CHAPTER VII
SUMMARY AND CONCLUSION

In recent years, many significant achievements have been realized in the field of nonlinear optics because of the development of laser technology and nonlinear optical materials of inorganic, organic and semiorganic types. The discovery of phenomenon of SHG in organic materials led to the development of many solution grown crystals like KDP, DKDP, ADP, urea etc. In the present thesis, glycine single crystals have been grown by slow evaporation technique. The primary aim was to study the effect of additives on growth and properties of γ-glycine, glycine nitrate, TGS and TGSP single crystals. This was achieved through the growth experiments with various concentration of additives. The additive concentration was optimized for the growth of each crystal with improved properties suitable for device application. The major problem encountered during growth of glycine nitrate was attaining large size crystal. This problem was overcome by optimizing growth condition. Nucleation parameters such as induction period, interfacial tension and critical radius were estimated for the growth of glycine nitrate crystals. The grown crystals were subjected to different characterization techniques to study their properties.

Single crystals of γ-glycine with good optical quality were grown in the presence of KCl, AgNO₃, H₃PO₄ and H₃PO₃ at various concentrations by adopting slow evaporation method. The crystals were transparent and their shape and size were sensitive to the amount of additive present in the solution during growth. The XRD studies confirmed the good crystalline nature and the phase purity. XRD data also confirmed that the crystals were hexagonal in structure with space groups of P3₂₁, a well-known non-centrosymmetrical space group, thus satisfying the requirements for second order NLO activity. Mixed crystal containing both α and γ-glycine grew in presence of the additive H₃PO₃. TG-DTA studies revealed that the phase transition temperature varies for various dopants viz; 170°C, 173°C, 192°C and 208°C for γ-glycine crystals grown in presence of KCl, H₃PO₃, H₃PO₄ and AgNO₃ respectively. These results depict that the γ-glycine crystal grown in presence of AgNO₃ was more stable. In FTIR spectra, the presence of carboxylate and ammonium ion clearly indicated that the glycine molecule exists in
zwitter ionic form in γ-glycine crystal. The γ-glycine crystals grown in presence of KCl exhibited excellent transmission (~100%) in the entire UV-Visible range studied (200-1100 nm). However, the relative second harmonic efficiency of these crystals was very less when compared to that of KDP. On the other hand, the SHG values of γ-glycine crystals grown in presence of AgNO₃, H₃PO₄ and H₃PO₃ were found to be 1.4, 1.3 and 1.1 times higher than that of KDP. The dielectric constant and dielectric loss of all the investigated γ-glycine crystals were found to decrease with increase in frequency. The dielectric constant of γ-glycine crystals grown in presence of H₃PO₄ was found to be higher than that of the crystals grown from all other additives. Similarly, γ-glycine crystals grown in presence of H₃PO₄ have higher mechanical strength when compared to crystals grown with other additives. Based on these facts it could be concluded that the AgNO₃ doped γ-glycine crystal has good propensity for nonlinear activity.

TGS crystals with and without HNO₃ addition (0.1 - 0.5M) were grown by slow evaporation method. The grown crystals' shape and size changed significantly with the change in the amount of HNO₃ in TGS solution. Single crystal and powder XRD studies confirmed that a certain amount of HNO₃ is doped into TGS and that there is saturation in the doping level already at 0.2M HNO₃ addition. Further increase in HNO₃ content in solution acted as habit modifier and enabled the changes only in crystal habit. The spectral investigations by FTIR and FT-Raman spectroscopy strongly suggested that the zwitter and glycinium ions were present in both pure and HNO₃ doped crystals. TG-DTA results suggested that the doped TGS loses its H₂SO₄ at 596°C which is about 100°C higher than that of pure TGS. HNO₃ doping in TGS leads to increase in dielectric constant value at low frequency region. The low value of dielectric loss confirmed the grown crystals were of good quality. The work hardening co-efficient (n) for nitric acid doped TGS crystal is less than that of pure TGS crystal which shows HNO₃ doped sample is harder than pure TGS crystal, which is desirable for device fabrication.

TGSP crystals were grown by slow evaporation method using L-lysine as additive. There was significant change in the growth rate and crystal morphology due to L-lysine addition. FTIR and FT-Raman studies revealed that no major shift or additional peaks occurs in their respective spectra which rules out the possibility of formation of any other complex compound in lysine doped TGSP crystals. Based on the broadening of the
peak in FTIR spectrum we confirm the co-existence of L-lysine in TGSP crystal. The lysine doped TGSP crystals had wide b plane, which is favorable for IR imaging applications. The XRD pattern of lysine doped TGSP crystals confirmed the phase purity and good crystallinity. TG-DTA studies showed a significant enhancement in the decomposition temperature. The lower value of dielectric constant in L-lysine doped was attributed to the increasing of dipole moments of the molecules constituting the admixture of L-lysine. The microhardness value of L-lysine doped TGSP crystal was higher than that of pure TGSP crystal.

Based on these findings, it can be concluded that the additives play important role on the growth rate, crystal habit and properties of γ-glycine and its family crystals. In case of γ-glycine, it was not possible to achieve improvement in desired properties such as transition temperature, SHG value, dielectric constant and hardness simultaneously. These factors vary from additive to additive. It is essential to do more such studies in order to find still better additive to achieve improvement in desired properties at once. Alternatively, two or more additives can be added simultaneously. Care has to be taken that the additives do not react independently and result in other products. In case of TGS and TGSP, the work can be extended with other aminoacids.