Doped L-Glycine Barium Chloride Single Crystal**" is entirely an original work and has been carried by us independently under the supervision and guidance of **Dr. K.C. Bright**, Assistant Professor, Department of Physics, Mar Ivanios College, Thiruvananthapuram during the academic year 2021-24 for the degree of Bachelor of Science in Physics, and this work has not been submitted for any other degree.

Thiruvananthapuram   Akarsh Mohan

Date: David Dann Isec

                                      Haridev S

                                      Naveen Muhammed F

                                      Vishnu B

CERTIFICATE

This is to certify that the project report entitled "**Non-Linear Optical Characterisation of Zn^{2+} Doped L-Glycine Barium Chloride Single Crystal**" is an authentic report of work carried out by **Haridev S**, **Akarsh Mohan**, **Vishnu B**, **David Dann Isec** and **Naveen Muhammed F** in the Department of Physics, Mar Ivanios College, Thiruvananthapuram under my supervision and guidance, as partial fulfilment for the award of the degree of Bachelor of Science in Physics.

Dr. John Jacob

Head of the Department

Department of Physics

Dr. K.C Bright

Assistant Professor

Department of Physics

Mar Ivanios College,

Autonomous

Signature of Examiners:

Thiruvananthapuram

1.

2.

ACKNOWLEDGEMENT

It is with great pleasure that we present our project entitled "Non-Linear Optical Characterisation of L-Glycine Barium Chloride Single Crystal". Primarily we would thank God for making us capable to complete this project successfully.

We would like to express our sense of gratitude and respect to **Dr.K.C. Bright**, Assistant Professor, Department of Physics, Mar Ivanios College, Thiruvananthapuram for his valuable advices and constant encouragement.

We record our heartfelt thanks to **Dr. John Jacob**, Assistant Professor and Head of the Department of Physics, Mar Ivanios College, Thiruvananthapuram who granted us lab facilities to do this project work.

We are also thankful to **Mrs. Aswathy G. S**, Research Scholar, for providing assistance and support for the experimental work of this project.

We extend our thanks to **Rev. Fr. Vincy Varghese**, Principal, Mar Ivanios College, Thiruvananthapuram for allowing us to do this project in our college.

We would also like to record the support and co-operation given to us by our family, friends, teaching and non-teaching staffs of Mar Ivanios College (Autonomous), who helped us directly and indirectly at various stages of this work.

TABLE OF CONTENTS

CONTENT   **PAGE NO.**

CHAPTER 1- INTRODUCTION TO NONLINEAR OPTICS AND CRYSTAL GROWTH TECHNIQUES

CHAPTER 2- CHARACTERIZATION TECHNIQUES

CHAPTER 3- GRAPHICAL ANALYSIS OF THE CRYSTAL

CHAPTER: 1

INTRODUCTION TO NONLINEAR OPTICS AND CRYSTAL GROWTH TECHNIQUES

1.1   INTRODUCTION

Crystals have always fascinated and benefited mankind and they are the unacknowledged pillars of modern technology. The field of crystal growth that had earlier been a relatively small area has now attained a unique status owing to the recent development of novel materials with user defined properties. Crystal growth is an interdisciplinary subject covering physics, metallurgy, crystallography, material science, chemistry, mineralogy, etc. In the recent years there has been an upswing in the development of photonics technology, which demands the synthesis and growth of high quality crystalline materials for the use of laser technology, optoelectronic process, photovoltaic devices, infrared detectors and other technologically important scientific applications. In the past few decades, there has been a growing interest in crystal growth process, particularly in view of the increasing demand for materials for technological applications. New materials are the life blood of solid state research and device technology **[1]**.

New materials are not usually discovered by device engineers or solid state theorists; they are mostly grown by crystal growers. An ideal crystal is one, in which the surroundings of any atom would be exactly the same as the surroundings of every similar atom. Real crystals are finite and contain defects. However, single crystals are solids in the most uniform condition that can be attained and this is the basis for most of the uses of these crystals. The uniformity of single crystals can allow the transmission without the scattering of electromagnetic waves. The strong influence of single crystals in the present day technology led to the recent development and advancement in the fields of semiconductors, solid state lasers, ultrasonic amplifiers, infrared detectors, transducers, nonlinear optic, piezoelectric, photosensitive materials, and thin films **[2]**.

All these developments could be achieved due to the availability of single crystals like silicon, germanium, and gallium arsenide and also with the invention of *nonlinear optical properties* in some inorganic, semi-organic and organic crystals. The desired physical phenomena for the fabrication of devices are exhibited only by certain single crystals. Hence in order to achieve high performance, good quality single crystals are needed. Therefore, researchers worldwide have always been in the search of new materials through their single crystal growth. The methods of growing crystals are very wide and mainly dictated by the characteristics of the material and its size. Atomic arrays that are periodic in three dimensions, with repeated distances are called single crystals. It is more difficult to prepare single crystal than poly-crystalline material and extra effort is justified because of the outstanding advantages of single crystals. Single crystals hold an upper hand over polycrystalline materials as they exhibit anisotropy, uniformity of composition, and the absence of boundaries. The strong influence of single crystals in the present day technology is evident from the recent advancements in the field of semiconductors, transducers, polarizers,

infrared detectors, ferrites, ultrasonic amplifiers, solid state lasers, non-linear optic, acoustic optic, photosensitive materials and crystalline thin films for microelectronics and computer industries. Growth of single crystals and their characterization towards device fabrication have taken a huge momentum due to their importance for both academic as well as applied research **[3-5]**.

1.2   CLASSIFICATION OF CRYSTAL GROWTH

Crystal growth is a controlled phase transformation, either from solid or liquid or gaseous phase to solid phase. The choice of a particular method for growing a desired single crystal critically depends on the physical and chemical properties of the substances. The consistency in the characteristics of devices fabricated from the crystals depends mainly on the homogeneity and defect present in the crystals. Thus, the process of producing single crystals, from homogeneous media with directional properties, attracts more attention and gains more importance than any other process. The method of crystal growth may range from a small inexpensive technique to a complex sophisticated technique. The basic methods of growing single crystals are:

- *Growth from melt*

- *Growth from vapour*

- *Growth from solution*

The basic methods to grow single crystals have been discussed in detail by several authors. In the solid growth of crystals, the important factor is conversion of a polycrystalline piece of a material into a single crystal by causing the grain boundaries to sweep through and pushed out of the crystal. The basic methods of growing single crystals are explained below **[2, 6,7]**.

1.2.1   Growth from Melt

A gas is cooled until it becomes a liquid, which is then cooled further until it becomes a solid. Polycrystalline solids are typically produced by this method unless special techniques are employed. In any case, the temperature must be controlled carefully. Knowledge of how crystals grow from the melt and the effects of the various factors which may influence crystal growth is a potentially important tool in interpreting textural and chemical features and crystallization histories of igneous rocks.

The first detailed study of crystal-growth phenomena was explained by *Tamman* (1899), who measured the rate of crystal growth from a melt **[8]**. He found that the rate is zero at the liquid state, increases to a maximum, and then decreases with decrease in temperature. Later in the year 1931, *Volmer* and *Marder* developed a simple theory to explain this relationship. Depending on the thermal characteristics, the following techniques are employed for the crystal growth:

1) *Czochralski technique*

2) *Bridgman technique*

3) *Kyropoulos technique*

4) *Zone melting technique*

5) *Verneuil technique*

Large crystals can be grown rapidly from the liquid elements using a popular method invented in 1918 by the Polish scientist ***Jan Czochralski* [9]**. One attaches a seed crystal to the bottom of a vertical arm such that the seed is barely in contact with the material at the surface of the melt. The arm is raised slowly, and a crystal grows underneath at the interface between the crystal and the melt. Usually the crystal is rotated slowly, so that inhomogeneities in the liquid are not replicated in the crystal. Large diameter crystals of silicon are grown in this way for use as computer chips. Based on measurements of the weight of the crystal during the pulling process, computer controlled apparatus can vary the pulling rate to produce any desired diameter. Crystal pulling is the least expensive way to grow large amounts of pure crystal. Synthetic sapphire crystals can be pulled from molten alumina. Special care is required to grow binary and other multi-component crystals; the temperature must be precisely controlled because such crystals may be grown only at a single, extremely high temperature. The melt has a tendency to be inhomogeneous, since the two liquids may try to separate by gravity.

The ***Bridgman method*[10-11]** is also widely used for growing large single crystals. The molten material is put into a crucible, often of silica, which has a cylindrical shape with a conical lower end. Heaters maintain the molten state. As the crucible is slowly lowered into a cooler region, a crystal starts growing in the conical tip. The crucible is lowered at a rate that matches the growth of the crystal, so that the temperature at the interface between crystal and melt is always same. The rate of moving the crucible depends on the temperature and the material. Then, the entire molten material in the crucible grows into a single large crystal. One disadvantage of this method is that, impurities are pushed out of the crystal during growth. A layer of impurities grows at the interface between melt and solid as this surface moves up the melt, and the impurities become concentrated in the higher part of the crystal.

In ***Kyropoulos technique***, the crystal is grown in a large diameter. As in the *Czochralski method*, here also the seed is brought in contact with the melt and is not raised much during the growth, i.e. part of the seed is allowed to melt and a short narrow neck is grown. After this, the vertical motionof the seed is stopped and growth proceeds. The major use of this method is the growth of alkali halides to make optical components.

Zone refining was developed by William Gardner Pfann [17] in Bell Labs as a method to prepare high purity materials for manufacturing transistors. In the zone melting technique, the feed material is formed into a mass by heat and pressure then the seed is attached to one end. A small molten zone is maintained by surface tension between the seed and the feed. The zone is slowly moved towards the feed. Single crystal is obtained over the seed. This method is applied to materials having large surface tension. The main reasons for the impact of zone refining process to modern electronic industry are the simplicity of the process, the capability to produce a variety of organic and inorganic materials of extreme high purity, and to produce dislocation free crystal with a low defect density.

