Chapter 5: Conclusions

This thesis is a detailed study of the mechanical and optical properties of Zinc (tris) Thiourea Sulphate (ZTS) crystals. As mentioned earlier in the introduction chapter, ZTS crystals belong to the class of "Semiorganics." The difficulty of growing large crystals due to phase transitions and poor UV transparency with a cut off around 450 nm is a major drawback with many inorganic crystals. Almost all of the organic compounds have poor optical transparency in the wavelength region less than 400 nm due to red shift of the UV absorption edge. Moreover, the conjugated planar structure of the large organic molecules inside the crystals makes the bonding force between the planes very weak. For this reason, these crystals have the characteristic strong tendency toward cleavage.[1] The interest in "Semiorganics" evolved to overcome the drawbacks of two major classes of high efficiency nonlinear optical crystals (organic and inorganic NLO crystals), which are currently being used in the ultraviolet (UV) to near infrared (NIR) wavelengths.

ZTS crystals used for this study were grown from aqueous solution of Zinc Sulphate and Thiourea. The aqueous solution method at room temperature yields crystals of good optical quality and can measure as large as 5 x 5.5 x 3 mm in 2-3 weeks without seeding. This method does not require highly sophisticated equipment and thus makes the growth process relatively inexpensive. For studying several direction-dependent properties of the crystal, preferential growth along specific directions is often required. Growth of the crystal depends on one or more variable conditions present in or imposed on the crystallizing system and causing one of a variety to change. An important variable for crystal growth that was investigated was the pH of the growth solution. In particular, the effect of pH on dislocation density, growth rate and optical absorption coefficient of ZTS crystals is reported in this thesis. 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 in the 3.6-3.8, yielding the lowest mass rate growth per unit mass per, were of highest quality. This indicates that slower growth rate is desirable to allow optimum atom rearrangement during crystal growth. Further the growth along the c-axis was found to increases with increasing pH.

Etching continues to be a powerful and relatively simple tool to study the structure and composition of materials and at the same time yields information about defect density and distribution. Formic acid, a new dislocation etchant for ZTS was discovered. This etchant was used to determine the activation energy by dislocation. The activation energy by etching was calculated to be 8.787 Kcal/mole. This value of the activation energy suggests that the etching reaction is diffusion controlled.

Mechanical hardness studies on this crystal were carried out as mechanical strength affects the growth, fabrication and use of the non-linear crystal. The hardness can effect how well a crystal can be finished. For instance, the vast majority of high temperature melt growth IR materials typically have low hardness values. This makes it difficult to polish surfaces to a high degree of flatness. It also demands that special procedures be implemented to protect the crystal surfaces from physical damage. From the hardness studies conducted in this thesis work, it can be concluded that ZTS possesses good hardness properties. It is observed that (100) plane is the hardest of the three planes studies, viz. (100), (001) and (010). The hardest and the softest directions on the three planes were analysed stereographically. The Vickers hardness of (100) and (001) planes exhibit significant surface anisotropy following the anisotropy in resolved shear stress on the active slip system of the crystal. The surface anisotropy coefficients of the Vickers hardness of (100), (010) and (001) planes have been found to be 0.35, 0.49and 0.42 respectively. The observed indentation creep agrees with the kinematic model proposed by Atkins *et al.* and the activation energy for creep is found to be 36.5 Kcal/mole. Strong correlation between the laser damage studies and microhardness was observed from the laser damage pattern. .

In early nineties ZTS received considerable attention due to the initial studies by H. O. Marcy and co-workers. A detailed study of second harmonic generation in ZTS was carried out and nonlinear coefficients with comparison to potassium dihydorgen phosphate were deduced. This early work concentrated on use of ZTS crystals in frequency doubling of the 1064 nm parent wavelength of an Nd:YAG laser.[2] Unfortunately, ZTS has a shallow absorption peak at 1040 nm. This eroded the use of ZTS crystal for frequency doubling applications at this wavelength. 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.[2] 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.[3] A detailed study of dopants for ZTS crystals is required to address this issue. To our knowledge, no such studies have so far been undertaken.

However, in recent years several suitable laser sources, including pulsed and cw laser diodes, have become available in the NIR wavelength range. This thesis work concludes that the standard ZTS crystals are suitable candidates for SHG from fundamental inputs in the 600-1000 nm wavelength region where the effects of the 1040 nm absorption peak are minimal. The preliminary studies in this thesis indicate Type-I second harmonic generation in as-grown ZTS crystals with near-IR fundamental inputs between 820 and 950 nm. For 100 fs fundamental pulsed input at 920 nm, the SHG angular acceptance is measured to be ~ 1.30 degrees. The average d_{eff} is estimated to be 0.37 pm/V by comparison with BBO. Without cutting or polishing the as-grown ZTS crystals an SHG output of ~ 0.3 mW is obtained with 100 fs femtosecond input at 76 MHz repetition rate and ~500 mW average power.

