CHAPTER 7

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

7.1 SUMMARY

A Satisfactory study on the synthesis, growth and characterisation of promising organic crystals like L-asparaginium picrate (LASP), Dimethyl aminopyridinium 4-nitrophenolate 4-nitrophenol (DMAPNP), L-valinium picrate (LVAP), L-argininium-4 nitro phenolate monohydrate (LAPM), N(-2 Chlorophenyl) 1-Propanamide (NCP) and Benzaldehyde 4 Nitro Phenyl Hydrazone crystals was made.

Single crystals of L-asparaginium picrate have been successfully grown by slow cooling solution growth technique. From the HRXRD results the incorporation of solvent into the growing crystal is elucidated which is common in solution grown crystal, is responsible for the very low angle boundaries. The occurrence of $\pi-\pi^*$ transition in the carboxyl group accounts for the nonlinearity in the title crystal. From FTIR spectrum, it is established that the presence of intermolecular hydrogen bonding which could enhance the nonlinear property of the material and it is found that picric acid necessarily protonates the carboxyl group. The morphology unveils the growth habits of the material. L-asparagine exhibits tautomerism due to weak intramolecular hydrogen bonding between OH group and imine N atom. Density functional theory calculations were performed for LASP crystal to evaluate the first order hyperpolarizability value. The calculated first order
hyperpolarisability of L-asparaginium picrate was found to be very high of
the order of $4.8152 \times 10^{-29}$ esu. It is due to the $\pi$-electron cloud movement
from donor to acceptor which makes the molecule highly polarized and the
intermolecular charge transfer interaction which is justified by the FTIR
spectrum. The theoretical factor group analysis of LASP predicts 216 total
vibrational optical modes that decompose into $\Gamma_{\text{total}} = 107A + 106B$ modes
among which three acoustic modes $\Gamma_{\text{acou}} = A + 2B$ are included that
correspond to the block transitions of the crystal. From the powder SHG
efficiency studies, it is clearly ascertained that LASP relatively ostentates
very high efficiency than KDP, Urea counterparts and its parent compounds.
The dielectric constant is drastically increased due to irradiation. The third
order nonlinear optical properties of LASP crystals were studied by Z-scan
technique using a 532 nm diode-pumped Nd:YAG laser. The measured
nonlinear refraction index coefficient ($n_2$), nonlinear absorption coefficient ($\beta$)
and susceptibility ($\chi^{(3)}$) are $-8.61 \times 10^{-8}$ cm$^2$/W, $-6.60 \times 10^{-3}$ cm/W
and $9.5 \times 10^{-5}$ esu respectively. The nonlinear absorption is due to saturable
absorption process while the nonlinear refraction leads to self-defocusing.

Single crystals of L-valinium picrate have been successfully grown
by slow evaporation solution growth technique. The morphology unveils the
growth habits of the material. The second order nonlinear optical properties of
LVAP crystals were demonstrated by quantum chemical calculations and also
by Kurtz and Perry powder SHG studies. The first order hyperpolarisability
($\beta$) of LVAP crystals were found to be $1.050 \times 10^{-29}$ esu using HF3-21G basis
set. Planar molecular structure and better conditions for electron conjugation
and charge transfer result in larger values of $\beta$ for this title crystal also. The
results of theoretical calculations are substantiated with powder SHG results.
The SHG efficiency results show a very high signal output of 1.3 V with input
laser power of 1.9 mJ/pulse when compared to just 9 mV of KDP.
A satisfactory study on the behaviour of dielectric constant, dielectric loss and ac conductivity of LVAP on the effect of irradiation was carried out. The effect of Ag$^{8+}$ and Si$^{8+}$ ion irradiation on LVAP can be summarized as follows:

The changes produced due to irradiation are dependent on the electronic energy loss. The dielectric constant is drastically increased. This could be due to breakdown of open hydrogen bonded network resulting in release of hydrogen. Increase in the dielectric constant makes the title crystal a better entrant for electro-optic modulators. Conductivity (ac) strongly depends on frequency. At high frequencies, the conductivity increases which is supported by the decrease in dielectric constant at high frequencies. There is a decrease in optical transmission irradiated crystals accounted by decrease in the optical bandgap. There is a slight enhancement in the efficiency of the irradiated crystals at low input energy.