In the ***Verneuil technique***, a fine dry powder of size 1-20 microns of the material to be grown is shaken through the wire mesh and allowed to fall through the oxy-hydrogen

flame. The powder melts and a film of liquid is formed on the top of the seed crystal. This freezes progressively as the seed crystal is slowly lowered. The art of the method is to balance the rate of charge feed and the rate of lowering of the seed to maintain a constant growth rate and diameter. This technique is widely used for the growth of synthetic gems **[12].**

1.2.2 Growth from Vapour

Crystals can be grown from vapour when the molecules of the gas attach themselves to a surface and move into the crystal arrangement. Several important conditions must be met for this to occur at constant temperature and equilibrium conditions, the average number of molecules in the gas and solid states is constant; molecules leave the gas and attach to the surface at the same rate that they leave the surface to become gas molecules. For the best growth, the gas solid chemical system must be in a non- equilibrium state such that there are too many gaseous molecules for the conditions of pressure and temperature. This state is called supersaturation. Molecules are more prone to leave the gas than to rejoin it, so they get deposited on the surface of the container. Supersaturation can be induced by maintaining the crystal at a lower temperature than the gas **[13]**. A critical stage in the growth of a crystal is seeding, in which a small piece of crystal of proper structure and orientation, called a seed, is introduced into the container. The gas molecules find the seed a more favourable surface than the walls and preferentially deposit there. Once the molecule is on the surface of the seed, it wanders around this surface to find the preferred site for attachment. Growth proceeds as one molecule at a time and one layer at a time. The process is slow; it takes days to grow a small crystal. The advantage of vapour growth is that very pure crystals can be grown by this method, while the disadvantage is that it is slow. Most clouds in the atmosphere are ice crystals that form by vapour growth from water molecules. In the laboratory, vapour growth is usually accomplished by sending a supersaturated gas over a seed crystal. Quite often a chemical reaction at the surface is needed to deposit the atoms.

1.2.3 Growth from Solution

The essential technique which produces large single crystals suitable for lot of applications at minimum cost is vital for research and commercial purpose. The selection of growth method is also important because it suggests the possible impurity and other defect concentrations to improve the physical and chemical properties of the material.

The crystal growth from solution falls into:

1) *Gel growth*

2) *Hydrothermal growth*

3) *Flux growth*

4) *Low temperature solution growth*

Growth of crystals from solution is an important process that can be used in laboratory, industry, research and development. In order to grow good quality single crystals by solution growth, the material should have high solubility and variation in solubility with temperature. The viscosity of the solvent solute system should be low. The materials used for the growth of crystal must not be a flammable one. Another aspect to consider is that the container and stirrer should be non-reactive with material. Among the various methods, growth from solution at low temperature occupies a prominent place owing to its versatility, simplicity and used to produce technically important crystals. Growth from solution at low temperature occurs close to equilibrium conditions and hence good quality bulk single crystals of utmost perfection can be grown easily **[14]**.

1.2.3.1 GEL GROWTH

It is an alternative technique to solution growth with controlled diffusion and the growth process is free from convection. Gel is a two component system of a semisolid rich in liquid and inert in nature. The material, which decomposes before melting, can be grown in this medium by counter diffusing two suitable reactants. Crystals with dimensions of several millimeters can be grown in a period of 3 to 4 weeks. The crystals grown by this technique have high degree of perfection and fewer defects since the growth takes place at room temperature **[15]**.

1.2.3.2 HYDROTHERMAL GROWTH

Hydrothermal implies conditions of high pressure as well as high temperature. Substances like calcite, quartz is considered to be insoluble in water but at high temperature and pressure, these substances are soluble. This method of crystal growth at high temperature and pressure is known as hydrothermal method. Temperatures are typically in the range of *400°C to 600°C* and the pressure involved is high. Growth is usually carried out in steel autoclaves with gold or silver linings. Depending on the pressure the autoclaves are grouped into low, medium and high-pressure autoclaves. The concentration gradient required to produce growth is provided by a temperature difference between the nutrient and growth areas. The requirement of high pressure presents practical difficulties and there are only a few crystals of good quality and large dimensions are grown by this technique. Quartz is the outstanding example of industrial hydrothermal crystallization. One serious disadvantage of this-technique is the frequent incorporation of OH ions into the crystal, which makes them unsuitable for many applications **[16].**

1.2.3.3 FLUX GROWTH

In this method of crystal growth, the components of the desired substance are dissolved in a solvent (flux). The method is particularly suitable for crystals needing to be free from thermal strain and it takes place in a crucible made of non-reactive metals. Crucibles are normally sealed in evacuated quartz ampoules or reactions take place in controlled atmosphere furnaces. A saturated solution is prepared by keeping the constituents of the desired crystal and the flux at a temperature slightly above the saturation temperature long enough to form a

complete solution. Then the crucible is cooled in order to cause the desired crystal to precipitate. Nucleation happens in the cooler part of the crucible. A disadvantage is that most flux method syntheses produce relatively small crystals **[17].**

1.2.3.4 LOW TEMPERATURE SOLUTION GROWTH

In the present investigation, the low temperature solution growth technique is employed and the fundamentals of the same are given below. Solubility and supersaturation are the two important parameters for the solution growth process. Solubility is defined as the maximum amount of substance dissolved in a particular solvent at a given temperature. Before starting the solution growth process, the solubility of the solute must be determined by dissolving the solute in the solvent at a constant temperature with continuous stirring. Solubility of the substance increases with increase in temperature for most of the materials. Either by cooling or evaporating the solvent, the solution attains its supersaturation. The solution is said to be in supersaturated state, if the concentration of the solution is greater than the equilibrium concentration. When the starting materials are unstable at high temperatures, low temperature solution growth is the most widely used method for the growth of crystals. The supersaturation is achieved either by temperature lowering or by solvent evaporation. This method is widely used to grow bulk crystals, from materials, which have high solubility and have variation in solubility with temperature.

Growth of crystals from solution at room temperature has many advantages over other growth methods. But the rate of crystallization is slow in this method. Since growth is carried out at room temperature, the structural imperfections in the grown crystals are relatively low. The ambient temperature of growth, the pH of the solution and the presence of deliberately added impurities are the essential additional parameters that determine the rate of growth and morphology of the crystal. Low temperature solution growth (LTSG) can be subdivided into the following categories:

- *slow cooling method*

- *temperature gradient method*

- *slow evaporation method*

Slow Cooling Method

Slow cooling method is one in which the solution is allowed to cool to a lower temperature in order to achieve supersaturated solution and the temperature of the solution is reduced in small steps. By doing so, the solution which is just saturated at the initial temperature will become a supersaturated solution. Once supersaturation is achieved, growth of single crystal is possible. The main disadvantage of slow cooling method is the need to use a range of temperature. The temperature at which such crystallization can begin is usually within the range 45-75°C and the lower limit of cooling is the room temperature. Wide range of temperature may not be desirable because the properties of the grown crystal may vary with temperature. Even though this method has technical difficulty of requiring a programmable temperature control, it is widely used with great success. The crystals produced by this method are small and possess unpredictable shape.

Temperature Gradient Method

This method involves the transport of the materials from hot region to a cooler region, where the solution is supersaturated and the crystal grows. The advantages of this method are that the crystal is grown at fixed temperature, this method is insensitive to changes in temperature (provided both the source and the growing crystal undergo the same change) and the cost of the basic materials are low. On the other hand, small changes in temperature difference between the source and the crystal zones have a large effect on the growth rate.

Slow Evaporation Method

In this process the temperature of the solution is not changed, but the solution is allowed to evaporate slowly. When the solvent begins to evaporate, the concentration of solute is increased and, therefore, supersaturation is achieved. The advantage of using this method is that the crystals grow at a fixed temperature. This method can effectively be used for materials having very low temperature coefficient of solubility. But inadequacies of the temperature control system still have a major effect on the growth rate.   In order to control the temperature of the system, constant temperature bath can be used. In spite of some of the disadvantages, this method is simple and convenient to grow bulk single crystals **[17-19]**.

CRITERIA FOR OPTIMIZING SOLUTION GROWTH

The growth of good quality single crystals requires optimized conditions; this may be achieved with the help of the following criteria:

- *material purification*
- *solvent selection*
- *solubility*
- *solution preparation*
- *crystal habit*

Solubility of the solute in the chosen solvent must be determined before starting the growth process.

Material Purification

Availability of the material with highest purity is an essential requirement for success in crystal growth. The impurity included into crystal lattice may lead to the formation of flaws and defects. Sometimes, impurities may slowdown the crystallization process. To harvest good quality crystals, material purification is a must. A careful repetitive use of standard purification methods of re-crystallization followed by filtration of the solution would increase the level of purity.

Solvent Selection

Solution is a homogeneous mixture of a solute in a solvent. Solute is the component present in a smaller quantity. For a given solute, there may be different solvents. Apart from high purity starting materials, solution growth requires a good solvent. The solvent must be chosen taking into account the following factors:

- *high solubility for the given solute*
- *low viscosity*
- *low volatility*
- *low corrosion*
- *low cost*
- *high purity*

Solubility

Solubility is an important parameter which dictates the growth procedure. If the solubility is too high, it is difficult to grow bulk crystals and too low solubility restricts the size and growth of bulk crystals. Hence solubility of the solute in the chosen solvent must be determined before starting the growth process.

Solution Preparation and Crystal Growth

After selecting the desirable solvent with high purity solute to be crystallized, the next important part is preparation of the saturated solution. To prepare a saturated solution, it is necessary to have an accurate solubility- temperature data of the material. The saturated solution at a given temperature is placed in the constant temperature bath. Wattman filter papers are used for solution filtration. The filtered solution is transferred to crystal growth vessel and the vessel is sealed by polythene paper in which 15–20 holes are made for slow evaporation. Then the crystallization is allowed to take place by slow evaporation at room temperature or at a higher temperature in a constant temperature bath. As a result of slow evaporation of solvent, the excess of solute which has got deposited in the crystal growth vessel results in the formation of crystals.

