ABSTRACT

In the modern world, the development of science and technology in many areas has been achieved through the availability of good quality single crystals. 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 optical (NLO) materials are expected to play a major role in photonics including optical information processing, sensor protector applications, data storage etc. High performance electro optical switching elements for telecommunications and optical information processing are based on the material’s properties. There are crystals with large NLO properties, but many of them do not have mechanical strength, thermal stability and perfection necessary for device fabrication. Hence, there is always a continuous search for new and better materials. In crystal growth, additive and dopant 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 potassium acid phthalate (KAP) crystals.

The potassium hydrogen phthalate [K(C₆H₄COOH-COO)] also called potassium acid phthalate (KAP) is a semi organic salt that belongs to orthorhombic class of alkali acid series. KAP crystallizes in an orthorhombic system with the space group Pca₂₁. It has unit cell dimension a=9.609 Å, b= 13.857 Å, c=6.466 Å and contains 4 KAP molecules. The habitual morphology of the crystal has 14 growth faces. It has a (010) face with a high
morphological importance on which spiral patterns could be easily observed due to the relatively high mono steps.

KAP crystals are diamagnetic along all the three main crystallographic directions at low temperatures and they exhibit piezoelectric, pyroelectric, ferroelectric, elastic and nonlinear optical properties with long term stability in devices. KAP crystals are also used as the second, third and fourth harmonic generators for Nd:YAG and Nd:YLF lasers. The crystals are widely used for electro-optical applications as Q-Switches for Nd:YAG, Nd:YLF, Ti:Sapphire and Alexandrite lasers, as well as for acoustic-optical applications. KAP crystals are frequently used as substrates for the deposition of thin films of organic nonlinear optical materials. KAP and other phthalate like cesium, rubidium and thallium acid phthalate are used in the preparation of buffer solutions. Nowadays KAP crystals are used as substrate for epitaxial growth of oriented polymers and hierarchical growth of organized materials.

Studies on the growth and structural characterization studies of this material have already been carried out, but the NLO and dielectric behaviour of this material have not been dealt with in detail. Amino acids contain chiral carbon atoms directing the crystallization in noncentrosymmetric space group and also possess zwitterion nature favouring crystal hardness. Some amino acids like glycine, L-alanine and L-arginine by itself have higher SHG conversion efficiency. The addition of amino acids in the semi organic material like KAP may perform modification or changes in the lattices or crystal behaviours and hence improving the NLO behaviour. Thus second and third chapter describes the growth and characterizations of KAP crystals grown in presence of amino acids. Several authors have investigated the crystallization of KAP in pure and doped form with various dopants in order to improve the crystal quality, morphology and physical properties. The metallic ion dopants (Fe$^{3+}$, Cr$^{3+}$, Zn$^{2+}$, Cu$^{2+}$, Na$^+$ and Li$^+$) on the
KAP crystals are reported to induce significant changes in optical, ferroelectric and non-linear optical behaviours. Thus fourth, fifth and sixth chapter describes the growth and characterizations of KAP crystals grown in presence of different metal ions (trivalent, divalent, monovalent, each three). In the present work, the author has carried out a systematic study on the effect of amino acid doping into KAP crystals and investigations on their thermal, structural and physical properties. In the second part, studies have been carried out on the effect of metal ions (trivalent, divalent, monovalent, each three) doping into KAP crystals and investigations on their thermal, structural and physical properties.

The first chapter gives brief discussion about nonlinear optics, ferroelectricity and dielectrics. 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 deals with the growth and characterization of KAP grown in presence of amino acids [L-alanine (LA: CH₃CH(NH₂)COOH), glycine (Gly: NH₂CH₂COOH) and L-tyrosine (LT: C₉H₁₁NO₃)]. The grown crystal were characterized using powder X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, ultra violet-visible near infrared (UV-Vis-NIR) spectroscopy, Thermogravimetric-Differential thermal analysis (TG-DTA), second harmonic generation conversion (SHG) efficiency, Vickers microhardness, and dielectric studies. Powder XRD studies confirmed the phase formation and amino acids doping into KAP crystals. The FTIR study confirmed
the presence of different functional groups of the molecule KAP. The optical absorption studies reveal that the LA doped crystals possess less absorption of visible ray than the pristine, Gly and LT doped KAP crystals. The optical spectra revealed that the transmittance is more for LA doped crystal than all the other crystals. TG-DTA studies show the decomposition temperatures to be 255, 232, 258 and 264°C for pure, LA, Gly and LT doped KAP crystals respectively. These variations have been attributed to the doping of certain amount of amino acids into KAP. Gly and LT doped crystals have a higher thermal stability. SHG efficiency of LA doped KAP crystal was found to be 1.1 times (31mV for KDP and 34mV for LA doped KAP) that of potassium dihydrogen phosphate (KDP) crystal. This is much higher when compared to that of undoped KAP crystal (12mV). Thus the LA doped crystals are suitable for device fabrication in nonlinear optical applications.

