ABSTRACT

The search for new advanced materials is an important area of contemporary research in numerous disciplines of science and development of many new technologies. Nonlinear optical (NLO) crystals have been a great deal of interest in recent years due to their potential applications in the domain of optoelectronics and photonic technologies.

The thesis consists of nine chapters discussing important and interesting issues in relation to growth and characterization of NLO crystals. A brief introduction to various growth methods with emphasis on low temperature solution growth and an overview on NLO crystals with their characteristics has been presented in detail.

The single crystal growth of organic bis(2-aminopyridinium) maleate (B2AM) by low temperature solution growth method and their characterization analysis are discussed. Crystalline perfection of the as-grown single crystal was studied through high-resolution X-ray diffraction (HRXRD) analysis. Dielectric measurements indicate that B2AM crystal has low values of dielectric constant and dielectric loss. The cutoff wavelength of B2AM at 354 nm is revealed by the optical transmission studies. The SHG efficiency of B2AM was found to be 4.2 times that of potassium dihydrogen phosphate (KDP).
The characterization analysis of $\gamma$-polymorph of glycine grown from aqueous solution of glycine and lithium acetate is described. The single crystal XRD studies illustrates that $\gamma$-glycine crystallizes in hexagonal system with noncentrosymmetric space group $P3_1$. Presence of various functional groups was identified by FTIR spectrum analysis. HRXRD studies indicate that the crystalline perfection of $\gamma$-glycine crystal is very good. The SHG efficiency of the grown crystal is 3.4 times that of KDP.

The studies on semiorganic NLO single crystals of tris(glycine) calcium(II) dichloride (TGCC) is presented. Transparent single crystals of TGCC were successfully grown by slow evaporation technique. The solubility and metastable zone width were determined with water as solvent. TGCC crystal belongs to the orthorhombic system with space group $Pb2_1a$. EDX analysis reveals the presence of calcium and chlorine. HRXRD analysis shows that crystalline perfection of TGCC crystals is quite good. Thermal studies of TGCC were determined. Chemical etching analysis on (001) face of TGCC crystal suggests four fold rotational symmetry. The SHG relative efficiency of TGCC is 1.5 times that of KDP. The reverse indentation size effect on the (001) plane of TGCC crystal was identified by mechanical studies.

The synthesis, growth and characterization of bis(2-aminopyridinium) sulfate (B2APS) single crystals is focused in the next section. Single crystal XRD studies reveal that B2APS crystal belongs to the orthorhombic system with space group $Fdd2$. The high-resolution diffraction
curve recorded for B2APS single crystal using (222) diffracting planes contains a single peak and indicates that the specimen is free from structural grain boundaries. Single diffraction curve with reasonably low value of FWHM indicates that the crystalline perfection is fairly good. Thermal studies reveal that B2APS melts at 210 °C. Chemical etching analysis suggests two fold rotational symmetry of the (010) face. The SHG relative efficiency of B2APS was found to be 2.6 times that of KDP.

The growth of potassium carbonate doped KDP crystals in different molar ratios is discussed. A good quality doped KDP (5 mol%) crystal of size 45 × 25 × 15 mm³ was grown by slow cooling method from aqueous solution by the rotation of the seed crystal (40 rpm) with the in-house built rotation assembly. The HRXRD analysis shows that the crystalline perfection of the crystal grown in these optimum conditions is extremely good without having any internal structural grain boundaries and mosaic nature. The crystals grown in these optimum conditions show positive effect in powder SHG, laser damage threshold and piezoelectric studies.

The growth and characterization analysis of KDP crystals grown with potassium thiocyanate as new additive is discussed. Nucleation studies show that the additive enhances the metastable zone width, induction period and growth rate of KDP crystals. The optimum addition of dopant increases the SHG conversion efficiency and optical transparency of KDP crystals.

The effect of the addition of amino acid materials L-arginine monohydrochloride and L-alanine as new additives in different molar
concentrations on ammonium dihydrogen phosphate (ADP) crystals, grown by seed rotation technique is discussed. The addition of these dopants suppresses the activities of the metal ion impurities present in the solution which enables larger metastable zone width and faster growth rate. HRXRD curves recorded for the crystals grown from 5 mol% doped solutions show that the crystals are having excellent crystalline perfection. It was observed that measured SHG efficiency and piezoelectric coefficient of doped ADP crystals are higher than that of pure ADP crystal. The summary of the present investigations and suggestions for future research activities are presented.