Crystal Habit

The growth of a crystal at approximately equivalent rates along all the directions is a prerequisite for its accurate characterization. This will result in a large bulk crystal. Such large crystals should also be devoid of dislocation and other defects. These imperfections become isolated into defective regions surrounded by large volumes of high perfection. In the crystals the imperfections grow as needles or plates, the growth dislocations propagate along the principle growth directions and the crystals remain imperfect. Change of habit in such crystals which naturally grow as needles or plates can be achieved by any one of the following ways:

- *changing the temperature of the growth*
- *changing the pH of the solution*

- *adding a habit modifying agent*

- *changing the solvent*

Achievement of the above parameters is of great industrial importance, where such morphological changes are induced during crystallization to yield crystals with better perfection and packing characteristics

ADVANTAGES OF LOW TEMPERATURE SOLUTION GROWTH TECHNIQUE

Low temperature solution growth is utilized for crystal growth due to its simplicity and versatility. Following are the important advantages of using low temperature solution growth technique:

- *Simple growth apparatus*

- *Growth of strain and dislocation free crystals*

- *Permits the growth of prismatic crystals by varying the growth conditions.*

- *This is the only method which can be used for substances that undergo decomposition before melting*

Following are the *disadvantages* of this technique

(a) The growth substance should not react with solvent

(b) This method is applicable for substances fairly soluble in a solvent

(c) Inclusions of solvent may present in the grown crystal

(d) Growth rate of this method is low

1.3   NONLINEAR OPTICAL MATERIALS

Optics is the study of interaction of electromagnetic radiation and matter. Nonlinear optics is the study of the phenomena that occurs as a consequence of the modification of optical properties of a material system by the presence of light. *Nonlinear optics (NLO)* has been an active field of research since the late 1960's with the advent of lasers followed by the demonstration of harmonic generation in quartz. Nonlinear optics extends the usefulness of lasers by increasing the number of wavelengths available. Nonlinear optical material is the medium on which a laser beam interacts. After the invention of laser, frequency conversion by nonlinear optical materials has become important and widely used technique. Nonlinear optics is the study of the interaction of intense electromagnetic field with materials to produce modified fields that are different from the input field in phase and frequency. Nonlinear optics is completely a new effect in which the light of one wavelength is transformed to the light of another wavelength.

In a linear material, electrons are bound inside a potential well, which acts like a spring, holding the electrons to lattice point in the crystal. If an external force pulls an electron away from its equilibrium position the spring pulls it back with a force proportional to the displacement. The spring's restoring force increases linearly with the electron displacement from its equilibrium position. In an ordinary optical material, the electrons oscillate about their equilibrium position at the same frequency of the electric field (E). Hence, these electrons in the crystal generate light at the frequency of the original light wave **[20-22].**

1.4 THEORETICAL EXPLANATION OF NONLINEAR OPTICS

When a beam of electromagnetic radiation propagates through a solid, the nuclei and associated electrons of the atoms create electric dipoles. The electromagnetic radiation interacts with these dipoles causing them to oscillate, which by the classical laws of electromagnetism, results in the dipoles themselves acting as sources of electromagnetic radiation. If the amplitude of vibration is small, the dipoles emit radiation of the same frequency as the incident radiation. As the intensity of the incident radiation increases, the relationship between irradiance and amplitude of vibration becomes nonlinear resulting in the generation of higher harmonics in the frequency of radiation emitted by the oscillating dipoles. Thus, *frequency doubling* or *Second Harmonic Generation (SHG)* and, indeed, higher order frequency effects occur as the incident intensity is increased. In a nonlinear medium, the induced polarization is a nonlinear function of the applied electric field. A medium exhibiting SHG is composed of molecules with asymmetric charge distributions arranged in the medium in such a way that a polar orientation is maintained throughout the crystal. At very low fields, the induced polarization is directly proportional to the electric field.

$$\mathbf{P} = \varepsilon_0\, \chi.\, \mathbf{E}$$

where 'χ' is the linear susceptibility of the material, '$\mathbf{E}$' is the electric field vector, 'ε_0' is the permittivity of free space. At high fields, polarization becomes independent of the electric field and the susceptibility becomes field dependent. Therefore, this nonlinear response is expressed by writing the induced polarization as a power series in the fields.

$$\mathbf{P} = \varepsilon_0\, \chi^1\, \mathbf{E} + \chi^2\, \mathbf{E}^2 + \chi^3\, \mathbf{E}^3 + \dots.$$

where χ^2, χ^3… are the nonlinear susceptibility of the medium. $\chi^1$is the term responsible for material's linear optical properties like, refractive index, dispersion, birefringence and absorption. χ^2 is the quadratic term which describes second harmonic generation in non-centrosymmetric materials. χ^3 is the cubic term responsible for third harmonic generation, stimulated Raman scattering, phase conjugation and optical instability. Hence the induced polarization is capable of multiplying the fundamental frequency to second, third and even higher harmonics **[21].**

Nonlinear optics is concerned with the interaction of intense electromagnetic radiation with materials. The electromagnetic field associated with electromagnetic wave induces a polarization in the material. In linear optics, where light having electric field E, induces an

instantaneous displacement (polarization) of the electron density away from the nucleus of the atom, resulting in a charge separation (an induced dipole), with moment μ. With small fields, the strength of the applied field is proportional to the displacement of charge from the equilibrium position and leads to the relation,

$$\textbf{Polarization, P} = \alpha \textbf{E} \qquad\qquad 1.1$$

where α is the linear polarizability of the molecule or atom. If the field oscillates with a frequency, then the induced polarization will have the same frequency and phase if the response is instantaneous.

Most applications and experiments in NLO are based on bulk or macroscopic materials and, in this case, the linear polarization is expressed as,

$$\textbf{P} = \varepsilon_0 \, \chi^{(1)} \textbf{E} \qquad\qquad 1.2$$

where ε_0 is the permittivity of free space, $\chi^{(1)}$ is the linear susceptibility of a collection of molecules.
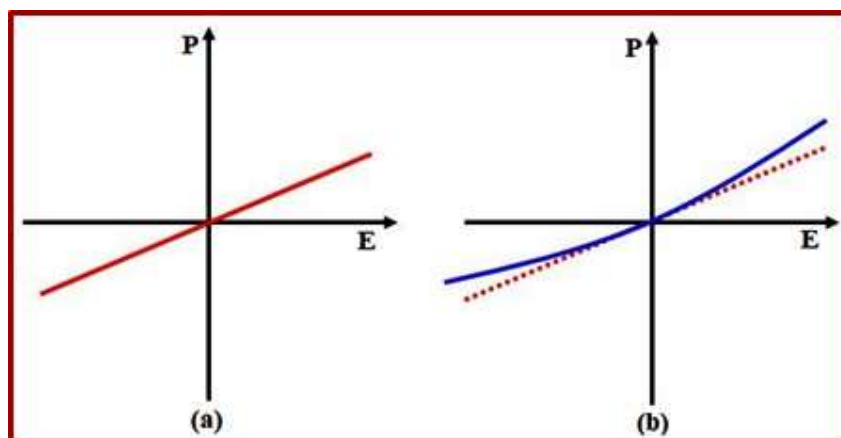

Figure 1.1 The P-E relation for (a) a linear dielectric medium and (b) a nonlinear medium

When a molecule is exposed to laser light (i.e., a very high intensity electric field), the molecule's polarizability can change and be driven beyond the linear regime as shown in figure 1.1. Therefore, the nonlinear polarization (which is a function of the applied field and leads to nonlinear effects) can be expressed as

$$\textbf{P}_{\textbf{molecule}} = \alpha \textbf{E} + \beta \textbf{E}^2 + \gamma \textbf{E}^3 + \ldots\ldots \qquad 1.3$$ where, β is the first-order hyperpolarizability and γ is the second-order hyperpolarizability. β and γ in equation 1.3, relates the polarisation to the square and the cube of the field strength respectively, are third and fourth-rank tensors, responsible for second-order and third-order NLO effects. With increasing field strength, NLO effects become more pronounced

$$P = \varepsilon_0 (\chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \ldots\ldots) \qquad 1.4$$

where ε_0 is the permittivity of free space; $\chi^{(n)}$ is the nth-order NLO susceptibility and is analogous to the molecular coefficients in equation 1.3.

The electric field of a plane light wave is given by,

$$E = E_0 \cos(\omega t) \quad 1.5$$

Equation 1.4 becomes,

$$P = \varepsilon_0(\chi^{(1)}E_0 \cos(\omega t) + \chi^{(2)}E_0^2 \cos^2(\omega t) + \chi^{(3)} E_0^3 \cos^3(\omega t) +..) \qquad 1.6$$

The quantities $\chi^{(3)}$ and γ are responsible for third-order nonlinear optical phenomena.

1.5 VARIOUS TYPES OF NLO EFFECTS

Some nonlinear optical processes are familiar to physicists, chemists and other scientists because they are in common use in the laboratories. Second harmonic generation is a nonlinear optical process that results in the conversion of an input optical wave into an output wave of twice as that of the input frequency. The process occurs within a nonlinear medium, usually a crystal (*KDP-Potassium Dihydrogen Phosphate*, *KTP-Potassium Titanyl Phosphate*, etc.). Such frequency doubling processes are commonly used to produce green light (532nm) using, a *Nd:YAG (Neodymium:Yttrium Aluminum Garnet)* laser operating at 1064 nm . Some of the NLO processes are given below [22-24]:

1) *Second harmonic generation*

2) *Sum frequency generation*

3) *Difference frequency generation*

4) *Optical parametric generation*

5) *Linear electro optic effect or Pockel's effect*

6) *Optical rectification*

1.5.1 Second Harmonic Generation (SHG)

The process of transformation of light with frequency 'ω' into light with double frequency 2ω and half the wavelength is referred to second harmonic generation. The process is spontaneous and involves three photon transitions. Second harmonic generation has been of practical interest ever since after it was demonstrated because of its efficient conversion from fundamental to second harmonic frequencies. This can be achieved by the available powerful sources of coherent radiation at higher to unattainable wavelengths.
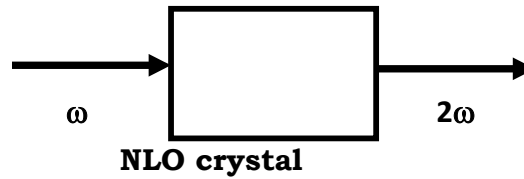
Schematic diagram of SHG

Most extensively studied conversion process of all has been the doubling of the 1.064 μm line obtained from the neodymium ion in various hosts. In particular, the doubling of the continuous wave Nd:YAG laser source has recently been the subject of intensive study, because the laser light itself is efficient and The powerful so that the green light obtainedby doubling is well placed spectrally for detection by photomultipliers.
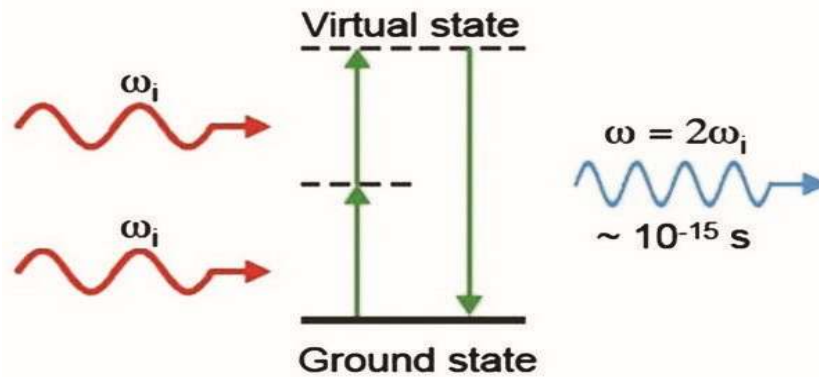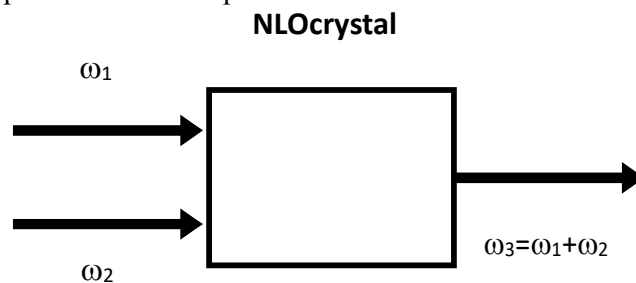

1.5.2 Sum Frequency Generation

It is a nonlinear optical process. Crystal materials with inversion symmetry can exhibit nonlinearity. In such NLO materials the sum frequency generation can occur. Fig. 2.2 illustrates the sum frequency generation.

