A Report on Growth And Spectroscopic Studies on The L-Tartaric Acid Doped Potassium Dihydrogen Phosphate Non-Linear Optical Single Crystals

S Arulmani¹, P Sanjay¹, E Chinnasamy¹, K Deepa², J Madhavan² and S Senthil¹

¹Department of Physics, Government Arts College for Men (Autonomous), Nandanam, Chennai - 600035
²Department of Physics, Loyola College, Chennai -600034
Email: ssatoms@yahoo.co.in

Abstract. In recent years study of non-linear optical (NLO) materials is gaining rapid momentum due to their needs in several device applications. Potassium Dihydrogen Phosphate (KDP) is a well-known NLO material, whose non-linearity is enhanced by doping with amino acids. In this present study, single crystal of L-Tartaric acid doped potassium Dihydrogen phosphate (LTKDP) have been grown by slow evaporation method at room temperature. Good quality transparent crystals were obtained with 27-30 days. The crystallinity and cell parameters were characterized by X-ray diffraction analysis (XRD), the shifts in frequency assignments of various functional groups of KDP due to the addition of L-Tartaric acid was analysed by Fourier transform infrared (FTIR) and Fourier transform Raman spectroscopic studies. The dielectric constant and the dielectric loss of the single crystals were studied as a function of frequency. Kurtz- Perry power technique was employed to determine the Second Harmonic Generation (SHG) efficiency of LTKDP single crystal.

1. INTRODUCTION
The rapid development in the field of science and technology necessitates searching for newer and efficient non–linear optical materials. Potassium dihydrogen phosphate (KDP) crystals have created interest because of its Piezo-electric, electro-optic, non-linear optical properties and its extensive application in x-ray monochromators [1, 2]. The electro-optic effect in KDP is used to obtain phase and amplitude modulations[3]. KDP crystal based world’s largest laser to generate UV beams has been demonstrated [4]. In order to get good quality crystals, many techniques have been introduced by several workers. The modern world is witnessing revolutionary advancements in the various aspects of science and technology. Organic non-linear materials are attracting a great deal of attention as they have large optical susceptibilities inherent ultra-fast response times and high optical thresholds for laser power as compared with inorganic materials [5]. A number of such materials have been reported in Literature for this potential application [6]. Among organic class of NLO materials, amino acids exhibits some specific features such as molecular chirality weak vanderwaals hydrogen bonds, absence of strongly conjugated bonds wide transparency range in the visible and ultraviolet regions, amenability for synthesis multi-functional substitution, higher resistance to optical damage and manoeuvrability for device application etc [7,8]. Among amino acids molecular are usually linked
through the hydrogen bond. The aim of the present study is to investigate the effect of L-Tartaric acid in KDP crystal by slow evaporation method at room temperature. The doping of L-Tartaric acid into KDP was achieved by adding 0.4wt %, this solution was prepared in double distilled water, and the solution was stirred for 3-4 hours to achieve homogenization. The solution was filtered and sealed with porous lid and placed in a dust free atmosphere for slow evaporation. The optically good quality and transparent crystals were harvested in 27-30 days. The crystals were characterized using powder x-ray diffraction studies, Fourier transform infrared (FT-IR) and FT- RAMAN analysis, Second harmonic generation (SHG), Dielectric studies etc.

2. EXPERIMENTAL METHODS

2.1. Crystal Growth

Single crystal of L-Tartaric acid doped KDP was grown by slow evaporation technique at room temperature. Higher grade KDP salt was dissolved in double distilled water and and 0.4% of L-Tartaric Acid was doped with KDP, the saturated solution of LTKDP was prepared in accordance with the solubility data. The solution was thoroughly stirred for homogenization and then filtered into a Borosil beaker using whatmann filter paper. The pH of the solution was noted. The saturated solution was closed with perforated cover and kept in a dust free atmosphere to allow slow evaporation of the solvent. Transparent and good quality LTKDP crystals were harvested. The photograph of as grown doped LTKDP crystal is shown in figure.1.