As applications of non-linear optical materials in laser technology involves high light intensities it is essential to study the damage caused by intense laser irradiation on to this materials. To evaluate the suitability of a material in laser applications it is necessary to determine its laser damage threshold. There are earlier reports of laser damage on ZTS crystals with ~ 40 ps pulses by using a 10 Hz Nd: YAG at a wavelength of 1064 nm.4 However the current commercially available low repetition rate Nd:YAG lasers have a typical pulse width of about 10 ns. At these time scales, thermal effects are likely to play in important role and the laser damage threshold is expected to be lower than that for the picosecond regime. Taking this into mind laser damage studies was carried on ZTS crystals at 532nm using a 10 Hz, 10 ns Nd: YAG laser. 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. The breakdown paths are parallel to [012], which is the hardest direction of ZTS crystal.[5] This indicates that there is a strong correlation of laser damage with the mechanical hardness anisotropy.[6] For ZTS 532 nm single shot damage occurred at an intensity of 50 GW/cm^2. This laser damage intensity saturates at 0.34 GW/cm^2 as the number of shots reach 10,000. Using the same laser, damage studies were also conducted at 1064 nm. For this wavelength, the damage threshold for single-shot is estimated to be at least 50GW/cm^2. Thermal lensing studies in this thesis work indicate that thermal effects compensate for the self-focusing effects due to kerr non-linearities and this possibly results in a high damage threshold in the NIR wavelength ranges. ZTS displays a high damage threshold that is comparable to the commercially available NLO crystals like KTP and BBO.

An important issue of a non-linear crystal is the characterization of the absorption in the spectral region of effective blue conversion particularly at the fundamental wavelength. Since the absorption in optical materials is usually very small, high sensitivity methods must be used for such characterization. This study demonstrates the suitability of thermal lens and z-scan techniques for measurement of small absorption in nonlinear optical crystals. In this thesis a pump-probe thermal lensing spectroscopy and thermal lensing Z-Scan experiments for the measurements of NIR spectrum and absolute absorption values of ZTS were conducted. A careful characterization 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 d*s*/d*T* is negative for ZTS. The negative d*s*/d*T* has important consequences for the damage threshold of nonlinear 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. A negative d*s*/d*T* is observed in other well-known SHG crystals with high laser damage thresholds, such as KTP and BBO.

The work reported in this thesis is a preliminary study on the mechanical and optical properties of the ZTS crystal. The ZTS crystals were used for laser damage and SHG studies in an as-grown state. The surface was not polished or antireflection-coated. On many samples in ZTS, the cleaved (100) surfaces show the presence of striations or steps, which could lower the damage threshold. The laser that was used for the damage studies described above has an average beam diameter of 5.5 mm. The beam from the unseeded Nd:YAG laser is not a TEM00 Gaussian profile. It is slightly elliptical (5.0 mm < diameter < 6.0 mm) with some non-uniformities in its profile. This results in higher intensity "hot spots" that could result in damage threshold estimate that is lower than the actual value. Second, the temporal profile of the laser pulses is nearly "top-hat." A Gaussian or a Lorentzian temporal profile delivers higher peak powers to the sample than the existing pulse shape. This factor was taken in to account while calculating the intensities corresponding to the incident pulse energies. Thus, it can be concluded that the damage threshold values reported in this work are conservative estimates and that the ZTS crystals can withstand impact of laser intensities at least up to these intensities.

A more precise study of optical properties in ZTS requires the crystals to be polished and appropriately cut. Proper anti-reflection coating should be applied on the surfaces to prevent reflections. The mechanical studies of ZTS indicate a high hardness value. This can make it convenient to polish the surfaces to a high degree of flatness. The hardness value of (100) plane is the highest. This suggests that mounting the crystal on this plane in an optical device can prevent damage of the ZTS crystal.

As ZTS crystal is grown by aqueous solution growth, it is possible that crystal can be affected by moisture. A similar problem is encountered in the case of KDP and BBO. For KDP a sealed housing typically used. For BBO moisture resistant coatings are applied. Similar techniques can be used for the ZTS crystal to prevent surface damage due to moisture. With these considerations taken in to account it should be possible to develop ZTS crystals for SHG device applications.

This work represents a renewed study to explore the feasibility of ZTS as a suitable material for second harmonic generation from near infrared laser sources to yield outputs in the blue and near UV wavelength range. This work shows that ZTS has good hardness properties and should make finishing the crystals for nonlinear optical applications straightforward. Laser damage threshold in ZTS is comparable to many other popular nonlinear optical crystals and shows very low absorption in the sub-micron near infrared wavelength range. Both these qualities should make intra-cavity laser use of this crystal possible.

REFERENCES

1. D. Xu, M. H. Jiang, J. T. Lin *et al*, SPIE Vol. **1104** , 188 (1989).
2. H. O. Marcy *et al*, Appl. Opt. Vol **31**, No. 24 (1992).
3. Ramabadran, U. B., McPherson, A. L. and Zelmon, D. E., J. Appl. Phys. **76**, 1150 (1994).
4. V. Venkataramanan, *et al*. J. Appl. Phys, **77** (11), (1995).
5. S. S. Gupte and C. F. Desai, Cryst. Res. Tech, **34**, 1329, (1999).
6. V. Venkataramanan, G. Dhanaraj, *et al*. Ferroelectrics, Vol. **155**, pp. 13-18,1994.