Chapter 1: Introduction

The search for crystals with valuable physical properties, study of their structure, and development of new techniques designed for their synthesis constitute one of basic lines of contemporary materials science and are important factors in technology. It is widely accepted fact that semiconductors and optoelectronics are two most important hardware areas supporting the information technology. The fast development in the field of optoelectronics has stimulated the search for highly new nonlinear optical crystals for efficient signal processing.

The Nonlinear optical materials have the unique ability to temporarily change their optical properties when they interact with light. The ability of these materials to amplify, steer, guide or otherwise change the optical characteristics of an incoming light beam has the potential to significantly impact laser technology[1], optical communication[2] and optical data storage technology.[3, 4]

The use of all-optical systems based on nonlinear optical materials will significantly increase the speed of the current telecommunications networks and can revolutionise the next generation systems for computing and image processing. It is known that the conversion of light signals to electrical signals and the use of electronic repeaters to amplify the signal significantly impede the speed of communications. However, even with an all-optical amplifier, processing equipments at either end will need to be fast enough to code and decode the light pulses. In general, the material base for all-optical systems is not sufficiently developed to permit the transition to a new generation of all-optical devices. Significant improvements in non-linear optical materials are needed before such devices and system of the future become possible.

Several inorganic crystals have shown their promise as nonlinear optical materials. However many of these materials require high temperature growth from melts and fluxes. The growth process is complex and the growth of large boules of crystals is tricky. In addition, these crystals generally tend to lose their transparency at wavelengths lower than the blue end of the visible spectrum. Due to these difficulties, the search for new frequency conversion materials over the past decade has sifted through organic compounds and many organic nonlinear materials were discovered. However, the implementation of single crystal organic materials in practical device applications has been impeded by their often inadequate transparency, poor optical quality, lack of robustness, low laser damage threshold and an inability to grow in large size crystals.[5]

Metal complexes of polarizable organic ligands are currently being explored for their nonlinear optical properties and commonly referred as "Semiorganics." Semiorganics share the advantage of both inorganics and organics 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 their high resistance to laser induced damage. Semiorganics can be considered to be compounds in which a polarizable organic molecule is stoichiometrically bonded within an inorganic host forming either an organic/inorganic salt or an organic ligand/metal ion complex. They are categorized as Type I and Type II semiorganics respectively. Examples of both types have been known for many years, and a few have recently been investigated for their NLO properties (e.g.; LAP [6], ATMB[7], L-Histidine tetrafluoroborate[8]).

Zinc (tris) thiourea sulphate (ZTS) is a type II semiorganic materials and is a non-linear optical crystal, which was first synthesised in 1972.[9] Later, in 1990, it drew considerable attention of researchers for potential applications in second harmonic generation[10] or as frequency converters and as electro-optic modulators[11] (Cleveland crystals) in general. ZTS crystallizes in the non-centrosymmetric orthorhombic space group Pca21 (point group mm2). The lattice parameters were reported to be a = 11.26 Å, b = 7.773 Å and c = 5.491 Å. The X-ray structural determination shows a zinc ion terahedrally coordinating three planar thiourea molecules and one oxygen from a sulfate.[9] There is also extensive inter- and intramolecular hydrogen bonding between N-H's and the sulphate O's and this feature most likely gives rise to the noncentrosymmetry, which is an essential property for second harmonic generation.[12] Previous reports on thermal gravimetric analysis and differential scanning calorimetry by H. O. Marcy and co-workers shows ZTS to be thermodynamically stable to 200° C. These results have been further confirmed by temperature–dependent dielectric constant measurements made over the range of 1-100 kHz, which show no change in the dielectric constant until 200°C. Thermal coefficient of expansion measurements also showed no evidence of structural phase transitions in ZTS before its decomposition at ~200° C.[10]

ZTS crystals are usually grown by solvent evaporation of aqueous solutions containing thiourea and $ZnSO_4.7H_2O$ in mole ratio 1: 3 at room temperature.[13, 10] The crystals so obtained are optically transparent, non-hygroscopic and free from inclusions. There are previous study reports on the influence of pH on the growth morphology of

ZTS crystals, with the pH value ranging from 3.15 to 6.54.[14, 15] A lower growth solution pH was reported to be preferable for better crystals where uniform growth along all crystal direction was assumed to be signature of better crystals. The present study investigates the influence of pH in the range 2.5 to 4.2, using the optical absorption coefficient and dislocation density as direct measures of crystal quality.

