PREFACE

Crystals are the unacknowledged pillars of modern technology. Without crystals, there would be no electronic industry, no photonic industry, no fiber optic communications, which depend on materials/crystals such as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries. Crystal growth is an interdisciplinary subject covering physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, etc.

In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications. Atomic arrays that are periodic in three dimensions, with repeated distances are called single crystals. It is clearly more difficult to prepare single crystal than poly-crystalline material and extra effort is justified because of the outstanding advantages of single crystals. The reason for growing single crystals is, 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. The strong influence of single crystals in the present day technology is evident from the recent advancements in the above mentioned fields. Hence, 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 as well as applied research.

Low-temperature solution growth is the simplest and in many cases the least expensive method for production of optical crystals. Historically, it was probably the first and the most widely used technique to produce artificial crystals for many applications, such as mass crystallization, production of pharmaceuticals, or growth of relatively small crystals for crystallographic and other physical studies. However, its use for growth of large, commercially important single crystals has been very much limited to a few inorganic water-soluble materials, examples of which include Rochelle salt, triglycine sulphate, or Potassium Dihydrogen Phosphate (KDP). For organic crystals, not soluble in aqueous solutions, the preference has been given to alternative methods, among which the Bridgman technique is the most common. Limited application of solution growth methods to pure organic systems might be explained by various reasons, such as difficulties in handling and purification of organic compounds and solvents, or, probably the most important, much slower speeds of traditional solution growth in comparison with growth rates of higher-temperature methods from melts. Modern availability of commercially produced high-purity organic solvents and recent development of accelerated techniques for solution growth, enables wider variations in growth methods to produce crystals of different materials. When large volumes of single crystal materials are needed for certain applications, solution growth methods may offer an advantage of easier scaling-up processes. For organic crystals, one such application relates to their use in radiation detection devices that deploy
scintillation properties of aromatic materials for high-energy neutron detection.

Nonlinear optical crystals (NLO) are very important for laser frequency conversion. KDP is suitable for higher harmonic generation of huge laser systems for fusion experiments because it can be grown to larger sizes and also it has a high laser damage threshold. Potassium Titanyl phosphate (KTP) is a useful NLO crystal to get efficient green light by the frequency doubling of Nd:YAG laser. It has high optical nonlinearity, large temperature and angular allowance and it is non hygroscopic and mechanically hard. The method of growing crystals varies widely; it is mainly dictated by the characteristics of the material and its size.

In recent years there has been considerable progress in the development of coherent UV sources based on non-linear optical processes. The demand for nonlinear optical crystals with superior properties is increasing due to quantum jump in the design of nonlinear optical devices with higher performance. With the progress in crystal growth technology, materials having attractive nonlinear properties are being discovered at a rapid pace. To enable a material to be potentially useful for NLO applications, the material should be available in bulk single crystal form. And so, crystal growths of new nonlinear optical materials and investigation into their properties have become most indispensable and efficacious disciplines in the field of materials science and engineering.
The rapid development of optical communication system has led to a demand for NLO materials of high performance for use as components in optical devices. NLO materials are used in frequency conversion, which is a popular technique for extending the useful wavelength range of lasers. The search for new materials has identified novel organic systems of considerable potential and high performance. There are three major stages involved in this research. The first is the production of pure materials and improved equipment associated with the preparation of these materials. The second is the production of single crystals first in the laboratory and then extending it to commercial production. The third is the characterization and utilization of these crystals in devices. The contribution from the delocalized π-electrons belonging to the organic legend results in wide optical transmittance and high nonlinear electro-optic coefficients. Many device applications of NLO require single crystals in the bulk form. This is achieved only with the organic crystals, which exhibit wide transparency, large and bulky crystal morphologies.

The most commonly experienced interactions of light with matter, such as refraction, reflection and diffraction, occur in the linear domain. This is to say, the magnitude of the observed effect changes linearly, with light intensity. Most optical nonlinear responses were not demonstrated until the advent of the laser, as a direct consequence of the extremely high photon fluencies that can be obtained under laser irradiation. The rapid development of optical communication system has led to a demand for NLO materials of high performance for use as components in optical devices.
The following objective has focused in the present research work. They are,

- To synthesis six organic crystals by solution growth technique.
- To study the structural properties of synthesized organic crystals using XRD technique.
- To characterize the optical properties of six organic crystals by UV, FTIR techniques.
- To study the Second order NLO properties and dielectric characterization of grown organic crystals.
- To study the micro hardness study of some organic crystals with help of Vickers hardness study apparatus.
- To calculate the energy gap of Glutamic acid and 3-pyridinecarboxamide crystals via Density Functional Theory calculation with GAUSSIAN03W version.

The NLO crystals were grown by conventional solution growth technique. The essential properties such as optical transparency and the second harmonic generation for the grown materials have been verified by recording optical transmission and Kurtz-Perry powder SHG efficiency studies. The grown crystals were subjected to vibrational analysis to study its bonding property. NLO processes can be viewed as dielectric phenomena. Hence dielectric studies were carried out for the grown crystals. Computational calculations were performed for the gap between HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest
Unoccupied Molecular Orbital) is calculated which is useful for estimating the efficiency of Second Harmonic Generation (SHG) of the grown crystal.

The proposed thesis is structured into **Nine Chapters**.

- **Chapter One** deals with introduction to crystal growth techniques.
- Characterization tools applied for the study were discussed in **Chapter Two**.
- Crystal Growth and Characterizations of 1,3-DCP-2,4-diene crystal were discussed in **Chapter Three**. In this chapter, the cell parameters were determined by powder X-ray diffraction analysis. FT-Raman and FT-IR analysis were used to confirm the presence of various functional groups in the grown crystal.
- **Chapter Four** discussed about Crystallization and characterization of nonlinear optical material of Glycolylurea organic crystals. In this chapter, the mechanical response of the crystal has been studied using Vickers microhardness technique.
- Growth of 1-Hydroxyurea Hydrate crystal and their structural and physicochemical properties were characterized by X-ray powder diffraction, Dielectric behavior, UV-Vis spectra and Hardness studies are explained in **Chapter Five**.
- **Chapter Six** deals with the growth of optically non-linear organic crystal Glutamic acid using water by slow evaporation of aqueous solution at room temperature. The mechanical response of the
crystal has been studied using Vickers microhardness technique. The elastic stiffness constant \( C_{11} \) were calculated for different loads using Wooster’s empirical formula. Static and dynamic hyperpolarizability values were calculated to confirm the suitability of the crystal for nonlinear applications.

- Crystal Growth and Characterizations of L-proline hydrate crystal were discussed in **Chapter Seven**. In this chapter, the hardness of the crystal has been studied using Vickers microhardness technique.

- The mechanical response of the crystal, the constant \( C_{11} \) and the HOMO-LUMO energy gap of 3-pyridinecarboxamide crystal were discussed in **Chapter Eight**.

- **Chapter Nine** gives the comparative conclusion of the present research work.