CHAPTER 9

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

9.1 SUMMARY

The successful demonstration of optical second harmonic generation in crystals by Franken et al in 1961 spurred rapid progress in nonlinear optics. Over the past decades, due to the rapid developments and simultaneous progress in laser technology, this field occupies a new branch of science. Nonlinear optical (NLO) materials have come upon the material science scene and are being studied by many research groups around the world. These new materials operate on light in a way very analogous to the way semiconductors operate on electrons to produce very fast electronic switching and computing circuits. With the emerging demand for information systems, nonlinear optical materials have been considered the key elements for the future photonic technologies of optical computing, telecommunications, optical interconnects, high density data storage, sensors, image processing and switching. Thus the nonlinear optical crystals have played an important role in laser science and technology. The search for new NLO crystals particularly for the ultraviolet and infrared spectral regions is still very active, even though intensive efforts in this field have been in progress for nearly fifty years. Scientists working in this field realize the extreme importance, in the search for new NLO crystals, of a thorough elucidation of the structure-property relationship between NLO effects and its microstructure.
Growth of single crystals is a standard and important technique in the optical industry involving the production of large crystals. This simple process yields bulk crystals with fewer defects. As the growth proceeds close to the room temperature, this technique results in high quality for device applications. Materials having moderate to high solubility can be grown by low temperature solution growth method.

In this thesis, low temperature solution growth of nonlinear optical single crystals of maleate and sulfate of 2-aminopyridine, γ-glycine, tris(glycine) calcium(II) dichloride, potassium carbonate doped KDP, potassium thiocyanate doped KDP, L-arginine monohydrochloride doped ADP and L-alanine doped ADP are reported and their characterization analysis are discussed in detail. 2-aminopyridine and glycine derivative single crystals were grown by slow evaporation method and doped KDP and ADP crystals were grown by slow cooling method with seed rotation technique. The first chapter contains a brief overview of the crystal growth processes with focus on low temperature solution growth technique. Nucleation, saturation and methods of crystallization in solution growth method are discussed. An introduction to nonlinear optical crystals and characteristics of organic, inorganic and semiorganic nonlinear optical crystals with broad perspective has been dealt in detail.

The second chapter discusses the growth of organic crystals of bis(2-aminopyridinium) maleate (B2AM) and their characterization analysis. Single crystal X-ray diffraction studies reveal that B2AM crystallizes in orthorhombic system with noncentrosymmetric space group Fdd2. Morphology of the grown crystals was identified. The solubility and metastable zone width of the material were determined for water solvent. HRXRD analysis shows that the crystalline perfection of the as–grown crystal is reasonably good. The FTIR analysis confirms the presence of functional
groups in the grown crystals. Dielectric studies show that B2AM has low values of dielectric constant and dielectric loss at high frequencies. TG-DTA and DSC studies show that B2AM melts at 137 °C. Optical spectrum reveals that B2AM crystal has good transmission window with UV cutoff wavelength at 354 nm. The SHG relative efficiency of B2AM was measured by Kurtz and Perry powder technique using Nd: YAG laser and it is found to be 4.2 times that of KDP, which is higher than the other maleate crystals.

The third chapter investigates the physico-chemical characterization analysis of single crystals of organic NLO material γ-glycine grown from aqueous solution of glycine and lithium acetate. The γ-phase was confirmed by single crystal XRD and powder XRD analysis. Presence of various functional groups was identified by FTIR spectrum analysis. HRXRD studies indicate that the crystalline perfection of γ-glycine crystal is very good. Thermal analysis was performed to study the thermal stability of the grown crystals. The dielectric properties of the crystals were determined. The microhardness measurements at different loads show that as–grown crystal exhibits the reverse indentation size effect in which the hardness value increases with the increasing load. The optical analysis shows that UV cutoff wavelength of γ-glycine is at 240 nm and it has a wide transparency window. The SHG efficiency of the grown crystal was observed to be 3.4 times that of KDP.

Semiorganic NLO single crystals of tris(glycine) calcium(II) dichloride (TGCC) were successfully grown by slow evaporation technique. The chapter four deals the growth and characterization of TGCC crystals. The presence of calcium and chlorine in the crystals was confirmed by EDX analysis. TGCC crystal belongs to the orthorhombic system with space group Pb2_1a. Morphology of the grown crystals was identified by the single crystal X-ray diffraction studies. The solubility and metastable zone width studies of
TGCC reveals that solubility increases with temperature and metastable zone width decreases with increasing temperature. HRXRD analysis substantiates the good crystalline perfection of the as–grown TGCC crystal. Thermal characteristics of TGCC were determined. Chemical etching analysis of TGCC crystal suggests four fold rotational symmetry of the (001) plane. The reverse indentation size effect on the (001) plane on TGCC crystal was confirmed from mechanical studies. Dielectric measurements indicate that TGCC crystal has low values of dielectric constant and dielectric loss. Optical studies reveal that TGCC crystals have good transmission window. The SHG relative efficiency of TGCC was found to be 1.5 times that of KDP.

The synthesis and growth of NLO bis(2-aminopyridinium) sulfate (B2APS) single crystals by slow solvent evaporation technique are discussed in fifth chapter. The solubility and metastable zone width were determined. Single crystal X-ray diffraction studies indicate that the crystal belongs to the orthorhombic system with space group Fdd2. Powder X-ray diffraction studies of B2APS was conducted and the powder XRD pattern was indexed. Morphology of the B2APS crystal establishes that the crystals have 8 developed faces out of which (010) and (0ã0) are prominent. The high-resolution diffraction curve recorded for B2APS single crystal using (222) diffracting planes contains a single peak and indicates that the specimen is free from structural grain boundaries. Single diffraction curve with reasonably low FWHM (19 arc s) indicates that the crystalline perfection is fairly good. Thermal studies show that B2APS crystal melts at 210 ºC. The dielectric constant and dielectric loss of B2APS crystal at different frequencies and temperatures were determined. Mechanical studies reveal that Vickers microhardness number increases with applied load. Chemical etching analysis on (010) face of the crystal suggests two fold rotational symmetry of the face. Linear optical spectrum elucidates that B2APS crystal has good
transmission window between 353 and 1100 nm. The SHG relative efficiency of B2APS was found to be 2.6 times that of KDP.

