

CHAPTER I

CRYSTAL GROWTH AND NONLINEAR OPTICS

1.1 INTRODUCTION

In the recent years, the progress of science and technology in several areas has been utilized for the growth of single crystals. The strong influence of single crystals in the present technology is evident from the latest progress in the fields of semiconductors, transducers, infrared detectors, ultrasonic amplifiers, solid state lasers, nonlinear optics, piezoelectric, acousto-optic, photosensitive materials and crystalline thin films for microelectronics and computer applications. All these developments could be achieved owing to the accessibility of single crystals such as silicon, germanium, gallium, gallium arsenide and the invention of nonlinear optical properties in a few organic, inorganic and semi organic crystals.

The growth of high eminence single crystals residues a demanding endeavor of materials science. For the purpose of fundamental research and practical functioning on microelectronic circuits, electro-optic switches and modulators, solid state lasers, light emitting diodes, sensors and many other devices (Fornar et al 2009), crystals of proper size with perfection are mandatory. The growth of most single crystals is a tricky procedure requiring important technical skills in the synthesis of novel materials, growth

processing and characterization (Byrappa et al 2003). It acts as a bond among science and technology for the practical device applications of single crystals as it can be seen from achievements in the contemporary microelectronics manufacturing.

Hence in this aspect, it is more suitable to state that the size and morphology of the crystals provide better results but moreover good quality crystals grown in clean environment with effective physical and chemical properties are essential in microgravity and space conditions. The optical, electrical, mechanical and thermal properties of materials ultimately conclude its effectiveness in device applications. In accordance with the available characterization facilities and in order to captivate the clarity, excellence and precision for the end users, every crystal researcher tries to grow ideal and bulk crystals with appropriate size and shape.

1.2 CRYSTAL GROWTH

Crystal growth requires the suspicious control of the phase changes. Hence, it may be definite three most important classifications of crystal growth methods.

Growth from solid → Processes involving solid-solid phase change

Growth from vapour → Processes involving vapour-solid phase change

Growth from liquid → Processes involving liquid-solid phase change

1.2.1 Growth from Solid

The solids are in common polycrystalline materials with very huge number of crystallites. They are able to be recrystallized by straining the materials and consequently by annealing or sintering. If a metal rod of fine grained structure is employed to strain at an elevated temperature, a few grains grow considerably at the expense of others which is called strain annealing. The recrystallization is probable only in those materials, which is constant at high temperature where appreciable diffusion can arise. This method is not appropriate for growing large size crystals.

1.2.2 Growth from Vapour

In vapour growth, the vapour obtained from a solid phase at a proper temperature is subjected to compress at lower temperature by utilizing the perception of chemical vapour transfer reaction. Vapour growth procedure may be subdivided into three major types. They are sublimation, vapour transfer and gas phase reaction. In sublimation, the solid is passed down to a temperature gradient and crystals grow from the vapour phase at the cold end of the tube. In vapour transfer, the solid material is passed down the tube by carrier gas. In gas phase reaction, the crystals grow as the creation of precipitate from the vapour phase as the result of chemical reaction between vapour species.

1.2.3 Growth from Liquid

The crystal growth from liquid falls into four divisions that are,

1. Melt growth
2. Flux growth
3. Hydrothermal growth, and
4. Solution growth methods

Many growth methods have been identified in each and every division. But solution growth technique at low temperature is considered as one of the oldest and widely used technique because of its simplicity and flexibility. The added advantages of solution growth are the control of growth temperature, control of viscosity and the high degree of crystal perfection, since these crystals grow at temperatures well below their melting point. Therefore, in accordance with these perspective crystals have been grown by low temperature solution growth method and presented.

1.3 GROWTH FROM SOLUTION

Solution growth method is considered as one of the majority primeval methods in the arena of crystal growth. Solution growth is most extensively application oriented process subsequently to melt growth. Several technologically essential crystals are fabricated only from low temperature aqueous solution method. The growth of crystal from the low

temperature solution requires a much additional time. There are two types of solution growth methods,

- a) Low temperature solution growth and
- b) High temperature solution growth.

Later, so many refinements and improvements have been made on the procedure of solution growth methods to harvest good quality crystals for the multiplicity of applications.