![Figure 1. Photograph of as grown LTKDP crystal](image)

3. RESULT AND DISCUSSION

3.1. Powder X-Ray Diffraction Studies (XRD)

The powder X-ray diffraction studies have been carried out to confirm the crystallinity and to determine the lattice parameter of the grown crystals. The powder x-ray diffraction (PXRD) analysis was carried out using XPERT–PRO Diffractometer with CuKα radiation of wavelength 1.5406 Å with the scanning rate 2degree per minute over the range of 10 - 70°. The PXRD studies for the grown crystal show the appearance of sharp and strong peaks which confirms the good crystallinity of the grown crystals, there are no other phases emerging besides the tetragonal system. The cell parameter value of the grown crystal is \(a = b = 7.433\)Å, \(c = 6.932\)Å with the angles \(\alpha = \beta = \gamma = 90°\) having space group 1.42 d and the calculated lattice parameter values are in agreement with the reported values. Powder x-ray diffraction pattern for LTKDP crystal is shown in figure (1).
3.2. **FT-IR and FT-RAMAN spectral analysis**

FT-IR and FT-RAMAN studies are very useful techniques for qualitative analysis and identification of compounds. The recorded FT-IR and FT-RAMAN spectra of LTKDP are depicted in Figure 3 and Figure 4. The spectral bands are interpreted and compared with the standard spectra of the functional groups[9]. The bands which appear in the spectral region 450-4000 cm\(^{-1}\) arise from the internal vibration of LTA, and water molecules, the vibration of O-H and O=H types of hydrogen bonds. In the high frequency region of IR spectra, the sharp peaks observed at 536 cm\(^{-1}\) are ascribed to PO\(_4\) stretching vibration in the crystal. Their Raman equivalents are observed in the region of 514 cm\(^{-1}\). In the IR spectra the peak will be observed at 3223 cm\(^{-1}\) are in O-H stretching hydrogen bonded of KDP. Their Raman equivalents are not observed due to insufficient detector sensitivity in the region above 3091 cm\(^{-1}\). An intensive IR bands assigned to the in-plane band vibration is observed at 1096 cm\(^{-1}\) with equivalent Raman band at 1295 cm\(^{-1}\). It is observed that some of the bands originate from both LT and KDP simultaneously. The IR bands at 2738 cm\(^{-1}\) is assigned to P-O-H asymmetric stretching vibration. In Raman it cannot be observed at this region. In IR bands the frequency of 2376 cm\(^{-1}\) in the doped crystal corresponds to P-O=H stretching [10]. The broad absorption peak at 1694 cm\(^{-1}\) is due to O=P-OH bending vibration. The O-H deformation and P=O stretching will be observed in the frequency of 1297 cm\(^{-1}\). In IR the absorption band at 912 cm\(^{-1}\) is due to P-O-H bending vibration in the doped LTKDP. In Raman the sharp peak will be observed at 1079 cm\(^{-1}\) are ascribed to P-O-H stretching molecule in the doped LTKDP crystal. In Raman spectra, the peaks will be observed at 681 cm\(^{-1}\) for O-H bending (out of plane). In the IR band 550 cm\(^{-1}\) and in Raman 514 cm\(^{-1}\) frequencies will be observed due to the P=O symmetric bending. The frequencies of 481 cm\(^{-1}\) in IR band and 402 cm\(^{-1}\) in Raman band.
3.3. *Second Harmonic Generation efficiency studies*

Kurtz and Perry second harmonic generation efficiency test (SHG) is performed for the comprehensive analysis of second order nonlinearity. Nonlinear optic measurements were carried out...
by using Kurtz powder technique. A Q-switched Nd: YAG laser beam of 1064nm wavelength with 1.9 mJ/pulse input power, 8ns pulse width and repetition rate 10Hz was used to estimate SHG efficiency of the grown crystals. The grown crystals of LTKDP were grounded into a fine powder and then packed in a micro-capillary of uniform bore and exposed to laser radiation. The fundamental input radiation (1064nm) was separated or filtered by a monochromator and the output was measured. Second harmonic radiation generated by the randomly oriented micro-crystals was focused by a lens and detected by a photo multiplier tube. SHG was confirmed by the emission of green light. Using the pure potassium dihydrogen phosphate (KDP) crystalline powder as reference material, the output of SHG range was compared and found the SHG conversion efficiency of LTKDP is 1.09 times greater than that of reference KDP.

