CHAPTER – VIII

SUMMARY, CONCLUSION AND FUTURE SCOPE

8.1 Introduction

Most of the complexes of amino acids are the nonlinear optical (NLO) materials which have the varieties of applications in connection with optical communication, optical computing, optical data processing and photonics. Amino acids and inorganic materials like cadmium sulphate, cadmium chloride, zinc sulphate, zinc chloride etc can be combined to form amino acid based metal organic crystals and these are also called as the semi-organic NLO materials and they have both the advantages of organic amino acids and inorganic metal complex salts. In this work, the amino acids like L-alanine or L-proline were considered to combine with cadmium chloride to synthesize metal organic NLO crystals like L-alanine cadmium chloride (LACC) and L-proline cadmium chloride (LPCC) crystals. To improve the physico-chemical properties of these crystals, organic materials like glycine, thiourea and L-tartaric acid were used as the dopants. Single crystals of pure and glycine or thiourea doped LACC and pure and L-tartaric acid doped LPCC were grown by solution method and the grown crystals were characterized by experimental studies.

8.2 Summary and conclusions

A total number of 10 samples were synthesized and single crystals of pure and doped L-alanine cadmium chloride and L-proline cadmium chloride were grown by solution method with slow evaporation technique. Saturated solutions of the synthesized salts were prepared and taken in the growth vessels for crystallization by slow evaporation using a constant temperature bath. Growth period for all the crystals is 20-30 days. The grown crystals are non-hygroscopic, stable, colourless and
transparent. The external appearance of undoped LACC and LPCC crystals seems to be different when compared to that of the doped crystals.

Nucleation kinetic studies were carried out for the samples to understand the nucleation process. It is noticed that adding dopants into the samples has affected the nucleation process and hence the induction period and the nucleation parameters of the grown samples are altered compared to that of pure LACC and LPCC crystals. The critical nucleation parameters such as Gibbs free energy change, nucleation rate, radius of critical nucleus, number of molecules in the critical nucleus of the samples have been determined by classical nucleation kinetic theory and the results were analyzed. Solubility studies in the temperature range 30 °C – 50 °C for the samples were done and it is found that solubility increases with increase in temperature and the samples show positive temperature coefficient of solubility. The solubility values of LACC and LPCC samples have been altered when LACC crystals are doped with glycine and thiourea and LPCC crystals are doped with L-tartaric acid.

The crystal lattice constants were obtained by XRD studies and from the results it is observed that the undoped (pure), glycine or thiourea doped L-alanine cadmium chloride (LACC) crystals crystallize in monoclinic structure and pure and L-tartaric acid doped L-proline cadmium chloride (LPCC) crystals crystallize in the orthorhombic structure. XRD results show that the lattice parameters are slightly altered when LACC and LPCC crystals are doped with organic dopants like glycine, thiourea and L-tartaric acid. The values of density of the grown crystals were found by floatation method and changes in the values of density of LACC and LPCC crystals indicate the dopants have entered into the host crystals.

UV-visible transmittance spectra of the samples were recorded using a Varian Cary 5E UV-Vis-NIR spectrophotometer in the range 200-1100 nm. From the
transmittance spectra, it is noticed that pure and doped LACC and LPCC crystals have
good transparency in visible region and hence they are useful in nonlinear optical
applications. The pure and glycine or thiourea doped LACC crystals are observed to
have the UV cut-off wavelength around 235-238 and the optical band gap values for
the samples have been determined. Linear optical constants such as reflectance (R),
refractive index (n) and extinction coefficient (k) were determined from the data of
optical transmittance. The values of reflectance, refractive index, extinction coefficient
of the samples have been altered when LACC and LPCC crystals are doped with
glycine, thiourea and L-tartaric acid. Second harmonic generation (SHG) efficiency
was measured for the samples by the Kurtz-Perry powder technique. SHG is
confirmed by emission of green light from the samples when the fundamental
wavelength from Nd:YAG laser is used. From the results, it is observed that when
LACC crystals are doped with glycine, a centrosymmetric material, the values of
SHG efficiency decrease. The SHG results show that the thiourea doped LACC
crystals and L-tartaric acid doped LPCC crystals have more SHG efficiency
compared to that of host crystals.

