ABSTRACT

With the advent of electronic devices, use of crystals became inevitable for developments in modern technology. Advances in solid-state physics have been responsible for the development of a wide range of crystals. Crystal growth has now been identified as a thrust area among the major areas of science and technology. This became true after the discovery of novel materials which bridge the gap between pure technology and their applications to human life. Crystals find applications in electronics, lasers, light valves, laser communication devices, light emitting diode (LED), thermal imaging, pyroelectric detectors, X-ray spectroscopy, etc. Large crystals are usually essential for device fabrication and it must be possible to grow crystals of good optical quality for utilization. Efforts are made to grow large crystals in short duration by fast growth techniques. Crystal growth techniques play a significant role in the development of many solid-state devices.

The developments of nonlinear optical (NLO) phenomena in crystals because possible only after the invention of laser. Now, NLO have been recognized for several decades as a promising field with important applications in the area of optoelectronics, photonics, memory devices, etc. High performance electro-optical switching elements for telecommunications and optical information processing are based on material properties. Hence, there is always a continuous search for new and better NLO materials. The goal is to find and develop materials presenting large nonlinearities, satisfying at the same time all the technological requirements for applications such as wide transparency range, fast response, high damage threshold, processability,
adaptability and interfacing with other materials. Hence efforts are being made recently towards producing new and efficient frequency conversion material. In this context of NLO, organic crystals possessing NLO properties which far surpass those of inorganic materials have been attractive for potential device applications. However because of the difficulty in growing bulk crystals of organic material, investigations on semiorganic NLO materials have been intensified.

From the stand-point of the search for newer NLO materials, amino acids offer a rich choice. All amino acids have a proton-donating carboxyl and the proton-accepting amino groups. Several new complexes incorporating the amino acid with different organic / inorganic acids are developed and are found to be very suitable for a number of NLO applications.

This thesis consists of nine chapters. The first chapter gives a brief introduction to crystal growth techniques and in particular, growth from solution. Overview of historical perspectives of nonlinear optical phenomena and criteria for NLO crystals are also discussed in this chapter. A discussion on new NLO materials built from organic, semiorganic and inorganic materials and their applications is also included in this chapter. The importance of amino acids as NLO materials has also been explored in chapter 1. Finally, an outline of work undertaken as research is discussed. The research is centred on the amino acid family, among which salts of β-alanine, L-leucine, L-cystine, L-phenylalanine, L-valine and glycine are chosen for study.

The second chapter deals briefly with the various analytical instrumentation techniques which are the backbone of crystal research
engineering. A discussion of the experimental techniques such as single crystal X-ray diffraction, powder X-ray diffraction, spectroscopic analysis like AAS, FTIR, FT Raman, FT NMR, CHNs, and ICP-OES is included. The basic principles of UV-Vis-NIR analysis and Kurtz powder SHG studies are also discussed. The principles and instrumentation technique of analyses like TGA, DTA and DSC have been included. Etching studies is also discussed to assess the perfection of the grown crystal. Finally, the experimental techniques of dielectric, Vickers hardness and laser damage threshold measurements are also presented.

The third chapter presents details of single crystal growth and characterization of an organic NLO crystal L-Leucinium Oxalate (LLO). Bulk form of the organic crystal (21 mm × 5 mm × 1 mm) has been obtained by using solution growth technique. The crystal data for the grown LLO crystal are determined by X-ray diffraction analysis. The powder XRD has also been used to confirm the crystal parameters of the LLO crystals. The confirmations of the functional groups in grown crystal by using spectral analyses like FTIR, FT NMR and CHNs have also been discussed. The optical behaviour of the crystal has been studied by using UV-Visible spectroscopy. The thermal stability and decomposition of the crystal are studied by TGA, DTA and DSC. LLO exhibits NLO behaviour and the efficiency is determined. The LLO crystals have excellent mechanical properties. The grown LLO crystal is also subjected to etching analysis. The dielectric behaviour of the crystal has been studied at room temperature in the frequency range from 70 Hz to 5 MHz. Laser damage threshold value of the LLO has also been measured using Nd:YAG laser.
In the **fourth chapter**, growth and characterization of new organic NLO material, L-Phenylalaninium Maleate (LPM), are discussed. Transparent, needle shaped crystal of dimensions 7 mm × 1 mm × 0.5 mm are obtained by solution growth technique. This organic crystal can be used as a potential candidate for second harmonic generation. The growth conditions are optimized and the crystals are obtained. The single crystal XRD and powder XRD studies confirm its crystalline nature. The functional groups present in the grown crystal are confirmed by FTIR, FT Raman, FT NMR and CHNs analyses. Etching analysis of the grown LPM crystal has also been carried out. The thermal stability of the crystal is analyzed with the aid of TGA-DTG and DSC analyses. The laser damage threshold value and SHG efficiency are also determined using an Nd:YAG laser.

