Abstract

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The thesis entitled **"Non-Linear Optical Hydrogen Phosphate Crystals: Growth and Characterization"**, representing an elaborated report of the author's research work, will be covering the following six chapters followed by suggestions for future work.

Chapter-1: Introduction of Crystal Growth and Non-linear Optics

This chapter provides a broad overview of the topic, crystal growth. The crystal growth section begins with a quick explanation of crystal growth before focusing on solution growth techniques for single crystal growth, such as slow evaporation, slow cooling, and so on, as well as the benefits and drawbacks of such procedures. The sub-section on non-linear optics provides an overview of non-linear optical phenomena, non-linear optical processes, and types of non-linear optical crystals. The relevance of various amino acids doped non-linear optical crystals is also discussed in this chapter. The author also provides a range of the literature on studies done in the last five years for amino acids doped hydrogen bonded KDP family crystals.

Chapter-2: Experimental Techniques

The many experimental approaches utilised to characterise the produced crystals are briefly described in this chapter. Powder X-ray diffraction (Powder XRD), Thermal Studies (TGA/DTA), Dielectric Analysis, Impedance Spectroscopy, Modulus Spectroscopy, Fourier Transform Infrared Spectroscopy (FT-IR), UV-Visible (UV-Vis) Spectroscopy, Photoluminescence Study (PL), Relative Second Harmoni Generation (SHG) Efficiency are all examples of these techniques.

Chapter-3: Effect of L-Cysteine on Structural, Thermal, Electrical and Optical Properties of Potassium Dihydrogen Phosphate (KDP)

This chapter represents a slow solvent evaporation technique at room temperature to grow and characterise pure and varied weight percentage (1 mol% and 2 mol%) L-Cysteine doped KDP crystals. Powder XRD spectra of pure and L-Cysteine doped KDP crystals revealed tetragonal symmetry, single-phase nature, and slight diffraction peak shifting, as well as minor changes in unit cell parameters. According to the TGA/DTA analysis, L-Cysteine added to pure KDP crystal improves its thermal stability; however, it decomposes faster than pure KDP crystal. The dielectric study reveals that L-Cysteine doping in KDP crystals reduces its electrical characteristics, such as dielectric loss, dielectric constant and conductivity, making

it acceptable for microelectronic applications. According to FT-IR spectroscopy, the doping of L-Cysteine in KDP crystal causes the absorption peak to shift, and the force constant was also calculated for O-H bond. The PL emission spectra of pure and doped KDP crystals show that L- and D- defects exist in doped and pure crystals. The electron and hole recombination at various photon energies has also been observed in PL emission spectra. The existence of Stokes shift and vibration relaxation phenomena indicates that doping has caused defects in KDP. In the UV-Visible and IR regions, the doped crystals have excellent transmittance. With doping levels of 1 mol% and 2 mol%, L-Cysteine in KDP crystals improves the bandgap from 3.41 eV to 4.40 eV and 4.50 eV, respectively, making it more appropriate for SHG application. The SHG efficiency of L-Cysteine doped KDP (1 mol%) crystal is two times that of pure KDP, implying that it could be used in frequency conversions and other applications. Thus, L-Cysteine doping improves the linear and non-linear optical (NLO) performance of KDP crystals, indicating that the doped crystals are promising candidates for diverse NLO applications.

Chapter-4: Effect of L-Arginine on Structural, Thermal, Electrical and Optical Properties of Potassium Dihydrogen Phosphate (KDP)

The pure and L-Arginine (1 mol% and 2 mol%) doped KDP crystals were successfully grown at room temperature with a slow evaporation technique. The obtained crystals were highly transparent. Powder XRD analysis revealed crystalline perfection and no substantial peak shifting, suggesting that the dopant L-Arginine atoms/molecules are accommodated adequately in the KDP crystal structure. The dielectric constant and dielectric loss decrease with applied angular frequency for all crystals due to electric dipole's inability to comply with the applied field and lattice defects produced within crystals. The a. c conductivity of doped KDP crystals is observed to be enhanced compared to pure KDP crystals suggesting the generation of defects in the lattice. From Jonscher's plots, we observed that L-Arginine doped KDP crystals follow the Correlation Barrier Hopping (CBH) conduction mechanism. Based on the conduction process taking place, we calculated the values of binding energy (W_m) and density of state at Fermi level [$N(E_f)$]. The incorporation of L-Arginine in the KDP lattice is confirmed by amino acid functional groups in the doped KDP spectra. Minor structural changes in the KDP crystalline matrix are caused by L-Arginine doping, evidenced by small shifts in vibrational frequencies in doped KDP crystal's FT-IR spectra. The bandgaps of L-Arginine (1 mol% and 2 mol%) doped KDP crystals are greater than pure KDP crystals. These findings

suggest that the materials are suitable for the manufacture of optical devices. Doping KDP crystal with L-Arginine (1 mol% and 2 mol%) successfully changed the transmittance cut-off, extinction coefficient, and refractive index in the visible area, which is critical for UV-tunable lasers, holographic data storage, and photonic devices. The huge magnitude of optical conductivity (10^{10} s^{-1}) confirms the presence of a very high photoresponsive nature of the material. Crystals with low Urbach energy (E_u) values have a high degree of crystalline perfection. The PL emission spectra of pure and doped KDP crystals show that L- and D-defects exist in doped and pure crystals. In the PL emission spectra, electron and hole recombination at various photon energies has been observed. The Nd:YAG laser was used to examine the NLO properties of pure and doped crystals. The SHG efficiency of L-Arginine doped KDP (1 mol%) crystal was three times that of pure KDP, suggesting that it might be used in frequency conversion and other applications.

