CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Basically the naturally grown crystals were recognized as the museum and ornamental gems pieces. This stimulated the crystal growers to grow more artificial crystals for the production and the fabrication. The crystal growth was scientifically approached from 1611 by Kepler, who interlinked the crystal structure and morphology to explain the properties of the crystals. Buckley in 1951 has kindly consigned the matter that “It is remembering the touch of the artist is important as the application of established scientific principles in the preparation of large crystals”. According to Gilman in the year 1963, the artificially grown crystal becomes a major commercial activity after the invention of the transistor. Later, Laudise and his coworkers in 1975 visualized that growing crystals are the technological application for the understanding and for the usefulness of the crystals. The crystals play more liability for the perfection with their symmetry in nature, due to the simplicity and from the high purity.

Due to their distinctive physical and chemical properties, a crystal acts a vital role in the field of electronics industries. As accordance with the court from String fellow in 1979, the crystals are an art than a science and many attempts are made for the fabrication of highly transparent and good crystals. The crystal growth processes, especially in the view of increasing demand for crystals applications were demonstrated by J.C Brice in 1986.
Improvement in crystal growth is highly demanded in the development of several important areas such as production of high efficient photovoltaic cells, for bright, long-lifetime light emitting diodes, for saving energy by wide use in illumination and traffic light detectors for alternative energy. The effect of grain boundaries in many single crystals is unseen or problematical. In the present studies, it is highly evident that the great persuade are implemented in the field of semiconductors, superconductors, optical devices, electronic devices and detectors.

1.2 REVIEW OF LITERATURE

Man has made the history for his extends to the art of crystallization in the past and antedates. Before the Christian period, it was recorded in the written documents that practice is made at many places in the prehistoric time by evaporating sea water to obtain a salt in the form of crystals and was considered as one of the oldest methods of transforming materials. The crystallization of a number of salts was narrated in “Natural is historia” by Roman Plinius. The preparation and their purification of various materials by the crystallization process by the sublime and the distillation was founded in the 12th century by Alchemist Geber. From the historical review, in the 17th century “the modern scientific development of crystal and its characteristic properties were revealed. During the 18th century considerable improvement was achieved in the crystal growth experiments and also in the systematic description. In 1602, Caesalpinus pragmatically studied that crystals are some kind of specific materials which exhibits different size, shape and also varies characteristic properties. Elwell and Scheel in 1975 and then followed by Scheel in 1993 shown the fundamental aspects of crystals. The theoretical understanding of crystallography and its thermodynamic studies revealed by Gibbs, Arrhenius, and Van’t Hoff in the 19th century.
Recent improvement, then advancement concerning societies over various sectors is established along the unexpected elevating on versatile materials. Materials shed a necessary characteristic between our periods in accordance with season desires, then because of our uplift about existence. Hence the exceptionally measured strategy, including on hand sophistical analytical gadgets yet equipment on the valuable research when the growth on the substance remains unchanged. For to distinguish the material properties and to find the various simulations on physiochemical residences, various kinds of characterizations such as mechanical, electrical, thermal, magnetic, optical, deteriorates and performance behavior of respective software have to be processed.

Franken and his coworker in 1961 defines the role of crystals and their applications in the field of communication, laser technology and optical imaging. The nonlinear optical properties of the newborn crystal substance lead to be the important characteristic among various utilities. So the analysis about substances together with massive Second Harmonic generation has been a choice up till now to the energetic discipline concerning research. NLO offers with the interaction about strong electromagnetic fields into an appropriate medium as on tunes various beyond the entire area among frequency, phase and amplitude were demonstrated by Zernike & Midwinter (1973) which followed by Munn and Iron side in 1994. The discipline concerning NLO results is extraordinarily applicable and desirable. To forgather the ever-growing functions between lasers, inclusive of optical conversation then statistics storage technology, Dryburgh (1987), conveys the Renaissance on optical fiber communication systems into inquire regarding nonlinear substances via the improvement regarding recent crystals. The supporter increase regarding unaccompanied crystal nonlinear optical substances has grown to be essential because of further lookup then technology. According to Seidel in the year 1988, the NLO properties of the
A wide range of optical materials are shown with respect to organic materials among the inorganic, organo-metallic and semi-organic materials. Due to the high time, polarizability and photostability, the organic-based materials embrace the huge difference in the scientific research in the development of new optical materials applications. There have been extended studies in the crystal growth with the organic materials. Here the crystals are grown with the consideration of organic and organo-metallic complexes by the slow evaporation solution growth technique. And the grown crystals are characterized for indispensable properties. The second harmonic generation and optical transparency of the grown crystal are used to find the nonlinear optical and linear optical studies with Kurtz-Perry powder technique from Kurtz and Perry approaches in 1968 and later considering the Sheik-Bahae et al. Approaches in 1989, by Z-Scan approach method, the magnitude and signal longevity regarding nonlinear intentness and refraction was once measured. Nonlinear optical characterization is the result concerning the oscillating electric discipline element of the obtaining light by way of Frisch et al., in the year 2004.