The **fifth chapter** presents the study of the new semiorganic NLO crystal L-Cystine Dihydrobromide. The crystal is successfully grown from aqueous solutions by slow evaporation method. Bulk sized crystals are grown and the SHG efficiency is found to be 0.38 times of the standard KDP crystal. The grown crystals are characterized by single crystal and powder X-ray diffraction analysis. Spectroscopic studies like FTIR and FT Raman are carried out and confirm the various functional groups present in the crystal. Optical behaviour of the crystal has also been investigated using UV-Visible spectroscopy. Laser damage threshold value has been measured. The mechanical strength and thermal stability of the grown crystal have been determined with the aid of Vickers hardness test and thermal analysis like TGA-DTA and DSC respectively.
Chapter six is devoted to the study of a new semiorganic crystal β-alanine zinc chloride grown by solution growth technique. It is a metal complex of amino acid. The structure of β-alanine zinc chloride is solved by direct methods and refined by a full-matrix least squares procedure based on 3172 reflections. SHELXS-97 and SHELXL-97 are applied. The R factor is determined as 0.0616. The confirmation of the structure of the grown crystal is carried out by powder XRD, FTIR, FTRaman, FT NMR, CHNs and AAS analyses. The thermal, optical and mechanical properties are also discussed in this chapter. Its SHG efficiency is 0.71 times of the standard KDP crystal. A study of another metal complex of β-alanine (i.e.) β-alanine cadmium chloride grown from aqueous solution is also presented in this chapter. The properties of the β-alanine cadmium chloride crystal are compared with β-alanine zinc chloride. Etching analyses are carried out on both crystals. Laser damage threshold have been determined at single shot mode for both crystals and reported in this chapter.

Chapter seven is devoted to an amino acid crystal, glycine, in its γ-polymorphic form which is grown from aqueous solution in the presence of strontium chloride. This crystallizes in perfect hexagonal morphology which is easily seen from the bulk growth of the crystal. Single crystal X-Ray diffraction analysis is used to measure the unit cell parameters. The grown crystals have also been subjected to powder X-ray diffraction study to identify the crystalline nature. The FTIR spectrum indicates the presence of all functional groups in the grown crystal. The confirmation of the molecular structure of γ-glycine by FT NMR study is also discussed in this chapter. The UV-Vis analysis indicates the wide transparency of the crystal. The phase
transition from $\gamma$ to $\alpha$ is found to take place at 192.3 °C, which is higher than the $\gamma$-glycine crystal grown in the presence of NaCl and KCl. Its mechanical strength is higher than that of crystals reported already. Surface morphology of the crystal is characterized by chemical etching. SHG efficiency is higher than that of KDP crystal. Though the XRD studies do not indicate the presence of strontium in the crystal, ICP-OES study confirms the presence of strontium in a minute quantity. The dielectric behaviour of the crystal has been determined at room temperature in the frequency range of 50 Hz to 5 MHz. Laser damage threshold value has been determined using Q-switched Nd:YAG laser operating at 1064 nm and with 13 ns pulse width in single shot mode.

Chapter eight presents the growth of L-valine grown in water and orthophosphoric acid as solvent. The phosphoric acid is used the solvent for better growth of crystals. The crystal structure of L-valine is determined by single crystal XRD and also powder XRD methods. The spectroscopic studies like FTIR are carried out to identify functional groups the grown crystals. The optical property of the grown crystal has been studied using the UV-Vis analysis. Hardness, etching and laser damage threshold have also been carried out on the grown crystals. The thermal properties of the grown crystal are also determined. The SHG efficiency has also been determined.

The ninth chapter summarizes the results of the present investigations and goes a step further by listing out the possible future work on these compounds.

The results of the above investigations have been published in the International journals and also presented in various national conferences.