The chapter six focuses on the growth of KDP crystal doped with potassium carbonate (K\textsubscript{2}CO\textsubscript{3}) as a new additive in different molar ratios using microcontroller based seed rotation technique. The metastable zone width of KDP solution with 5 mol% K\textsubscript{2}CO\textsubscript{3} was determined and compared with the pure system. A good quality 5 mol% doped KDP crystal of size 45 × 25 × 15 mm\textsuperscript{3} was grown by the slow cooling method from aqueous solution by the rotation of the seed crystal with the in-house built rotation assembly. Dielectric measurements were carried out on pure and doped KDP crystals at various temperatures in the range 313–423 K by the parallel plate capacitor method and it indicates that 5 mol% K\textsubscript{2}CO\textsubscript{3} addition leads to low dielectric constant value dielectrics. The addition of 5 mol% K\textsubscript{2}CO\textsubscript{3} and proper rotation of seed crystal (40 rpm) improves the quality of the crystal. The HRXRD analysis shows that the crystalline perfection of the crystal grown in these optimum conditions is extremely good without having any internal structural grain boundaries and mosaic nature. The crystals grown in these optimum conditions show positive effect in the various characterization techniques. The transmission spectrum reveals that the crystal has sufficient transmission in the entire visible and IR region. A positive effect is observed in the nonlinear optical properties like powder SHG and laser damage threshold. The piezoelectric coefficient (d\textsubscript{33}) value of 5 mol% K\textsubscript{2}CO\textsubscript{3} doped KDP crystal was found to be 1.6 times that of pure KDP crystal.

The effect of the addition of potassium thiocyanate (KSCN) in different molar concentrations on KDP crystals, grown from aqueous solution by the temperature lowering method using seed rotation technique was discussed in seventh chapter. Nucleation studies show that the additive enhances the metastable zone width and the induction period of pure KDP.
The addition of KSCN can make KDP solution more stable and increase the growth rate of KDP crystals. The absence of additional peaks in the powder XRD spectrum of doped KDP crystals shows the absence of any additional phases due to doping. Dielectric measurements were carried out on pure and doped crystals at various temperatures in the range 313–423 K and compared. The crystalline perfection of the grown crystal was studied by HRXRD analysis. The optimum addition of dopant increases the SHG conversion efficiency and optical transparency of pure KDP crystals.

The chapter eight discusses the growth of ADP crystals with amino acid materials L-arginine monohydrochloride (LAHCl) and L-alanine as new additives in different molar concentrations. It is found that these additives effect the nucleation of ADP from aqueous solutions. The addition of these amino acids enhances the metastable zone width and induction period of pure ADP. Also, during the experiment it was observed that the number of tiny crystals formed by spontaneous nucleation was appreciably reduced in the case of doped solution. It is believed that the addition of these amino acid materials suppresses the activities of the metal ion impurities present in the solution which enables larger metastable zone width and faster growth rate. X-ray powder diffraction patterns of pure ADP and doped ADP crystals are identical without any additional peaks showing the absence of any additional phases due to doping. The FTIR spectrum shows that amino acid additives have entered into the ADP crystals. The high-resolution X-ray diffraction curves recorded for 5 mol% amino acid additives doped crystals show that the crystals are having excellent crystalline perfection. The transmission spectrum reveals that the crystal has sufficient transmission in the entire visible and IR region. Dielectric measurements of pure and doped ADP crystals shows that LAHCl and L-alanine doped ADP crystals have lower values of $\varepsilon_r$ and dielectric loss compared to pure. It was observed that measured SHG
efficiency and piezoelectric coefficient of doped ADP crystals are higher than that of pure ADP crystal.

9.2 SUGGESTIONS FOR FUTURE WORK

The synthesis and crystal growth of other 2-aminopyridinium and glycine derivatives can be attempted. The crystal structures are available in literature for compounds that contain both a 2-aminopyridine and a carboxylic acid moiety. In these ionic compounds, proton transfer occurring to the aromatic nitrogen of the 2-aminopyridine moiety. The bulk growth of these materials is not reported so far. These materials should be interesting candidates for NLO applications due to their large SHG efficiency. These materials can be grown as usable size crystals. Design of new semiorganic materials with glycine as the organic host molecule can be attempted. For example, complexes of glycine with rare earth metal halides are interesting materials for nonlinear applications. The other glycine calcium halide crystals can be attempted. The bulk growth of these crystals is not reported in literature so far.

The nucleation parameters in addition to solubility and metastable zone width of B2AM, γ-glycine, TGCC and B2APS crystals can be investigated. FT-Raman and NMR spectra of the grown crystals may be studied. The excitation and emission spectra of B2AM, B2APS and TGCC single crystals can be identified by the photoluminescence studies of the same. The grown crystals may be subjected to the refractive index measurements for different wavelengths.

SHG optical elements can be fabricated from grown KDP and ADP crystals doped in optimized conditions and their energy conversion efficiency can be determined. Attempts can be made to optimize and grow KDP and ADP crystals with other amino acid additives in different molar
concentrations. The effect of these additives on the growth and properties of parent materials can be studied. The grown crystals can be subjected to various studies like phase matching, laser damage threshold, birefringence studies etc., which may lead to very interesting results.