By using 03W Gaussian application package dipole moment, polarizability, Millikan values, Crystal packs factors, overexcited polarizabilities values, Highest Occupied Molecular Orbital, it can also be termed as HOMO and Lowest Occupied Molecular Orbital, it is also known as LUMO are computed and studied with the support of an experimentally decided correction factor. During the current study, the investigation made on the linear and nonlinear systems with Centrosymmetry and noncentrosymmetry, organic and organometallic crystals then the grown crystals were subjected to various crystalline properties. The crystal growth with increasing demands such as chemical processing engineers, electrical with the mechanical based engineers, instrumentation and material researchers, numerical simulation specialists, physicists and crystallographers
possibly will be fulfilled when they come to know the internal structural properties for the development of for large and high quality NLO crystals, ferro-electric and piezo electric single crystals with inhomogeneities and with the minimum defects for any applications.

In former era, Scientist Scheel and Fukuda in 2003 has tactfully studied the most types of single crystals and they also have shown their usefulness as in the field of computers' memories, in medical devices and in miracles communication systems with the support of semiconductor crystals, oxide crystals, alkali halide crystals and non-linear optical crystals and its epitaxial layers. Then, the large amount of generation of the single crystals are grown, processed, and is characterized to reach required significant technical skills in the communication and general applications, which was explained by Byrappa & Ohachi (2003).

With the material specification and from their significant properties such as melting point, decomposition temperature and the solubility of salt in solvents, etc. there are various methods for crystallization process and they takes place by three steps:

i) By the achievement of supersaturation,

ii) From the formation of crystal nuclei and

iii) Finally from the growth of crystal.

All the above steps occur concurrently with the different regions in crystallization units. The study of the phenomenon of undercooling and supersaturation was documented in the 18th century by Lowitz and Fahrenheit. Ostwald in 1893 and 1897 measured the existing range of undercooled melts and solutions with the corresponding metastable region and the same was explained by Miers (1906). Young (1911) and 1913 described the effect of
friction on the width of this Ostwald–Miers region. By the process of slow cooling, by evaporation way and from the addition of precipitant, the supersaturated crystals mechanism is achieved.

Hans Scheel & Tsuguo Fukuda (2003) described that the impact of stirring on metastable region very essential in crystallization of sugar, salt and various chemicals.

1.3 GROWTH OF SINGLE CRYSTALS

Many attempts have been made to synthesis newborn crystals with high efficiency in research areas with low cost and by recently available rare earth materials with the process of transformation and creation or combination. The growth of first successful crystal was developed in the middle of the 19th century, it was named as carat sized crystals and they are grown for high temperature solutions. Historically, attempt has made on the growth of single crystal of ruby from high temperature solutions and the grown crystal was not in the quotable seized. So, Verneuil comes through the enabled large sized ruby crystals grown from the melt phase than the liquid phase. Later, many of the scientific and industrial fields involved in the production of large single crystals. For example, in the industrial field, it is highly essential for the metallurgists to grow the single crystal of metals for the study their properties. Other examples are optic and piezoelectric crystals of large dimensions which were grown and they are employed in the optic and electric communication technology. In Sato et al. (2001) are the first to achieve the large growth of single crystals such as quartz, ADP and KDP for the optical and for piezoelectric applications.
1.4 CLASSIFICATION OF CRYSTAL GROWTH

Many of the researchers and industrialist are making attempts for to grow the highly crystalline materials with complete geometrical parameter of atomic arrangements for the study of optically based properties. There are some selective reasons for the premeditated growth of crystals and that are

- Their phase transformation
- The effect of grain boundaries and
- Due to physical properties and internal symmetry of crystal structure.

Buckley (1951) and Mullin (1976), determined the properties of the crystalline materials and they showed that crystal growth process and the size of crystals varies from materials to materials.

Based on the phase transition, the crystal growth methods are categories into three, they are as follows

i) Growth of crystals from solid to solid phase transformation (i.e., growth from solid)

ii) Growth of crystals from liquid to solid phase transformation (i.e., growth from solution)

iii) Growth of crystals from vapor to solid phase transformation (i.e., growth from vapor)

Among these different methods of growing single crystals, the solution growth phase transition plays a prominent role because of the
versatility and its simplicity. Since the growth takes place at low temperature, which owing to at near saturation conditions and hence they are highly perfected.

1.4.1 Low Temperature Solution Growth

The solution growth technique is more commonly and practically used method for growing single crystals. Materials with the instability and at very high temperature are preferred for this method to product highly transparent optical single crystals, which suggested by Feigelson et al in the year 1988. The materials must crystallize from solution with prismatic morphology from this method. The supersaturation is achieved by evaporation of the solvent. James and Kell in 1975 and then Chernov in 1984, they reported that bulk crystals were grown by this method with high solubility and of large variations in temperature. The crystals which are grown by slow evaporation solution growth method have various advantages. That is, the rate of crystallization is slow because it is carried out at room temperature and has the structural imperfection which is relatively low.

Further, the grown mechanism has subdivided into three types, namely

- Crystallization by Slow cooling method,
- Crystallization by Slow evaporation method and
- Crystallization by Temperature gradient method.

