Studies on Structural, Optical and Thermal Properties of L- Histidine Doped Potassium Hydrogen Phthalate Single Crystal

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***Abstract*— Semi organic Potassium Hydrogen Phthalate single crystal with amino acid L-Histidine as a dopant was grown by slow evaporation technique. The grown crystal was subjected to powder X-ray diffraction analysis and the result confirms its structure and lattice parameters. The optical transparency of grown crystal was studied by UV-Visible spectroscopy and the molecular structure was confirmed by FTIR analysis. TGA and DTA studies reveal thermal stability and the mechanical strength of the grown crystal was estimated by Vickers hardness test. The improved SHG efficiency of L-Histidine doped Potassium Hydrogen Phthalate crystal could enhance the nonlinearity behavior. The low value of dielectric constant of the grown crystal also proved the enhanced NLO properties.**

Keywords*— Crystal Growth, Dielectric constant, FTIR, KHP, SHG, Thermal studies, UV, XRD.

I. INTRODUCTION

The search for new conversion materials for various device applications has led to the discovery of many organic, inorganic and semi-organic non linear optical (NLO) materials. But recent interest is focused on the development of the new semi organic materials with improved properties. Semi organic materials posses the advantage of both organic and inorganic materials in terms of high thermal and mechanical stability as well as broad optical frequency range, higher SHG and high threshold damage [1-2]. Crystals of phthalic acid derivatives are potential candidates for NLO and electro optic applications. Potassium Hydrogen phthalate (KHP), a semi organic material is one of the important NLO crystals in the alkali metal acid phthalate family which are used for long wave x-ray spectrometers [3-5]. Recently amino acid family crystals are playing an important role in the field of non linear optics and several new complexes incorporating the amino acid have been crystallized [6-7]. In the present work, the structural, optical and thermal properties of amino acid L- Histidine doped KHP single crystal, which was grown by slow evaporation technique at room temperature has been studied in detail.

II. SYNTHESIS & CRYSTAL GROWTH

Analytical reagent (AR) grade sample of pure KHP and L-Histidine along with triple distilled water were used for the growth of single crystal. The solution of KHP salt was prepared in a slightly under saturation condition at 30 ˚C with one mole percent of L-Histidine as dopant and then stirred well for 4 h. Then the solution was filtered using a filter paper. The solutions were kept undisturbed by covering with a thick porous sheet of paper and placed in a dust free atmosphere for controlled slow evaporation. Optically transparent crystals were harvested in 15-20 days. The photograph of L-Histidine doped KHP crystal is shown in Fig 1. The grown crystals were subjected to different characterizations such as Powder XRD, FTIR analysis, UV–visible spectral studies, TG & DT analyses, SHG efficiency and dielectric constant.

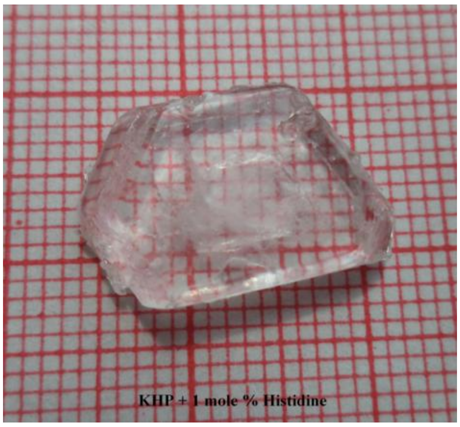

Fig. 1. Photograph of 1 mole % Histidine doped KHP crystals.

III. RESULT AND DISCUSSION

A. *Powder XRD Analysis*

The powder X-Ray diffraction pattern (Fig. 2) of L-Histidine doped KHP crystal was recorded using *Philips X'pert Pro* with *Cu Kα1* radiation (λ = 1.54056 Å) for phase analysis. This study reveals that the grown crystal belong to orthorhombic system and its cell parameters are a=9.7125 Å, b=13.3929 Å, c=6.5266 Å and cell volume V=848.97 $Å^3$. The cell parameters were good agreement with the reported values

[8] from the database of International Centre for Diffraction Data (ICDD). As compared with original pattern it is observed that there is slight shift in the peak positions, slight change in the relative intensities, cell volume and lattice parameters and these slight changes are due to the doping of L-histidine in KHP crystal.

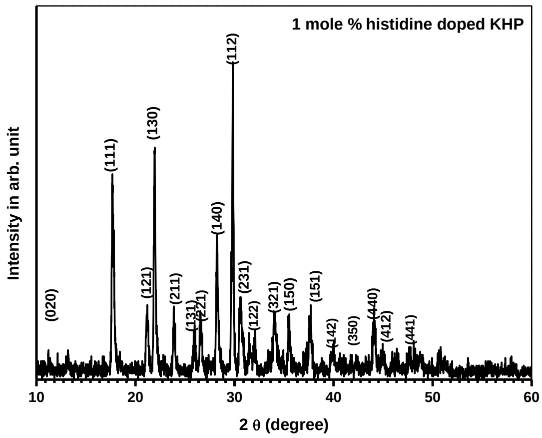

Fig. 2. Powder XRD pattern of 1 mole % histidine doped KHP.

