SUMMARY

This thesis deals with an investigation of Zinc (tris) Thiourea Sulphate (ZTS) a non-linear optical crystal. ZTS belongs to a class of semi organic materials, which mate the non-linear optical properties with the mechanical robustness of inorganic crystals. New non-linear optical frequency conversion materials can have a significant impact on laser technology, optical communication, and optical data storage.

Metal complexes of polarisable organic ligands, commonly referred to as semiorganics, were explored in the early nineties for their nonlinear optical properties. Semiorganics share the advantage of both inorganic and organic materials, which include extended transparency (down to UV), high optical nonlinearity, amenable crystal growth, good mechanical hardness and chemical inertness. Another remarkable advantage of this class is the high resistance to laser induced damage. Zinc (tris) Thiourea Sulphate (ZTS) is a semi-organic, nonlinear optical crystal. ZTS has drawn considerable attention of researchers due to its potential for second harmonic generation and as a frequency conversion material in general

In the work reported in the thesis, ZTS crystals were solution grown by solvent evaporation method at room temperature. The characterisation studies of ZTS crystals in this work indicate that this crystal has the necessary qualities required for nonlinear optical applications. These properties include extended transparency in the UV region up to 300 nm, high second order optical nonlinearity, amenable crystal growth, good mechanical hardness, chemical inertness and high resistance to laser induced damage.

A detailed study was conducted to determine the influence of the growth solution pH on the quality of the solution-grown ZTS single crystals. Using the absorption coefficient and the dislocation density as measures of crystal quality it was observed that the crystals grown from solutions with pH values between 3.6-4.2 were of the best quality. Further the growth along the c-axis was found to increase with increasing pH.

Etching continues to be a powerful and relatively simple tool that yields information about dislocation in crystals, their density and distribution. A new dislocation etchant, namely formic acid, for the (100) plane is reported. Formic acid was found to be more suitable than the earlier reported dislocation etchants such as methanol.

This thesis reports on Vickers hardness variation as a function of applied load and a detailed study on the surface anisotropy on three different planes, namely, (100), (001) and (010). The surface anisotropy of hardness has been explained on the basis of the effective resolved shear stress on the slip system of the crystal, developed by the hardness indentor. The effect of temperature and loading time on the microhardness of Zinc (tris) Thiourea Sulphate crystal was also studied and the activation energy of plastic flow in the observed timed-dependent deformation has been determined.

As non-linear optical applications of ZTS in laser technology involve high intensities, it is essential to study the damage caused by intense laser irradiation on this material. The report describes the results obtained, for the first time, on the laser damage on ZTS using 8 nanosecond pulses by a single-shot and multiple-shot laser irradiation. Damage thresholds were determined for varying number of shots from single shot to 10,000 at 10Hz-repetition rate at 532 nm. Single shot damage occurred at an intensity of ~ 3.0 GW/cm^2. This laser damage intensity saturates at ~ 0.5

GW/cm^2 as the number of shots reach 10,000. It is reported earlier that the damage pattern in ZTS reflects the mirror symmetry of the plane of damage and the dominant cause for the damage is dielectric breakdown with the damage propagating as stress fractures.

A detailed study of ZTS by H. O. Marcy *et al.* reports on the second harmonic generation in ZTS crystals. However their work concentrates on the 1064 nm wavelength by a Nd:YAG laser. The present thesis reports on preliminary studies of the second harmonic generation in ZTS using the input from a femtosecond pulsed laser for fundamental wavelengths in the 880-980 nm NIR region, producing blue laser light in the 440-490 nm region. Presumably this is the first study of its kind on the ZTS crystal system in this wavelength range for femtosecond inputs. This process of blue light generation was identified to be TYPE-I SHG. The acceptance angle for SHG under femtosecond input was determined to be around 0.6 degrees, which allows for easy tunability of the output wavelength. For 150 fs input pulses at 76 MHz repetition rate and average power of ~ 500 mW second harmonic outputs of up to 0.3 mW were obtained.

Transparency of the crystal is an important characteristic for optical materials. Therefore optical absorption studies were carried out on ZTS. IR absorption spectra were determined from 510 cm^{-1} and 4000 cm^{-1}. From this data the band gap in ZTS was found to be 3.0 eV in good agreement with earlier reported values. Visible to near-UV absorption spectra show an UV cut-off wavelength at around 300 nm. This study demonstrates the suitability of thermal lens and z-scan techniques for measurement of small absorption in non-linear optical crystals. A careful characterisation of NIR absorption of ZTS indicates a maximum absolute absorption coefficient of 0.04 cm^{-1} at 820 nm. This absorption is very small and should not hinder the use of ZTS for nonlinear applications requiring high intensity laser inputs at NIR wavelengths. The Z-scan results show that the coefficient ds/dT is negative for ZTS. The negative ds/dT has important consequences for the damage threshold of non-linear optical crystals. It was concluded that the negative d*s*/d*T* possibly contributes to the high damage threshold for ZTS by compensating for the self-focusing effects caused by Kerr non-linearities.

Zinc (tris) Thiourea Sulphate was investigated as a non-linear optical crystal in the early nineties particularly as a second harmonic generation material for the 1064 nm Nd:YAG laser. The unfortunate presence of a small N-H vibrational absorption overtone hindered further development of this material. With recent availability of several NIR solid-state laser sources there was a need for evaluating ZTS for second harmonic applications in this wavelength range. This thesis therefore revisits this subject and indicates that suitability of ZTS for as a frequency doubling crystal at fundamental inputs in the 880-980 NIR wavelength range.