6.1 SUMMARY

In the present investigation, the nucleation kinetics, crystal growth, characterization and irradiation of technologically important non-linear optical single crystals were dealt. The single crystals of m-Nitroaniline, Benzimidazole, N-Bromosuccinimide, Benzil and O-Nitroaniline doped Benzil have been grown, among which thermally stable m-Nitroaniline, Benzimidazole and Benzil crystals were grown by the vertical Bridgman technique. To grow the defect free crystals, the knowledge about the nucleation kinetics is of prime importance. Hence the nucleation kinetics of m-Nitroaniline, Benzimidazole, N-Bromosuccinimide and Benzil crystals were studied, based on the classical nucleation theory. The grown crystals were irradiated with different ions at varying fluences. The characterization studies were done to analyze the grown crystals.

m-Nitroaniline (m-NA) crystals exhibit second harmonic generation. m-Nitroaniline crystallizes in the orthorhombic structure, with the cell parameters $a = 6.370\text{Å}$, $b = 19.240\text{Å}$, $c = 5.081\text{Å}$ and space group is Pbc$_2$. The solubility of m-Nitroaniline was determined in various solvents such as acetone and ethanol. The solubility of m-Nitroaniline in acetone was found to be higher than that of ethanol; consequently the metastable zonewidth was measured using the acetone. The thermodynamical parameters such as interfacial energy, induction period, number of ions in the nucleus and critical
radius were calculated. The bulk single crystals were grown with acetone solvent (dimensions 10 × 2 × 3 mm³). From the thermal studies, the melting and decomposition point of m-Nitroaniline was found to be 114°C and 153°C, respectively.

The vertical Bridgman technique was used for growing the m-Nitroaniline crystals from melt. The two zone furnace was exclusively constructed for the growth of m-Nitroaniline and the temperature profile was measured. Using the optimized conditions, device quality m-Nitroaniline crystals were grown with the dimensions of 23 × 10 × 5 mm³. The grown m-Nitroaniline crystals were confirmed by the single X-ray diffraction studies and FTIR studies. The presence of vital functional groups was observed in the FTIR spectrum of m-Nitroaniline crystals. The optical absorption studies show that the m-Nitroaniline crystal is transparent in the entire visible region. The relative SHG conversion efficiency of m-Nitroaniline crystal is 2.5 times that of urea. The first order hyperpolarizability value of m-Nitroaniline crystals were found by using the GAUSSIAN 98W. The conversion efficiency of m-Nitroaniline was 10 times higher than that of urea. The discrepancy in the experimental and the theoretical value of first order hyperpolarizability can be due to the cancellation of some dipoles in the crystalline m-Nitroaniline.

The m-Nitroaniline crystals were subjected to irradiation studies using the ions of Ag⁷⁺ and Li³⁺ with varying fluences of 1×10¹¹ ions/cm² and 1×10¹² ions/cm². To analyze the modifications of m-Nitroaniline on irradiation, the irradiated crystals were subjected to various investigations. The powder X-ray diffraction analysis shows that the columnar defects are created on irradiation. In the case of Li³⁺ ion irradiation the defect is less than the Ag⁷⁺ ion irradiation. It can be concluded that the strain developed due to the created defects is responsible for the modification of different properties
of the m-NA crystals. The optical absorption increases with increasing fluence of ion irradiation and with the reduction in $E_g$ by increasing ion fluence arises due to the effect of band tailing, owing to the defects produced during irradiation. The blue shift occurs in the m-NA crystals when subjected to irradiation. The blue shift is the net result of the effects of charge separation and band filling occurring due to the Auger effect. The energy gap values in the photoluminescence study are compatible with the UV-Visible study, which ascertains the formation of the defects on irradiation. Hence with Li$^{3+}$ ion irradiation (rather than Ag$^{7+}$ ion) on m-NA crystals, it is possible to create electrically transparent windows along with the optical activity of laser structure without any damage to the active region. The mechanical strength of pure and irradiated m-NA crystals was studied. The increase of the dielectric constant of m-NA crystals on Li$^{3+}$ ion irradiation implies that the irradiation with the Li$^{3+}$ ion can be used to construct more efficient electro-optic modulators. The ion irradiated m-NA crystals had the radical ions generated, leading to the charge separation, hence the irradiated samples resulted in higher SHG efficiency compared to that of the pure sample.