The Novel second order NLO material DMAPNP has been grown successfully. From the molecular structure of DMAPNP, it is inferred that the main component of the crystal to provide enhanced NLO efficiency is due to p-nitrophenol. The thermal analysis recommends that the material can be placed for any application below 128 °C. The measured laser damage for the grown crystal was 2.24 GW/cm². The calculated first order hyperpolarisability of DMAPNP was found to be very high of the order of $9.53 \times 10^{-30}$ esu which is nearly 49 times that of Urea. It is due to the $\pi$-electron cloud movement from donor to acceptor that makes the molecule highly polarized and the intermolecular charge transfer interaction which is justified by the FTIR spectrum. The formal classification of fundamental mode predicts 564 internal vibrations which can be distributed as $(141A + 141B_1 + 141B_2 + 141B_3)$ and 24 external modes such as $(3A+3B_1+3B_2+3B_3)$ translational, $(3A+3B_1+3B_2+3B_3)$ vibrational and $(B_1+B_2+B_3)$ acoustic modes. The effect
of Ag\(^{8+}\) and Si\(^{8+}\) ion irradiation on DMAPNP can be concluded as follows. The changes produced due to irradiation are dependant on the electronic energy loss. The dielectric constant is drastically increased. This could be due to breakdown of open hydrogen bonded network resulting in release of hydrogen. More increase in dielectric constant is envisioned due to Ag\(^{8+}\) ion irradiation than Si\(^{8+}\) ion irradiation and due to high fluence than low fluence of irradiation. Increase in the dielectric constant makes the title crystal a better entrant for electro-optic modulators. Conductivity (ac) strongly depends on frequency. At high frequencies, the conductivity increases which is supported by decrease in dielectric constant at high frequencies. Dielectric constant, and conductivity increase with increasing fluence of both Ag\(^{8+}\) and Si\(^{8+}\) ions. There is a slight enhancement in the efficiency of the irradiated crystals at low input energy. With high input energy, the SHG signal output decreases than the pristine crystals indicating the decrease in Laser damage threshold due to irradiation. Based on these facts it could be proposed that this material can be better accommodated for second order non-linear optical applications.

Optical quality single crystals of LAPM were grown by solution growth technique and the structure is reported for the first time in the literature. The morphology unveils the growth habits of the material. The second order nonlinear optical properties of LAPM crystals were demonstrated by quantum chemical calculations and also by Kurtz and Perry powder SHG studies. The first order hyperpolarisability (β) of LAPM crystals were found to be \(9.002 \times 10^{-29}\) esu using HF3-21G basis set. Planar molecular structure and better conditions for electron conjugation and charge transfer result in larger values of β for this title crystal. The results of theoretical calculations are substantiated with powder SHG results. The SHG efficiency results show a high signal output of 312 mV with input laser power of 1.9 mJ/pulse when compared to just 9mV of KDP. From FTIR spectrum, it is
established that the presence of intermolecular hydrogen bonding which could enhance the nonlinear property of the material.

Good quality transparent crystals of N-(2 Chlorophenyl)-(1-Propanamide) were grown by slow cooling solution growth technique. From the crystal structure it is evident that carbonyl group is protonated. Hence, $\pi-\pi^*$ transition occurs in the carbonyl group, which may give rise to the NLO properties in this type of complex of NCP. The dielectric studies reveal that dielectric constant decreases ceaselessly with increase in frequency succeeded with a frequency independent behavior at high frequencies. The useful transmission range makes NCP valuable for applications that require blue-green light. The Damage threshold studies disclose that the damage threshold of NCP is many a time higher than KDP but many times less than BBO and more or less equal to that of BMZ. The drastic increase in dielectric constant of NCP crystals after ion irradiation may be correlated to the defects created along the ion tracks and the structural modifications induced in the surrounding regions.

The Benzaldehyde 4-nitro phenyl hydrazone was synthesised and grown by slow cooling solution growth technique. The structural properties of single crystals of BPH have been studied by powder X-ray diffraction technique. SHG signal energy output for BPH with that of standard KDP and Urea shows a high efficiency of BPH crystals than KDP and Urea counterparts.

### 7.2 SUGGESTIONS FOR FUTURE WORK

In the present investigation a preliminary report on the effect of irradiation on organic nonlinear optical crystals have been presented. Further characterisation studies like Photoluminescence, AFM and SEM can be
performed for defect analysis and surface modifications. The possibility of waveguide like propagation in the irradiated crystals can be performed by measuring the refractive index. New class of compounds of picrates can be synthesised by reacting picric acid with various amino acids like L-Leucine, Glycine etc.