NON-LINEAR OPTICAL HYDROGEN PHOSPHATE CRYSTALS: GROWTH AND CHARACTERIZATION

Synopsis of the Thesis to be submitted

to

THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA

For the Award of Degree of Doctor of Philosophy

in

Physics

by

MAHADIK ASHWINI

Reg. No FOS/1998

Under the Guidance of

Dr. P. H. Soni

Department of Physics, Faculty of Science

The Maharaja Sayajirao University of Baroda

Vadodara-390002 (Gujarat), India

Introduction:

Crystals and research on crystals and their properties have always been fascinating. The enchanting colours, the smooth surfaces with scintillating reflections of light, the definite and varied shapes with sharp edges, the deep transparency of some perfect crystals, all together aroused the aesthetic sense of the early man who used them as ornaments. Crystals are unacknowledged pillars of modern technology. Crystal growth is an interdisciplinary subject which has great importance in physics, chemistry, material science, crystallography, mineralogy, etc. In the past few decades, there has been growing interest on various crystal growth processes, due to the increasing demand of materials for technological applications. Growth of single crystal has a prominent role to play in the present era of rapid technical and scientific advancements.

In the non-centrosymmetric class of crystals, ionic crystals exhibit the phenomenon of electric polarization due to its inherent permanent electric dipoles. In such crystals there can be induced polarization which is normally proportional to the applied electric field whereas, the susceptibility is independent of the field. In practice, this is always the case at low fields. However, at high fields, the polarization exhibits nonlinear dependence on the field and hence the susceptibility starts depending on the field. This phenomenon at high electric fields gives rise to Nonlinear Optics (NLO) property. At high light intensity, the graph representing the dependence of optical polarization on the light field amplitude deviates from straight line and adopts curvature. Thus, Non-Linear optics deal with behavior of light in non-linear media, i.e., the media in which the dielectric polarization P responds non-linearly on the applied electric field. A primary criterion of selection of an NLO material is that the non-linear susceptibility should be quite large. NLO crystals can be suitable for higher harmonic generation of high intensity huge laser system for fusion experiments (for example, because crystals can be grown to larger sizes and can have high laser damage threshold). The demand for non-linear optical crystals with superior properties is increasing due to quantum jump in the design of non-linear optical devices with higher performance.

KDP (Potassium Dihydrogen Phosphate), KH_2PO_4, is a water-soluble salt of potassium and dihydrogen phosphate ions making it useful as a fertiliser, a food additive and a fungicide. It is a source of phosphorus and potassium. Single crystals of KDP are para-electric at room temperature. At temperatures below −150°C (−238 °F) they become ferroelectric. KDP crystals have a high laser damage threshold, a large non-linear optical coefficient, good structural quality and mechanical properties. KDP is an efficient angle tuned dielectric medium for optical harmonic generation in the visible region.

There has been considerable increase in interest over last few years for water-soluble crystals. These water-soluble crystals contain complex organic molecules which can be used for simulation of crystal growth process. Other than this, these crystals can also be used for investigation of phase transitions in crystals [1-4]. There are many studies and investigations reported on crystal habit modification with the use of additives, dopants and specific metallic anions or cations which can influence the crystal growth rate as well as the shape of crystals. Specifically, for potassium dihydrogen phosphate (KDP), it has been observed that some dopants and additives show a selective adsorption to a specific growth surface; for example, prismatic segment (100) or pyramidal segment (101) [5, 6].

Due to ample number of hydrogen bonds in KDP, we can observe various optical, electrical and structural influences in the presence of dopants or additives using different characterization techniques. With a suitable dopant and growth condition, we can enhance certain properties of KDP crystals. This enhancement of properties of KDP can lead to different device applications. Also, we can analyse the change in non-linear properties due to presence of suitable dopants or additives. KDP and Ammonium Dihydrogen Phosphate (ADP) single crystals are already well-known materials having wide range of applications in different fields like non-linear optics, photonics, etc.

Amino acids exhibit NLO property and are widely found in biological substances. Their molecules contain α-amino acid and guanidyl groups. They are promising materials for NLO applications. Complexes of amino acid with inorganic salts are considered to be novel materials for Second Harmonic Generation (SHG) and they are found most of the time to be as promising as KDP or better.