The fourth chapter describes the role of another three amino acids [L-cystine (LC: C₆H₁₂N₂O₄S₂CY), histidine (HI: C₆H₉N₃O₂) and L-lysine (LY: C₆H₁₄N₂O₂.H₂O)] on the growth of KAP crystal. The grown crystals have been subjected to extensive physical characterizations. The optical transmittance spectra revealed that the transmittance is more for HI doped crystal in 300 to 600 nm range than all the other crystals. TG-DTA studies show the decomposition temperatures to be 255, 260, 247 and 230°C for pure, LY, HI and LY doped KAP crystals respectively. These variations have been attributed to the doping of certain amount of amino acids into KAP. LY doped crystal have a higher thermal stability. The dielectric constant and dielectric loss studies showed that all the doped crystal change the dielectric behaviour of KAP crystal significantly. Grown crystals were subjected to FTIR and microhardness studies. The values of the SHG efficiencies obtained
by Kurtz powder method confirmed that all the doped crystals are suitable for nonlinear optical applications.

*Fifth chapter* explains the growth and properties of three trivalent metal ion (Al$^{3+}$, Cr$^{3+}$ and Fe$^{3+}$) doped KAP crystals. Powder XRD results proved that the crystals belong to orthorhombic system. Elemental analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES) confirmed the metal ions doping into the grown KAP crystals. The FTIR spectrum confirmed the presence of functional groups in the pure and doped compounds. The decomposition begins at 255, 270, 258 and 287°C for pure, Al$^{3+}$, Cr$^{3+}$ and Fe$^{3+}$ doped KAP crystals respectively. These variations have been attributed to the doping of metal ion into KAP. The optical transmission analysis revealed that the pure and doped KAP crystals have transmittance in the entire visible region, which is very essential for NLO applications. The microhardness values increased with increase in load for Al and Fe doped KAP crystals. The variation of dielectric constant and dielectric loss were studied as a function of frequency.

The *sixth chapter* consists the growth and characterization of three divalent metal ion (Ba$^{2+}$, Ca$^{2+}$ and Mg$^{2+}$) doped KAP crystals. Elemental analysis by ICP-OES proves the incorporation of these impurities into the grown crystals. Powder XRD studies confirmed the phase formation and metal ions doping into KAP crystals. TG-DTA show the onset decomposition temperatures to be 255, 238, 251 and 250°C for pure and Ba$^{2+}$, Ca$^{2+}$ and Mg$^{2+}$ doped KAP crystals respectively. The results revealed that the onset decomposition temperature of Ba-KAP is lower (238°C) and its total weight loss (98 wt.%) is higher when compared to that of Ca and Mg doped KAP crystals. The result suggests that Ba-doping into KAP reduced its thermal stability. The optical transmission studies confirmed that the metal ion doping reduces the optical quality of the KAP crystal. Ca-KAP crystal
exhibited the highest second harmonic generation (SHG) conversion efficiency of 16 mV with the output power of nearly half of the standard potassium dihydrogen phosphate (KDP) crystal. Among the three investigated metal ion impurities, Ca$^{2+}$ ion seem to have positive influence on the growth, mechanical, thermal, dielectric and SHG characteristics of KAP which makes it suitable for applications.

*Seventh chapter* reveals the growth and characterization of monovalent metal ion (Ag$^+$, Li$^+$ and Na$^+$) doped KAP crystal. Transparent KAP crystals were grown by slow evaporation method from the individual mixtures of AgCl, LiCl, NaCl and KAP. These crystals were characterized using XRD, TG-DTA, FTIR, UV-Vis-NIR, microhardness, dielectric studies and SHG. XRD results suggest that there is no change in the crystal system due to doping. The presence of functional groups in the crystal has been observed by FTIR. The UV-Vis-NIR spectrum confirms the optical quality of grown crystal. Dielectric properties have been measured as a function of frequency for pure and doped KAP crystals at temperatures 50, 100 and 150°C. The optical transmission analysis, microhardness and dielectric constant were higher values for Na doped KAP crystals. The results support that the Na$^+$ doped KAP crystal is more preferable for NLO applications.

*Eighth chapter* comprises the summary and conclusion. The results of the investigations have been published in the international journal and presented in conferences.