1.4.1.1 Crystallization by slow cooling method

This method is used to grow bulk single crystals. The supersaturation was attained by the temperature changes and the process of crystallization explains in such a manner that the temperature dependence concentration orient to the metastable state within the saturation region with
the low solubility along all possible directions. When the nature of the crystal is almost finite and the amount of substance is saturated, then the system cooling takes place on supersaturation stage. The temperature dependence of solubility and the volume of crystal are studied on the basis of crystallization process; it was explained with the help of thermostatic crystallization.

As the room temperature with a lower limit of cooling and within the range of 45 to 75°C, the crystallization process was takes place.

1.4.1.2 Crystallization by solvent evaporation

By this method, the difference within the rates of solvent evaporation and the solute can be utilized by establishing the excess of the given solute for crystal growth. Here on this method the volume of the solution decreases during the evaporation process and hence the solution loses the particles which are loosely bounded with the other particles in the crystal matrix. Petrov in 1969 reported the evaporation of the solvent is more rapid and also the solution becomes soon supersaturation. The vapour pressure of the solvent is greater than the vapour pressure of the solute in the phase changes.

This is one of the oldest method which effectively be used for the materials having a reasonable solubility coefficient. And it is very simple and easy method to grow the crystals by allowing the vapor formed above with the solution to escape freely into the atmosphere. The formation of crystal is due to evaporation of solvent from the solute about few mm³ per hour with the temperature stabilization upto ±0.05°C.
1.4.1.3 Crystallization by temperature gradient method

In this method, when the solution becomes supersaturated and the crystal is starting to grow due to the transport properties of the movement of crystalline substance from a hot region to a cooler region. This temperature difference makes the crystal zones to have a large effect during the growth process. The small change in temperature between the source and growing crystal gives the outcomes of large crystal effect on the growth rate mechanism. The crystals grow at constant temperature and the economy of solvent and solute are the major advantages of this method.

1.5 FUNDAMENTAL OF SOLUTION GROWTH

1.5.1 Nucleation

The term nucleation is the formation of crystals in liquid phase begins with nucleation, which may occurs induced artificially and due to the spontaneity in the crystallization process. There are two types of nucleation namely homogeneous and heterogeneous nucleation. They both come under primary nucleation and they are amorphous in manner. In the metastable phase transition, the generation of nucleation occurs which are capable of developing the structural formation of the crystalline materials. This nucleation is the study of the kinetics of the crystal growth.

In the formation of the crystallization process, there are three basic steps,

- Attainment of supersaturation (supercooling)
- Arrangement of crystalline nuclei and
- Successive growth of crystals of the distinct structure
1.5.2 Solvent Selection and Purification

Selecting Solvent in the solution growth method is a very important factor and is highly necessary for to grow optically good transparent crystals. Solvent classified into two types, they are polar and non-Polar solvents. The non-polar solutes which are more stable than the polar solvent. Nearly 90 percentages of the crystals are grown from low temperature solutions using water as a solvent. The solubility level of supersaturation for solvent with advantages as follows

- It should have been good solubility for the given solute
- It obeys the temperature coefficient of solute solubility
- Is should Non-toxic, Non corrosiveness, Non volatility
- It acts as Non flammability
- It has Maximum stability and Less viscosity
- Low Cost

The selection and the purification of material with suitable solvents is the initial process in crystal growth mechanism. The purity of the material will be high and the presence of impurity in the materials is to be only in the range of 10-100 ppm. If the impurity concentration increases, then the contamination and dislocation in the crystal lattice arrangement occur. The process like recrystallization would raise the level of purity of the material and the fractional recrystallization of the solute using pure solvent is the simple crystallization process for purification.

1.5.3 Solution Preparation

Preparing solution is the most important process in crystal growth studies. For solution preparation, it is most essential to have the soluble factor
at different temperatures suitable for the material. The sintered glass filters are used for solution filtration, which made of different pore sizes. Finally, the ultra-clear solution is taken in a pure glass beaker which is saturated at the desired temperatures.

1.6 CHARACTERIZATION TECHNIQUES FOR THE GROWN CRYSTALS

The characterization of the crystals which gives the significance role in the study of high quality grown crystal with the standardized parameters such as interatomic packaging structures, defects in the crystalline materials, highly transparency and chemical ratio. For the technological applications and for general optical applications, these basic characterizations have been considered. The structural, electrical, thermal and mechanical properties also studied for the grown crystals.

In present investigations the newly born crystals were considered for various crystallographical analyses such as

- An x-radiation diffraction (XRD) study is a versatile and Non-destructive method to find the crystalline structure and its dependent crystalline parameters.
- Fourier Transform Infrared (FT-IR) and Fourier Transform Raman (FT-Raman) spectral analyses used to find the functional group analysis and the atomic bonding vibration frequencies with an intensity of vibrations.
- Ultraviolet-visible-Near infrared spectroscopy is a UV-Vis-NIR spectrophotometer used to measure the cutoff wavelength from the cutoff wavelength.
- Photoluminescence analysis was used to perform the structural behavior of the grown crystals. The absorption of light results in a transition from the ground state to an excited state of an atom or molecule.