- Amino acids exhibit specific features of interest as follows:

1. "Molecular Chirality" which secures non-centrosymmetric crystallographic structure
2. "Absence of strongly conjugated bond" which leads to wide transparency range in the visible and UV spectral regions
3. "Zwitter Ionic nature of the molecule" which favours crystal hardness required in device applications

The amino acids possess large non-linearity and favourable optical properties. This is mainly due to the presence of proton acceptor amine group (NH_3^+) and proton donor carboxyl group (COO^-) [7]. Materials like amino acid which possess high non-linear coefficients can enhance the second harmonic generation (SHG) efficiency by introducing organic molecules into the matrix of KDP crystal. They can also augment the crystal morphologies as well as microscopic changes in KDP. There are number of evidences which depict that hydrogen bonds such as O-H and N-H/O bonds play a vital role in optical non-linearities of inorganic crystals [8]. Requirement of both the bulk form and notably nanoform crystals has increased in last few decades due to their applications in optoelectronic and microelectronic industries. This demand widely depends on overall stability as well as performance of crystals.

The reason for requirement of huge KDP crystals is that huge KDP crystals are suitable for use in large aperture laser systems. KDP also holds advantage of growing into large size crystal from a small single crystal. Habit modification through different techniques and growth process controls are frequently required for suitability of the grown crystals for their use in devices. Incorporation of a dopant in the crystal bears its effects in terms of physical, optical, electrical and mechanical properties depending on dopant type, its concentration, distribution and accommodation in the host crystal. The dopant's functional groups can help amplify properties of the crystal. The atoms or molecules of a dopant may accommodate in the crystal lattice in such a way that they can affect optical transparency as well as growth rate of the crystal. Thus, dopants or additives play vital role in enhancing some properties of the crystal.

Present work

Potassium dihydrogen Phosphate and Ammonium Dihydrogen Phosphate are two most well-known non-linear optical crystals. The main objective of the present work is to improve and enhance certain properties of KDP like the ionic conductivity, thermal, optical and electrical properties with a suitable dopant. However, selecting an appropriate dopant which can enhance or improve the qualities of KDP without deforming crystal lattice is a difficult task. This is so because dopants may augment certain properties only. Hence selection of the dopant is important and it should be such that it improves most of the desirable properties of KDP.

KDP single crystals can be grown using different crystal growth techniques. In the present work, conventional slow evaporation technique was used for growing doped as well as pure KDP crystals. KDP holds a very important place in non-linear optics and in laser optics. For many years several efforts have been made to modify its properties as new various applications of non-linear optical crystals come up day by day. There are many organic and inorganic materials which can be used as non-linear optical materials; however, there are certain drawbacks of both the organic and inorganic materials. There are some inadequacies of KDP crystals like SHG efficiency in need of improvement, narrow transparency range, etc., which can be removed with inclusion of suitable dopants or additives. Discovery of many inorganic, organic and semi-organic non-linear optical (NLO) materials with high susceptibilities has been proving fruitful for various device applications. KDP has been an interesting material for ages because of its interesting dielectric and optical properties, ease of crystallization and structural phase transitions. Thus, over many years it has become subject of intense investigation [9, 10]. The most important factor in solution growth of crystals is high supersaturation. At high supersaturation, large number of growth nuclei tends to form and adversely affects growth of the main crystal and can also terminate the growth run. This problem of solution stability also poses a challenge for rapid growth [11]. Amino acids have been reported to enhance some properties of KDP; therefore, it is be of interest to dope KDP with amino acids, as has been done in the work presented in the thesis. The thesis would consist of six chapters.

Chapter 1: Introduction

This chapter overviews reports of work done so far on KDP crystals with different dopants and growth conditions. The chapter also outlines history of KDP crystals and their applications in different areas. The objectives of the work are also explained in this part of the thesis.

