ABSTRACT

Crystal growth forms a crucial part of materials science. The single crystals play a very important role in the present day technology to the extent that it can be said ‘single crystals are the pillars of modern technology’. In the recent high technology era, novel devices are made using single crystals of nonlinear optical, dielectric, ferroelectric, semiconductor, superconductor, piezoelectric and acousto-optical materials.

Nonlinear optics and ferroelectrics have been recognized for several decades as promising fields with important applications in the area of opto-electronics, photonics, memory devices etc. High performance electro-optical switching elements for telecommunications and optical information processing are based on material’s properties. Hence, there is always a continuous search for new and better materials. In crystal growth, the additive plays an important role. For example, trace amount of additives present in crystalline solids have a profound influence on their structural, mechanical, electrical, thermal and optical properties. In proposed thesis, the author has investigated the effect of different chemical additives on the growth, structural, spectral, thermal, dielectric and nonlinear optical properties of some glycine family crystals such as γ-glycine, triglycine sulphate (TGS) and triglycine sulphophosphate (TGSP).

Glycine (CH$_2$NH$_2$COOH), the simplest aminoacid is known to crystallize in three different polymorphs: α, β and γ. These polymorphs differ in the way how $^{+}$NH$_3$-CH$_2$-COO$^{-}$ zwitter-ion is linked together via hydrogen-bonds networks. While α and β forms crystallize in centrosymmetric class, the γ-glycine crystallizes in non-centrosymmetric space group P3$_2$ making it a potential candidate for nonlinear optical applications.
especially for optical second harmonic generation. The metastable \( \alpha \)-glycine grown from aqueous solution transforms into \( \gamma \)-form spontaneously. To induce crystallization of the \( \beta \)- and \( \gamma \)-polymorphs of glycine it is necessary to destroy the dimers present in glycine solution, which direct the crystallization towards the formation of the \( \alpha \)-form. This can be achieved by applying electric field or by changing solvents or by adding specially selected impurities. The \( \beta \)-form transforms rapidly to \( \alpha \)- and \( \gamma \)-forms in presence of moisture at room temperature. The \( \gamma \)-form transforms to \( \alpha \)-form on heating around 165°C.

The first chapter gives brief discussion about nonlinear optics and ferroelectrics. The second chapter gives brief discussion about crystal growth. Low temperature solution growth is a well-established technique due to its versatility and simplicity. It is possible to grow large crystals of high perfection as the growth occurs close to equilibrium conditions. It also permits the preparation of different morphologies of the same materials by varying the growth conditions. The proposed thesis deals with the growth of crystals from aqueous solution. Hence, in the first chapter, low temperature solution growth technique has been described in detail.

The third chapter explains the importance of glycine crystals and effect of additives on glycine crystals. \( \gamma \)-glycine crystallizes in the hexagonal system with non-centrosymmetric space group. This makes \( \gamma \)-glycine a candidate for nonlinear optical applications with second harmonic efficiency more than that of well-known NLO material potassium dihydrogen phosphate (KDP). A survey of literature shows that the \( \gamma \)-glycine can be crystallized only in presence of additives. The author has grown, for the first time, \( \gamma \)-glycine single crystals in presence two different electrolytes (KCl and
AgNO₃). Both KCl and AgNO₃ selectively inhibits growth of crystal faces with favorable adsorption site and effectively changes the morphology. These additives preferentially adsorbed on (011) face of α-glycine crystal and subsequently inhibit its growth along c-axis. It changes the actual morphology to the extent that it enhances the growth along the ‘a’ direction and reduces the growth along ‘c’, thus leading to the formation of γ-glycine.

The co-existence of KCl and AgNO₃ in the crystal lattice of γ-glycine was confirmed by FTIR, FT-Raman, TGA and XRD analyses. There has been a significant difference in the physical properties of the γ-glycine crystals grown from these two additives. For example the transition temperature i.e. transition from γ-glycine to α-glycine got enhanced from 165°C to 208°C for glycine crystal grown in presence AgNO₃ whereas there is no significant change in the crystals grown from KCl. Kurtz powder SHG test confirmed the frequency doubling of the glycine crystal grown in presence of AgNO₃ and its efficiency was 1.4 times higher than that of KDP. Similarly, the second harmonic generation (SHG) efficiency value was found to be significantly low for the crystals grown from KCl. Owing to its wide transparency range, high thermal stability, high hardness value with relatively high SHG efficiency, AgNO₃ doped γ-glycine appears to be a promising material for laser application and fabrication of electro-optic devices. The results have been discussed in detail.

In fourth chapter the growth and characterization of γ-glycine grown in presence of inorganic acids (H₃PO₃ and H₃PO₄) have been discussed. The effect of H₃PO₃ and H₃PO₄ addition on structure has been analyzed by single and powder X-ray diffraction studies. The effect on vibrational band is analyzed by FTIR and FT-Raman spectroscopy. Thermal analysis and microhardness measurement have also been done for glycine
crystals. The TG-DTA results indicate that the phase transition temperature enhances from 165°C to 191°C for crystals grown in presence of H₃PO₃ and H₃PO₄. SHG efficiency for glycine crystals grown in presence of H₃PO₃ and H₃PO₄ were found to be 1.1 and 1.3 times respectively higher than that of KDP crystals. In addition, large single crystals of glycine nitrate have been grown and FTIR, XRD, UV and TGA results have been discussed in third chapter. The nucleation parameters, such as interfacial tension and radius of the critical nucleus have been estimated for the growth of glycine nitrate single crystal. Second harmonic generation conversion efficiency has been determined and the output power generated by the crystal was compared with that of KDP crystal.

Glycine and its methylated analogues form complexes with mineral acids exhibiting interesting physical properties like ferroelastic, ferroelectric or antiferroelectric behavior. Triglycine sulphate (NH₂CH₂COOH)$_3$H₂SO₄, is one of the well-known ferroelectric materials in glycine family which is useful for room temperature IR detector application. The main disadvantages of the TGS crystals are; (a) depolarization with time and (b) low Curie temperature (49°C). But these can be overcome by substituting suitable dopant(s). Thus fifth chapter discusses about growth and properties of HNO₃ doped triglycine sulphate (TGS) crystals. 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 at around 0.2M HNO₃ addition. Further increase in HNO₃ content in solution acted as additive and enabled the changes only in crystal habit. The spectral investigations by IR and Raman spectroscopy strongly suggested that the zwitter and glycinium ions were present in both pure and HNO₃ doped
crystals. The dielectric studies confirmed that dielectric constant of TGS crystal got enhanced due to HNO₃ doping.

Partial substitution of sulphate with phosphate ion results in triglycine sulphophosphate (TGSP) crystal which has an improved transition temperature of 51°C. The \( b \)-plane is wider in TGSP crystal which can be used for fabrication of pyroelectric detectors. Substitution of molecules similar to glycine improves dielectric and ferroelectric property of TGSP crystal. The optically active dipolar L-lysine have similar structure as glycine. Here, the author has studied the substitutional effect of L-lysine in TGSP and the results concerning the crystal growth and properties are presented in sixth chapter. There was significant change in the growth rate and crystal morphology due to L-lysine addition in TGSP. The lysine doped TGSP crystals had wide \( b \) plane, which is favorable for IR imaging applications. The lower value of dielectric constant in L-lysine doped TGSP is attributed to the increasing of dipole moments of the molecules constituting the admixture of L-lysine.

Seventh chapter concludes with summary and conclusion.

The major findings have been published/submitted for publication in reputed International journals.