6. SUMMARY, CONCLUSIONS AND FUTURE SCOPE

An overall summary of the present research work is provided here along with giving the various conclusions derived. Also, the future scope is dealt with.

6.1 Summary and Conclusions

The subject Crystal Growth and Characterization forms a frontier area of research in science and technology, owing to their vivid physical and chemical properties. The availability of appropriate crystalline materials is a crucial factor for the development of advanced technologies as well as for breakthrough in applied and basic sciences. Nonlinear optical (NLO) materials capable of efficient frequency conversion of infrared based radiation to visible and ultraviolet wavelengths are given vital importance in view of their potential use in various applications in the modern era which includes telecommunication, optical computing, optical data storage and optical information processing.

Metal complexes of polarizable ligands are currently explored for their nonlinear optical properties. These have been commonly referred to as semiorganics, as their physical and chemical properties set them apart from the usual organic and inorganic materials. The search for new frequency conversion materials over the past decade has led to the discovery of many semiorganic materials. Semiorganics share advantages of both organic and inorganic materials, which include extended transparency, high optical nonlinearity, good mechanical hardness and chemical inertia.
Bis(thiourea)cadmium chloride (BTCC) and bis(thiourea)cadmium iodide (BTCI) are two semiorganic nonlinear optical materials. For BTCC the transmission range extends from 285 to 900 nm. The crystal has a good transmission in the entire visible region. BTCC is 110 times more nonlinear than quartz. The reported value of single shot damage threshold of BTCC crystal is 32 Gw/cm$^2$ and that of multiple shot damage threshold is 6 Gw/cm$^2$. BTCC possesses a wide transparency range in the UV-Vis region with lower cut off value down to 324 nm and can find applications in optical devices.

With an aim of discovering new useful NLO materials, we have grown pure and mixed crystals of BTCC and BTCI, (BTCC)$_x$ (BTCI)$_{1-x}$ with $x = 0.8$, 0.6, 0.5, 0.4 and 0.2 and urea doped BTCC crystals by the free evaporation method. A total of eleven crystals were grown and characterized by different characterization techniques such as single crystal XRD, PXRD, FTIR spectral, EDAX, AAS, UV-Vis-NIR spectral, SHG efficiency, thermogravimetric, dielectric and DC conductivity measurements.

Single crystal XRD and PXRD results reveal that pure BTCC and mixed crystals with compositions $x = 0.8$ and 0.6 and urea doped BTCC crystals (0.25 mol% doped, 0.50 mol% doped, 0.75 mol% doped and 1.0 mol% doped) are orthorhombic in structure and belong to $Pmn2_1$ space group. The remaining crystals (BTCI and mixed crystals with $x = 0.5$, 0.4 and 0.2) are monoclinic in structure and belong to $P2_1/c$ space group. In the case of doped BTCC crystals, small variations in the lattice parameter values were observed indicating the presence of impurity molecules in the crystal lattice. Optical absorption (UV-Vis-NIR) spectra of pure and mixed BTCC –
BTCI crystals reveal that these crystals possess a wide optical transmission window from 300 to 900 nm, which is suitable for NLO applications. Optical absorption spectra of urea doped BTCC crystals reveal that the UV - cutoff wavelength of pure BTCC crystal is reduced much by adding urea as impurity. For the doped crystals the optical transmission window is within 275 to 1900 nm which is more suitable for NLO applications. Also, SHG measurements show that the SHG efficiency of doped BTCC crystals is greater than that for the mixed (BTCC-BTCI) crystals. The thermal parameters are found to vary nonlinearly with composition. The functional groups were identified with the FTIR spectral data. EDAX and AAS measurements indicate the chemical composition of the grown crystals.

DC electrical conductivities were measured for all the eleven grown crystals at various temperatures ranging from 40 to 100°C by using the conventional two-probe method. Activation energies were also determined. The conductivity for the grown mixed crystals and urea doped BTCC crystals is found to increase with the increase in temperature. The observed nonlinear variation of DC conductivity, and activation energy with the composition of the mixed crystals could be explained as due to the enhanced diffusion of charge carriers along dislocations and grain boundaries which are more in mixed crystals. Urea addition leads to random orientation of hydrogen bonds and consequently the nonlinear variation of $\sigma_{dc}$ with impurity concentration.

Capacitance and dielectric loss tangent (tan $\delta$) measurements were carried out for all the eleven grown crystals at various temperatures ranging from 40 to 100°C using an LCR meter with frequencies 100 Hz, 1 kHz, 10 kHz, 100kHz and 1 MHz.
Dielectric constants, AC electrical conductivities and activation energies were determined from the measured capacitance and tan δ values.

The εᵣ and tan δ values are found to increase with the increase in temperature and decrease with increase in frequency for all the crystals, indicating a normal dielectric behaviour. However, the composition of mixed crystal has complicated influences on the dielectric constant, tan δ, σ_ac and E_ac values. This nonlinear variation with composition has been attributed to the enhanced diffusion of charge carriers along dislocations and grain boundaries. The nonlinear variation of dielectric parameters with impurity concentration in the case of doped crystals could be explained as due to random orientation of hydrogen bonds caused by the urea molecules. σ_ac is found to be more than σ_dc which is expected for a normal dielectric material. This indicates that the grown crystals are normal dielectric materials. The conductivity property of the grown crystals could be explained as due to the protonic movement and the temperature dependence observed could be attributed to the temperature dependence of the proton transport. The variation of dielectric parameters observed with temperature could be understood as essentially due to the temperature variation of ionic polarizability.

The present study was aimed at developing a newer variety of NLO crystals. The preliminary SHG efficiency studies and optical properties strongly favour the use of these crystals in photonics technology. The present study indicates that proper solid solutions can be prepared directly from the reactants taken at suitable proportions even if the end members have lattice mismatching.
6.2 Future Scope

Crystal growth is an important field of materials science which has got scientific as well as technological importance. Scientific importance of the subject is mainly related to the growth of single crystals and its characterization while the technological importance is dealing with the growth of large single crystals and its application on device fabrication. The present research work (reported in this thesis) is scientific in nature and not technological.

It is possible to grow large size crystals of (BTCC - BTCI) mixed crystals with improved quality by carefully adopting either the SR method or some innovative techniques with modified apparatus. The effect of pH value on the growth conditions and morphology of the grown crystals can be investigated. Since the nucleation studies for these samples are not carried out, attempts can be made in future to investigate the nucleation parameters such as metastable zone width, induction period, interfacial tension, etc to improve and investigate the optimized growth parameters for industrial crystallization. Attempts can be made to identify suitable dopants, which could provide better optical properties and thereby enhance the NLO property of these crystals. It will be interesting to study the microhardness studies for different orientations of the grown crystals. The grown crystals can be subjected to Z-scan studies to estimate the absorption coefficient. Grown crystals could also be subjected to Nuclear Magnetic Resonance (NMR), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) studies to visualize the structure and defect mechanisms. Etching studies can be made on different crystallographic faces of the crystals with suitable etchants in order to identify the dislocations. Several studies are to be carried out on the fabrication of devices with the grown crystals.