Growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic as well as applied research. In the modern era single crystals are largely used in the areas such as telecommunication, optical computing, optical data storage and optical information processing etc. Further progress in crystal growth technology is required for significant contributions to the energy crisis. Besides, the dream of laser fusion energy and other novel technologies can only be realized after appropriate progress in the technology of crystal. The strong influence of single crystals in the present day technology is evident from the recent advancements in the above mentioned fields. Hence, in order to achieve high performance from the device, good quality single crystals are needed.

The rapid development of optical communication system has led to a demand for Nonlinear Optical (NLO) materials of high performance for use as components in optical devices. NLO materials are used in frequency conversion, which is a popular technique for extending the useful wavelength range of lasers. The search for new materials has identified novel systems of considerable potential and high performance and the improvements in the properties of the known crystals is a never ending process. Therefore, special consideration is given not only to the possibility of changing significant functional characteristics of the crystal, but also to the creation of properties which is new to the pure crystal by adding different
impurities. Potassium Hydrogen Phthalate (KHP) is a model system for nonlinear optical device application, it continues to be an interesting material both academically and industrially and is extensively studied from various aspects. Its excellent qualities such as high nonlinear conversion efficiency, wide optical transmission range with low cut-off wavelength and high laser damage threshold has drawn the attention of several crystal growers. Many research works have been resulted in the modification of KHP properties and growth rates by varying the growth conditions and by adding suitable impurities.

**9.2 SUMMARY AND CONCLUSION**

In the present work, the slow solvent evaporation technique is used for the growth of pure and doped KHP crystals. The inorganic dopants are SrCl$_2$, BaCl$_2$, CdCl$_2$ and the organic dopants are Thiourea, L-Histidine, and L-Glutamine. The study of solubility curves for pure and doped KHP solutions are presented. The kinetics of nucleation is also discussed and it has been observed that the induction period as well as nucleation parameters for the doped crystals are higher than the pure KHP crystals.

The crystal structure of grown crystals was confirmed by single crystal and powder XRD. All the grown crystals belong to orthorhombic system. Powder XRD is used to study the variation in the unit cell parameters and the possibility of presence of any extra phase due to doping in KHP crystals. All samples have showed the single phase nature and not much variation in unit cell parameters of KHP is observed due to doping.
CHN studies reveal the presence of C and H for all grown samples. Atomic absorption studies and EDS analysis reveal the presence of Sr$^{2+}$, Ba$^{2+}$ and Cd$^{2+}$ metal ions in the doped KHP crystals. Surface morphological features were studied by SEM and for doped crystals, the empty space increases which in turn reduces the dielectric constant of that materials.

The density of the pure and doped KHP crystals was determined by floatation method. Again it was found that the densities of doped KHP crystals were high as compared with pure KHP. The density variation shows clearly that the impurity molecules have entered proportionately into the KHP crystal matrix nearly as per the impurity considered in the solution used for the growth of single crystals.

For any device application, various mechanical properties are very important. The variation of Vickers micro hardness with applied load is studied. As the applied load increases the Vickers micro-hardness also increases. Since the work hardening coefficient of all the grown crystals are greater than 1.6, the grown crystals of this work belong to the category of soft materials.

FT-IR spectroscopy studies of pure and doped KHP crystals are reported, which confirms the successful achievement of doping in KHP. From FTIR analysis, the functional groups and their interactions in the crystal are confirmed through hydrogen bonds. The existence of functional groups and bonding nature of all the grown crystals were studied by FTIR spectral analysis. It was observed that there was slight shifts, broadening and narrowing of absorption peaks in FTIR spectrum of doped KHP crystals. This may be due to the incorporation of dopants into the lattice of KHP.
SHG describes the nonlinear optical properties of grown pure and doped KHP crystals. The Kurtz and Perry powder method has been used to determine the second harmonic generation. A Q-switched mode locked Nd:YAG laser of 6 mJ pulse at 1064 nm fundamental radiation is passed through the powdered samples filled in a fine capillary and the radiation emitted by the samples is detected by photodiode detector. The second harmonic radiation intensity is compared with the standard KDP sample. It has been found that for all doped materials, SHG efficiency was higher than that of pure KHP crystals. In addition to this, the increase in SHG in the case of all doped KHP crystals may also be attributed to the central ion in metal organic complex which offers a certain anisotropic field to keep NLO active chromopores and vary the hyperpolarizibility value.