The nucleation parameters like critical radii, induction period and interfacial energy were calculated and the growth conditions were optimized for BMZ crystals. The BMZ crystals were grown by solution growth using the methanol as the solvent. Bulk single crystals of BMZ of dimensions (10×3×3) mm$^3$ were grown. The thermal analysis was carried out on BMZ and it was found that BMZ melts at 172°C. The BMZ crystals were grown by the vertical Bridgman technique by using a specially designed two zone furnace. The defect free crystals of dimensions of (20×15) mm$^3$ were grown. The grown crystals were characterized by various characterization methods, such as X-ray diffraction analysis, FTIR analysis, optical absorption studies, mechanical and electrical studies. From the optical studies it is noted that the BMZ crystals have less absorbance in the entire UV and visible region, which
makes BMZ a valid candidate for the NLO applications. BMZ crystals exhibit reverse indentation size effect and the geometry of the cracks formed are of Palmqvist type. The average value of yield strength is 1.516 MNm\(^{-2}\). The quality of the grown crystals was assessed by the high resolution X-ray diffraction analysis, which supports that the grown crystals are of good quality. From the Kurtz-Perry powder technique, it is inferred that the relative conversion efficiency of second harmonic generation is 4.5 times that of the KDP. The theoretical calculations of the first order polarizability of BMZ using GAUSSIAN 98W shows that the second order efficiency is about three times that of the KDP, this discrepancy can be due to the strong hydrogen bond formation and the N-H bond which aids in the strong intermolecular bonding. Single shot laser damage threshold was estimated to be 2.7 ± 0.1 GW/cm\(^2\). For the case of multiple shot laser damage threshold, it was found to be 1.4 ± 0.1 GW/cm\(^2\).

The melt grown BMZ crystal was subjected to irradiation study. The silicon (Si\(^{7+}\)), lithium (Li\(^{3+}\)) and silver (Ag\(^{7+}\)) ions were used for irradiating the BMZ crystals. The creation of point defects was identified by the high resolution X-ray diffraction analysis. On irradiation the N-H bond weakens, which was aiding in the strong intermolecular hydrogen bonding. The MeV ion irradiation produces point defects such as vacancies, anti-site defects and interstitials, causing lattice damage. Hence, the reduction in \(E_g\) with increasing ion fluence may arise due to the effect of band tailing, owing to the defects produced during irradiation. In fact, the MeV ions excite the electrons from both the lone pair and bonding states to the higher-energy states. Vacancies created in these states are immediately filled by the outer electrons with Auger processes that, in turn, induce more holes in the lone pair and bonding orbital, leading to a vacancy cascade process. The increase in dielectric constant on heavy ion irradiation may enhance the electro-optical
property of the non-linear optical crystals. Thus the irradiation of swift heavy ions on BMZ increases their utility in various non-linear optical applications.

N-Bromosuccinimide (NBS) is a source of free-radical or positive bromine, used primarily in the bromination of organic substrates. The NBS was synthesized by mixing succinimide with sodium hydroxide in equimolar ratios and the resulting compound was brominated, which yielded N-Bromosuccinimide. The solubility of NBS was determined in various solvents such as acetone and water; it was found that acetone is the best solvent for the growth of the N-Bromosuccinimide crystals. The nucleation kinetics was studied for the N-Bromosuccinimide crystals. The good quality transparent NBS crystals of dimension (3 × 4 × 7 mm³) were grown by the low temperature solution growth technique. The lattice parameters of the grown crystals were confirmed by single crystal X-ray diffraction analysis, from which it is confirmed that the NBS crystallizes in orthorhombic crystal structure with space group P2₁2₁2₁. The UV-visible spectrum shows that the NBS crystals are highly transparent in the region of 325 nm to 1100 nm. The photoluminescence study reveals the presence of the intrinsic defects in the forbidden region of the energy gap. The first order hyperpolarizability values were calculated theoretically which shows that the value of β is 7.4122 × 10⁻³¹ esu, and the dipole moment value is 3.112 Debye. The Kurtz-Perry powder technique was used for studying the relative SHG efficiency of KDP and it was 240 mV and NBS had 350mV at given pulse energy of 5 mJ/sec.