1.3.1 Low Temperature Solution Growth

Initially, it was observed that material gets unbalanced at high temperatures. Therefore, to overcome this difficulty, low temperature solution growth method is extensively studied (Pamplin 1979). This technique needs that the materials must crystallize from solution with prismatic shape. In common, this technique involves seeding, growth in a saturated solution. The driving force i.e., the supersaturation can be achieved by both i.e., temperature lowering and solvent evaporation. Low temperature solution growth method is widely used to grow bulk crystals as it possess high solubility (James et al 1975). However it was observed that the crystals grown at room temperature have quiet low structural imperfections (Brice 1972). The low temperature solution growth can be divided into the following categories,

1. Slow cooling method
2. Slow evaporation method and
3. Temperature gradient method.

1.3.1.1 Slow cooling method

This is the finest method along with others to grow bulk single crystals from solution. In this process, supersaturation is achieved by varying the temperature generally in the entire crystallizer. The crystallization process is carried out in such a way that the point on the temperature reliance on the concentration which moves into the metastable region beside the saturation curve in the direction of lowers the solubility. Because, the volume of the crystallizer is limited and the quantity of substance positioned in it is restricted, the supersaturation requires systematic cooling. It is achieved by using a thermostated crystallizer and volume of the crystallizer.

1.3.1.2 Slow evaporation method

In this method, excess of a specific solute is established by utilizing the difference between the rate of evaporation of the solvent and the solute. In distinction to the cooling method, in which the total mass of the system remain constant, in the solvent evaporation method, the solution loses particles, which are weakly bound to previous components and therefore the volume of the solution decreases. In almost all cases, the vapour pressure of

the solvent above the solution is superior to the vapour pressure of the solute and therefore the solvent evaporates more quickly and the solution becomes supersaturated. Generally, it is adequate to permit the vapour produced above the solution to get away freely into the atmosphere. This is the oldest method of crystal growth and technically, it is very simple.

1.3.1.3 Temperature gradient method

This technique is performed in a specially projected chamber which contains a bottom hot zone in which the source material to be grown is kept and a cooler region where the solution achieves supersaturation state inducing the crystal to grow. The benefit of this growth technique is that bulk crystal can be grown at ambient temperature and its solvent and solute are economically cost effective. It is inert to the change in temperature provided both the source and growing crystal have the same atmosphere.

1.4 SOLUTION PREPARATION

In low temperature solution growth method for growing crystals, preparation of saturated solution is the main key factor. A saturated solution enables the possibility of solute particles to come together and appear a nucleus which would effect in the creation of crystal. Tremendous care must be taken to prepare the solution in order to attain good quality crystals. It is improved to use a concentrated solution with as much solute as that can be dissolved, that is a saturated solution. It is also probable in a few cases that

the nucleation is achieved by involving solute particles in the solution without any assistance, which is termed as unassisted nucleation.

However, the assisted nucleation must be provided in order to increase the possibility of forming crystals. To prepare saturated solution, it is necessary to have the solubility data for different temperatures. Watman filter papers are used for solution filtration. The clear transparent solution, saturated at the required temperature is taken in a growth container. The growth container is hermetically conserved to avoid the evaporation of the solvent. The solution is experienced for saturation by suspending small test seed crystal in the solution. If the system is not in balance, the seed crystal either dissolves or the solute will crystallize on the seed. By adjusting the temperature, the needed equilibrium state is achieved and the test seed crystal is separated and a new seed crystal is introduced for crystal growth.

1.5 NONLINEAR OPTICS

In the current period, nonlinear optics plays a major role, the nonlinear optics has been evolved with the detection of second and third harmonic generations. The nonlinear behaviour will start once the perturbation to the interatomic field becomes significant. At fields very much below that of the atomic field, the probation is not enough to produce a measurable nonlinear effect.

Nonlinear optics is a novel and well established effect in which light of one wavelength is transformed to light of another wavelength. Mostly, the nonlinear optical materials are dealing with light and matter. Consequently interaction of light with matter takes place through the valence electrons in the external shells of electron orbital. Light wave is an electromagnetic radiation containing a magnetic field and an electric field component. When a light wave interacts with a medium, it motives the charged particles of the matter to oscillate. This perpetuates localized optical variations in the medium that the light is driving through the medium. The magnitude of such an induced polarization (P) at modest field strengths will be proportional to the applied field and expressed as

$$P = \epsilon_0 \chi^{(1)} \cdot E \quad (1.1)$$

where $\chi^{(1)}$ is the linear susceptibility of the material, E is the magnitude of the electric field vector, ϵ_0 is dielectric constant.

