ABSTRACT

There is a need for new lasers with exciting combination of light properties such as wide spectral tuning ranges and large bandwidth for communication systems. While a variety of materials including inorganic, organo-metallic, organic and polymeric have been studied for their NLO activity, the organic materials have been receiving the maximum attention because of their ultra fast response time, photo-stability and large first order hyperpolarizability ($\beta$) values. In this direction, organic NLO crystals were grown by conventional low temperature solution growth technique. The essential properties such as optical transparency and the second harmonic generation for the grown crystals have been verified by recording optical transmission spectra and measuring SHG efficiency using Kurtz-Perry powder method. Some of the grown crystals were subjected to swift heavy ion irradiation and the effects were studied mainly focusing on the dielectric constant. This thesis is structured into seven chapters.

The first chapter deals with the introduction of crystal growth methods, nonlinear optics, some aspects of nonlinear interactions, materials perspective, characterization tools involved, theory of hyperpolarisability calculations and methodology of swift heavy ion irradiation.

The second chapter presents the synthesis and growth of L-asparaginimum picrate (LASP) crystals grown by slow evaporation solution growth technique. Single crystals of LASP have been grown from the
saturated solution (pH = 2.01) of the synthesized salt of LASP by the slow evaporation technique at 30°C using a constant-temperature bath having the control accuracy of ±0.01°C. LASP (Molecular formula C₄H₉N₂O₃⁺. C₆H₂N₃O₇⁻) belongs to the monoclinic crystal system with space group P2₁ having two molecules in the unit cell with the unit cell parameters a = 10.332 Å, b = 5.121 Å, c = 13.093 Å and β = 92.9°. The powder SHG test of LASP gives an output voltage of 599 mV for an input power of 1.9 mJ/Pulse. The microscopic nonlinearity was calculated by the density functional triply parameter hybrid model DFT/B3LYP using GAUSSIAN 98W. The 6-31G (d,p) basis set has been employed. The calculated first order hyperpolarisability of LASP is 4.815 × 10⁻²⁹ esu. L-asparaginium picrate was subjected to 100 MeV Ag⁸⁺ and 50 MeV Si⁸⁺ ions. The dielectric constant of LASP increases enormously after 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 third chapter is devoted to the synthesis and growth of L-valinium picrate (LVAP) crystals by solution growth technique. The nonlinear optical properties of LVAP crystals are reported for the first time in the literature. Single crystals of LVAP have been grown from saturated solution of mixed solvent of acetone and water in 1:1 ratio by slow evaporation solution growth technique. The LVAP (molecular formula C₅H₁₂NO₂⁺.C₆H₂N₃O₇⁻) crystallizes in the monoclinic crystal system with space group P2₁ and the lattice parameters are a = 9.970 Å, b = 6.313 Å, c = 12.591 Å and β = 110.99°. The first order hyperpolarizability of LVAP is
calculated using 3-21G (d,p) basis set based on finite field approach. The calculated first order hyperpolarizability of LVAP is $1.050 \times 10^{-29}$ esu. The factor group analysis was performed for LVAP crystals. The SHG signal energy output for LVAP was 1.3 V for an input pulse of 1.9 mJ/Pulse. The grown crystals were subjected to irradiation of 100 MeV Ag$^{8+}$ and 50 MeV Si$^{8+}$ ions which resulted in a drastic increase in dielectric constant and almost uniform reduction in transmission.

The fourth chapter deals with the synthesis and growth of Dimethyl amino pyridinium 4-nitrophenolate 4-nitrophenol (DMAPNP). Single crystals of DMAPNP have been grown from saturated solution (pH = 3.26) of the synthesized salt of DMAPNP by the slow evaporation solution growth technique at 30 °C using a constant temperature bath having a control accuracy of ± 0.01°C. Thermal, optical, laser damage threshold, dielectric behaviour and second harmonic generation properties of DMAPNP were studied. The SHG signal energy output for DMAPNP was 135 mV for an input pulse of 1.9 mJ / Pulse. It is observed that the damage threshold of DMAPNP (2.24 GW/cm$^2$) is many times higher than KDP (0.20 GW/cm$^2$). DMAPNP was subjected to 100 MeV Ag$^{8+}$ and 50 MeV Si$^{8+}$ ions irradiation. The dielectric constant and conductivity increase with increasing irradiation fluence.

The fifth chapter presents the synthesis, growth, crystal structure determination and characterization of L-argininium phenolate monohydrate (LAPM). LAPM crystals were grown from aqueous solution by slow cooling solution growth technique. LAPM (Molecular formula $C_{12}H_{21}N_{5}O_6$) belongs
to the orthorhombic crystal system with space group $P2_12_12_1$ with the unit cell parameters $a = 5.125 \, \text{Å}$, $b = 9.368 \, \text{Å}$ and $c = 31.514 \, \text{Å}$. The hyperpolarizibility calculations were performed using density functional theory methods. The thermal, optical and vibrational analyses of LAPM were performed.

The sixth chapter discusses the synthesis, growth, crystal structure determination and characterization of N-2 Chlorophenyl 1-Propanamide (NCP) single crystals and growth and characterization of Benzaldehyde 4 Nitro Phenyl Hydrazone single crystals. NCP crystal belongs to the monoclinic crystal system with molecular formula $C_9H_{10}ClNO$. The grown crystals were subjected to FT-IR and FT-Raman analyses for vibrational frequency assignments, UV-Vis spectral studies for optical transmission, dielectric studies for the study of dependence of dielectric constant and conductivity with frequency and temperature and Laser damage threshold studies. The Benzaldehyde 4 Nitro Phenyl Hydrazone (BPH) crystal belongs to the monoclinic crystal system with the molecular formula $C_{13}H_{11}N_3O_2$, space group $Cc$, $a = 6.049\,\text{Å}$, $b = 23.320\,\text{Å}$, $c = 8.507\,\text{Å}$, $\beta = 92.2^\circ$. The crystals of BPH have been synthesized and grown by slow cooling solution growth technique using ethanol as solvent at 32°C. The grown crystals were subjected to FT-IR and FT-Raman analyses for vibrational frequency assignments, UV-Vis spectral studies for optical transmission.

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