- Thermogravimetric, differential Thermal Analysis and Differential Scanning Calorimetry were used to determine the thermal behavior of the grown crystals.

- Materials have an exceptional value of electrical characteristics that depends on its insulation or dielectric properties. The ability of an insulator to store electrical energy was studied by this technique.

- Micro hardness is a very important solid state property used to determine the mechanical strength of the materials and the resistance to local deformation.

- The etching studies reveal the origin and character of crystalline defects such as grain regions, plastic flow and slip planes, dislocation which relies heavily on etching phenomena.

- Nonlinear optics is the basic phenomenon to know the modification in the optical characterization of the material with the presence of optical radiation.

- The third harmonic generation was measured by the Z-scan technique, this technique is used to determine both the nonlinear absorption coefficient ($\beta$) and nonlinear refraction ($n_2$).
1.6.1 Single Crystal X-ray Diffraction

X-ray diffraction is the analytical technique to study the structural properties of the crystalline materials. In the crystal, the atomic arrangements of the atoms are highly regularized in way. The internal atomic structure of the crystalline substances with the basic cell parameters are studied by Non-destructive technique is called crystal X-ray diffraction method. There are two ways through with the crystal structures can be determined, first the single crystal X-ray diffraction method and the second is Powder X-ray diffraction method.

In single crystal X-ray diffraction technique, the data for the grown crystal was obtained from X-ray analysis. They are interpreted and distinguished to get the structure of the crystal. Then grown single crystals were subjected to single crystal XRD using an Oxford-Diffraction X-Calibur with a sapphire CCD detector and enhance diffractometer equipped with graphite monochromated Mo Kα radiation of $\lambda=0.71073\text{A}$.

In XRD diffractometer, the goniometer equipped with $\phi$, $\omega$, $\chi$ and $2\Theta$ axes through which the crystal starts rotated. The grown crystals were cut with the sharp blade which mounted on a glass fiber with the cyanoacrylate. From the known 36 frames, the unit cell parameters were determined by collecting diffracted intensities obtained from three different crystallographic zones form the crystals. X-rays are oscillated by a cathode ray tube which altered to produce monochromatic radiation than it is collimated to concentrate and falls directed toward the sample. The interaction of the incident rays of the single crystal produces the constructive interference or diffraction ray, when the conditions satisfy the Bragg's Law.
The condition is \( n = 2d \sin \mu \). The diffracted X-radiation is then counterpart and detected for data processing. The angle between the incident and the diffracted rays are the key components for all diffraction studies.

**1.6.2 Powder X-ray Diffraction Studies**

Powder X-ray diffraction method is the non-destructive technique used to study and for to measure of phase identification, quantitative analysis, study of three dimensional micro structural properties, structure imperfections and crystal structures of a crystalline material and to find information on unit cell dimensions of the crystalline materials. It works on the principle of Bragg’s law. According to this law, when a sharp and highly intense beam of monochromatic source of X-rays tends to fall on grown crystals, then each atom becomes a source of scattering radiations. The Bragg’s law conditions are fulfilled by altering d-spacing in polycrystalline materials on by varying the diffracted angle theta.

![Figure 1.1 The schematic diagram of single crystal X-ray diffractometer (Source: Google)](image)

**Figure 1.1 The schematic diagram of single crystal X-ray diffractometer** (Source: Google)
In our present study, Rich Seifert diffractometer with CuK$_\alpha$ radiation of wavelength, λ=1.5418 Å were used to verify the correctness of lattice parameter values. In this, the taken sample is made into fine powder contains thousands of atomic grains with irregularly orientations. The sample was scanned through an angle of 10° to 80° at a running rate of one degree per min, to find the diffraction associated with different atomic spacing. A plot is introduced between the angular positions and intensities of the resultant diffracted peaks of radiation; a pattern is obtained which characterize the crystalline nature of the sample. An Investigation made on the basis of X-ray diffraction, which provides the structural, physical and chemical information about the crystal material.

1.6.3 Fourier Transform Technique

For to elucidate the molecular structure of the grown crystal the most important tool used is vibrational spectroscopy. In this, the bands are assigned to various vibration molecular modes. Here, the comparison has been made between spectral bands with characteristic functional group frequencies to assign the variation in the molecular crystal with the presence of obtaining functional groups. The intermolecular interactions between the functional group elements, frequency and intensity transition and chemical kinetics are observed to find the position of the bands which are directly associated to the chemical bonding.