$\omega_1 + \omega_2 = \omega_3$ $\longrightarrow$
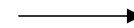
When two electromagnetic waves with the frequencyω_1 and$\omega_2$interact in a NLO medium, a nonlinear polarizability can be induced. The NLO material generates an optical wave of frequency$\omega_3$which is equal to the sum of the two input wave frequencyω_1 andω_2. The energy of output wave is represented in the equation.
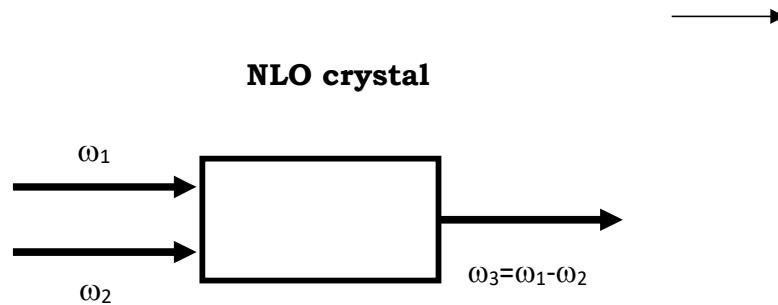
NLOcrystal

Schematic diagram of sum frequency generation

1.5.3 Difference Frequency Generation

The process of difference-frequency generation is described by the following equation.

$\omega_1 - \omega_2 = \omega_3$

NLO crystal

ω_1

ω_2

$\omega_3 = \omega_1 - \omega_2$

Schematic diagram of difference frequency generation

1.5.4 Optical Parametric Generation

Optical parametric generation is an inverse process of sum frequency generation and described by the following equation. It splits one high-frequency photon (pumping wavelength λ_p) into two low-frequency photons (signal wavelength λ_s and idler wavelength λ_i)

$\omega_s + \omega_i = \omega_p$

NLO crystal

ω_s

ω_p

ω_i
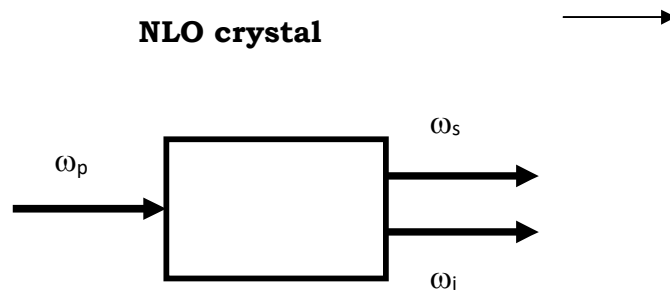
Schematic diagram of optical parametric generation

1.5.5 Linear Electro Optic Effect

The Pockel's effect is a linear change in the refractive index of a medium in the presence of an external electric field. Here a dc field is applied to a medium through which an optical wave propagates. The change in the polarization due to the presence of these two interacting field components effectively alters the refractive index of the medium.

1.5.6 Optical Rectification

The optical rectification is defined as the ability to induce a dc voltage between the electrodes placed on the surface of the crystal when an intense laser beam is directed into the crystal.

1.6 NONLINEAR OPTICAL MATERIALS

The search for new and efficient materials has been very active since second harmonic generation (SHG) was first observed in *single crystal quartz*. The discovery of inorganic photorefractive crystals such as *potassium niobate (KNbO₃)*, *potassium dihydrogen phosphate (KH₂PO₄)*, *barium titanate (BaTiO₃)*, *lithium niobate (LiNbO₃)* and their optimization during the last thirty five years have led to numerous demonstrations of variety of optical applications. At the end of 1968, *Kurtz and Perry SHG method* was introduced and a powdered sample is irradiated with a laser beam and scattered light is collected and analysed for its SHG efficiency. So, the stage was set for a rapid introduction of new materials, both inorganic and organic. For the optical applications, a non-linear material should have the following requirements:

- *Wide optical transparency range*

- *Ease of fabrication and high nonlinearity*

- *High laser damage threshold*

- *Ability to process into crystals and thin films*

- *Good environmental stability*

- *Fast optical response time*

- *High mechanical and thermal stability*

The nonlinear optical materials are broadly classified into [23-28]:

1) *Organic crystals*

2) *Inorganic crystals*

3) *Semi-organic crystal*

1.6.1 Organic Crystals

Over recent years, the search for new NLO materials has concentrated primarily on organic compounds owing to their high nonlinearity as compared to inorganic materials. The organic materials are molecular materials that consist of chemically bonded molecular units interacting in the bulk media through weak van der Waal interactions. The organic molecules which contain both conjugated bonds and acceptor group on one side and a donor group on the other side are known as nonlinear optical (NLO) materials. The NLO properties of large organic molecules have been the subject of extensive theoretical and experimental investigations during the past two decades and they have been investigated widely.

Organic NLO materials have numerous advantages like high second –order nonlinear optical efficiency, great resistance to damage in the laser beam, birefringence, inherent synthetic flexibility. Despite the advantages, these materials have shortcomings that cannot be neglected. They include poor physicochemical stability, low hardness and cleavage tendency which can hinder their device application.

In order to retain the merits and overcome the shortcomings of organic materials, some new classes of NLO crystals such as metal organic or semi-organic complex crystals have been developed. The relatively strong metal ligand bond permits the complex crystals to combine the advantages of inorganic crystals, such as good stability, with the advantages of organic crystals, such as high nonlinearity and molecular engineering features.

1.6.2 Inorganic Crystals

Inorganic materials are mostly ionic with high melting point, high degree of chemical inertness, high thermal and mechanical stability. It is always easier to synthesize inorganic materials. The phenomenon of SHG in inorganic materials was first reported in 1961 by *Franken and co-workers*. The inorganic NLO materials have some advantages like high bulk susceptibility and compatible physical properties but on the other hand these materials suffer from disadvantages like absorption in the visible region, poor response time and degradative photorefractive effects, low laser damage threshold and poor optical transparency. The examples of inorganic NLO crystals are *lithium niobate (LiNbO$_3$)*, *potassium niobate (KNbO$_3$)*, *barium titanate (BaTiO$_3$)*, *potassium titanyl phosphate (KTiOPO$_4$)*, *potassium dihydrogen phosphate (KH$_2$PO$_4$)*, *ammonium dihydrogen phosphate (NH$_3$PO$_4$)*, *lithium iodate (LiIO$_3$)*, etc.

1.6.3 Semi-Organic Crystals

The widest search for new compounds and crystals led to the development of many amino acids based semi-organic single crystals. In comparison with inorganic crystals, semi-organic crystals are less hygroscopic and can be easily grown as single crystals. *L-arginine phosphate monohydrate (LAP)* is one of the potential nonlinear optical crystals among the amino acid based semi-organic materials. Monaco et al synthesized LAP and its chemical analogs are the strongly basic amino acid and various other acids. All the compounds in this class contain an optically active carbon atom, and therefore all of them form acentric crystals. All the crystals are optically biaxial and several among them give second harmonic signals greater than quartz. Different organic and inorganic acids were introduced into *L-alanine and L-histidine* and many new nonlinear optical materials were reported with a better NLO efficiency compared to inorganic KDP crystals. LAP crystals are usually grown from aqueous solution by temperature lowering technique. LAP Crystals possess high nonlinearity, wide transmission range (220-1950nm), high conversion efficiency (38.9%) and high laser damage threshold. Metal-organic crystals form a new class of materials under semi-organics. Compared to organic molecules, metal complexes offer a larger variety of structures, the possibility of high environmental stability, and a diversity of electronic properties by virtue of the coordinated metal center.

1.7 Application of Nonlinear Optics

The application of nonlinear optics plays a major role in laser, information and materials technology (Garmire 2013).

1.7.1   Application in Laser Technology

- Laser Frequency Conversion
- Laser Pulse Compression
- New Laser Devices
- Laser Transportation
- Laser Protection

1.7.2 Application in information technology

- *Optical Communication*
- *Optical Computing*
- *Optical Sensing*

1.7.3 Application in material technology

- Micromachining of Material
- Optical limiting
- High Resolution Spectrum Analysis

AIM AND SCOPE OF THE RESEARCH WORK

Crystals are the unacknowledged pillars of modern technology. Without crystals, there would be no electronic industry, no photonic industry, and no fiber- optic communications. The reason for growing single crystals is that many physical properties of solids are obscured or complicated by the effect of grain boundaries. The chief advantages are the anisotropy, uniformity of composition and the absence of boundaries between individual grains, which are inevitably present in polycrystalline materials. In order to achieve high performance from the device, good quality single crystals are needed. Growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic and applied research.

Perspectives of the structure-activity relationship and hyperpolarizability are originated from the nonlinear study of molecules. Explaining their structural features using vibrational spectroscopic methods with the aid of quantum chemical computations are of recent origin. The primary aim of the present research is to investigate the structure-property relations and evaluate the molecular nonlinearities of certain NLO materials on recognizing the active IR

and Raman bands that are accountable for their NLO behaviour. Natural bond orbital analysis has been performed to elucidate the correlation between the intra molecular charge transfer and π-conjugated electron delocalization of the molecule. Polarizability and hyperpolarizability were calculated and compared with the second harmonic generation to identify the non-linear optical property of the material. Charge analysis and HOMO-LUMO analysis were also performed to validate the structural activity relationship. In addition to molecular electrostatic potential was also investigated using *Density Functional Theory (DFT)* calculation.

