CHAPTER 6

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

Nucleation studies on pure and amino acid doped TGS crystals have been done. The classical theory of homogeneous nucleation has been employed to evaluate the nucleation parameters. The rates of nucleation were evaluated experimentally by the induction time measurements for pure and amino acid doped TGS crystals. It has been observed from the experimental results that the induction time $\tau$ reduces while doping with L-alanine and L-valine. This has been attributed to the enhanced rates of nucleation. The interfacial energy for pure and doped solutions has been calculated from the slopes of $\ln \tau$ versus $(\ln S)^2$.

Growth conditions and stability of pure and amino acid doped TGS crystals have been investigated. An investigation has been made on the basic growth parameters such as solubility and metastable zone width. It has been found that both the solubility and metastable zone width reduce with doping of amino acids. Computer controlled optically heated constant temperature bath with a high precision temperature control to an accuracy of $\pm 0.01^\circ C$ has been fabricated. For the growth of bulk crystals, the type of seed used plays a vital role in the external habit formation of the crystal. Seeds of different orientations such as [001], [010] and [100] have been experimentally investigated during growth. It has been found out that while using [010] and [100] seeds the crystal ended with more inclusions and less growth rate. While using a [001] seed, the crystal ended with a wide b-plane and the crystal yield was high which is a favourable one for IR detector and imaging applications. Highly transparent TGS crystals of size $9 \times 5 \times 4 \text{ cm}^3$. 
were grown by using [001] seeds. Morphology and growth rate changes have been observed while doping the crystals with L-alanine and L-valine.

The electrical and mechanical characterization of pure and doped TGS crystals have been investigated. In order to find out the suitability of TGS crystals for IR detection, pyroelectric and dielectric studies have been carried out. The doping of L-alanine and L-valine has enhanced the pyroelectric coefficient. Also the ferroelectric transition temperature ($T_c$) has been shifted to a higher value. This is a favourable one for applications in room temperature operated IR detectors used in military systems. The shift observed at Curie temperature is attributed to the change in macroscopic polarization and increase in electrical conductivity. The capacitance and dielectric loss were measured at different temperatures for pure and amino acid doped TGS crystals at different frequencies and subsequently the permittivity ($\varepsilon_r$) and loss factor ($\varepsilon''$) were calculated. Amino acid doped crystals were found to be less permeable to electric flux compared to pure TGS crystal and the temperature at which the permittivity was maximum was also found to be changed on amino acid doped crystals. It has been observed that while doping with amino acids $\varepsilon_{max}$ is lowered and $T_c$ shifted to higher temperature. This is attributed to the asymmetric strain field produced during doping of L-alanine and L-valine. The dielectric loss ($\varepsilon''$) was higher for pure crystals than for the doped crystals. Lattice parameters have been calculated from single crystal X-ray diffraction studies. Microhardness measurements were made for pure and doped crystals which reveal a reduction of hardness due to doping with amino acids. The presence of dopants in the crystal were qualitatively investigated by the FTIR studies. The doping with L-alanine and L-valine causes much broadening of the peaks in the spectra when compared to the pure TGS crystal. The spectra also reveal reduction in the crystal hardness as a result of doping incorporation - this has been evident in the hardness measurements for pure and doped crystals. It is inferred that the modes due to polar groupings, for example COOH, COO' are more broadened compared to the modes of
non-polar groupings illustrating that the doped crystals reject more degree of interaction for the polar groupings rather than for non-polar groupings.

Growth and characterization of Benzophenone and Urea doped TGS crystals have been investigated. Optical quality single crystals of Benzophenone and Urea doped TGS were grown. The doping of crystals has affected the growth rate and the morphology. In the case of Benzophenone doped TGS (BTGS) crystal the growth rate along (010), (001) and (100) were less; when compared to that of pure TGS crystal. In the case of Urea doping (UTGS) the growth rate was enhanced much higher in the (010) direction leading to a wide (110) face; the crystal yield was also higher compared to pure TGS crystal - a favourable one for IR detection fabrication. The pyroelectric coefficient has been measured as a function of temperature. BTGS and UTGS have higher pyroelectric coefficients than pure TGS. Also the ferroelectric transition temperature has been enhanced to 51°C. The dielectric constant and loss has been measured as a function of temperature. It has been found that Benzophenone doping has increased the dielectric constant ($\varepsilon$). The low permittivity of Urea doped TGS crystal results in a higher pyroelectric figure of merit than pure TGS crystal. The increase of dielectric constant in BTGS crystal lowered its figure of merit, which is lesser than that of pure TGS crystal. This is attributed to the symmetric structure of Benzophenone which prevents a locking of dipoles thereby preventing the internal bias field. Microhardness studies were made for the doped crystals. BTGS and UTGS crystals have higher hardness than pure TGS crystal. The relative increase in hardness values for doped crystals make them more suitable for the fabrication of (010) plates for IR detection.

SUGGESTIONS FOR FUTURE WORK

TGS crystals have been grown successfully to a dimension of 9×5×4 cm$^3$ by slow cooling method. For the fabrication of IR imaging systems b-cut plates of dimensions (1×1×0.5) cm$^3$ in large numbers are
necessary; for which bulk TGS crystals of wide b-plane are required. In the conventional growth technique the size of the crystal is limited to the length of [001] direction seed, hence the length of [001] direction should be increased. A novel grafting technique can be adopted in which two [001] direction seeds can be attached lengthwise and used for growth. By this technique bulk TGS crystal of wide b-plane can be grown. From these bulk crystals many [001] seeds can be obtained and used for further growth runs.

In TGS, one of the major disadvantages is the low transition temperature ($T_c = 49^\circ C$). Due to this drawback, the crystal cannot be used in IR detectors operated at room temperature. One possible way to overcome this problem is to grow crystals in heavy water (DTGS), where the transition temperature is enhanced from 49°C to 60°C. Attempts can be made to grow pure and doped TGS in heavy water.

Many pure and doped TGS crystals have been grown. The doping of crystals in general has enhanced the device quality characteristics for IR detectors. Attempts should be made to fabricate single and multi element IR detectors. The device parameters such as voltage responsivity, current responsivity, minimum detectable power and detectivity should be measured for pure and doped TGS crystals. The fabricated IR detectors should be tried in specific applications such as military systems and FTIR spectrometers.