1.6.3.1 Fourier Transform Infrared (FT-IR) spectroscopic analysis

It is one of the most important parameters to study the functional groups of pure, doped materials. There are two methods for characterizing the functional properties of matter with infrared frequencies.
They are in general,

- Dispersive type
- Fourier transform infrared

In the dispersive type by using a grating monochromator, the infrared light is dispersed into individual frequencies. But in the Fourier transform infrared, the infrared frequencies where interacts with the matter to produce an interference pattern that then analyzed using a Fourier transformer to study the individual frequencies and their variation in the intensities. It gives the comparative result for the compounds with the presence of elements. The electromagnetic interaction between the incident radiation and with the matter was studied in it. Due to the interaction between the radiation and matter, the electromagnetic radiation attributes of the interacting system may be absorbed or emitted. The data recorded with respected to the frequency of the wavelength to the intensity of radiation, which characterized the radiation absorbed or emitted by the material medium and these data are interrelated with the geometrical structure of the material.

![Figure 1.2 FT-IR spectrophotometer (From Google Source)](image-url)

**Figure 1.2** FT-IR spectrophotometer (From Google Source)
The FT-IR spectrum of grown crystals was recorded in the wave number range 400 - 4000 cm\(^{-1}\) using SHIMADZU FT-IR spectrometer is shown in Figure 1.2. The spectrometer contains an interferometer within the source and sample holder. The sample holder is located inside the interferometer and the sample detector. The sample is pelletized with KBr pellet way for to record the functional group elements and then the signals are recorded.

By experiment when we place the sample material in the path of the infrared radiation, the absorption in the material takes place which characterize the frequencies of the functional group elements and there is reduced intensities in the interferometer which resulting Fourier transform is the infrared absorption spectrum of the sample. The infrared spectrum of the sample can be measured with the moving mirror for the very short time even in a few milliseconds. The collected Fourier spectrum data are digitized and is calculated.

1.6.3.2 Fourier Transform Raman (FT-Raman) spectroscopic analysis

Raman spectroscopy is the analytical instrument based on the principle of inelastic scattering of photon energies by atomic molecules. It is used to detect of functional groups in the samples which concerns with the scattering of radiation rather than an absorption process. It was recorded in the frequency range 4000 - 400 cm\(^{-1}\) using BRUKKER RFS27 FT-Raman spectrometer (Figure 1.3). There should be some change in polarizability of the molecules through which the Raman transition can be achieved. It is suitable for heteronuclear diatomic molecules. It shows that the diatomic molecules do not have the permanent electric dipole and they are undetectable. According to Clark in the year 2007, the energy of the rotational transitions is lesser than the vibrational transitions.
UV-Visible-Near Infrared Spectroscopy is the dispersion of the light beam which gets reflected from the surface of the sample or after penetrates through the sample using Perkin Elmer Lamda 35 spectrophotometer (Figure 1.4). Spectrophotometer measures the intensity light incident on before and after the sample. The intensity of light before passes to the sample is given by I and the intensity of the light after passing through the sample is $I_o$. Therefore, the ratio of $I/ I_o$ measures the transmittance of the light on the sample to the certain intensity and frequency values. Thus, it gives the comparison among intensity of the transmitted light to that of the incident light.

The relation $I/ I_o$ is known as the transmittance and is generally defined in terms of percentage (% T). It is given
\[ A = -\log\left(\frac{\%T}{100}\right) \] (1.1)

Where, A is the absorbance which based on the transmittance of the light from the sample.

Basically, spectrophotometer consists of some parts as like incident light source, sample container, monochromator to separate the variation in the wavelength of light and the detector. The source of radiation used is often a Tungsten filament with the wavelength range of 300 to 2500 nm. A deuterium arc lamp is used as a source which covers the ultraviolet frequency region of the order of 190 to 450 nm. The Xenon lamp used for to cover the visible wavelengths. The charge couple device or photodiode is used as a detector with the monochromators for to filter the light ray of a single wavelength, reaches the detector. Along with the charge coupled device a diffraction grating is used which collects the light of different wavelengths.

![Figure 1.4 UV-Visible spectrophotometer (From Google Source)]
UV-Visible-Near Infrared Spectroscopy or spectrophotometer is of two beams, can be either single or double beam. A single beam spectrophotometer is the oldest technique and it is still used in general and industrial laboratories. The spectrophotometer contains only single beam for the measurement of intensity of light. The entire light beam is passed through the sample as a single beam. The intensity of the light ($I_o$) is measured by removing the sample.

But, in the double beam spectrophotometer the incident beam has resolved into two beams before it falls over the sample, they are

- Reference beam and
- Sample beam

The reference beam intensity is the ratio of the two beam intensities and is measured as zero absorbance or 100% transmittance and the sample beam intensity is the measure of variation in the intensities from the sample. Since the sample beam and the reference beams are measured at the equal time. Following the escalation, the reference beam gives signal to dynode voltage regulator and be diverse to keep the constant reference signal and amplifiers in required operating limits. The out coming signal from the sample is moreover process throughout a logarithmic converter for absorbance or used directly for transmittance measurements.

1.6.4.2 Photoluminescence (PL) studies

Photoluminescence (PL) is one of the most important characterization tools for measuring material properties. The photoluminescence measurement was executed using a RF-5301 spectrofluorometer instrument (Figure 1.5) to study the emitted spectrum of photo generated minority carriers by the radioactive recombination process.
The high pressure Xenon lamp is used to measure continuous spectrum; it provides the continuous outputs from 200 nm to 800 nm. From the emitted spectrum, the spectral dependence intensity provides the information about energy level coupling and the lifetimes of the material. (Ricbard Brundle 1992). From the known PL emitted defect level transitions, the defects in the material are estimated.