B. *FTIR Spectral analysis*

FTIR spectra of L-Histidine doped KHP crystal were recorded in the range 40-4000 cm using KBr pellet in a *Perkin Elmer spectrometer* and FTIR spectrum is shown in Fig. 3.

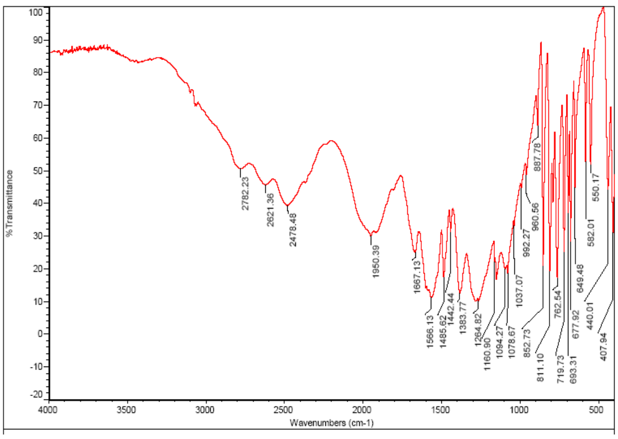

Fig. 3. FTIR spectrum of 1 mole % histidine doped KHP.

A very slight shift in some of the characteristic vibrational frequencies is obtained and this is due to lattice strain produced as a result of doping and using FTIR analysis the presence of the functional groups in the compound has been confirmed [9].

C. *UV Spectral Studies*

The UV –VIS spectrum of crystal was recorded in the region 100 to 1550 nm using *Perkin Elmer mode Lambda 35 spectrometer* and the recorded spectra are shown in Fig. 4.

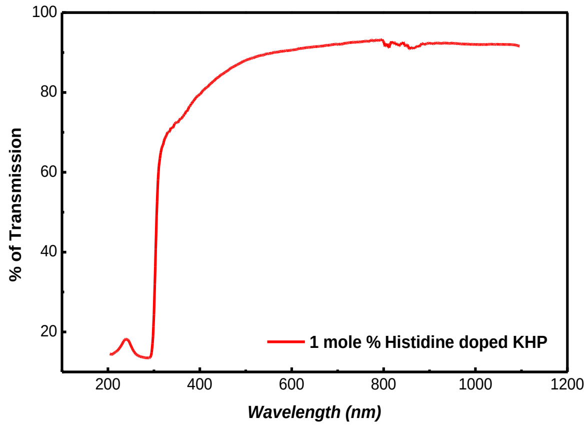

Fig. 4. The UV-Vis spectra of L-Histidine doped KHP.

High transparency and better lower cut off wavelength noted confirms that the L-Histidine doped KHP crystal is a good candidate for electro optic applications [10].

D. *Micro hardness test*

To estimate mechanical hardness, the indentation hardness is measured as the ratio of applied load to the surface area of the indentation. The hardness values of the crystal samples were found to increase slowly with the applied loads. A plot drawn on hardness value and corresponding load is shown in Fig. 5(a).

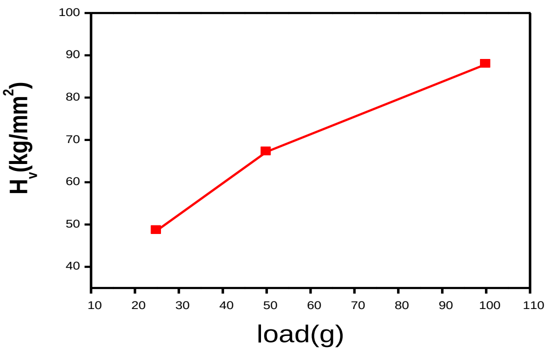

Fig. 5(a). The variation of hardness number with load for L-Histidine doped KHP crystal.

It is observed that the hardness number increases with increase in load and it reveals that the doped KHP crystal exhibits reverse indentation size effect. Higher hardness value for doped KHP crystal indicates that greater stress is required to form dislocations. The plot of log(P) against log(d) is almost a straight line as shown in Fig. 5(b) and from the slope of this plot, the work hardening coefficient is found to be n=3.486. It shows that the material is not belongs to the category of hard materials.

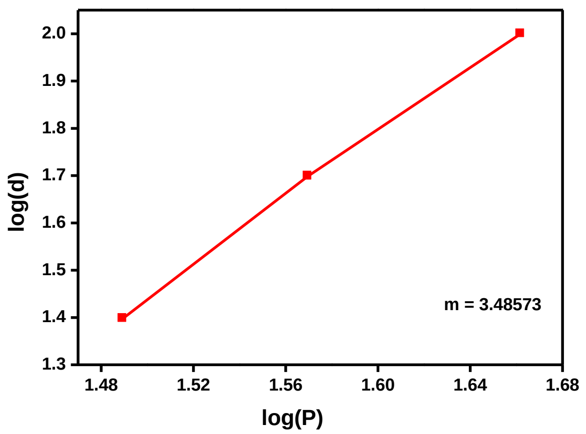

Fig. 5(b). The plot log(P) against log(d) for L-histidine doped KHP crystal.

