ABSTRACT

The applications of ultraviolet (UV) lasers in the fields like optical data storage, telecommunications, medical diagnostics and entertainment have increased in higher quantum in the recent years. The nonlinear optical crystals act as the best alternative to excimer lasers for the production of UV laser frequencies, since the usage of excimer lasers pose great complications in usage and involve corrosive gases. Several nonlinear optical (NLO) single crystals based on semi-organics are being worked world-wide by several research groups.

The present thesis consists of six chapters. A brief review on semi-organic amino acid halide single crystals employed in NLO applications is summarized. An introduction to Non-linear optics, amino acids and semi-organic crystals is given. The crystal growth techniques involved in the present investigations are discussed.

The growth of L-glutamic acid hydro chloride (L-gluHCl) crystals, from low temperature solution growth has been carried out and characterization studies were performed. The synthesis of L-gluHCl polycrystalline material was done and confirmed through powder X-ray diffraction (XRD) analysis. The growth of L-gluHCl single crystals was carried out from the Petri dish. L-gluHCl single crystals with good dimensions were obtained. Solubility of L-gluHCl in water was determined. The grown L-gluHCl single crystals were characterized by using powder X-ray diffraction studies. The lattice parameters of the grown crystals were identified by single crystal X-ray diffraction. The cutoff wavelength of the L-gluHCl crystal is around 235 nm. FTIR and Raman analysis were
performed for the as grown L-gluHCl crystal and its functional group assignments were carried out. The FTIR and Raman spectrum of the crystal revealed the presence of the necessary bond vibrations in the L-gluHCl compound. Vicker’s micro-hardness studies were performed for the as grown crystals of L-gluHCl. High resolution X-ray rocking curves were recorded for as grown L-gluHCl and from its FWHM value the crystalline quality of the grown crystals was determined. Etching studies were carried out for the L-gluHCl crystal. The etching time was 3 s and 5 s. ‘Pit-like’ patterns were observed on the etched L-gluHCl crystal and the crystal possesses step growth pattern. The Kurtz powder SHG test performed on the L-gluHCl crystal revealed that the crystal has the SHG efficiency similar to that of KDP.

The growth of Tu doped L-gluHCl was carried out and the characterisation was performed. The crystals were grown by solvent evaporation method and the crystals were harvested after a week’s time. As grown thiourea doped L-gluHCl crystals were also found to be transparent and slightly hygroscopic in nature. Powder X-ray diffraction pattern was recorded for the as grown sample. The Tu: L-gluHCl sample is subjected to FTIR analysis to determine the bond vibrations of the compound. From EDAX analysis it is determined that 0.05 weight percentage of thiourea is incorporated in the L-gluHCl crystal. From the UV-Vis-NIR spectral analysis, it is observed that the transparency of the Tu: L-gluHCl single crystals decrease due to the presence of thiourea and it retains the cutoff at 235 nm. The high resolution x-ray diffraction (HRXRD) studies revealed the crystalline perfection of the crystals (FWHM=28 arc s). Vicker’s micro-hardness study was carried out and from the results it is observed that the hardness ($H_v$) is decreased compared to pure L-gluHCl crystal. Powder SHG
test was carried out by using the Kurtz-Perry technique. Thiourea doped L-glutamic acid hydrochloride crystals were found to possess SHG, and the SHG efficiency is similar to that of pure L-gluHCl crystal. In this experiment potassium di hydrogen phosphate (KDP) was used as the reference material. Thiourea doped L-gluHCl crystals were also subjected to etching analysis and it is observed that the crystal possesses step growth pattern which is analogous to the pure L-gluHCl crystal.

The synthesis and growth of L-glutamic acid hydrobromide (L-gluHBr) crystals from low temperature solution growth was carried out and characterization studies were performed. The synthesis of L-GluHBr material was confirmed by FTIR analysis, the bond vibrations in L-gluHBr compound was determined and their peak positions were assigned. Solubility of L-gluHBr in water was determined in the temperature range 30 °C to 50 °C. L-gluHBr single crystals with the good dimensions were obtained. The lattice parameters of L-gluHBr crystals were identified using single crystal X-ray diffraction analysis. Reflections from a few planes were collected and the morphology of the grown crystal is determined. Bond angle, bond length and atomic co-ordinates of the L-gluHBr were also determined. From the HRXRD analysis, it is observed that the grown crystals are of good quality with the FWHM value of 25 arc s. From the UV-Vis-NIR studies, the lower cutoff wavelength of the L-gluHBr crystal is around 260 nm and the long wave length cutoff is around 1580 nm. Dielectric studies for the as grown crystals of L-gluHBr were carried out in the frequency range of 50 Hz to 500000 Hz, at different temperatures ranging from 35 °C to 95 °C and the effects are studied. From etching analysis, it is found that the crystal possesses step growth pattern. Vicker’s micro-hardness analysis shows that the hardness
number increases with increase in the indenter load. The Kurtz powder SHG test was carried out for the L-gluHBr crystal and it is observed that the crystal is NLO active.

The growth of L-gluHCl and L-gluHBr crystals was carried out by using the novel uniaxial crystal growth method of Sankaranarayanan and Ramasamy (SR). A brief review on SR method and its importance in growing technologically important crystals are given in this chapter. The L-gluHCl single crystal was grown by SR method with slight modifications in the growth apparatus. A brief discussion is given on the experimental setup and growth of the material. The crystalline perfections of the crystals were analyzed by HRXRD studies (for L-gluHCl, FWHM=6 arc s; for L-gluHBr, FWHM=22 arc s) and the results are presented. From the TG/DTA analysis, it is observed that both the crystals are stable up to 200°C and decomposes on further increase in temperature. UV-Vis-NIR spectrum was recorded for the SR method grown crystals and the results are compared to that of conventionally grown crystals. Dielectric studies and specific heat measurements were carried out for SR grown L-gluHCl single crystals and the results are presented. Vickers hardness measurements and etching analysis were carried out for the as grown samples of SR grown L-gluHCl and SR grown L-gluHBr and the results are presented.

The summary of the present investigations and the suggestions for future works are also discussed and presented.