CHAPTER 6

SUMMARY AND SUGGESTION FOR FUTURE WORK

6.1 SUMMARY

The technological needs are increasing every day, and the demand for crystals in the electronic industries is always on the rise. With the progress of laser technology, a new branch of science called Nonlinear Optics have come up, which insists on the breakthrough of nonlinear optical materials and their crystallization. Therefore the ultimate role of crystal growers is to grow perfect single crystals with desired morphology and properties in order to realize the quality and application prospects in demand. An efficient approach in the crystal growth technique is the modification of nucleation, growth rate and morphology in order to develop the desired physical characteristics of a crystalline material.

In order to meet the requirements, a variety of organic, inorganic and semiorganic materials were developed and grown into crystals. Organic materials have been of specific interest due to their flexibility in designing novel materials with promising properties. On the other hand, the class of semiorganic crystals offers a number of tantalizing openings in the application aspect. In the fast developing world of technology, research on the crystal growth techniques and search for new materials has been the mission of crystal growers.
In this stream of research, crystals growers started introducing different methods of crystal growth in order to grow new crystals of interest. One of the simplest methods of crystal growth is the low temperature solution growth. As the crystallization takes place close to the ambient temperature, defects arising due to thermal fluctuations are highly minimized and optically transparent crystals suitable for device applications can be grown.

The first chapter gives an overview of different methods in the crystal growth. An elaborate discussion was made on the low temperature solution growth methods which include solvent evaporation method, temperature reduction method and gel diffusion method. The basic theory of crystal growth was studied and crystal growth parameters such as solubility, saturation, supersaturation, nucleation phenomena and metastable zone width were described. The various crystal characterization techniques such as, single crystal X-ray diffraction, powder X-ray diffraction, Fourier transform infrared spectroscopy, ultraviolet-visible-near infrared spectroscopy, thermogravimetric and differential thermal analysis, dielectric studies, second harmonic generation, Vickers microhardness test were introduced. A brief introduction of nonlinear optics was also presented.

The second chapter investigates the synthesis and growth of urea-3-nitrobenzoic acid in the presence of m-nitroaniline and p-xylene by solvent evaporation technique. Morphologically good and highly transparent crystals were obtained in this system compared to pure system of urea-m-nitrobenzoic acid. The complete structure of the crystal was obtained by single X-ray diffraction analysis. The material grown was found to be a novel material and the crystal data was deposited in Cambridge Crystal Data Center (CCDC 764102). The existence of very strong hydrogen bonding between the hydrogen atom of urea molecule and 3-nitrobenzoic acid were confirmed, due to which the tendency of hydrogen bond formation of urea with water molecules in the moisture is prevented. Therefore urea-3-nitrobenzoic acid
crystal is non-hygroscopic unlike urea. The FTIR analysis confirmed the finger prints of functional groups in the parent material. Optical spectrum has showed that urea-3-nitrobenzoic acid crystal has an excellent transmission window with a UV lower cutoff wavelength at 264 nm. The melting point of the crystal was determined as 152 °C using TGA-DTA analysis. Vickers hardness test has listed the urea-3-nitrobenzoic acid crystals in soft category with the Mayer’s number 1.84.

The third chapter reports the growth and properties of L-proline doped KDP single crystals and elaborately discusses the influence of doping on the optical, electrical and mechanical anisotropies of grown crystal. L-proline doped KDP single crystals were grown by temperature reduction method and slow evaporation method. An average growth rate of 5.25 mm/day was recorded in slow evaporation method. The effect of doping was found to be more prominent in determining the growth rate and growth direction. The functional groups present in the crystal were confirmed by FTIR analysis. All the observed frequencies were assigned with respect to the different vibrational modes. A strong interaction of L-proline with the –OH group of KDP was observed. In the case of second harmonic generation, the efficiency increases with increase in the concentration of L-proline.

The anisotropy in optical, electrical and mechanical properties of the grown crystal was studied in a-axis, b-axis and c-axis directions, and the optimized direction of the L-proline doped KDP single crystal for nonlinear optical applications was identified. The studies have shown a normal dielectric behavior of NLO crystals. High percentage of optical transmittance and high mechanical hardness along the a-axis suggests this axis as more appropriate for optical applications. The chemical etching analysis have shown anisotropy in the etch patterns of different faces. It shows a growth difference that has occurred from the molecular level leading to anisotropic
mechanical strain distribution at different faces. The role of L-proline was very active in attaining fast c-axis growth of the KDP and thus resulting in less strained prismatic planes suitable for optical and mechanical applications.

The fourth chapter reports the influence of series of amino acids, viz. L-histidine, L-proline and glutamine on the growth and properties of ZTS single crystals. Zinc tris(thiourea) Sulphate (ZTS) was synthesized and grown as single crystals in pure form and in doped form by slow evaporation method. The amino acid dopants were found to influence the nucleation rate, growth morphology and NLO properties of ZTS to a greater extent. Single XRD studies have revealed that the crystals belong to orthorhombic crystal system with space group Pca2₁. The obtained cell parameters of pure and amino acid doped ZTS single crystals were in good agreement with the literature values. The UV-vis-NIR studies have shown a variation in the transmittance percentage due to amino acid doping. All the grown crystals show good optical transmittance with a lower cutoff of 270 nm. The transmittance percentage of pure and amino acid doped ZTS was found to vary in the order of L-histidine doped ZTS > Pure ZTS > L-proline doped ZTS > Glutamine doped ZTS. FTIR studies were done and all the observed frequencies were assigned with respect to their vibrational modes. The influences of amino acids were marked by a small shift in the absorption peaks. The SHG studies have shown that the relative SHG efficiency of L-histidine doped ZTS, L-proline doped ZTS and Glutamine doped ZTS were 1.42 times, 1.06 times and 1.48 times respectively that of pure ZTS.