Figure 1.5 Spectrofluorometer (From Google Source)

1.6.5 Thermal analysis

The thermal changes in the material are characterized with three methods, namely

- Thermo Gravimetric analyzer
- Differential thermal analyzer
- Differential Scanning calorimetric
1.6.5.1 Thermo-gravimetric analysis

The Thermo Gravimetric Analysis (TGA) is the basic instrument used to measure the mass of the sample as a function of temperature. It is one of the most significant and powerful apparatus in solid chemistry and in materials science. When the sample is heated or cooled with the controlled rate of measures, then the weight loss or weight gain is calculated with the basis of temperature or time. Here the Perkin Elmer thermal analyses were used to find the thermal behavior of the given sample between 35°C to 800°C in the nitrogen gas atmosphere at a heating rate of 10°C/min. It used in the determination of Crystallization of materials, kinetics of mechanism, oxidation and reduction, etc. Thermo Gravimetric Analyzer (TGA) contains of

- Thermo balance,
- Microfurnace,
- Temperature programmer and
- Data recorder.

TGA diagram is shown in Figure 1.6. The thermobalance used to measure the weight accurately for thermal procedure and the purpose of using micro furnace to change the temperature in a controlled manner with specific rate (Gilson 1970).

An automated temperature programmer is inbuilt in the system for the calibration. The temperature of the furnace is calibrated with Ni and Fe elements and is maintained with standard Curie points with a small horseshoe magnet which placed around the microfurnace. The calibrated values are recorded by TG PC-7 series analyzer.
1.6.5.2 Differential thermal analysis

Differential Thermal Analysis (DTA) measures the temperature difference between a reference (inert) and the sample as a function of temperature. It detects the variation in the heat content of the sample. This instrument is used in an extensive range for

- Identification of melting point
- Composition analysis
- Purity
- Reactivity
- Phase diagrams,
- Hydration and dehydration,
- Thermal stabilization and
- Polymerization

The differential thermal curve is parallel till the sample does not undergo any physical or chemical change of state. Once the temperature reaches the limit of excitation, there will be some change in the physical and chemical properties of the material and the changes are indicated in different peak signals.

1.6.5.3 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) measures the enthalpy changes in the sample with quantitatively as a function of time or temperature. The nitrogen atmosphere is used in this method for to measure the changes in the melting point, decomposition temperature and dehydration process. It is often used to detect the changes which do not involve weight loss like polymorphic transformations, para-ferroelectric phase transitions.

1.6.6 Dielectric Measurement

We know each and every material have unique electrical characteristics depends on the insulating or dielectric properties of the materials. The impedance measurements are the basic means of dielectric or insulation properties. Faraday first invented the term dielectric by suggesting that when the external field is applied through a capacitor, the charged particles in the capacitor acquired the field energy and then it becomes polarized only when the insulator converts into charging conductors. The
resulting magnitude of dielectric medium depends on the total degree of polarization charge displacement takes place in the crystal.

Dielectric studies were carried out on the grown crystal using an LCR meter at various frequencies in the range from 50Hz to 5MHz and at different temperatures ranging. Dielectric studies furnish a great deal of information about perfection, crystal structure and chemical composition. A study of the dielectric properties of solids gives information about the electric field distribution within the solid. The action of an electric field brings the charges of the molecules of the dielectric into a certain ordered arrangement in space. The study of dielectric constant of a material gives an insight into the nature of bonding in the material. Defect-free and transparent crystal was selected and used for the dielectric measurement. The capacitance and dissipation factor of the sample were measured for various frequencies, in the range 50 Hz to 5 MHz.

The relative dielectric constant $\varepsilon_r$ is

$$\varepsilon_r = \frac{Cd}{A\varepsilon_0}$$  \hspace{1cm} (1.2)

Where, $C$ is the capacitance, $d$ is the thickness of the crystal, $\varepsilon_0$ is the free space permittivity and $A$ is the area of the crystal.

The dielectric constant has high values in the lower frequency region and decreases with an increase in frequency. In accordance with Miller rule, the lower value of dielectric constant is a suitable parameter for the enhancement of SHG efficiency. The variation of $\varepsilon_r$ with temperature is generally attributed to the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defects. The low value of dielectric constant at high frequencies indicates the low power dissipation and that the crystal can be highly suitable for electro-optic applications. The
dielectric loss very much depends on temperature and frequency. The
dielectric loss also depends on the frequency of the applied field like
dielectric constant.

