SUMMARY AND FUTURE SCOPE OF WORK

I. SUMMARY

The thesis focuses the growth of bulk nonlinear optical single crystals and a comprehensive investigation on the correlation between their crystalline perfection and physical properties. To accomplish the aim, pure and doped single crystals of LiNbO$_3$ (LN), Benzophenone and ZTS have been grown and subjected to the characterization for crystalline perfection and physical properties. The crystalline perfection of single crystals has been assessed very precisely by an in-house designed and developed multicrystal high resolution X-ray diffractometer (HRXRD); a stringent requirement for device application. The conclusions made from the investigations carried out in the thesis have been discussed as follows.

The Czochralski (CZ) growth of crack free LN bulk single crystals has been successfully performed on an indigenously developed CZ puller. In view of the growth of large size LN crystals, a two zone furnace has been developed. A low thermal gradient in the entire growth zone of furnace has been achieved by installing a coaxial resistive heater just above the radio-frequency furnace, which in turn provided a homogeneous slow post growth cooling of the entire crystal boule. A resistive furnace with precise temperature control has been developed for the growth of pure and liquid crystals (LC) induced Benzophenone single crystals by CZ method.

The grown pure, Zn and Fe doped LN crystals have been characterized for crystalline perfection by HRXRD and found that all the crystals were almost perfect. The pure and Fe-doped crystals were free from the structural grain boundaries but predominantly having vacancy defects, whereas, the Zn-doped crystal possessed a low angle grain boundary. The concentration of Li ($C_{Li}$) evaluated by Raman technique in all crystals was found well correlated with the lattice strains as investigated by HRXRD. The tuning of optical transparency and band gap of LN by Zn and Fe doping was also found to have a direct correlation with the dopants/point defects. In case of pure and Zn doped LN the evaluated defectiveness (Li vacancies and Nb$_{Li}^{4+}$ antisitic defects) using optical cut-off wavelength were in tune with defects analyses by X-ray
methods. The concentration of OH\(^{-}\) ions in the crystals’ lattice due to incorporation of protons (H\(^{+}\)) has shown a direct bearing with the crystalline perfection. The refractive indices and birefringence of the grown crystals measured by prism coupler and ellipsometry, respectively, found to be significantly varied with doping and have been successfully correlated with the HRXRD and powder XRD results.

The high ordering/aligning capability of LC has been exploited to grow the nearly perfect bulk single crystals of BP by CZ technique by adding a small quantity of LC in the charge during growth. The structural grain boundaries, commonly found in the pure BP single crystal could be successfully eliminated by an application of LC addition to the charge during crystal growth which leads to the significant enhancement of its optical transparency. The birefringence nature of LC induced BP crystal was also found to be slightly improved.

The effect of urea doping on the NLO properties on ZTS crystals was found to be very prominent. At lower doping concentrations, urea is incorporated statistically at interstitial sites in the lattice of ZTS crystal, whereas, at higher concentration it leads to the formation of structural grain boundaries and at very high concentration the crystal acquired the mosaic structure. The enhanced SHG efficiency at low concentration of urea was found which might be due to charge redistribution in the crystal lattice. At high concentration the strains in the lattice got relaxed by segregation of urea along the grain boundaries. However, SHG efficiency was found to be increased which could be due to the high SHG efficiency of urea itself.

The chromium doping in ZTS crystal leads to the enhancement of refractive index and makes it suitable for the photorefractive applications. In this investigation, the actual concentration of Cr\(^{3+}\) incorporated into the ZTS crystal lattice differed significantly compared to that added in the solution during crystal growth and distributed statistically in the lattice. Formation of vacancies at higher doping concentration has been attributed to the charge neutrality of crystal and lead to the decrease in optical transparency due to the trapping of photons. Slight increase in optical band gap was found which may be attributed to the removal of localized states in band gap.
II. FUTURE SCOPE OF WORK

The grown NLO single crystals are of good quality and suitable size for the fabrication of various devices for photonic applications and hence these can be used in various device applications as discussed below:

The Zn-doped LN with good crystalline perfection and enhanced optical transparency/band gap can be used to make periodic poled lithium niobate (PPLN) structures for frequency conversion applications. The Fe-doped LN crystals with good crystalline perfection are found to be suitable for the photorefraction applications and hence these can be used for the holographic data storage. The waveguides also can be fabricated by using the grown pure and doped LN crystals.

The Benzophenone single crystals with high crystalline perfection and optical transparency obtained by the addition of liquid crystals to the charge during growth, can be suitably used for the fabrication of SHG elements as these crystals have three times more SHG efficiency than that of standard KDP. The concept of addition of liquid crystals for improving the crystalline perfection may be tried with many strategic crystals.

The ZTS single crystals with good crystalline perfection and enhanced SHG efficiency can be suitably used for the SHG applications. The large single crystal of urea doped (≤ 2.5 mol% in solution) ZTS with high NLO property can be grown by suitable methods. Urea can also be used to enhance the SHG efficiency of other organic/semiorganic NLO crystals, required for tailor made applications.