This research is motivated by the application of optical and electro-optical device based on NLO materials in telecommunications and optical processing industries. Today, there are large number of nonlinear optical materials of specific wavelengths with various thresholds and optical characteristics. Keeping this in view, attempts have been made to grow and study the structure, functional groups, optical and NLO properties of different crystals. This approach has a wide scope for further expansion of the cited ambition. In future, attempts will be made to design and develop highly efficient NLO materials which are suitable for applications in telecommunication, signal processing and advanced optical storage devices.

The present investigation is aimed at

i.   Synthesizing the chosen material for the growth of single crystals.

ii.   Growing bulk size single crystals by purification and re-crystallisation.

iii. Estimating the lattice parameters of the grown crystals using powder and single crystal X-ray diffraction method.

iv.   Characterizing the grown crystals by FT-IR, NMR and optical transmission studies.

v.   Determining the SHG efficiency of the crystals by *Kurtz-Perry powder technique*.

REFERENCES

1)   Laudise R.A. (1970), '*The Growth of Single Crystals*', Prentice Hall, Eaglewood Cliffs, New Jersey.

2)   Brice J.C. (1986), '*Crystal Growth Processes*', John Wiley and Sons, New York.

3)   Nalwa H.S and Miyata S. (1996), '*Nonlinear Optics of Organic Molecules and Polymers*', CRC Press Inc., New York.

4)   Buckley H.E. (1951), '*Crystal Growth*', Wiley, New York.

5)   Mullin J.W. (1976), '*Industrial crystallization 78*', Plenum Press, and New York.

6)   Santhanaraghavan P., and Ramasamy P. (2003), '*Crystal Growth Processes and Methods*', KRU publications, Kumbakonam.

7)   Mullin J.W. (1972), '*Crystallization*', Second Edition, Academic Press, London.

8)   Pamplin B.R. (1980), '*Crystal Growth*', Pergman Press, London.

9)   Czochralski J. (1918), '*A New Method for the Measurement of Crystallisation Rate of Metals*', Z. Phys. Chem. 92, 219.

10)   Bridgman R.W. (1925), '*Certain Properties of Single Crystals of Tungsten, Antimony, Bismuth, Tellurium, Cadmium, Zinc and Tin*', Proc. Amer. Acad. Arts. Sci., 60, 305-383.

11)   Stockbarger D.C. '*The Production of Large Single Crystals of Lithium Fluoride*', (1936), Rev. Sci.   Instrum., 7, 133-136.

12)   W.G.Pfann. (1958), '*Zone Melting*', Wiley, New York.

13)   Schafer H., and Wiese U. (1971), '*The Chemical Transport of Pt with CO+Cl2 (Br2)*', J. Less Common Metals, 24, 55-61.1

14)   Ohara.M., and Reid R.C. (1973), '*Modeling Crystal Growth Rates from Solution*', Prentice Hall, Eaglewood Cliffs, New Jersey

15)   Pamplin B.R. (1979), '*Crystal Growth*', Pergamon Press, Oxford.

16)   James J.A., and Kell R.C. (1975), '*Crystal Growth*', Pergamon Press, New York.

17)   Chernov A.A. (1984), '*Modern Crystallography*', III-Crystal Growth Springer Series, Solid State, 36, Berlin.

18)   Brice J.C. (1972), '*The Growth of Crystals from Liquids*', Wiley, New York.

19)   Christian.R. (1990), '*Solvents and Solvent Effects in Organic Chemistry*', VCH, New York.

20)   Zernike F., and Midwinter J.E. (1973), '*Applied Nonlinear Optics*', John Wiely& Sons, New York.

21)   Munn R.W., and Ironside C.N. (1994), '*Principles and Applications of Nonlinear Optical Materials*', CRC Press, Inc., USA.

22)   Franken P.A., Hill A.E., Peters C.W., and Weinreich G. (1961), '*Generation of Optical Harmonics*', Phys. Rev. Lett., 7, 118-119.

23)   Eaton D.F. (1991), '*Nonlinear Optical Materials*', Science, 253, 281-287.

24)   Silfvast W.T. (1998), '*Laser Fundamentals*' Cambridge University press, New Delhi.

25)   Chemla D.S. and Zyss J. (1987), '*Nonlinear Optical Properties of Organic Molecules and Crystals*', Academic Press, New York.

26)   P. Paramasivam, '*Studies on the Growth and Characterization of Some Optical Crystals*', M.Phil thesis, Post graduate & Research department of physics, Government Arts College, Tamil nadu.

27)   Robert. W. Boyd, '*Nonlinear Optics'*, Third edition.

28)   G. Marudhu, '*Growth and Characterization of Nonlinear optical 4-APMP, Amino acids Doped with NaAP and DGBCM Single Crystals*', B.S Abdur Rahman University, March 2015.

[1]   Christian.R. (1990), '*Solvents and Solvent Effects in Organic Chemistry*', VCH, New York.

[2]   Eaton D.F. (1991), '*Nonlinear Optical Materials*', Science, 253, 281-287.

[1]   Chemla D.S., and Zyss J. (1987), '*Nonlinear Optical Properties of Organic Molecules and Crystals*', Academic Press, New York

CHAPTER 2

CHARACTERIZATION TECHNIQUES

2.1 INTRODUCTION

Characterization is a tool for the measurement of physical and chemical properties of materials. Characterization provides a basis for understanding and improving the characteristics of material for specific applications. Characterization of a material essentially depends on the characterization and experimental techniques involved with tools of sophisticated technology. Today scientists and researchers have powerful and elegant tools for obtaining qualitative and quantitative information about the composition and structure of matter. The development of these tools began over two centuries ago and the search still continues. The use of instrumentation is an exciting and fascinating part of any analysis that interacts with all the areas of chemistry and with many other fields of pure and applied science.

Characterization of a crystal essentially consists of determination of chemical composition, structure, defects and study of their optical properties. Crystal studies such as structural analysis, investigation of growth defects, and measurement of linear and nonlinear optical properties are essential in understanding the nature and properties of the grown crystals. In order to obtain good quality single crystals pertaining to specific applications enhancement of the desired properties must be done. Hence, in this chapter, the various instruments with different techniques involved in the characterization of the grown crystals with their working principles are discussed.

2.2 SINGLECRYSTALX-RAYDIFFRACTION(SXRD)STUDIES

Single crystal X-ray Diffraction is a non-destructive analytical technique which provides detailed information about the internal lattice of crystalline substances, including unit cell dimensions, bond lengths, bond angles and details of site ordering. Directly related is single crystal refinement, where the data generated from the X-ray analysis is interpreted and refined to obtain the crystal structure.

2.2.1 Principles of X-ray Diffraction

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference and a diffracted ray, when conditions satisfy *Bragg's Law*. This law relates the wave length of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. The Bragg's condition for reflection can therefore be written as

$$2d\sin\theta = n\lambda$$

where,

n-Order of diffraction

λ-Wave length of the X-ray used

θ-Bragg's angle

d–Inter‑planar spacing

These diffracted X-rays are then detected, processed and counted. By changing the geometry of the incident rays, the orientation of the centered crystal and the detector, all possible diffraction directions of the lattice should be attained.

In the study of crystals, the single crystal X-ray diffraction is used for four purposes:

- *to prove the crystallinity*

- *to determine the structure*

- *to determine the perfection*

- *to determine the lattice parameters*

2.2.2 Sample Selection and Preparation

Samplesforsingle-crystaldiffractionshouldbeselectedfromunfractured, optically clear crystals. This can be determined by viewing the samples under crossed polars on a petrography microscope. Crystals can bebroken off a larger sample and the best

fragment selected. Samples should be between 30 and 300 microns, with ideal crystals averaging 150-250 microns in size.

2.2.3 Sample Mounting

Samples are mounted on the tip of a thin glass fiber using an epoxy or cement. Care should be taken to use just enough epoxy to secure the sample without embedding it in the mounting compound. Then the fiber is attached to a brass mounting pin, usually by the use of modeling clay, and the pin is then inserted into the goniometer head.

2.2.4 Sample Centering

The goniometer head and sample are then affixed to the diffractometer. Samples can be centered by viewing the sample under an attached microscope or video camera and adjusting the x, y and z directions until the sample is centered under the cross-wire for all crystal orientations.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays.
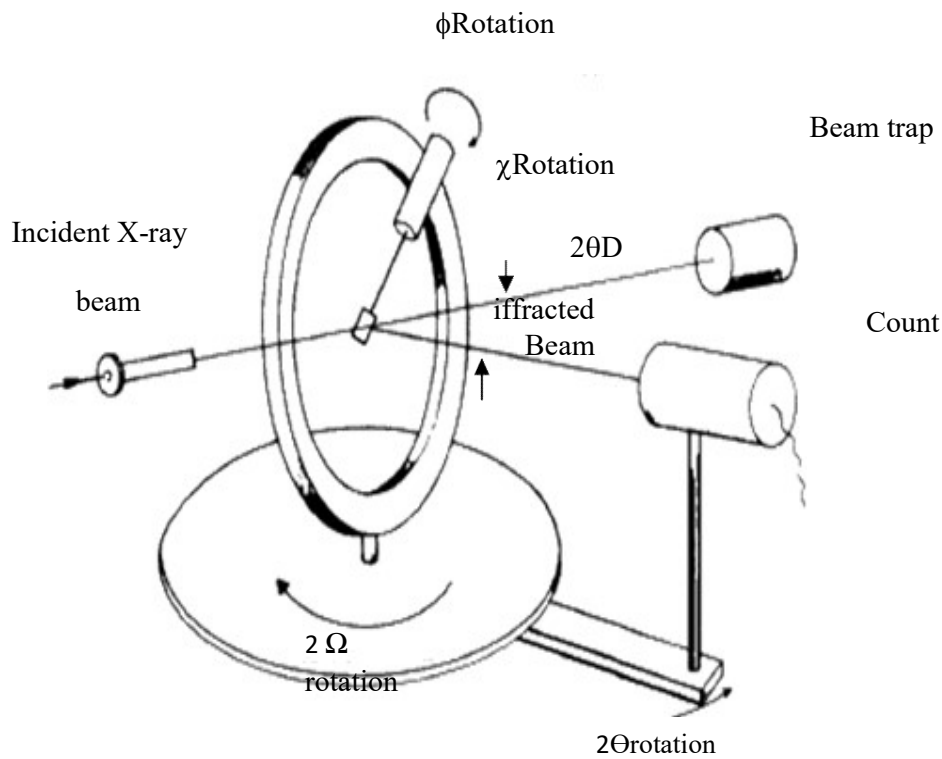

Fig 2.1 Experimental arrangement of Single Crystal X-Ray Diffractometer

Single crystal diffractometers use either 3 or 4 circle goniometers (Fig.3.1). These circles refer to the four angles (**2θ, χ, φ, and Ω**) that define the relationship between the crystal lattice, the incident ray and detector. Samples are mounted on thin glass fibers which are attached to brass pins and mounted onto goniometer heads. Adjustment of the x, y and z directions allow centering of the crystal within the X-ray beam.