The transmission spectrum for a ZTS crystal shows a UV cut-off below 0.290 μm. Also the spectrum indicates a shallow N-H vibrational overtone absorption at ~1.04 μm. This absorption peak has been an impediment for the use of ZTS as a suitable frequency doubling crystal for the 1064 nm parent wavelength of the Nd:YAG laser. H.O. Marcy and co-workers have tried to shift the 1.040 μm absorption peak to ~0.400 μm towards longer wavelengths by deutration.[10] Attempts to shift the 1040 nm vibrational overtone to about 1400 nm by deuterating to yield *d*-ZTS crystals have not been satisfactory since this process leads to a lowering of the acceptance angle for SHG and also makes non-critical phase matching impossible.[16]

When a real crystal is formed many factors prevent the formation of a perfectly regular lattice. Thus, departures from the ideal structures, known as defects, appear in a real crystal. In the field of semiconductor and opto-electronic materials line defects are particularly pronounced, playing a key role in determining the yield and performance of devices fabricated from such materials.[17] Dislocation etching continues to be a powerful and relatively simple tool to study and yield information about dislocation density and distribution. A dislocation etchant, namely methanol, for the (100) plane has been reported.[13] However, the action of methanol was found to be generally too fast with a tendency to make the etch pits overlap. In the present study, a complete new dislocation etchant is investigated. Using this etchant and the dislocation density is determined by etch-pit count method. The estimation of the activation energy of dislocation etching has also been obtained.[18]

Mechanical hardness of a nonlinear optical crystal dictates the temperature differential it can withstand, how well it can be polished, the measures that are needed to protect its surface and the optimum mounting arrangement in a nonlinear optical device. This makes the mechanical hardness an essential field of study. The Knoop hardness anisotropy of ZTS on the (100) plane was reported by V. Venkataramanan.[13] Particularly there are no reports on surface anisotropy in Vickers hardness of this important NLO crystal. Using Vickers hardness as a measure to study the hardness property, material the author reports, for the first time, the hardest and the softest directions in the major habit plane (100) of this crystal.[18] Since plastic deformation is known to be accommodated by dislocation slip mechanisms, the effective resolved shear stress developed by the hardness indentor on the slip system of this crystal has also been reported in the thesis. The observed anisotropy variations are then explained by the author, on the basis of effective resolved shear stress on the active slip system in the crystal.[19] Also the Vickers microhardness on major habit plane (100) of ZTS has been measured as a function of temperature and loading time in this thesis. The results indicated indentation creep phenomenon taking place. The activation energy of the plastic flow has been evaluated from the data obtained.

ZTS crystal is essentially uniaxial-negative, with indices in the crystallographic *a*-axes and *c*-axes being equal (within experimental error) at 1.782, while the index along the *b*-axis is 1.701(at 600nm)[12,20]. Detailed work on the evaluation of ZTS for second harmonic generation (SHG) devices, complete refractive index data for ZTS, including two pole Sellmeier fits, calculation of phase matching loci and non-critical wavelengths and their experimental verification is reported by H. O. Marcy et. al.[10]. However, this work is concentrates on the Nd:YAG 1064 nm fundamental wavelength for the Type-II second harmonic generation. The values of d_{eff} and β_0 and the damage threshold for SHG were reported H. O. Marcy *et al.*[21] This thesis reports, for the first time, Type-I second harmonic generation at 920 nm wavelength for a femtosecond laser on the as grown ZTS crystals.

Laser damage on ZTS was carried by V. Venkataramnanan *et al.*[22] These earlier reports of laser damage on this crystals are with ~ 40 ps pulses by using a 10 Hz Nd: YAG at a wavelength of 1064 nm. However the current commercially available low repetition rate Nd:YAG lasers have a typical pulse width of about 10 ns. Since thermal effects begin to manifest themselves at nanosecond time-scales the damage behaviour for 10 ns pulses is likely to be different from 40 ps pulses. With this goal in mind, the present study reports on the laser damage in ZTS crystals at 532nm using a 10 Hz, 10 ns Nd: YAG laser.

A report on studies of thermal properties on ZTS crystal concludes the principal coefficient of thermal conductivity to be largest in the polar *c*- axis and the smallest in the *a*-axis.[23] Ramabadran *et al.*, studied the electro properties, piezo-electric and dielectric properties of ZTS and have reported the electro-optic piezoelectric, and dielectric constants of ZTS.[24] Vibrational spectroscopic characterization has also been carried out on ZTS and the effect of metal complexation on thiourea vibrations has also been studied.[25]

One important issue of a nonlinear crystal is the characterization of the absorption in the spectral region of the fundamental source used for effective blue conversion. This is particularly needed if the NLO crystal is to be used for intra-cavity applications. The presence of the N-H Vibrational overtone at 1040 nm in ZTS opens the possibility of higher order modes giving rise to absorption peaks in the near-infrared spectrum. Therefore a careful characterization of the optical absorption in the near-infrared spectral region is essential. As is well known, thermal nonlinearities depend greatly on the absorption of the material. Since usually this absorption is small it is possible, provided other material parameters are known, to measure small absorption coefficients using a thermal lensing technique. The author have measured the absorption spectrum of zinc (tris) thiourea sulphate in the near infrared region (700 nm-980 nm) using a pump-probe thermal lensing spectroscopy[26, 27, 28] and Z-scan techniques[29, 30, 31] and demonstrates low absorption of the crystal in the spectral region that is typical for second harmonic generation of blue light.

Combined with the earlier known studies of the ZTS crystal, the present thesis completes several studies that are required to evaluate this material for second harmonic generation devices. This study demonstrates suitability of ZTS as an effective second harmonic generation material for a wide range of near-infrared fundamental wavelengths. This clears the way for further studies on ZTS for other nonlinear applications including generation of higher-order harmonics, difference frequency generation and applications involving third order non-linearities. Studies on this crystal with suitable dopings to further enhance its properties for specific applications can now be undertaken.

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