The NLO phenomena arise at sufficiently enormous fields. As the applied field strength becomes greater the polarization response of the medium, it is no longer linear as exposed by the Equation (1.1). The induced polarization (P) becomes a function of the applied field and is given by

$$P = \epsilon_0 \{ \chi^{(1)} E + \chi^{(2)} E \cdot E + \chi^{(3)} E \cdot E \cdot E + \dots \} \quad (1.2)$$

In expression of nonlinearity, the result of two or additional oscillating field gives oscillation at grouping of frequencies.

$$P(-\omega_0) = \epsilon_0 \{ \chi^{(1)}(-\omega_0; \omega_1) \cdot E(\omega_0) + \chi^{(2)}(-\omega_0; \omega_1, \omega_2) \cdot E\omega_1 \cdot \omega_2 + \chi^{(3)}(-\omega_0; \omega_1, \omega_2, \omega_3) \cdot E\omega_1 \cdot \omega_2 \cdot \omega_3 + \dots \} \quad (1.3)$$

where $\chi^{(2)}$ and $\chi^{(3)}$ coefficients represent the second and third order susceptibilities of the medium respectively. The nonlinear susceptibilities have decreasing magnitudes as their order increases at $\chi^{(1)} : \chi^{(2)} : \chi^{(3)}$. The first order susceptibility $\chi^{(1)}$ is the linear optical properties such as refractive index, absorption, dispersion and birefringence of the medium. The second order $\chi^{(2)}$, provides the second harmonic NLO property (SHG), frequency mixing and parametric generation, while the third order nonlinear optical susceptibility $\chi^{(3)}$ gives rise to third harmonic generation (THG), motivated to Raman scattering, conjugation and optical bistability.

1.6 NONLINEAR OPTICAL MATERIALS

In the current arena, nonlinear optical materials imply an effective role in the field of nonlinear optics and it has created huge impact on laser science and industrialized applications. However, in the recent period, this research has also unlimited towards the applied features of nonlinear optics. This can be effectively detected by the performance of NLO materials. The advancement of new techniques for the invention and growth of non-natural materials used for NLO applications has considerably afforded to

this way. Thus, the intention is to grow new crystals with high nonlinearities and fulfilling the technological needs for device manufacturing. The fundamental desires for optical device fabrications are large transparency range, rapid response, and immense laser damage threshold. In accumulation to the method capability, flexibility and interfacing with other materials, enhancement in nonlinear optical device manufacturing has led the manner to investigate NLO properties and the initiation of recent approaches.

Nonlinear optical materials have captivated and extended its usefulness in several photonic applications. NLO crystals have been distinguished as a favorable one in many optical and electro optical materials. Nonlinear optical materials have recognized in many aspects with the introduction of a large number of laser sources. The development of knowledge is emergent in progress and quicker processors and mass storage appliances are in exhaustive research and advancement. Basically, NLO materials are allocated into three distinct categories such as Organic, Inorganic and Semi-organic materials. Currently, organic nonlinear optical materials have exposed high optical susceptibility, ultrafast response and improved laser damage resistance as compared with their inorganic counterparts. In this deference, materials by higher nonlinear optical response are predicted to play a major role in permitting optoelectronic and photonic technologies.

1.7 ORGANIC NONLINEAR OPTICAL MATERIALS

Huge work was initiated during the 1970s to use the scientific advent, known as molecular engineering and it directed towards the invent of tailor-made materials for nonlinear optics, based on the understanding of structure-property associations. A diversity of measurements on molecular systems of different geometries, polarizability and charge transfer feature were performed. Many chemically bonded molecular units present in organic materials interact through weak van der Waals interactions. Organic materials have elevated themselves as the alternative materials because of their low cost, ease of fabrication and incorporation into devices and intrinsic tailor capacity which permit one to fine tune the chemical structure and properties for a given NLO progression. The organic materials acquire intrinsic synthetic flexibility, high optical damage thresholds and large NLO response over a wide range of frequency equivalent to those of their inorganic counterparts. Based on the organic material, the NLO property of these organic molecules is converted by the NLO characteristics of the molecular chromophores. It is observed that chromophores consisting of donor and acceptor substituents are pertained by an intervening π -backbone. 5-Sulfosalicylic acid has been intensively studied due to the possibility of formation of proton transfer organic salts and it has three potential coordination centres: $-\text{COOH}$, $-\text{SO}_3\text{H}$ and $-\text{OH}$, allowing a large number of different coordination modes and proton transfer in organic salts are assumed mainly with N-hetrocyclic bases, leading

to tunable optical properties (Ma et al 2003, Liu et al 2006). In the recent years, organic nonlinear optical materials have been established from the benzenesulfonic acid extraction (Minemoto et al 1992). The centric molecules such as, piperidine, 2-phenylethylamine, p-methylaniline and creatinine form centro crystalline complexes with 5-sulfosalicylic acid.