E. Thermal analysis

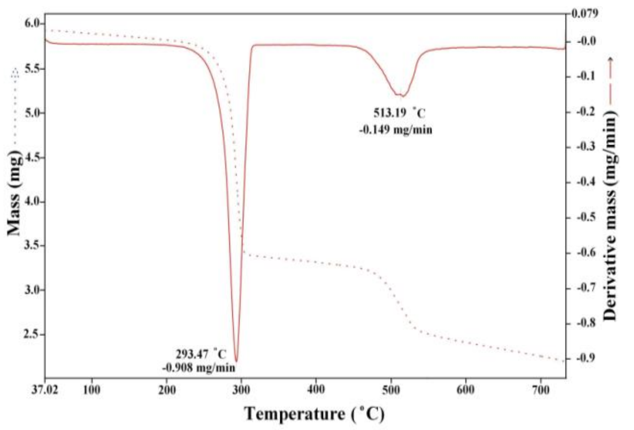

Fig. 6. The TG-DTA curves for L-Histidine doped KHP.

The TGA and DTA curves for L-Histidine doped KHP are shown in fig. 6. It is noticed that there is strong endothermic peak at 293.47 ˚C reveals the decomposition of doped KHP structure which is closer to the melting point of pure KHP (290 ˚C). There is an endothermic peak of DTA is observed at 513 ˚C, which shows the bulk decomposition of the compound at this temperature and various gases like CO, CO_2, NH_3, Cl_2, etc., are liberated.

F. Dielectric study

Good quality single crystals of L-Histidine doped KHP were selected for dielectric measurements using *Agilent 4284A* precision LCR meter. The selected samples were cut using a diamond saw and polished on both faces to make a capacitor with the crystal as a dielectric material [11-12]. The variation of dielectric constant was studied as a function of frequency for L-Histidine doped KHP crystals at different temperatures and the results are shown in Fig.7. From the figure it was clear that the dielectric constant increases as the temperature increases and then decreases when temperature becomes equal to 373.7 K. This decrease is due to paraelectric to ferroelectric phase transition. The dielectric constant has high values in the low frequency regions. The high values of dielectric constant at low frequencies may be due to the presence of all four polarizations namely, space charge, orientation, electronic and ionic polarization and its low values at high frequencies may be due to the loss of these polarizations.

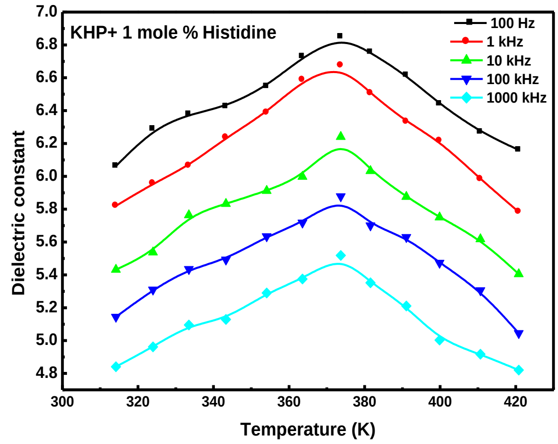

Fig. 7. The dielectric constant for L-Histidine doped KHP.

But from 313 to 373 K, there is an increase in the value of dielectric constant and this type of the behavior is due to the stray in the capacitance, which is an essential parameter for the enhancement of NLO property of the material [12].

G. Second Hormonic Generation efficiency

Table 1: Comparison of SHG signals energy output.

Input power (J)	KDP ref (mJ)	KHP Pure (mJ)	L - Histidine doped KHP (mJ)
0.68	8.8	3.2	5.1

To confirm the nonlinear optical property of the sample, the powder form of L-Histidine doped KHP crystals were subjected to NLO test obeying the Kurtz and Perry powder technique [13]. The Second Harmonic Generation (SHG) was confirmed by the emission of green light (λ=532 nm). The powder SHG efficiency of L-Histidine doped KHP crystals are compared with KDP and it was found that the SHG efficiency of doped KHP was 0.58 times that of KDP and it was very much greater than (1.6 times) that of pure KHP (Table 1). This SHG conversion efficiency makes the grown crystal a potential material for device application in the field of optoelectronics.

IV. CONCLUSION

Good optical quality single crystals of L-Histidine doped KHP have been grown by slow evaporation method under room temperature. The powder XRD confirms its structure and lattice parameters. The molecular structure was confirmed by FTIR spectral analysis. The optical transmission spectrum shows that L-Histidine doped KHP crystals have high transmission in the entire visible region and have low cut off wavelength. The thermal study reveals that an L-Histidine doped KHP crystal is thermally stable up to 293.47 ˚C. The temperature dependent dielectric constant measurement shows the normal behaviour of ferroelectric properties and also enhancing the NLO properties. All these studies promising that the doping of L-Histidine in KHP enhances the thermal, optical and electrical properties of KHP, and thus considered as a potential candidate for optoelectronic device fabrication.

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