Fourier transform IR spectra of pure and doped LACC and LPCC crystals
were recorded in the range 400-4000 cm$^{-1}$ employing a Perkin-Elmer spectrometer in
the form of solid dispersed in KBr pellet technique. From the results, it is observed that
NH$_2$ groups of L-alanine and L-proline molecules in the samples are protonated
by COOH group giving rise to NH$_3^+$, the broad envelope in the higher wave number
region between 3400 and 2900 cm$^{-1}$. The functional groups such as NH$_3^+$, OH, COO,
CH$_2$, CCN, C-C etc present in the samples have been identified by FTIR studies.

Laser damage threshold (LDT) studies for the samples were carried out using
an Nd:YAG laser (1064 nm, 18 ns pulse width). From the results, it is observed that
the values of laser damage threshold are more for the glycine doped LACC crystals and LDT values are low for the thiourea doped LACC crystals than that of undoped LACC crystal. The results show that L-tartaric acid doped LPCC crystal has more than that of pure L-tartaric acid.

Dielectric constant, dielectric loss and hence AC conductivity values were measured using an LCR meter at different frequencies and temperatures. High values of dielectric constant and loss factor at low frequencies are observed for all the samples of this work and this may be due to presence of space charge polarization. The dielectric parameters like dielectric constant and dielectric loss factor are found to be decreasing with increase of frequency and these values are observed to be increasing with increase of temperature of the samples. Doping of LACC with glycine and thiourea and LPCC crystals with L-tartaric acid is found to increase dielectric constant and loss factor appreciably. The low value of dielectric loss at high frequency reveals the high optical quality of the crystals with lesser defects, which is the desirable property for NLO applications. AC conductivity values of the samples have been determined using the data of dielectric constant and loss factor and the results show that the conductivity increases when LACC and LPCC crystals are doped with the organic dopants like glycine, thiourea and L-tartaric acid. Using the values of conductivity, activation energy has been calculated for all the samples and the activation energy of the doped crystals is found to be low compared to that of pure LACC and LPCC crystals. The impedance data were obtained for the samples at different frequencies and temperatures using an impedance analyser. The results show that the real part and imaginary part of impedance of the samples decrease with increase of frequency and with increase of temperature. The decrease of impedance with increase of temperature of the samples indicates the negative temperature
coefficient of resistance behavior. The relaxation frequency has been calculated for the samples and the values indicate that the relaxation frequency increases as the temperature of the samples increases.

Third order nonlinear parameters like nonlinear refractive index, nonlinear absorption and third order susceptibility were found by Z-scan technique for pure and doped samples of LACC and LPCC. Microhardness studies have been carried out for the grown samples and the results proved that all the crystals obey reverse indentation size effect. The mechanical parameters like hardness, work hardening coefficient, stiffness constant and yield strength of the samples have been determined. The photoconductivity studies for the grown crystals were carried out by measuring dark and photo currents at different applied electric fields. It is noticed that the values of dark current and photo current increase with increase of applied electric field. The pure LACC and LPCC crystals have negative photoconductivity because photo current is less than dark current and the similar behavior is also observed for the doped LACC and LPCC crystals. The melting point/decomposition point values of the grown crystals have measured using a melting point apparatus and results show that the decomposition point of the doped samples are more than that of the undoped LACC and LPCC samples.

8.3 Suggestions for the future work

In this work, the single crystals of pure and doped LACC and LPCC crystals were grown by solution method and in the future these crystals will be grown by unidirectional crystal growth method (S-R method of growth). Also the samples of this work will be grown by other methods like gel method, slow cooling method etc. LACC and LPCC crystals could be grown by adding other suitable dopants like rare earth elements dyes to improve the NLO properties. Etching studies can be made on
different crystallographic faces of the crystals with suitable etchants in order to identify the dislocations. SEM, HRXRD and etching studies could be carried out for the samples in the future. Effects of gamma ray irradiation and X-ray irradiation on the samples can be investigated. The impedance parameters like admittance, electric modulus, complex permittivity, complex conductivity of the samples could be analyzed. Phase matching and higher harmonic generation studies for the samples can be carried out in the future. The grown NLO crystals of this work could be used in second-order, third-order NLO devices and in the development of other nonlinear optical devices.