Piperidine is a heterocyclic amine organic compound, which is the derivative of pyridine and it comprise of a six-membered ring containing five methylene bridges ($-\text{CH}_2-$) and one amine bridge ($-\text{NH}-$). Phenethylamine (PEA), is also known as β -phenylethylamine and 2-phenylethan-1-amine. Phenethylamines are the group of phenethylamine derivatives which contain phenethylamine as a backbone. p-methylaniline contains a proton acceptor amino (NH_2) group, which can create a strong hydrogen bond with organic acids and forms N-H--O, an anilinium group (Jovita et al 2013). Creatinine or creatine anhydride is a breakdown product of creatine phosphate. The loss of water molecule from creatine results in the formation of creatinine. A current class of nonlinear optical energetic materials has been achieved through crystal liberation of various organic materials trailed in it. The present investigation is focussed on the combination of 5-sulfosalicylic acid with various organic bases and synthesis, growth, physical and chemical properties of compounds have been studied through various characterizations.

1.8 CHARACTERIZATION TECHNIQUES

1.8.1 High Resolution X-ray Diffraction

The crystalline perfection of single crystals can be analyzed by high resolution X-ray diffraction (HRXRD) using a multi-crystal X-ray diffractometer. The divergence of the X-ray beam rising from a fine focus X-ray hose (Philips X-ray Generator, $0.4 \times 8 \text{ mm}^2$, 2kW Mo) is first condensed by a lengthy collimator fitted with a couple of fine slit assemblies. The foreshortening angle of the rising beam from the objective is kept at three degrees as a substitute of the standard value of six degrees, though the intensity is expected to be lesser in the vision of having better resolution. Mo target (objective) has been preferred as a substitute of generally used Cu as the wavelength of $\text{MoK}\alpha_1$ (0.70926 \AA) is less than half of that of $\text{CuK}\alpha_1$ (1.54056 \AA). This collimated beam is diffracted double by two Bonse-Hart type of monochromator crystals and the thus diffracted beam has well resolved $\text{MoK}\alpha_1$ and $\text{MoK}\alpha_2$ components.

The $\text{MoK}\alpha_1$ beam is isolated with the help of fine slit arrangement and approved to advance diffract from an independent third Si monochromator crystal set in dispersive geometry (+,-,-). All the three (111) Si monochromator crystals are plane crystals and set for diffraction for (111) planes in symmetrical Bragg geometry. The specimen crystal is aligned in the (+,-,-,+) configuration, in which the sample crystal is in

non-dispersive geometry with respect to the third monochromator. Due to dispersive configuration of the third monochromator crystal with respect to the second monochromator, the spectral eminence of diffracted beam emerged from the third monochromator is highly perfect ($\Delta\lambda/\lambda \sim 10^{-5}$, horizontal divergence $\gg 3$ arc seconds) and the lattice constant of the monochromator crystal and the specimen are different, the unnecessary experimental dispersion broadening in the diffraction curve of the specimen crystal [$\Delta\text{FWHM} = \Delta\lambda/\lambda (\tan\theta_M - \tan\theta_S)$, θ_M and θ_S are being the Bragg diffraction angles of monochromator and the sample crystals] is insignificant. The advantage of dispersion configuration (+,-,-) over the non-dispersive configuration (+,-,+) of monochromators has been established (Bhagavannarayana et al 2010). It may be mentioned that as the third monochromator stage is independent and positioned at a huge distance of approximately 75 cm from the Bonse-Hart crystals, the unwanted divergent $\text{MoK}\alpha_1$ and scattered radiation (though most of them are stopped by the slit assembly after the second monochromator) from the tails of the first and second monochromators are eliminated to a great extent.

All the monochromators are symmetrical cut crystals and aligned for symmetrical Bragg diffraction for crystal planes. The specimen can be rotated about the vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arc sec. The diffraction or rocking curves (RCs) are recorded by changing the glancing angle (angle

between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position θ_B (taken as zero for the sake of convenience) starting from a suitable arbitrary glancing angle and ending at a glancing angle after the peak, so that all the meaningful scattered intensities on both sides of the peak are included in the diffraction curve. RC curve can be recorded by the omega (ω) scan wherein the detector is kept at the fixed angular position $2\theta_B$ (θ_B being the Bragg diffraction angle) with wide opening for its slit. The slit width is kept around 1 mm through which the intensity distribution for an angular range up to around 500 arc sec on both sides of the 2θ position (of the detector which is at a distance of around 165 mm from the sample) can be received which could cover all the peaks due to various grain boundaries. It may be mentioned, when the residual direct beam which may emerge through the crystal is stopped, even if the slit width is much more than 1 mm, the observed RC along with the scattered intensity along the tails of the RC does not change as observed experimentally.