Chapter 2: Experimental Techniques

This chapter deals with synthesis of KDP with different dopants/additives and of different growth methods/techniques normally used. It is found that certain dopant changes the morphology of KDP crystals abruptly. Also, some optical as well as electrical properties of KDP are enhanced with the inclusion of suitable dopant or additive.

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

This chapter describes changes in structural, thermal and optical properties of L-Cysteine doped KDP crystals as compared to pure KDP crystal. L-Cysteine differs from all other amino acids, particularly sulfur amino acids, in that it has a sulfhydryl group in its molecular structure making it very strongly reactive and serving as a strong reducing factor, while its chirality would expectedly enhance the charge symmetry feature of the non-centrosymmetric crystal. The structural analysis with powder X-ray diffraction (XRD) data is given. This chapter also throws light on the property acquired by the dopants themselves when incorporated in pure KDP crystal without changing the crystal structure. The L-Cysteine doped KDP crystals exhibited elongation along the C-axis as compared to pure KDP. The good overall improved high transmittance of the crystals in the entire visible region suggests its suitability a potential alternative in NLO devices. The amine functional groups of L-Cysteine were present and it was confirmed with the help of Fourier Transform Spectroscopy (FTIR). Photoluminescence (PL) analysis offers information regarding the point or lattice defect nature of L-Cysteine doped as well as pure KDP crystal. It has been observed that there is increase in peak intensity of emission spectra of doped KDP crystal which may be due to increase in concentration of heterovalent impurities with L-Cysteine dopant percentage. The phenomenon indicates that the increase in the concentration of impurities results in orientational defects of L and D types in the vicinity of the impurity atoms to compensate for the excess charge. Interestingly, L-Cysteine (1 mol% and 2 mol%) doping in KDP crystal increases the band gap from 3.78 eV to 5.13 eV and 5.34 eV. The thermal analysis shows that inclusion of amino acid, particularly L-Cysteine in pure KDP crystal enhances its thermal stability; however, the crystal starts decomposing faster than pure KDP crystal does. It was observed that SHG efficiency of L-Cysteine doped KDP (1 mol%) crystal is 2 times that of the pure KDP, suggesting its application for frequency conversion, etc. As a consequence of wider band gap and increased SHG efficiency, these crystals are suitable for photonic and optical applications [12]

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

This chapter deals with optical, electrical and structural changes in KDP due to inclusion of L-Arginine amino acid in different proportions. The changes in crystal morphology or habit modification of L-Arginine doped as well as pure KDP crystals are explained in this chapter. Also, there is no major peak shifting observed in XRD analysis; so, we can say that the dopant L-Arginine atoms/molecules well accommodate in KDP crystal lattice. The functional groups of L-Arginine present in doped KDP crystals divulge the unification of dopant in KDP. There are some functional groups of L-Arginine which are overlapping the functional groups of KDP. Like in the case of L-Cysteine, inclusion of L-Arginine in KDP also enhances its band gap from 3.78 eV to 5.83 eV and 5.95 eV. It is observed that the intensity of PL emission spectra increases as the concentration of amino acid dopant is increased confirming the incorporation of the dopant in the KDP crystal. Dielectric constant, d. c. conductivity, activation energies and tan δ are calculated and plotted and results are discussed. Dielectric constant and D.C conductivity of L-Arginine doped KDP crystal tend to increase with increasing temperature. From the dielectric calculations, it is observed that the values of dielectric constant and D.C conductivity of L-Arginine doped KDP crystal are larger as compared to those of the pure KDP crystal. The lower value of dielectric constant can find its application in low power consumption devices. The values of d. c conductivity can find application in energy storage devices, etc. It is observed that of L-Arginine plays a significant role as a dopant in enhancing SHG efficiency of the KDP crystal.