X-rays leave the collimator and are directed at the crystal. Rays are either transmitted through the crystal, reflected off the surface or diffracted by the crystal lattice. A beam stop is located directly opposite the collimator to block transmitted rays and prevent burn-out of the detector. Reflected rays are not picked up by the detector due to the angles involved. Diffracted rays at the correct orientation for the configuration are then collected by the detector. Modern single crystal diffractometers use *CCD (Charge-Coupled Device)* technology to transform the X-ray photons into an electrical signal which are then sent to a computer for processing. In the present study, single crystal X ray diffraction analyses were carried out using *ENRAF NONIUS CAD 4 / Brucker Kappa APEX II CCD* diffractometer.

2.3 POWDERX-RAYDIFFRACTION(PXRD)STUDIES

The discovery of diffraction of X-rays by crystals led to the development of a powerful and precise method for the exploration of the internal arrangement of atoms in a crystal. X-rays are still the principal source of new information about the crystallography of solids and are supplemented by electron and neutron diffraction. The diffraction of X-rays by the atoms in a solid is a completely analogous phenomenon, the wave length of electromagnetic radiation in the case being of the order of inter atomic distance in solids is 1Å. X-rays are used as a tool for investigating the crystal structure was first suggested by *Von Laue* in 1912 and further developed by *Bragg and W.L Bragg*. X-ray diffraction gives the appropriate internal structure of the crystal. There are three main X-ray diffraction methods by which the crystal structure can be analyzed.

- *Laue method which is applicable to single crystals.*
- *The rotating crystal method which is applicable to single crystals.*
- *The powder method is applicable to polycrystalline powdered specimen*

The principle of powder X-ray diffraction is a tool for accurate determination of lattice parameters in crystals of known structure and for the identification of elements and compound If one uses X-rays having strong monochromatic components and a sample

consisting of many tiny, randomly oriented crystals, the equation **nλ=2dsinθ** will be fulfilled because some of the crystals will be oriented to give reflections without need of rotation. The most common powder technique is the *Debye – Scherrer method*.

Instrumentation

X-ray diffractometers consist of three basic elements; an X-ray tube, a sample holder, and an X-ray detector. All X-ray tubes contain two electrodes, an anode (the metal target) maintained with few exceptions, at ground potential, and a cathode, maintained at a high negative potential, normally of the order of 30,000 to 50,000 volts.

Copper is the most common target material for single crystal diffraction, with CuK_α radiation 1.5418 Å. The X-rays produced from the X-ray tube 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 the Bragg equation, constructive interference occurs and a peak in intensity appears. 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 computer monitor. Peak positions occur where the X-ray beam has been diffracted by the crystal lattice. The unique set of d-spacing derived from this pattern can be used to '*finger print*' of the material.

The geometry of an X-ray diffractometers is such that the sample rotates in the path of the collimated X-ray beam at an angle $\boldsymbol{\theta}$ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of $2\boldsymbol{\theta}$.The instrument used to maintain the angle and rotate the sample is termed a *goniometer*. For typical powder patterns, data is collected $2\boldsymbol{\theta}$ from 5° to 90°; angles that are pre-set in the X-ray scan.

In the present study, *Enraf Nonius CAD-4 MV31Bruker Kappa Apex II* single crystal X-ray diffractometer has been used.

It is a fully automated four circle instrument controlled by a computer. It consists of an FR 590 generator, a goniometer, CAD4F interface and a microVAX3100 equipped with a printer and plotter. The detector is a scintillation counter. A single crystal is mounted on a thin glass fiber fixed on the goniometer head. The unit cell dimensions and orientation matrix are determined using 25 reflections and then the intensity data of a given set of reflections are collected automatically by the computer. Mo and Cu targets are available. Maximum X-ray power is 40 mA x 50 KV. Polaroid camera is also available.

Fig 2.2: Enraf Nonius CAD-4 MV31 Bruker Kappa Apex II Diffractometer

2.4 UV-visible Absorption Spectroscopy

The spectrofluorometer is an instrument which takes advantage of fluorescent properties of some compounds in order to provide information regarding their concentration and chemical environment in a sample. A certain excitation wavelength is selected and the emission is observed either at a single wavelength or a scan is performed to record the intensity versus wavelength, also called an emission spectrum. Generally, spectrofluorometers use high intensity light sources to bombard a sample with as many photons as possible. This allows for the maximum number of molecules to be in the excited state at any one point in time. The light is either passed through a filter, selecting a fixed wavelength, or a monochromator, which allows to select a wavelength of interest to be used as the exciting light. The emission is collected at a point perpendicular to the exciting light. The emission is either passed through a filter or a monochromator before being detected by a photomultiplier tube, photodiode, or charge-coupled detector. The signal can either be processed as a digital or an analog output. Ultraviolet-visible spectroscopy refers to the absorption or reflectance spectroscopy in the ultraviolet-visible spectral region. It means it

uses light in the visible, near UV and near IR region. Visible light absorption causes objects to be colored. A blue dye appears blue because the light at the red end of the spectrum is absorbed, leaving the blue light to be transmitted. Visible light lies in the wavelength range of 400-700nm. In this region molecules undergo electronic transitions. Hence through this technique, information regarding electronic bonding inside the molecule can be obtained.

A molecule of any substance has an internal energy which can be considered as the sum of the energy of its electrons; the energy of vibration between its constituent atoms and the energy associated with the rotation of the molecule. It means an electronic energy level consists of number of vibrational energy levels which in turn consists of number of rotational energy levels. A change of level requires the absorption or emission of an integral number of a unit of energy called a quantum or a photon. The electronic energy levels of simple molecules are widely separated and only the absorption of high energy photon can excite a molecule from one energy level to another. In complex molecules the energy levels are more closely spaced and photons of near ultraviolet and visible light can excite the electron.

The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the *Beer-Lambert's law*. For most spectra the solution obeys Beer's law. This states that the light absorbed is proportional to the number of absorbing molecules. This is only true for dilute solutions. The lamberts' law tells us that the fraction of radiation absorbed is independent of the intensity of the radiation. Combining these two laws gives *the Beer-Lambert law.*

$A = \log I_0/I = kcL$

where k is the extinction coefficient, c is the concentration of the absorbing species and L is the path length of the absorbing solution.

The instrument measures the intensity of light passing through a sample (I) and compares it with the intensity of light before it passes through a sample (I_o). The basic parts include a light source, a sample holder and a diffraction grating. Instead of a single lamp two light sources are used to cover the required range rating in a monochromator and a detector. A hydrogen or deuterium discharge lamp covers the ultraviolet range and a tungsten filament, or more recently light emitting diodes are used for the light in the visible range. The radiation is separated according to the wavelength by a diffraction grating followed by a narrow slit which ensures that the radiation is of very narrow waveband. In double beam instrument the light splits into two before it reaches the samples. One beam is used as the reference and the

other beam passes through the sample. The reference beam intensity is taken as hundred percent transmitted and the measurement displayed is the ratio of the two beam intensities.
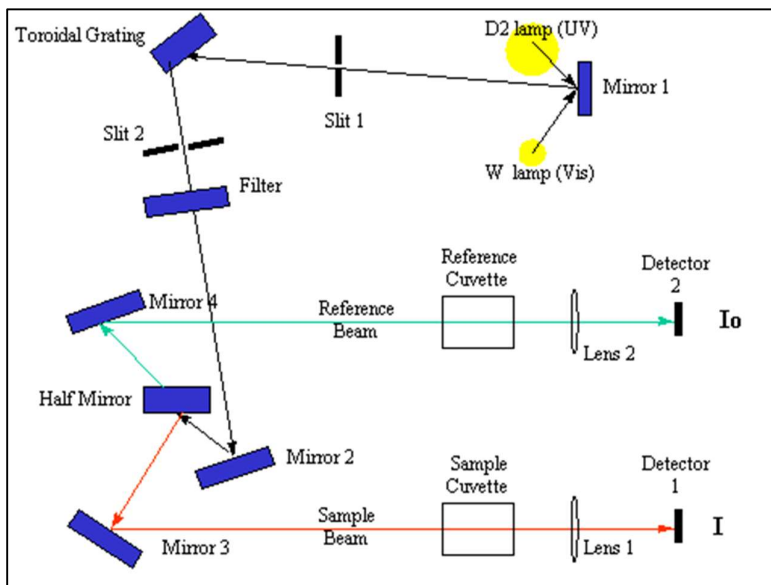

Fig 2.3: Schematic Representation of UV-visible spectroscopy

Samples are placed in a transparent cell, known as a cuvette. The most widely applicable cuvettes are made of high quality fused silica or quartz glass since they are transparent for the UV, visible and near infrared regions. Glass and plastic curettes are also common, although they have limited use, as they show absorbance in the UV region. Detection of the radiation passing through the sample or reference cells can be achieved by either a photomultiplier or a photodiode, that converts photons of radiation into tiny electrical currents or a semiconducting cell that emits electrons when radiation is incident on it followed by an electron multiplier similar to those used in mass spectrometers. The spectrum is produced by comparing the currents generated by the sample and the reference beams.

In this study, Cary 5000 UV-Vis-NIR spectrophotometer has been used to carry out UV-Visible absorption studies.

Fig 2.4: Cary 5000 UV-Vis-NIR spectrophotometer

The Cary 5000 is a high-performance UV-Vis-NIR spectrophotometer with superb photometric performance in the 175-3300 nm range. Using a *Pb Smart* detector, the Cary 5000 extends its NIR range to 3300 nm making it a powerful tool for materials science research. The large sample compartment can be expanded to hold large accessories and integrating spheres for spectral and diffuse reflectance. The *Lock Down* mechanism makes it possible to quickly change and position accessories for reproducible results.