The UV-Vis spectra show that the materials have wide optical transparency in the entire Visible region. The dopant does not affect or change the optical transmittance of the crystals. The SHG efficiency of doped KHP crystals possesses higher second harmonic generation efficiency and hence it can be used as an efficient frequency conversion material.

The TGA and DTA studies have been carried out for the pure and doped KHP crystals. There is no significant weight loss till the melting point. Strong endothermic peak at 290 °C reveals decomposition of pure KHP. There was gradual weight loss in different stages due to the liberation of various gases like CO, CO₂, Cl, NH₃ etc. It is evident from TG/DT analyses, the dopants have slight influence on the thermal stability of KHP crystal and hence the doped compound could be used for the fabrication of any optical devices with better thermal stability. Another important observation is that there is no phase transition till the material melts and
this aspect enhances the temperature range for the utility of the crystal for NLO applications.

The dielectric study is carried out for the pure and doped KHP crystals at room temperature by varying the frequency of applied field in the range from 100 Hz to 100 kHz. From the electrical studies, it is observed that the values of dielectric constant and dielectric loss decrease with increase in frequency of applied field. At low frequency, all the four types of polarizations were present (especially the space charge polarization). As the frequency increases, space charge cannot comply with external field and dielectric constant decreases. There is a phase transition from paraelectric to ferroelectric at Curie temperature for pure and doped KHP crystals. It have also been observed that the values of dielectric loss and dielectric constant are less for doped samples in comparison to the pure KHP sample and decrease with increase in doping level. As the frequency increases, the capacitive reactance decreases and hence the dielectric loss decreases. The low value of dielectric loss at higher frequency suggests that the grown crystal possesses enhanced optical quality used for NLO application. The variation of a.c. conductivity with applied frequency is also presented. The AC activation energies were increases with the addition of impurities and it takes high values for the doped crystals. The low dielectric loss values in doped crystals have indicated that the doping do not introduce major defects in the crystals. The lowering of dielectric constant values due to doping makes the crystals good candidates for electro-optic applications, which needs lower dielectric constants.
9.3 SUGGESTIONS FOR FUTURE WORK

Since the dielectric constant of the pure KHP is low, it can be used as intermetal dielectric material. The microelectronic industry is searching for low dielectric constant materials. So the bulk crystals of KHP which is free from defects can be grown by slow evaporation technique or by other methods. The dielectric properties along the three principle directions can be calculated and hence it can be used for microelectronic applications. Before use it for real applications its linear as well as non-linear optical properties along the three principle axis should be studied and the actual values for the non-linear optical susceptibility tensor will need to be measured in future.

Crystalline perfection can be determined by HRXRD analysis and laser damage threshold studies. Dislocation, surface defects and morphology can be characterized by chemical etching followed by etch pit examination using optical microscopy. Irradiation effect on the dielectric properties of doped KHP crystals can also be investigated.

The optical properties such as refractive index, birefringence and phase matching of the pure and doped KHP crystals can be studied in future to confirm their optical utility.

Again the dielectric constant can be increased or decreased, depends on the need by doping it with smaller ionic radii metal ions or higher ionic radii metal ions, respectively. Serious attempts can be made in this regard with many other smaller as well as higher ionic radii metal ions in future.
The grown crystals can be subjected to Z-scan studies to estimate the absorption coefficient. Grown crystals could also be subjected to Nuclear Magnetic Resonance (NMR), and Atomic Force Microscopy (AFM) studies to visualize the structure and defect mechanisms. Studies such as ESCA/AUGER near the phase transition temperature will be very much useful in understanding the mechanism involved during the phase transition. NLO parameters such as phase matching, higher harmonic generation, etc. could be estimated. Photo-acoustic studies could be carried out on grown crystals. The second harmonic efficiency of the doped KHP crystals can be improved by adding many more different doping concentration with pure KHP.

Since the nucleation studies for these samples are not carried out, attempts can be made in future to investigate the nucleation parameters such as metastable zone width, induction period, interfacial tension etc., to improve and investigate the optimized growth parameters for industrial crystallization. In future, attempts can be made to improve the quality of the grown crystals; etching studies can be made on different crystallographic faces of the crystals with suitable etchants in order to identify the dislocations.