Chapter 9
Summary

In recent years, lot of attention has been paid to grow novel and high quality nonlinear optical (NLO) crystals, especially organic and semi-organic crystals, since these crystals generate highly efficient second harmonic blue-violet light in laser diodes. Therefore in the present work attempts have been made to synthesis, grow and investigate the physicochemical properties of some promising organic and semi-organic NLO crystals. The organic NLO crystals of 4-nitrophenyl hydrazone and 3-[(1-(2-phenylhydrazinylidene)ethyl]-2H-chromen-2-one, organic NLO crystals of pure L-alanine alaninium nitrate (LAAN) and doped with lanthanum oxide (La$_2$O$_3$), sodium chloride (NaCl), urea (CH$_4$N$_2$O), glycine (C$_2$H$_5$NO$_2$) and thiourea (CH$_4$N$_2$S) were grown. The semi-organic NLO crystals of L-alanine cadmium chloride (LACC) and L-alanine sodium nitrate (LASN) were also grown. In addition, the inorganic NLO crystals of potassium dihydrogen orthophosphate (KDP) doped with L-alanine and L-arginine were grown. The crystals were grown from low temperature solution growth technique by slow evaporation method. The grown crystals were characterized by different characterization techniques. The X-ray diffractometers (single crystal and powder) were used to find the structure and crystalline nature of the grown crystals. The Fourier transform infrared (FTIR) spectrometer was used to identify the presence of various functional groups. In order to study the thermal and optical properties of the grown crystals, the thermal analyser and UV-Vis-spectrometers were used. The morphology and the elements present in the crystals were studied using scanning electron microscope and energy dispersive X-ray (EDX) analysis respectively. The dielectric measurement was carried out using high frequency LCR Meter. The dc conductivity measurement was carried out using Keithley dual channel source meter model 2636A. Further, the microhardness measurement was carried out using Vicker's microhardness tester. The Kurtz and Perry powder technique was used to measure the second harmonic generation conversion efficiency of the grown crystals.

In addition to the growing of novel NLO crystals, it is important to understand the radiation effects on NLO crystals, since the crystals need to work in radiation environment. Some of the NLO crystals like LACC, L-alanine and L-arginine doped KDP were irradiated with different doses of Co-60 gamma radiation using gamma
chamber 5000 at Pondicherry University, Puducherry. The LASN crystals were irradiated with different doses of 100 MeV oxygen ions using 15 UD 16 MV Pelletron Accelerator at Inter University Accelerator Centre (IUAC), New Delhi. The irradiated crystals were characterized to understand the radiation effects on physical and structural properties.

This chapter summarizes the main results obtained in this work along with the useful suggestions that can be carried out in future on these crystals.

9.1. Organic Nonlinear Optical Crystal: 4–Nitrophenyl hydrazone

- 4–nitrophenyl hydrazone was synthesized and needle shaped crystals were grown by slow evaporation technique using acetone as a solvent.

- The single crystal XRD study confirmed that the compound crystallizes in Orthorhombic crystal system with space group Pca2₁ which is recognized as non-centro-symmetric and the lattice parameters were found to be $a = 10.3152(3)$ Å, $b = 9.5469(2)$ Å, $c = 8.0198(4)$ Å, $\alpha = \beta = \gamma = 90.00(0)$°.

- The powder X-ray diffraction analysis confirmed the crystallinity of the sample.

- The FTIR and NMR studies confirmed the presence of functional groups in the grown crystal. The chemical composition of the grown crystal was confirmed by energy dispersive X-ray (EDX) analysis.

- The UV-visible spectrum revealed that the grown crystal is transparent in the entire visible region.

- The thermal stability of crystal was analyzed and it indicates that the crystal is stable up to 146°C.

- The emission of green radiation from the grown crystal confirmed that the second harmonic signal generation and the 4–nitrophenyl hydrazone single crystal shows high SHG conversion efficiency of 15.39 times when compared to KDP crystal.
9.2. **Organic Nonlinear Optical Crystal: 3-[(1-(2-phenylhydrazinylidene) ethyl]-
2H-chromen-2-one**

- 3-[(1-(2-phenylhydrazinylidene)ethyl]-2H-chromen-2-one was synthesized and
  needle shaped crystals were grown by slow evaporation technique using acetone
  as a solvent.