NBS crystals were subjected to irradiation with various ions such as Li³⁺ and Ag⁷⁺ at different fluences. The 70 MeV Li³⁺ and 100 MeV Ag⁷⁺ ion irradiation modifications in the optical, mechanical and electrical properties of NBS single crystals have been analyzed. The optical absorption decreases with increasing fluence of ion irradiation and with
reduction in energy gap by increasing ion fluence arises due to the effect of band tailing, owing to the defect produced during irradiation. Hence by Ag$^{7+}$ ion irradiation (rather than Li$^{3+}$ ion) on NBS crystals, it is possible to create electrically transparent windows along with the optical activity of laser structure without any damage to the active region.

Benzil (BZ) is a simple organic compound with hexagonal structure. This diketone is used as an intermediate in organic synthesis. The solubility of benzil was obtained in different solvents, and it was found that ethanol yields device quality crystals. The nucleation kinetics of the benzil crystals were carried out. Good quality transparent crystals of benzil were obtained. The grown crystals were confirmed by the single crystal X-ray diffraction technique and Fourier transform infrared analysis. The theoretical first order hyperpolarizability values were calculated for the benzil crystals using the GAUSSIAN 98W, which shows that the value of β is $1.5335 \times 10^{-30}$ esu and the dipole moment value is 4.5202 Debye units.

The effect of doping O-nitroaniline to Benzil was studied. O-nitroaniline (O-NA) is more easily reduced than p-nitroaniline. This behavior is due to the effect of hydrogen bonding involving the nitro and amino groups. When the O-NA is doped with benzil, the lone pair of electrons in the carbonyl group of benzil forms the hydrogen bond. A comparative analysis between the Benzil and O-nitroaniline doped Benzil crystals were made, to study the effect the dopant on Benzil. The single X-ray diffraction analysis made on O-NA doped Benzil crystals showed the shift in the values of the cell parameters. The doped O-NA in benzil is evidenced from the C-N stretch at 1095.5 and 1072.3 cm$^{-1}$, while the band at 1170.7 cm$^{-1}$ is attributed to the phenyl-C stretch in aromatic ketones. The color change from light yellow to greenish yellow on addition of O-NA of the crystal could explain the donor acceptor complex formation. The doping of O-NA induced
significant changes in the spectrum of benzil, which could be associated to the weak van der Waals bond, stronger interaction could exist between the guest and host molecule by the hydrogen bonding. The PL intensity is highly dependent on the crystallinity and composition of the ratio of the dopant. It is found that incorporation of O-NA in the lattice has enhanced the crystallinity of Benzil crystals. The third order non-linearity studies were performed by using the Z-scan technique. The values of non-linear refractive index $n_2$ of benzil and O-NA doped benzil are $-9.4 \times 10^{-9}$ and $-6 \times 10^{-7}$ cm$^2$/W respectively and from the open Z-scan curve, the values of non-linear absorption co-efficient $\beta$ of benzil and O-NA doped benzil are $-78 \times 10^{-3}$ cm/W and $-22 \times 10^{-3}$ cm/W respectively. The increase in mechanical hardness on O-NA doped benzil may be due to strong hydrogen bond formed on doping of O-NA.

6.2 SUGGESTIONS FOR THE FUTURE WORK

A systematic analysis of nucleation, crystal growth, irradiation and characterization of m-Nitroaniline, Benzimidazole, N-Bromosuccinimide and Benzil has been made. Effect of different dopants on the material synthesis, growth aspects and also characterization of the grown crystals may be carried out to obtain novel NLO crystals. The effect of gold, oxygen and hydrogen ions on the aforesaid non-linear optical crystals can be studied. The concentration of the dopants can be varied and the corresponding changes can be recorded.