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

This chapter deals with L-Leucine doped KDP crystals. An L-Leucine doped KDP crystal was dissolved in de-ionized water to conduct paper chromatography. Purple coloration was obtained with the help of ninhydrin, implying the presence of amino acid in doped KDP crystals; the presence of L-Leucine was further confirmed with the help of FTIR spectroscopy. The powder XRD analysis implies that there is no change in the crystal structure of KDP even after doping it with L-Leucine up to 2mol%. The sharp diffraction peaks of pure and doped KDP crystals indicate very good crystalline perfection [13]. L-Leucine doped KDP crystals also follow the same trend of increased band gap like L-Cysteine and L-Arginine doped crystals. At low temperatures, the conductivity is due to vacancies and feebly attached impurities in the crystal lattice. Due to the addition of L-Leucine in KDP, the conductivity is observed to have increased. However, we can say that in the higher temperature region, the water molecules present in the crystals vanish and the conductivity observed is due to intrinsic defects. The increase in conductivity of the L-Leucine doped KDP crystals with increase in temperature has also been observed in the cases of KDP crystals doped with urea, thiourea, etc. [14, 15].

Chapter 6: Effect of Growth under Electric Field on Structural, Electrical and Optical Properties of L-Cysteine and L-Arginine doped Potassium Dihydrogen Phosphate (KDP) crystals.

When L-Cysteine and L-Arginine dopants are added to the KDP solution for crystal growth under applied D. C. electric field, the prism sides of the growing crystal are elongated along the z-axis. We can say that adsorption of amino acid and forced orientation of its moment in presence of electric field apparently may be the causes of elongation. It has been observed that (100) and (010) planes contain highest phosphate reticular density whereas the z-plane (001) has the least phosphate reticular density [16]. With the help of powder XRD analysis, it is observed that there is almost no variation in the inter-planar spacings and lattice parameters in the doped crystals grown in presence of electric field, in agreement with the reported lattice parameters of pure KDP. From the FTIR spectra, it is observed that some of the frequencies get slightly shifted due to KDP bands overlapping the amino acid vibrations and also a few bands of KDP become broader. The qualitative evaluation of impurity amalgamation and the consistency of grown crystals can be interpreted with photoluminescence analysis. One of the optical phenomena that can be investigated using absorption of photoluminescence at a certain wavelength is the recombination attending electronic transitions. When KDP is doped with L-Arginine, the dopant incorporates in the lattice and engenders L-defects. The formation of L-defects depends mainly on the proton transport mechanism [17]. Lokshin [18] assumed that HPO_4^{2-} ions are also the reason for generation of vacant H-bonds (L-defects). Also, impurity addition in the crystal lattice entails replacement of cations by L-Arginine. KDP is protonic mainly due to the anions [$H_2PO_4^-$ ions] and not the cations [K^+ ions]; the additional H-bonds getting created to aid the proton movement. Due to this reason the conductivity increases with increasing dopant concentration [19]. We observe that the SHG efficiency is enhanced for L-Arginine (2 mol%)

doped KDP crystals grown in the presence of an electric field and is 5 times that of pure KDP crystal grown in absence of electric field. We may say that this is due to the zwitterionic nature of amino acid. It may be possible that the molecular alignment of L-Arginine doped KDP crystal grown in presence of an electric field enhances the nonlinearity as a result of which the SHG efficiency is boosted. The high value of SHG efficiency provides promise for potential application of crystals in laser fusion experiments as well as in frequency conversion experiments.

Chapter 7: Future Scopes

Recommendation for future work can be summarised as follows:

- Various ion beam irradiation or implantation study can be done on KDP (pure and doped) to explore the structural, nonlinear optical and electrical properties modification of such crystal in pre and post manner.
- Using the density function theory (DFT), it is possible to study the hydrogen bonding defect chemistry of amino acid doped as well as pure KDP crystals more closely.
- The higher order nonlinear optical susceptibility may also be explored in the crystal implanted with suitable dopant ions.
- Various properties of KDP doped with suitable nanoform impurities of the types organic or inorganic dyes, metal ions, etc., can be studied.
- In the presence of electric field and ultrasound, efforts can be made to grow the pure and doped KDP crystals and variations in growth and properties of KDP crystal can be studied.

References:

1. Y. Velikhov, I. Pritula, I. Ganina, M. Kolybayeva, V. Puzikov, A. N. Levchenko, Growth and Properties of Dye Doped KDP Crystals, Cryst. Res. Technol. 42 (2007) 27-33.