- The single crystal XRD study confirmed that the compound crystallizes in
  triclinic crystal system with space group P1 which is recognized as non-centro-
  symmetric and the lattice parameters were found to be
  \[ a = 13.0088(5) \, \text{Å}, \, b = 14.0416(5) \, \text{Å}, \, c = 26.0976(10) \, \text{Å}, \, \alpha = 76.763(2)^\circ, \, \beta = 88.963(2)^\circ, \, \gamma = 70.629(2)^\circ. \]

- The powder X-ray diffraction analysis confirmed the crystallinity of the sample.

- The FTIR and NMR studies confirmed the presence of functional groups in the
  crystal. The chemical composition of the grown crystal was confirmed by EDX
  analysis.

- The thermal stability of the crystal was analyzed by DTA and TGA techniques
  which indicate that the crystal is stable up to 196°C.

- The good transmittance property of the crystal in the entire visible region
  ensures its suitability for second harmonic generation application.

- The emission of green radiation from the crystal confirmed the second harmonic
  signal generation and the SHG efficiency of the grown crystal was found to be
  3.3 times that of KDP.

9.3. **Pure and Doped Organic Nonlinear Optical Crystal: L-Alanine Alaninium
Nitrate (LAAN)**

- The single crystals of pure LAAN and doped with lanthanum oxide, sodium
  chloride, urea, glycine and thiourea were grown by slow evaporation method.

- The solubility of the doped LAAN crystals were found to be less than that of
  pure crystal.
The single crystal XRD confirmed that there is no change in the (monoclinic) phase structure of the doped samples; however slight changes in lattice parameters were observed for the doped samples compared to the pure sample.

Comparison of IR spectrums of pure and doped LAAN shows slight shift in absorption bands which may be due to the presence of doping.

The percentages of transmittance in doped samples were found to be more when compared to the pure sample.

The incorporation of dopants into the crystalline matrix was observed by EDX analysis.

The dielectric constant, ac and dc conductivity were found to be more in doped crystals than in pure LAAN crystals.

The refractive index (RI) values of the crystals were found to decrease slightly after doping.

The Vickers microhardness was found to increase after doping for all loads.

The thermal analysis showed that doped LAAN crystals were slightly more stable than pure crystals.

The SHG conversion efficiency measurement shows that the dopants enhance the SHG efficiency of LAAN.

9.4. Semi-organic NLO Crystal: L-Alanine Cadmium Chloride (LACC)

The LACC single crystal was grown by slow evaporation technique using double distilled water as a solvent.

The single crystal XRD study confirmed that the compound crystallizes in the monoclinic system with the space group C2 which is recognized as non-centro-symmetric and the lattice parameters are a = 16.415 (3) Å, b = 7.279 (1) Å, c = 7.989 (1) Å; α = γ = 90.00(0)°, β = 116.53 (2)°.

FT-IR spectrum confirmed the presence of various functional groups in the crystal and the presence of NH$_3^+$ is very easily identified in the FT-IR spectrum.
The lower cut-off at 224 nm combined with the very good transparency in the range 224–800 nm, attests the usefulness of this material for optoelectronics applications.

The dielectric constant and dielectric loss were found to be higher at lower frequencies and decreases with increase in frequency.

The ac and dc conductivity were found to increase with increase in temperature.

The microhardness of LACC was found to decrease linearly as the applied load increases and the LACC crystal belongs to the hard material category.

The thermal studies showed that the compound is stable up to its melting point 137.47°C.

The SHG conversion efficiency of LACC was confirmed using Kurtz Perry method and is 0.68 times that of KDP crystal.

9.5. Semi-organic Nonlinear Optical Crystal: L-Alanine Sodium Nitrate (LASN)

The single crystal of LASN was grown by slow evaporation technique using double distilled water as a solvent.

The single crystal XRD study confirmed that the compound crystallizes in the orthorhombic system with the space group P2₁2₁2₁ which is recognized as non-centro-symmetric and the lattice parameters are a = 6.845(4) Å, b = 12.215(6) Å, c = 6.357(4) Å; α = γ = β =90.00(0)°.

The presence of functional groups of the grown crystal was confirmed by FTIR.

There is no considerable absorption of light to any appreciable extent in the visible range of electromagnetic spectrum.