The omega scan is suitable to record the small range order scattering caused by the defects or by the scattering from local Bragg diffractions from agglomerated point defects or owing to low angle and very low angle structural grain boundaries (Bhagavannarayana et al 2010). In case of 2θ - θ or 2θ - ω scan, the experimentally obtained RC is having the information about a single grain. The rocking curve is expected to be very sharp as the detector with narrow slit will not obtain diffracted

intensities from the other grains which are misoriented to the grain below investigation (i.e. align for diffraction) or the diffuse scattering from point defects and their aggregates. Wherein the comparatively simple omega scan, with sufficiently broad slit for the detector, if the crystal contains structural grain boundaries, all the peaks in the RC are obtained. On the other hand a single sharp peak can be obtained in omega scan, it really confirms that the specimen crystal has a single domain with single orientation. The schematic diagram of HRXRD is depicted in Figure 1.1.

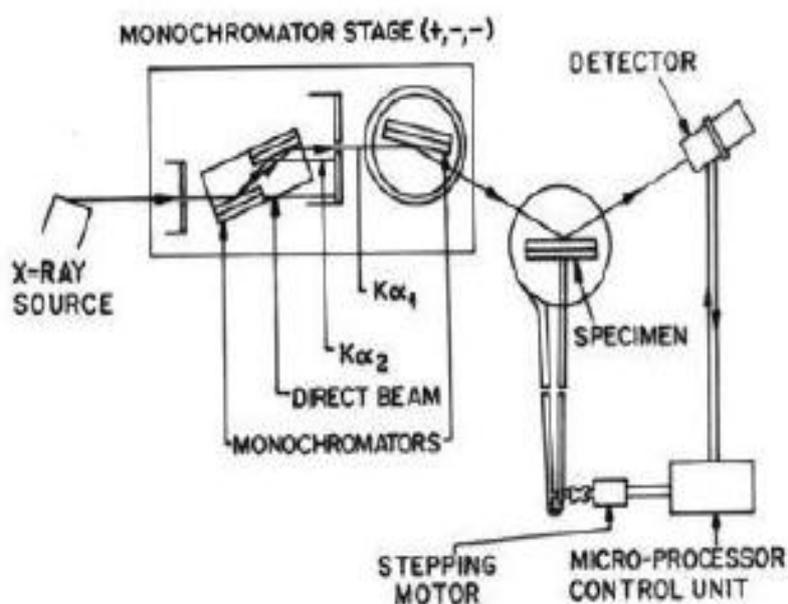


Fig.1.1 Schematic diagram of HRXRD

1.9 SCOPE OF THE THESIS

The investigation on the nonlinear optical materials has been of extreme interest in the current years because of their frequent latent

applications. Extensive research have been employed to design a highly competent nonlinear optical crystals for visible and ultraviolet regions in the areas such as laser and material processing. The most extensively investigated ionic crystal in salicylic family is 5-Sulfosalicylate. There has been a systematic endeavour to widen new sulfosalicylate crystals for efficient NLO applications.

Usually organic nonlinear optical molecules have higher nonlinear optical coefficient, so they are considerably used in optical device diligence which are similar to optical communication, information data storage, optical switching, optical limiting etc. The organic materials have high ultrafast response time, photo-stability and large hyperpolarizability (β) values. In exacting, the π -conjugated systems involving a donor and an acceptor confirm large NLO response and for this reason they have been well premeditated.

In the present investigation, 5-Sulfosalicylate derivative compounds Piperidinium 3-carboxy 4-hydroxy benzenesulfonate (PBS), 2-phenylethylaminium 5-sulfosalicylate (2PE5S), p-methylanilinium 3-carboxy 4-hydroxy benzenesulfonate (PMBS), Creatinium 5-sulfosalicylate (C5SS) compounds have been synthesized and their structural, spectral and optical properties have been inferred.

To grow single crystals of PBS, 2PE5S, PMBS and C5SS, slow evaporation solution growth technique has been employed. The crystal structure, lattice parameters and crystalline perfection of grown crystals have been analyzed by powder X-ray diffraction and HRXRD studies.

FTIR study has been performed on the grown crystal to find functional groups present in grown crystal. Thermal property of the grown crystals have also been identified.

The optical studies like UV-Vis-NIR, photoluminescence, laser damage threshold, THG of PBS, 2PE5S, PMBS and C5SS crystals have been performed.

Dielectric and micro-hardness properties of grown crystals have been studied. All the studies have been made to find the diverse properties to explicate NLO performance of the materials.