3.4. Dielectric Studies
Every material has a unique set of electrical characteristics that are dependent on its dielectric properties. The variation of dielectric constant of the sample with frequency is studied at room temperature using H10K1 3532 LCR HITESTER in the frequency range 300HZ to 3MHZ and is shown in figure 5. The high value of dielectric constant at high frequency may be due to the presence of all the four polarizations namely space charge, orientation, electronic and ionic. The dielectric characteristic of a crystal is determined by the dielectric constant. The dielectric constant determines the share of the electric stress which is absorbed by the material. It is the ratio between the permittivity of the medium and the permittivity of free space. If $E_0$ is the applied electric field, $E_p$ is the electric field produced due to polarization of the material, then the dielectric, $\varepsilon = \frac{E_0}{E_0 - E_p}$. The dielectric constant $\varepsilon$ has no units and it is a measure of the polarization in the dielectric material. Any small change in dielectric constant with respect to temperature can be attributed to the transition of the material. When the temperature raises, the orientation of the dipoles is increased and this increases the dielectric constant $\varepsilon$. Potassium dihydrogen phosphate (KH$_2$PO$_4$) has very good photorefractive performance and electro-optic properties due to its high dielectric constant. Figure 6 shows the variation of dielectric loss with frequency. The crystal possesses enhanced optical quality with lesser defects and this parameter play a vital role for the fabrication of nonlinear optical device because of low dielectric loss with high frequency for the samples.

![Figure 5. Variation of dielectric constant of LTKDP](image-url)
Second International Conference on Materials Science and Technology (ICMST 2016) IOP Publishing
IOP Conf. Series: Materials Science and Engineering 360 (2018) 012043 doi:10.1088/1757-899X/360/1/012043

Figure 6. Dielectric constant of LTKDP

4. Conclusions
High quality and transparent LTKDP single crystal has been grown by slow evaporation method at room temperature. Powder XRD studies shows that the grown crystals are tetragonal in structure. The transmission spectrum reveals that the crystal has sufficient transmission in the entire visible and IR region. The vibrational frequencies were assigned from FT-IR and FT-RAMAN spectral analysis which confirms the presence of functional groups. The SHG efficiency of the grown crystal was measured by Kurtz and Perry power method and its efficiency was found to be 1.09 times that of the pure KDP crystal. All the above results strongly attributes LTKDP is a novel material for non-linear optical applications.

Acknowledgment
The authors acknowledge University Grand Commission (UGC), India for funding this research project- F.No.4-4/2015-16 (MRP/UGC-SERO) – 2914.

References
[1] Dhumane N R, Hussaini S SDongre V G, Ghughare P, Shirsat M D, 2009 Growth and characterization of glycine doped bis thiourea cadmium chloride single crystal Research and Technology 44269–27
[2] Suresh Kumar B, .RajendraBabu K, 2008 Effects of L-Arginine, L-Histidine and Glycine on the growth of KDP single crystal and their characterization Indian Journal of Pure & Applied Physics, (IJRST).46123-126.
[3] Parikh K D, Parekh B B, .Dave D J, Joshi M J, 2007 Thermal, FT-IR AND SHG efficiency studies of L-Argine doped KDP Crystals Bulletin of Materials science 30 105-112
[4] Ferdousi Akhtar and Jiban Podder, 2011A Study on Structural, Optical, Electrical and Etching Characteristics of Pure and L-Alanine Doped Potassium Dihydrogen Phosphate Crystals Journal of Crystallization Process and Technology. 1 55-62.

[5] Jagadish P and Rajesh N P, 2011J. Effect of L-proline on the growth and NLO properties of KDP crystal Journal Of Optoelectronics And Advanced Materials. 13 962.

[6] Muley G G, 2012. Study on Growth Habit, SHG and Thermal properties of urea Phosphate Doped KDP Crystal Journal of Science and Technology. 2109-113

[7] Dhumane N R, Hussaini S S, Dongre V G, Ghugare P, Shirsat M D 2009 Growth and Characterisation of L-Alanine doped Zinc Thiourea Chloride Single Crystal (ZTC) Applied Physica A 95 727-732.

[8] Dave d J, Parikh K D, Parekh B B, Joshi M J, 2009 Growth and spectroscopic, thermal, dielectric and SHG studies of L- threonine doped KDP crystals Journal Of Optoelectronics And Advanced Materials, 11602 – 609.

[9] Dhanaraj P V, Rajesh N P, Mahadevan C K and G. Bhagavannarayana, 2009 Growth and Characterization of Non Linear Optical Crystal: L-Alanine Doped KDP Physica B. 40 404.

[10] Kumaresan P, Moorthy Babu S. Anbarasan P M, 2008 Thermal, dielectric studies on pure and amino acid L-glutamic acid,L-histidine, L-valine doped KDP single crystals Journal of Crystal. Growth. 30 1361–1368.