2. K. Maeda, A. Sonoda, H. Miki, Y. Asakuma, K. Fukue, Synergy of organic dyes for KDP crystal growth, Cryst. Res. Technol. 39 (11) (2006) 1006-1013.

3. Kahr, R. W. Gurney, Dyeing crystals, Chem. Rev. 101 (2001) 893-952.

4. I. V. Shnaidshtein, B. A. Strukov, S. V. Grabovski, T. V. Pavlovskaya, L. Carman, Effect of an organic dye on the ferroelectric phase transition in KH_2PO_4 (KDP), Phys. Solid State 43 (2001) 2276-2279.
5. X. Zhao, C. Sun, Y. Si, M. Liu, D. Xue, Crystallization behaviors of ferroelectric and piezoelectric materials, Mod. Phys. Lett. B 23 (2009) 31-32.
6. D. Xu and D. Xue, Morphology control of KDP crystallites, Physica B 370 (2005) 84-89.
7. P. Selvarajan, J. Glorium Arul Raj, S. Perumal, Characterization of pure and urea-doped γ-glycine single crystals grown by solution method, J. Cryst. Growth 311 (2009) 3835-3840.
8. D. Xue and S. Zhang, Effect of hydrogen bonds on optical nonlinearities of inorganic crystals, J. Chem. Phys. Lett. 301 (1999) 449-452.
9. J. D. Lindl, Development of the indirect-drive approach to inertial confinement fusion and the target physics basis for ignition and gain, Physics of Plasmas 2(11) (1995) 3933-4024.
10. D. Eilmerl, Electro-optic, linear, and nonlinear optical properties of KDP and its isomorphs, Ferroelectrics 72(1) (1987) 95-139.
11. N. Zaitseva and L. Carman, Rapid Growth of KDP-Type Crystals, Prog. Cryst. Growth Char. Mater. 43 (2001) 1-118.
12. S. Suresh, A. Ramanand, D. Jayaraman, S. M. Navis Priya, Growth kinetics and optical and mechanical properties of glycine lithium sulphate (GLS) crystals, J. Miner. Mater. Charact. Eng. 9 (12) (2010) 1071-1080.
13. M. S. Pandian, K. Boopathi, P. Ramasamy, G. Bhagavannarayana, The growth of benzophenone crystals by Sankaranarayanan-Ramasamy (SR) method and slow evaporation solution technique (SEST): A comparative investigation, Mater. Res. Bull. 47 (2012) 826-835.
14. G. Deepa, T. H. Freeda, C. Mahadevan, Ind. J. Phys. 76(A) (2002) 369.
15. A. Anne Assencia, C. Mahadevan, D. C. electrical conductivity measurements on ADP single crystals added with simple organic compounds, Bull. Mater. Sci 28 (2005) 415-418.
16. Harry J. Kolb and Joseph J. Comer, Habit Modification of Ammonium Dihydrogen Phosphate Crystals during Growth from Solution, J. American Chem. Soc., 67 (1945), 894-897.

17. L. B. Harris, G. J. Vella, Direct current conduction in ammonium and potassium dihydrogen phosphate, J. Chem. Phys. 58 (1973) 4550-4557.

18. E. P. Lokshin, Crystallography Reports 41 (1996) 1070.

19. M. Meena and C. K. Mahadevan, Growth and electrical characterization of L-arginine added KDP and ADP single crystals, Cryst. Res. Technol. 43 (2008) 166-172.

LIST OF PUBLICATIONS:

1. Habit modification in L-arginine doped potassium dihydrogen phosphate crystal growth under applied electric field
   Ashwini Mahadik, P. H. Soni and Ketan Chaudhari
   AIP Conference Proceedings 2265 (2020) 030421.

2. Thermal, optical and electrical properties of pure and L-Cysteine doped KDP crystals
   Ashwini Mahadik, P. H. Soni and Ketan Chaudhari
   AIP Conference Proceedings 2220 (2020) 060014.

3. Effect of L-Cysteine doping on growth and some characteristics of potassium dihydrogen phosphate single crystals
   Ashwini Mahadik, P. H. Soni and C. F. Desai
   Journal of Physica B, Volume 527 (2017) 61-65.