Dielectric studies were conducted using parallel plate capacitor method. Dielectric constant and dielectric loss factor were calculated by varying the temperature and frequency. The order of grown crystals according to the observed dielectric constant was; pure ZTS > L-proline doped ZTS > L-histidine doped ZTS > Glutamine doped ZTS. Dielectric loss of the crystal was found to decreases with increase in ac frequency. In particular, the low
dielectric loss is a sign of the good crystalline quality with fewer defects. The order of grown crystals according to dielectric loss factor is, L-histidine doped ZTS > Glutamine doped ZTS > pure ZTS > L-proline doped ZTS. The results of Vickers microhardness test have shown that the hardness of the grown single crystals increases with increase in load. It also validates the results of dielectric studies and suggests that Glutamine doped ZTS is superior to the others grown crystals for NLO applications.

Growth of copper and potassium ion doped ZMTC single crystals by gel method and the influence of doping on the crystal morphology, NLO properties and thermal behavior of grown crystal are discussed in fifth chapter. Single crystals of copper doped ZMTC and potassium doped ZMTC were grown in silica gel medium. K doped ZMTC were grown at three different pH. The crystals grown in the pH of 2.8 were found to be better in size and transparency. Cu doped ZMTC crystals were grown in the pH 2.8 in silica gel medium. Morphological change has occurred and NLO property was enhanced as a result of doping. The metal incorporation in the crystal was confirmed by EDAX analysis and the approximate weight percentages of dopants were determined. The functional groups present in the molecule were identified using FTIR spectrum and all the frequencies were assigned with respect to their vibrational modes. A slight distortion was observed in the frequencies due to distorted tetrahedra. The structure of the grown crystals was confirmed by their cell parameters and compared with the reported values in the literature. Solid morphology diagram of the crystals were drawn and all the faces were indexed. The UV-vis-NIR spectral studies show a high percentage of transmittance with lower cut off wavelengths 260 nm for Cu and K doped ZMTC. The TGA-DTA analysis have shown that the thermal decomposition of the grown crystal involve multi-step process with high thermal stability of the crystals compared to pure ZMTC crystals.
The main objectives of the present work are to grow and characterize organic, doped inorganic and semiorganic single crystals, and to study the influence of dopants on their physical properties. To achieve these objectives, organic crystals of urea-3-nitrobenzoic acid were grown by co-crystallization technique using slow evaporation method. Growth conditions were optimized to improve the size and quality of crystals. As a fruitful outcome, the harvested urea-3-nitrobenzoic acid crystals were nonhygroscopic with well developed faces and good in size. Subsequently, to grow doped inorganic crystals, L-proline was chosen as dopant for KDP single crystals. The influence of L-proline on the properties of KDP was studied. It was interesting to observe that the growth rate and NLO properties of KDP was enhanced. Following this work, the influence of L-histidine, L-proline, L-glutamine on the growth and properties of ZTS single crystals were studied. A reasonable increase in NLO properties and change in crystal morphology was found in ZTS as a result of doping. Finally, potassium doped ZMTC and copper doped ZMTC single crystals were grown by single diffusion gel method. Metal dopants were expected to bring a perturbation in the bimetallic thiocyanate system to achieve enhanced NLO property. All the main objectives of this work were achieved and their physical interpretations were made with reference to the literature.

6.2 SUGGESTIONS FOR FUTURE WORK

Synthesis of urea co-crystals with other organic NLO materials can be attempted. Proton transferable bulk aromatic groups can be preferred to enhance the NLO property of urea. Another method of utilizing the urea material for NLO application is by the formation of adducts. Suitable guest molecules can be identified to fit into the urea host and new urea systems can be generated. The urea-3-nitrobenzoic acid crystal has high optical birefringence, which can be studied and interpreted for suitable
optical applications. Other characterizations such as high resolution XRD, photoluminescence studies and ferroelectric studies can be performed on this crystal.

In L-proline doped KDP crystals, the morphological studies can be done to explore the changes in the growth habits. As the NLO property has shown an improvement with L-proline doping, an attempt of crystal growth can be made by increasing the percentage of doping in KDP. The grown crystal can be subjected to other characterizations such as photoluminescence, phase matching, laser damage threshold and atomic force microscopic studies. The doping can be extended with other amino acids also.

Zinc tris (Thiourea) Sulphate crystal is an efficient NLO material. This system has shown a high response to the doping agents. It was observed that, the growth morphology abruptly changed with respect to L-histidine. So, the morphological significance can be studied in detail and can be reported. Metal dopants can be attempted with ZTS. The grown crystals can be characterized with high resolution XRD and photoluminescence studies. New systems of thiourea sulphate can be synthesized and studied for NLO properties.

The zinc mercury thiocyanate crystals are easily grown by gel method. The crystals grown by this method are smaller in size due to which the characterization becomes challenging. Growth optimization can be done by trying with different gel mediums in order to grow considerably larger crystals. This may open up the way to study the crystals using various characterizations, where larger size crystals are required. In addition to the metal doping of ZMTC, amino acids can be used as dopants and their influences can be studied.