Preface

The fast developments in the field of optoelectronics and photonics have stimulated an intense search for efficient nonlinear optical (NLO) crystals for laser technology, optical communication, signal processing and optical data storage. This has led to the innovations of various non-linear optical materials. It is evident from literature that of the many organic and inorganic NLO crystals investigated no one species has proved to be all encompassing with advantages for one application being negated by disadvantages for another. However in recent years semi organic materials through their unique characteristics have found success and brought new dimension to this area. Thiourea and glycine are interesting inorganic matrix modifiers due to their large dipole moment and have the ability to form an extensive network of hydrogen bonds. The metal coordination complexes of thiourea and glycine are the recently developed semi organic NLO crystals.

Among the non-linear optical phenomena, frequency doubling by second harmonic generation (SHG) is the most important process. The basic requirement for a material to be suitable for NLO applications is that it must have very high non-linearity. The general requirements for a material to be useful in second order NLO applications are:

- It must be transparent at the required wavelength range.
- It must exhibit low optical losses at the frequencies involved
- It must be phase matchable
- It must have high damage threshold
- It must possess large non-linear coefficient in the phase matching direction
Criteria essential for large hypolarizability of second order NLO materials are

- The material must be highly polarizable
- Charge distribution must be asymmetric
- There must be a path way for pi conjugated electrons
- The material must crystallize in noncentro symmetric structure

However most of the organic and inorganic crystals failed to meet the standards required for the practical use in device applications. Hence, there is a need to synthesize various new materials and to grow good quality single crystals needed for NLO applications. Among some novel semi organic NLO crystals reported for their SHG, thiourea and glycine based inorganic complexes are noticeable materials for their excellent non-linear optical properties and relatively good crystal quality. In this view, five new semi organic materials have been synthesized and single crystals were grown using solution and gel technique at ambient temperature. The grown single crystals were characterized using different physical techniques.

The design of a new class of semi organic materials is based on a highly polarisable organic molecule thiourea and glycine. Thiourea, which is incapable of generating second harmonic frequency, is converted into a high efficient second harmonic crystal by forming complexes with inorganic salt. Glycine is an interesting amino acid and forms complexes when combined with inorganic salts. Synthesized thiourea and glycine based complexes crystallize in noncentro symmetric structure and have the advantages of both organic and inorganic materials.
The thesis consists ten chapters; First chapter gives detailed information about crystal growth and fundamentals of non-linear optics. Different methods used for the growth of crystals are discussed briefly. The principle of non-linear optical effect such as fundamentals of non-linear polarization, second harmonic generation, phase matching etc., are presented in brief. The motivation and scope of the present research work are also presented in this chapter.

The second chapter describes the growth of thiourea mixed ammonium dihydrogen phosphate (TADP) crystal. The principles of crystal growth process, morphology of grown crystals is also presented in this chapter. Nucleation parameters of TADP crystal and its metastable zone width have been determined. The variation of nucleation parameter under identical conditions for the pure Ammonium Dihydrogen Phosphate (ADP) and TADP are studied. Metastable zone width for different saturation temperatures for pure ADP and TADP are studied and the results are presented.

The characterization of TADP crystals are discussed in the third chapter. X-ray diffraction, Fourier Transform Infra Red spectral, thermal and mechanical techniques are used to identify and assess the optical quality details of the grown crystal.

Chapter four describes the optical and dielectric studies of TADP crystal. The linear optical properties such as refractive index, optical transmittance of the crystal have been studied. From the transmittance optical characteristics of the TADP crystal, it is found that TADP crystals are highly transparent in the visible region. The non-linear properties of the TADP crystal...
is measured using Nd:YAG laser. The second harmonic conversion efficiency of the crystal is three times that of ADP. Electrical conductivity and dielectric properties of the TADP crystal are also described in this chapter.

Chapter five presents the structural investigations of thiourea mixed ADP crystal. Data collected on a Bruker SMART 6000 sealed-tube system comprise a three-circle platform goniostat, an HOG crystal monochromator, a four kilopixel by four kilopixel single-chip CCD-based detector, a K761 high voltage generator, and a PC interface running Bruker's SMART software. The variation of lattice parameters of ADP with the addition of different molar concentration of thiourea has been compared with pure ADP crystal. The intermolecular bond length, bond strength etc., have been measured.

The sixth chapter deals with crystal growth, optical and structural properties of thiourea mixed antimony bromide (TAB). Thiourea mixed antimony bromide crystals are grown using gel technique. The primary characterization of the grown crystals has been discussed employing various techniques such as FTIR, EDX etc. Experiments and results of room temperature measurement of refractive indices, dispersion, birefringence, optical absorption and second harmonic generation (SHG) have been explained. The structure of thiourea mixed antimony bromide is determined using single crystal X-ray diffraction technique.

The investigation of growth of single crystals of thiourea mixed bismuth chloride (TBC) in gels using a chemical reaction method at ambient temperature has been presented in chapter seven. Linear optical properties
of this material such as refractive indices, birefringence and absorption characteristics are measured in the wavelength range 200nm – 1400nm. No dispersion of the birefringence is observed within the experimental accuracy. The second harmonic generation efficiency of TBC is two times that of quartz. Single crystal structure of TBC is also determined.

Eighth and ninth chapters present the study of growth and characterization of glycine mixed sodium nitrate and barium chloride respectively. Investigations about the growth mechanism such as growth rate, kinetics, morphology of the glycine complexes are described in this chapter. Thermal properties like low temperature differential scanning calorimetry, thermo gravimetric analysis have been studied and the results are appended. The electrical conductivity and dielectric measurements at varying temperatures are carried out and the results are discussed. Non-linear properties like second and third harmonic generation in these crystals are also discussed.

Chapter ten gives the overall summary of the present investigations and the scope for further study. Each chapter ends with conclusions, references are listed at the end of each chapter.

The results of the present investigations are published in refereed journals and some are presented in the national and international conferences/seminar.