The dielectric constant and dielectric loss were found to decrease with increase in frequency and were found to increase with increase in temperature.
• The ac and dc conductivity were found to increase with increase in temperature.

• Vicker's hardness test shows that the hardness value of the grown crystal was found to increase with increase in load.

• Thermal studies revealed that LASN crystal does not decompose before melting and is suitable for NLO applications up to 281.9°C.

• SHG measurement has shown that the crystal possesses second harmonic efficiency and the efficiency is 0.36 times that of KDP crystal.

9.6. Co-60 Gamma Irradiation Effects on LACC, L-alanine and L-arginine Doped KDP NLO Crystals

• Some of the NLO crystals were exposed to Co-60 gamma radiation in the dose of 100 Krad to 6 Mrad and the crystals were characterized with different techniques.

• The single crystal XRD study confirmed that, there is no change in the phase structure of the irradiated samples; however there are slight changes in the lattice parameters.

• The transmittance of LACC was found to decreases with increase in radiation dose. There is no systematic behaviour in the optical transmittance of L-alanine and L-arginine doped KDP single crystals.

• The LACC crystals are the most affected by radiation and this was also visible by change in its colour from transparent to yellow colour with increase in dose and this inturn degrades the optical transmittance in the visible wavelengths.

• The dielectric constant and ac conductivity of the crystals were found to increase with increase in radiation dose.

• The dc conductivity of LACC and L-alanine doped KDP was found to increase with increase in radiation dose where as in case of L-arginine doped KDP crystals, the dc conductivity was found to decrease with increase in radiation dose.
• The RI values of the crystals were found to increase slightly up to the total dose of 600 krad. After 600 krad dose, RI was found to decrease with increase in radiation dose.

• The values of Vicker’s microhardness of the crystals were found to decrease with increase in radiation dose and it indicated that irradiation had made crystals softer.

• Thermal studies confirm the same chemical entity in the crystal lattice after irradiation without any modification in its structure.

• The SHG efficiency of LACC crystal was found to decrease with increase in radiation dose where as in case of L-alanine doped KDP crystals, the SHG efficiency was found to increase with increase in radiation dose. The SHG conversion efficiency of L-arginine doped KDP crystals are almost unaffected by irradiation.

9.7. 100 MeV O\(^{7+}\) Ions Irradiation Effects on LASN Crystal

• LASN crystals were irradiated with 100 MeV O\(^{7+}\) ions in the dose range of 1 Mrad to 10 Mrad.

• The single crystal XRD study confirmed that, there is no change in the phase structure of the irradiated samples; however there are slight changes in the lattice parameters.

• The optical absorption of LASN crystal was found to increase with increase in radiation dose.

• The dielectric constant, ac and dc conductivity of the crystal were found to increase with increase in radiation dose.

• The modification in the RI due to irradiation implies the possibility of fabricating optical waveguides using LASN single crystal and the hardness of the crystal was found to increase after irradiation.
• The DSC studies reveal that the melting point remains unaffected due to irradiation and the crystal does not decompose as a result of irradiation.

• The SHG conversion efficiency of LASN crystals was found to decrease with increase in radiation dose.

9.8. Suggestions for Future Work

In the present investigation, the 4-nitrophenyl hydrazone and 3-[(1-(2-phenylhydrazinylidene)ethyl]-2H-chromen-2-one were grown by slow evaporation technique using acetone as a solvent. As these crystals exhibit thermal stability, it can be tried to grow highly pure, large size and good quality crystals by melt method.

Attempts would be made to improve the SHG efficiency of LAAN NLO crystal by incorporating different concentrations of rare earth metal ions such as Lanthanum (La), Cerium (Ce), Ytterbium (Yb), Terbium (Tb), for better frequency conversion devices.

The single crystals of LACC and LASN are extensively studied in terms of their growth, optical, electrical, mechanical and thermal properties. The growth of single crystals of NLO material can be tried by Sankaranarayanan-Ramasamy (SR) method in order to obtain still better quality crystals. A comparative study can be made on the crystals grown from solution method and SR method and their linear and nonlinear properties and their thermal stability can be studied for their suitability for NLO applications.

It would be very interesting to study the effects of high energy ions irradiation effects on LACC, L-alanine and L-arginine doped KDP NLO crystal. A comparative study can be made on the effect of Co-60 gamma and high energy ions on these crystals.