The dielectric loss which is low at high frequencies reveals that the
crystal is of good quality with lesser defects. The dielectric constant and
dielectric loss of the crystal increases in temperatures for a constant frequency
due to the contribution of a number of dipoles and weakening of inter force
between the dipoles. The alternating current conductivity is calculated using
the relation

\[ \sigma_{ac} = \omega \varepsilon_0 \varepsilon_r \tan \delta, \]

Where \( \omega \) is the angular frequency, \( \omega = 2\pi f \), \( f \) is the frequency, \( \varepsilon_0 \) is the
permittivity of the free space, \( \varepsilon_0 = 8.854 \times 10^{-12} \) Faraday per meter, \( \varepsilon_r \tan \delta \) are
relative permittivity and dielectric loss respectively at a frequency (f).

1.6.7 Vicker’s Hardness Measurements

Microhardness is one of the important mechanical properties of the
crystal. Also, it gives a great role in the manufacturing of device fabrication.
Micro hardness test is a microprobe technique for evaluating the bond
strength, apart from being a measure of bulk strength. Highly transparent and
well-polished crystals with crack free surface were selected for the
microhardness measurements and the same crystal was mounted on the base
of the microscope. All the indentations were made at room temperature. The
applied load \( P \) is variable between 10 to 100 g, and all the indentation time
was kept as 9s for all the loads. The intended impression of Vicker’s was
approximately square in shape. The shape of the impression is dependent on
the structure, face and materials used. The Vicker’s microhardness number
was calculated using the given expression
Where \( P \) is the applied load, \( d \) is the diagonal length of the indented impression (\( \mu \text{m} \)) and 1.8554 is a constant of a geometrical factor for the diamond pyramid

### 1.6.8 Etching Studies

The structural perfection of the crystal was studied by chemical etching technique and visualizes the dislocations in the single crystal (Sangwal 1987). Etch pits are formed at the dislocation centres on the surface of the faces where the chemical complexes are present in the solution. The etching was carried out on single crystals as to know the symmetry of the crystal from the shape and size of the etch pits. The linear layered etch pits without water etchant captured on the surface of the crystal due to reduced dislocation density. The surface etchant taken at time intervals of 30 and 60 seconds on crystal and it is cleaned gently using tissue papers. The etch pits slightly disappear on the faces where the additives are bounded, this gives the dislocations in the crystal. From these recorded etching patterns, the possible reasons for large size etch pits in crystal may be due to the crystalline perfection.

### 1.6.9 Second Harmonic Generation (SHG)

The working mechanism of SHG was first studied with the powder method by Kurtz & Perry in 1960. Chemla & Zyss in the year 1987 given the history of NLO material. The principle of SHG was first achieved in 1961, when the piezoelectric sample investigated under pulsed laser radiation.

The experimental observation was first studied by Peter A. Franken in the year 1961. According to him, 3 kW pulsed beam of red laser radiation
focused on the quartz crystal, the frequency of the incident beam get double the input, which enables the extended range of laser wavelength into as the blue and UV spectrum. Such way is called frequency doubling.

Second harmonic generation is the process of transformation of light with frequency ‘ω’ into double frequency ‘2ω’ with a powerful source of coherent light at higher wavelengths. Nd: YAG laser was used to find the doubling frequency with input light radiation of 1.064 μm. Thus the output green light is obtained by this process and is highly efficient and more powerful.

![Figure 1.7 Schematic diagram of SHG (Source: Google)](source)

Here the powder sample for SHG study was irradiated with high intense radiation to emit light of scattered radiation. Then the scattered radiation is further collected and studied with the filtration process for use of harmonic content. The materials with good NLO property exhibit the principle of NLO. NLO materials possess some important optical applications and in accordance with Namwa and Miyata NLO material have highly transparence, have a high nonlinear figure of merits and large laser threshold frequency, etc.
1.6.10 Z-Scan Measurements

The measure of Z scan was first observed by the scientist Sheik-Bahae et al during the periods 1989 and 1900, they studied the optical absorption and optical refraction in the solids and liquids medium. The third harmonic generation of the grown crystals was measured by the Z-scan technique. The basic idea behind the Z-scan technique is the self-focusing or self-defocusing. The study of nonlinear refraction by the Z-scan method is based on the intensity dependence of the investigated thin sample along a focused Gaussian laser beam. The beam propagation direction is taken as the Z direction and the sample moves along that direction, and, hence this technique is known as the Z-scan technique.

Figure 1.8 Schematic diagram of Z Scan (Source: Google source)

Generally, this technique is used to determine both the nonlinear absorption coefficient ($\beta$) and nonlinear refraction ($n_2$). A CW He-Ne laser with a fundamental wavelength of 532 and 632 nm with a repetition rate of 1 KHz was used an excitation source. In this study, the sample has been translated to the Z-direction along the axis of a focused Gaussian beam and the far field intensity has been measured as a function of the sample position.
It is used to obtain the normalized transmittance value (T) with an open and closed aperture of distance Z along the lens axis. The peak and valley transmittance (ΔT\text{p-v}) difference is written in terms of phase shift \(|\Delta \phi|\) is given by

\[
\Delta T_{\text{p-v}} = 0.406 (1-S)^{0.25} |\Delta \phi|
\]

(1.5)

Where, \(\Delta \phi\) is the on-axis phase shift and \(S\) are the linear aperture transmittance and it is given by

\[
S = 1 - \exp \left(\frac{-2r_a^2}{\omega_a^2}\right)
\]

