ABSTRACT

Nonlinear optical (NLO) materials play a overwhelming role in nonlinear optics and various information technology and industrial applications, in particular they have a great impact on optical telecommunication, data storage, manipulation and transmission. In the last decade, however, this effort has also brought its fruits in applied aspects of nonlinear optics. This can be essentially traced to the improvement of the performances of the NLO materials. The understanding of the nonlinear polarization mechanisms and their relation to the structural characteristics of the materials is considerably important in the study of new NLO effects and related concepts in non linear devices. Since there is a vast demand for solid-state devices efforts have been directed in recent years towards producing larger size crystals. The new development of techniques for the fabrication and growth of non linear optical materials has dramatically contributed to this evolution. The organic materials is presenting good nonlinearities and satisfying the technological requirements for applications such as wide transparency range, fast response, and high damage threshold. In this direction, the present work is aimed at growing various pyridine and aldehyde based NLO crystals by slow evaporation technique using various solvent at room temperature and various investigations have been carried out to explore the different properties of grown crystals. This thesis is constructed with seven chapters.

The first chapter gives the introduction of crystal growth methods, basic aspects of nonlinear optics and nonlinear interactions, materials perspective, and a brief description of characterization techniques involved.

The second chapter deals with growth and characterization of 3-hydroxypyridinium tartrate mono hydrate NLO crystal. Good quality single
crystals of 3HPTMH were obtained with space group of \( P2_12_12_1 \) by slow evaporation method using mixed solvent of water and ethanol. Unit cell parameters of the grown crystal were obtained by single crystal X-ray diffraction analysis that elucidates the non centrosymmetric nature of the crystals. The first order hyperpolarizibility of 3HPTMH is \( 1.28109 \times 10^{-30} \) esu. HOMO and LUMO calculations were performed for grown crystals using Gaussian 03 software. The presence of various functional groups is confirmed by FTIR and FTRaman which establishes the presence of intermolecular hydrogen bonds in 3HPTMH. The satisfactory factor group analysis was performed and hence the possible degrees of freedom were calculated. Lower cut off wavelength (308 nm) and optical transparency window in grown crystals were identified using UV-Vis spectra. Thermal analysis confirms the stability and absence of phase transition before melting (75°C). The decrease in dielectric constant and dielectric loss establishes the dielectric behaviour of 3HPTMH. The relative SHG efficiency of the material (80 mV) is equivalent to Potassium Dihydrogen Phosphate (KDP).

The third chapter presents the synthesis and growth of 4-chlorobenzylidene Tosylhydrazide crystal. A NLO material 4CBTH was grown from solvent ethanol using slow evaporation technique at room temperature. Single crystal XRD analysis was performed and results reveals that the crystal grown with cell parameter of \( a = b = 10.8907(3) \) Å, \( c = 21.4542(7) \) Å with non centrosymmetric space group \( P6_1 \). Various functional groups of compound were analysed using FTIR and FTRaman spectral analysis. The molecular structure was confirmed by \(^1\)H NMR study. Total number of vibrational modes is exhibited by 4CBTH. The thermal property of the sample was analysed by TG and DTA analysis and was found that the 4CBTH crystalline compound is stable up to 175°C. The cut off wavelength of the grown material is 340 nm and shows a low absorption in the near IR region. Hyperpolarizibility, HOMO–LUMO analysis were performed using DFT calculations using Gaussian 03 software. Dielectric and hardness studies
were also studied. The SHG relative efficiency was found to be 0.76 times of KDP. Thus, the characterization of the grown crystal reveals the suitability of material for NLO applications.

The fourth chapter presents the crystal growth and characterization of 2’,3,4,4’,5-Pentamethoxychalcone NLO crystals. The single crystals of PMC have been grown by slow evaporation method in well defined morphology with dimension 13×10×3 mm$^3$. Solubility analysis were performed and based on the result DMF was chosen as suitable solvent for crystallisation process. Powder X-ray diffraction analysis confirmed the lattice parameters of the crystal and it is found that crystal belongs to the orthorhombic system with P2$_1$2$_1$2$_1$ space group. FTIR and FRaman spectroscopy ascertain the presence of various functional groups in the sample. The chemical construction of the grown crystal has been confirmed by $^1$H NMR analysis. Theoretical calculation for vibrational mode was performed using factor group analysis. The dielectric studies indicate that the grown crystal of PMC possess good optical quality and lesser defect. The UV cut off range is determined by optical absorption study, the observed cut-off wavelength 243 nm indicate that this material is potential one for generation of blue-violet light. Thermal stability of the grown crystal is analysed by TG-DTA studies. Photoluminescence study is also performed. NLO behaviour of PMC crystals has been studied using Kurtz powder technique and SHG efficiency is found to be 2.02 times higher than that of KDP.

The fifth chapter is devoted to synthesis and growth of organic NLO crystal of Toluidine tartrate by slow evaporation technique using ethanol as solvent. The cell parameters are confirmed by the single crystal X-ray diffraction studies. The various functional groups presence in the grown crystal and the molecular structure were confirmed with FTIR, FRaman and NMR analysis. From the thermal studies it is observed that the material has suitability for NLO application up to 201°C. The optical absorption study confirms the low cut-off wavelength (239 nm). Further factor group analysis
has been performed to calculate number of vibrational modes exhibited by TT. Dielectric constant and dielectric loss is calculated for TT crystal and the values of dielectric parameters reveal that dielectric constant decreases with increase in frequency due to the influence of various types polarization. Hardness test confirms the mechanical stability of TT. SHG efficiency of the material has been confirmed by the Kurtz and Perry powder method, using KDP as reference material.

The sixth chapter discusses the growth and characterization of 3-hydroxy pyridinium nitrobenzoate crystals. A well defined crystal of 3HPNB is grown by slow evaporation technique using ethanol as solvent. Solubility test confirms ethanol as the best solvent for crystallization process. The cell parameters for the grown crystal were confirmed using single crystal X-ray diffraction. FTIR, FTRaman and \(^1\)H NMR spectral studies was carried out to confirm the functional groups present in 3HPNB. The theoretical factor group analysis of 3HPNB predicts 552 total vibrational optical modes that decomposes into \(\Gamma_{\text{total}} = 275A_g + 275A_u\) along with two acoustic mode \((A_g + A_u)\). Thermogravimetric analysis reveals that titled compound melts at \(195^\circ C\). The observed UV cut-off wavelength 387 nm of the grown crystal confirms the suitability of this material for optical applications. The dielectric constant and dielectric loss of 3HPNB establishes the normal dielectric behaviour. The mechanical study for the sample was carried out. Emission of green light and low value of second harmonic conversion efficiency of the sample of 3HPNB in Kurtz and Perry method reveals that the suitability of the crystal for NLO applications.

The summary of the present investigations and suggestions for future work are presented in the seventh chapter.