2.5 APPARATUS FOR SHG

The study of second harmonic generation in powders has been shown to yield useful information on the non-linear optical properties of solids. For exhibiting SHG, there are two factors, in materials, which determine the existence or absence of efficient SHG. Firstly, and fundamentally, the material should crystallize with a non-Centro-symmetric crystal structure. Secondly, for maximum SHG efficiency, crystals should possess phase matching properties (i.e., the propagation speeds of the fundamental and harmonic waves should be identical in the crystal).

The *Kurtz-Perry* powder technique is widely used for the rapid characterization of newly grown nonlinear optical materials available in powder form. It assesses the effective nonlinear susceptibility of randomly oriented powder in comparison with a reference material. This technique becomes especially versatile when equipped with a broad wavelength range and intensity tenability because it provides key NLO properties of

the material under study, such as the frequency dispersion of the NLO susceptibility, phase-matching range and laser-induced damage threshold as a guideline.

The ability of this technique to sort out new phase-matching materials having large nonlinear coefficients makes it attractive since the difficult requirement in obtaining single crystals of optical quality has been removed.

Experimental Setup

The fundamental beam is divided into two identical beams by a beam splitter. One of them illuminates the sample under study and the other one illuminates a reference sample. The two samples are powders of the same calibration placed in identical holders. The second harmonic powder diffused by the sample under test is measured as a function of second harmonic powder diffused by the reference sample when the pump beam power is increased by rotating a half-wave plate between two parallel polarisers.

Since SHG coefficient of the reference sample is known, the effective second harmonic coefficient of the sample under test can also be found out. The output powers diffused by the sample under test and the reference are proportional to the square of their effective coefficients, the square of the incident beam power of the fundamental wave and also to a factor that depends upon the refractive indices of the sample.
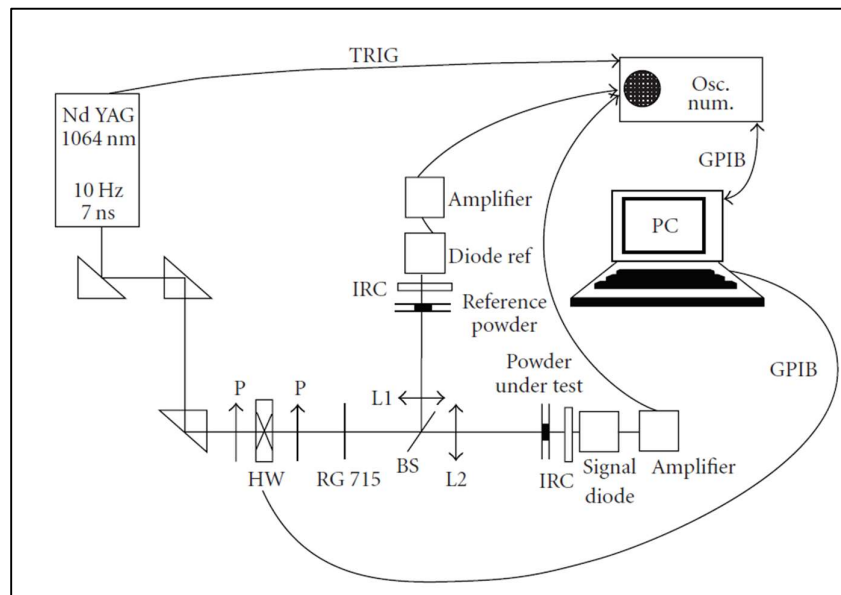

Fig 2.5: Kurtz-Perry powder SHG experimental setup.

REFERENCES

1) H.P. Klug L.E. Alexander, X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials, 2ndEdn, John Wiley and Sons, New York, 1954.

2) G.H. Stout and L.H. Jensen, X-Ray Structure Determination, Macmillan, New York, 1968.

3) M.M. Wolfson, An Introduction to X-ray Crystallography, Cambridge University Press, Cambridge, 1970.

4) Jag Mohan, Organic Spectroscopy, Narosa Publishing House, New Delhi, 2001.

5) C.N.R. Rao Ultraviolet and Visible Spectroscopy, Butterworths, London, 1961.

6) Firdous Anwar, The Assessment of Urea Related Compounds as Non-linear Optical Materials and The Single Crystal Growth of Urea and NN' dimethyl Urea, Ph.D Thesis, Dept of Pure and Applied Chemistry, University of Strathclyde, U.K. 1988.

7) S. Chemla, J. Zyss, Non-linear Optical Properties of Organic Molecules and Crystals, Vol. 1-2, Academic Press, Orlando, New York, 1987

CHAPTER 3

GRAPHICAL ANALYSIS OF THE CRYSTAL

3.1 INTRODUCTION

Single crystals having high SHG and THG response are good candidate for surface nonlinear optics and nonlinear optical microscopy in addition to nonlinear integrated optics [1]. The metallic part of the metal-organic ligand plays a vital role in optical properties. Amino acids are interesting materials for NLO applications, as they contain an asymmetric carbon atom which makes them optically active [2]. In the present work our aim is focused towards the growth of Zinc chloride doped glycine barium chloride single crystal.

3.2 Experimental Methods

The Zn^{2+} doped L-Glycine Barium Chloride single crystal was grown by slow evaporation solution growth technique. The appropriate amount of L- Glycine and Barium chloride is dissolved in double distilled water in the stoichiometric ratio of 1:1. Then 0.2 mol% of zinc chloride is added to the beaker. These reactants are stirred well about 5 hours and the filtered solution is heated at an optimum temperature of 45^0C. The super saturated solution of the sample has been dried after the evaporation of H_2O. Then the obtained adduct was dissolved in double distilled water and the solution was left stand by for several days at room temperature thereby good quality transparent crystals were obtained in a period of about 25 days. The image of the obtained crystal is shown in **fig1.**
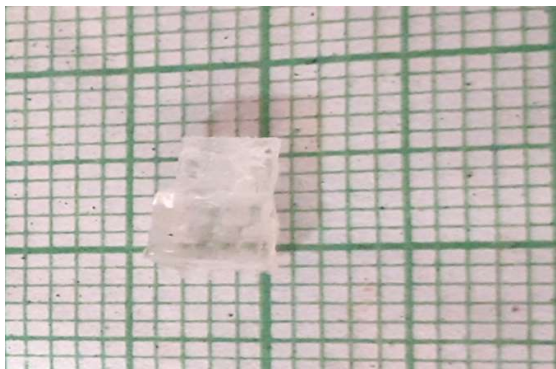

Fig.1. Image of Zn^{2+} doped LGB single crystal

3.3 Characterization Techniques

The Lattice parameters and space group of pure Zn^{2+} doped L- Glycine Barium Chloride single crystal were recorded by Enraf Nonius cad-4 Mv31 Bruker Kappa Apexll Diffractometer. The PXRD pattern of pure &doped L-Glycine Barium Chloride crystal is recorded by Pan analytical X'pert-Pro diffractometer. Energy dispersive X ray analyzer [Carl Zeiss Evo 18 Research] is used to confirm the presence of dopant in the lattice. The effect of Zn^{2+} doping on absorbance , transmittance and optical conductivityis identified by Perkin Elmer Lambda 950 UV/VIS/NIR Spectrometer. Pulsed Nd-YAG laser is used for the conformation of SHG.

3.4 Result & Discussion

3.4.1 Single Crystal X-Ray Diffraction

Single Crystal XRD has been carried out to determine the structure and cell parameters of the synthesized crystal. SXRD data confirmed that the crystal belongs to orthorhombic crystal system and the lattice parameters are a= **8.28 Å, b= 9.31Å, c= 14.85 Å, α= β =γ= 90 ^{0}**. The increased lattice parameters of the Zn^{2+} doped LGB crystal is due to the incorporation of the Zn^{2+} dopants into the crystal lattice of LGB crystal **[3]**. The lattice parameters of the pure LGB crystal are **a= 8.26 Å, b= 9.29Å, c= 14.82 Å, α= β =γ= 90 ^{0}[4].**

Fig.2. SXRD image of Zn^{2+} doped LGB Crystal

3.4.2 Powder X-Ray diffraction

The powder X- ray diffraction analysis was carried out to determine the crystallinity and purity of theZn^{2+} doped LGB crystal. Powder XRD pattern was recorded by scanning the sample over the range $10-80^0$. The recorded PXRD pattern of Zn^{2+} doped LGB crystal is shown in **fig.3**. The crystalline nature of the synthesized crystal has been confirmed by the strong and well defined peaks in powder XRD pattern. The lattice parameters estimated from the PXRD data are found to be in good agreement with the results of SXRD data. From the **fig.3** it is clear that the incorporation of $Zn^{2+}$is responsible for the change in intensity and the position of the diffraction peaks **[5].**
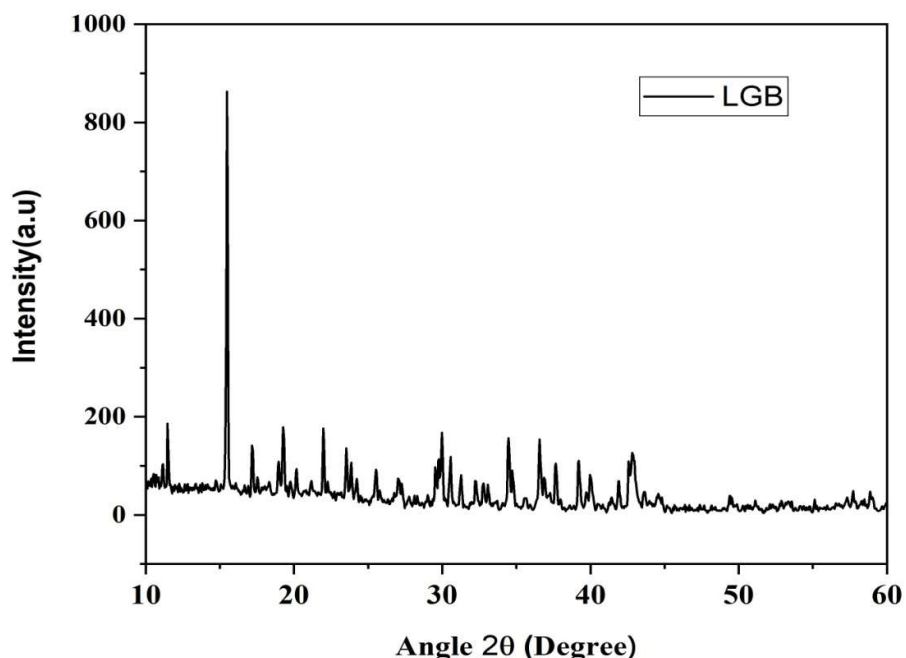