(1.6)

Where, \(r_a\) is the radius of the aperture and \(\omega_a\) is the beam radius at the aperture. The third order nonlinear refractive index \((n_2)\) was evaluated by the following relation

\[
n_2 = \frac{\Delta \phi}{k I_0 L_{\text{eff}}}
\]

(1.7)

Where, \(k=2\pi/\lambda\), the wavelength of the laser is \(\lambda\), the on-axis irradiation at the focus (\(Z=0\)) is \(I_0\) and the effective thickness of the sample is \(L_{\text{eff}}\).

\[
L_{\text{eff}} = \frac{1-e^{-\alpha L}}{\alpha}
\]

(1.8)

Where, \(\alpha\) is the linear absorption coefficient and the thickness of the sample be \(L\). From the open aperture curve nonlinear optical absorption coefficient \((\beta)\) was evaluated

\[
\beta = \frac{2\sqrt{2 I_0 \Delta T}}{I_0 L_{\text{eff}}}
\]

(1.9)

The real and imaginary parts of the third order nonlinear optical susceptibility was determined by the below relations
\[ Re \chi^{(3)}(esu) = 10^{-4} \frac{\epsilon_0 C^2 n_0^2 \alpha^2}{\pi} \left( \frac{cm}{W} \right) \tag{1.10} \]

\[ Im \chi^{(3)}(esu) = 10^{-2} \frac{\epsilon_0 C^2 n_0^2 \lambda \beta}{4\pi^2} \left( \frac{cm}{W} \right) \tag{1.11} \]

Where, \( \epsilon_0 \) the vacuum permittivity and the velocity of light in vacuum is \( C \).

The absolute value of \( \chi^{(3)} \) was obtained from the following relation

\[ |\chi^{(3)}| = [(Re \chi^{(3)})^2 + (Im \chi^{(3)})^2]^{\frac{1}{2}} \tag{1.12} \]

1.6.11 Gauss View – Software Overview

The Gauss overview software is the graphical representation interface device used to give the graphical analytical reports for the given crystal parameters. It is a supported software mode which assists the Gaussian measures rather than the front and back end processor. This Gaussian interface device by Frisch and his coworker in 2000. Some of the parameters under the Gaussian studies are Structural orbital measures, a carrier density measure of electrons and surface measure of the electrostatic potential. The electrons from the ground state excite to the higher state by wave function analysis. According to this analysis, the electron from the highest occupied molecular orbital state to the electron from the lower occupied molecular orbital state is studied and the structural changes are indicated in the atomic presence of highest occupied molecular (HOMO) orbital to the atomic presence of lowest unoccupied molecular orbital (LUMO) analysis.

1.6.12 HOMO-LUMO Orbitals

The electrons donor and acceptor representations are studied with HOMO and LUMO analysis. The term HOMO indicates the ready donation of the electrons in the orbital structure while the term LUMO indicates the acceptance of the electrons in the orbital structure. The changes in the HOMO
and LUMO study narrate the dislocation of the crystal structure with their parameters.

1.6.1 Molecular Electrostatic Potential

Scientists Politzer and Murray in the year 2002 stated that the electrostatic potential is a physical property which relates to molecular interactions in the crystal. The molecular size and shape of the crystal with orientations gives the electronic availability and the distribution of an electron charge under the molecular level. It represents the delocalization charges in the crystal. The molecular electrostatic potential is an electronic energy interaction between the positively charged nucleus and the negatively charged spices. Such attraction between the charged particles will be electrophilic attack.

1.7 SCOPE OF THE THESIS

In this present work with the potential organic and inorganic chemical substances the growth and characterizations of Cesium sulfamate, Cesium Hydrogen Tartrate and N’-((E)-(4-Bromophenyl)(phenyl)methylidene)-4-methylbenzenesulfonyldrazide, Yttrium doped triglycine sulphate crystals (YTGS) and 2-Aminopyridinium copper acetate crystals (2APC) have been studied.

These grown crystals are characterized by Single crystal and Powder X-ray diffraction studies. SHG study was carried by Kurtz-Perry powder techniques were used to find the NLO conversion efficiency for the crystal samples. The functional group analysis was performed for the grown crystals to find the parameters such as a crystalline structure with the basis of molecular atomic arrangements, the interatomic bonding between the molecules, the dislocation of the atomic molecules on the presence of infrared radiations, modes of atomic vibrating during the transmittance of the infrared
radiations, etc. The electrical and optical properties of the grown crystals were also performed. The harmonic generation study such as third order nonlinear harmonic generation was also executed by Z-scan measure. Thermo gravimetric (TG/DTA) MEASUREMENTS, Vcker’s Microhardness, UV-Vis-NIR studies, Dielectric, Z-Scan and Etching studies. Only for 4BBTH crystal the molecular polarizability, and hyperpolarizability (β), the molecular range, the studied on energy difference between the highest and lowest molecular orbits of HOMO - LUMO, the molecular orbital energy different for the stability of the material are studied in the present chapter.