Chapter-5: Effect of L-Leucine on Structural, Thermal, Electrical and Optical Properties of Potassium Dihydrogen Phosphate (KDP)

Using the slow evaporation growth technique at room temperature, good quality crystals of pure and L-Leucine (1 mol% and 2 mol%) doped KDP crystals were successfully grown. By doping L-Leucine amino acid into the KDP crystal, its optical and dielectric characteristics are found to be enhanced usefully for its applicability in various NLO device applications. The tetragonal structure and minor changes in lattice parameters of doped KDP crystals were verified with XRD analysis. Due to the inability of electric dipoles to comply with the applied field and lattice defect developed within crystals, the dielectric constant and dielectric loss decreases with applied angular frequency for all crystals. The a. c conductivity of KDP crystals doped with the amino acid L-Leucine is observed to be enhanced due to the generation of lattice defects. With the help of Jonscher's power law, it is observed that pure and L-Leucine doped KDP crystals follow the Correlation Barrier Hopping (CBH) conduction mechanism. The values of binding energy (W_m) and density of states at Fermi level [$N(E_f)$] were calculated. For all the crystals, the a. c conductivity behaviour signifies a thermally induced mechanism. The Nyquist plots reveal one depressed semi-circle for all crystals investigated, successfully represented by one R-CPE parallel circuit. Complex impedance spectroscopy analysis shows that even a small amount of L-Leucine doping in KDP crystal causes significant changes in the bulk resistance and capacitance values and the conduction mechanism. The presence of amino acid functional groups in the doped KDP spectra confirms

the inclusion of L-Leucine in the KDP lattice. L-Leucine doping causes minor structural changes in the KDP crystalline matrix, as seen by slight shifts in vibrational frequencies in FT-IR spectra of doped KDP crystals. Due to the addition of L-Leucine (1 mol% and 2 mol%), the optical transmittance of pure KDP crystal is increased by 2% and 3%, respectively. It is observed that the bandgaps of L-Leucine (1 mol% and 2 mol%) doped KDP crystals are more than that of the pure KDP crystal. The results indicate that the materials may prove good for use in optical devices. L-Leucine (1 mol% and 2 mol%) doping successfully adjusts the transmittance cut-off, extinction coefficient and refractive index of KDP crystal in the visible region, which is important for photonic devices, UV-tunable lasers and holographic data storage. The presence of a very high photoresponsive nature of the material is confirmed by the large magnitude of optical conductivity (10^{11} s^{-1}). The low values of Urbach energy (E_u) suggest that crystals have high crystalline perfection. The L-Leucine doped crystals' SHG conversion efficiency is higher than that of the pure KDP crystal and is improved with increasing doping concentration. These investigations imply that L-Leucine doping significantly improves crystalline perfection, SHG efficiency and optical transparency, with a considerable correlation between crystalline perfection, optical transparency and SHG.

<u>Chapter-6:</u> Effect of Growth under Electric Field on Structural, Electrical and Optical Properties of L-Cysteine and L-Arginine Doped Potassium Dihydrogen Phosphate (KDP) Crystals

The pure and doped KDP crystals grown using the slow evaporation method in the presence of an electric field. have good quality and transparency. An elongation along the c-axis [100] was observed in L-Cysteine and L-Arginine doped KDP crystals. The impurity causes this elongation in crystals which are grown in the presence of an electric field. Powder XRD analysis verified crystalline perfection. No significant peak shifting indicates that the dopant L-Cysteine and L-Arginine atoms/molecules are satisfactorily accommodated in the KDP crystal structure. The formation of lattice defects increases the a. c conductivity of KDP crystals doped with the amino acids (L-Cysteine and L-Arginine). Using Jonscher's power law, it was observed that pure, L-Cysteine, and L-Arginine doped KDP crystals follow the Correlation Barrier Hopping (CBH) conduction mechanism. The binding energy (W_m) and density of state at the Fermi level [$N(E_f)$] were calculated. The a. c conductivity indicates a thermally induced mechanism for all the crystals under study. Based on complex impedance spectroscopy analysis, it is noted that even a small amount of L-Cysteine and L-Arginine

doping in KDP crystal generates substantial changes in the bulk resistance and capacitance values, as well as the conduction mechanism. The Nyquist plots indicate one depressed semi-circle for all crystals studied, successfully represented by one R-CPE parallel circuit. The FTIR spectra show that the doped crystals contain the amino acid with an amine functional group. Based on the value of force constant measured for O–H vibration in doped KDP crystals, it is found that the L-Cysteine and L-Arginine atoms/molecules have not disrupted the lattice structure of KDP. Using the emission spectra of the crystals, the electronic transition resulting from light absorption by intrinsic impurities that generate colour-centre emissions can be investigated. The relative SHG efficiency of L-Arginine (2 mol%) doped KDP crystals grown in an electric field was found to be around five times that of pure KDP crystals. The high value of SHG efficiency suggests that crystals might be used in laser fusion and frequency conversion investigations.

Future Scopes:

This chapter gives an overall view of the future works which can be executed on the grown crystals.