Fig.3. PXRD image of Zn^{2+}doped LGB single crystal

3.4.3 EDS Analysis

The synthesized crystals have been subjected to EDS analysis for recognizing all the elements present in the crystal lattice. Energy peaks corresponding to the various elements present in the Zn^{2+}doped LGB crystal is shown in **fig4.**
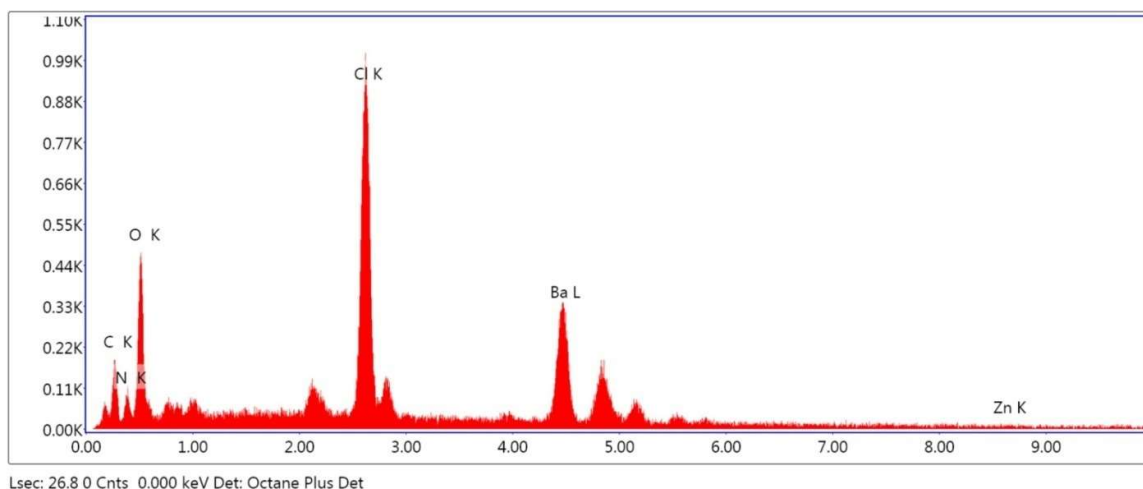
Lsec: 26.8 0 Cnts 0.000 keV Det: Octane Plus Det

Fig.4. EDS spectra of Zn^{2+} doped LGB single crystal

3.4.4 UV-VIS-NIR Spectral Analysis

Optical absorption analysis by UV –visible spectrophotometer is used for finding the effect of Zn^{2+} doping on the linear optical properties of the synthesized material.UV-Visible absorption and transmission spectra of Zn^{2+} doped LGB single crystal is recorded in the wavelength range 200-800nm. The lower cut off wavelength and wide optical transparency of pure and Zn^{2+}doped LGB crystal suggested the usefulness of this material for different applications in optoelectronics **[6].**
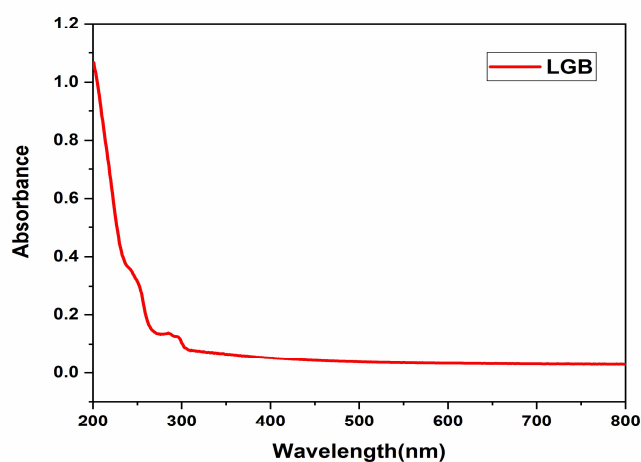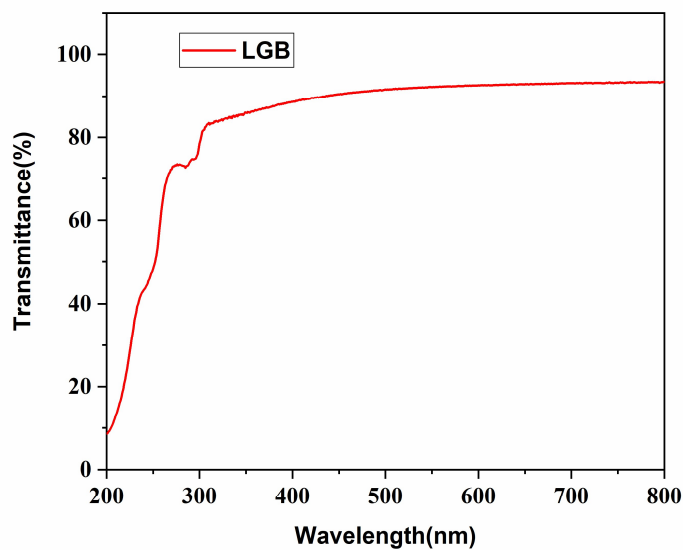
Fig.5 & Fig.6 Absorbance and Transmittance spectra of Zn^{2+} doped LGB single crystal

The absorption coefficient was determined from the transmittance T using the relation

$$\alpha = \frac{2.303 * \log\left(\frac{1}{T}\right)}{t}$$

Where 't' is the sample thickness. In order to understand the nature of the band gap the following equation was used.

$(\alpha h\nu)^2 = A(h\nu - E_g)$

The band gap of pure and Zn^{2+} doped L- Glycine Barium Chloride single crystal was calculated from the graph plotted between $(\alpha h\nu)^2$ and energy. From the graph it is found that the band gap of pure LGB crystal is 5.36eV and that of Zn^{2+} doped crystal is 5.1eV.
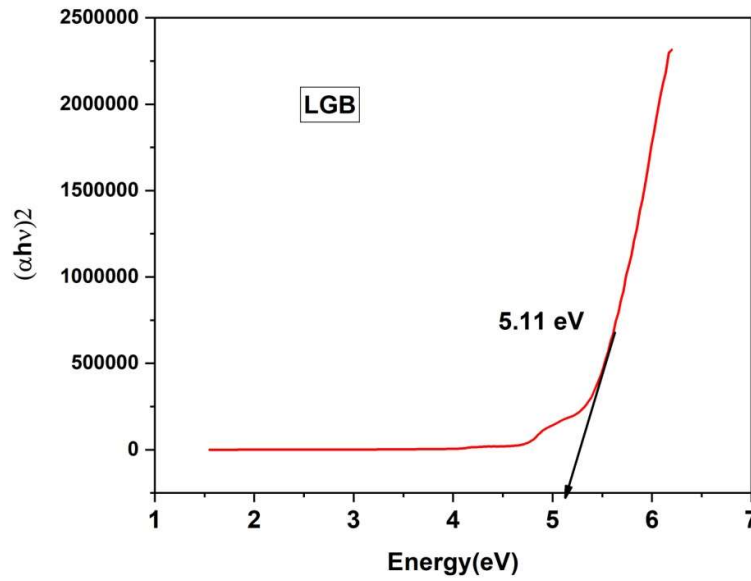
Fig.7. Tauc Plot of Zn^{2+} doped LGB crystal

3.4.5 SHG Analysis

The SHG conversion efficiency of the pure and Zn^{2+} doped LGB single crystal was determined by Kurtz-Perry technique. In this method the input energy is given by a pulsed Nd –YAG laser of wavelength 1064 nm. The laser source provides an input energy of 1.2 mJ/pulse. The fine powder of synthesized crystal was packed in a capillary tube and is exposed to the laser source. The same quantity of KDP powder was used as the reference material for SHG efficiency measurement. The SHG efficiency of pure and Zn^{2+}doped LGB crystal is found to be 0.5 and 0.75 times that of KDP. TheZn^{2+}doping is responsible for the increased SHG efficiency of the LGB crystal **[7].**

3.5 Conclusion

In summary, good quality single crystals of Zn^{2+} doped LGB single crystals have been synthesized from the aqueous solution through slow evaporation method. The lattice parameters of the pure and doped crystal are determined from the single crystal X ray diffraction analysis and which has been in a well harmony with the results of PXRD analysis. The UV-Visible spectrum revealed the optical qualities such as band gap, transmittance and

optical conductivity of pure and doped LGB crystal. The band gap of the Zn^{2+} doped crystal is estimated to be 5.11 eV. The SHG efficiency of the crystal is found to be increased on Zn^{2+} doping.

Acknowledgement

REFERENCES

1. Robert Boyd, Nonlinear optics, Third edition, Academic Press (2018).
2. M. Abila Jeba Queen, K.C Bright, S Mary delphine, P. Aji udaya: Specroscopic investigation of supra molecular organometallic compound: Spectrochimica acta part A: molecular and biomolecular.117802(2019).
3. J.H Joshi, G.M Joshi, M.J Joshi, J.O Jethva, K.D Parikh: Raman, Photoluminescence, A.C Electrical Studies of Pure and L-Serine Doped Ammonium Dihydrogen Phosphate Single crystals: The Understanding of Defect Chemistry in Hydrogen Bonding:New J. Chem.(2018).
4. Anu Elizabath Jose, Gayathri Mohan K V, Suresh Kumar M R: Structural and Optical properties of di glycine chlorides of Barium and Magnesium Crystals: IJERT, ISSN: 2278-0181.
5. J.H Joshi, S.Kalainathan, D.K Kanchan, M.J Joshi, K.D Parikh: Effect of L-threonine on Growth and Properties of Ammonium Dihydrogen Phosphate Crystal: Arabian Journal of Chemistry (2017).
6. P.Jayaprakash, M. Peer Mohammed, M. Lydia Caroline, Growth, Spectral and optical Characterization of a novel nonlinear optical organic material: D-alanine DL-Mandelic acid single crystal. Journal of Molecular structure (2016).
7. RK Raju, P Beena, H S Jayanna: Growth, Characterization and optical properties of potassium iodide doped potassium hydrogen phthalate single crystals for optoelectronic applications: Material science Poland, 37(3), 2019.