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Effect Of Dopants On The Optical Properties Of An Efficient NLO Single Crystals: Potassium Hydrogen Phthalate

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ABSTRACT
Pure potassium hydrogen phthalate (KHP),L-Arginine doped potassium hydrogen phthalate (LA-KHP) and L-Histidine doped potassium hydrogen phthalate (LH-KHP) single crystals were grown by slow evaporation method. The grown crystal crystallizes in orthorhombic system which is confirmed by single crystal XRD analysis. Optical studies reveals that the doping of amino acids decreased the optical band gap value of KHP single crystal. The optical constants such as extinction coefficient, reflectance and refractive index were estimated. The existence of SHG is confirmed by powder Kurtz Perry and Q-switched Nd-YAG laser technique.
KEY WORDS: Single crystals, Optical property

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I. INTRODUCTION

Potassium Hydrogen Phthalate or Potassium Acid Phthalate abbreviated as KHP/KAP is a semiorganic crystal which belongs to alkali acid phthalate series with chemical formula $K[C_6H_4COOH\text{-}COO]$. Potassium Hydrogen Phthalate crystallizes in orthorhombic system with space group $Pca2_1$. Potassium Hydrogen Phthalate (KHP) is intensively studied as it is used as X-ray analyzer and monochromator in high resolution X-ray instruments [1,2]. Its cleavage faces find applications as substrates for the growth of highly orientated film of conjugated polymers with high nonlinear optical susceptibility with non-hygroscopic nature [3].

In order to improve the crystal quality, morphology, to enhance the optical and other physical properties, crystallization of pure and doped Potassium Hydrogen Phthalate has been investigated [1-7]. Some organic compounds exhibit large NLO response than widely known inorganic materials. They also offer the flexibility of molecular design and the promise of virtually an unlimited number of crystalline structures. Among organic crystals for non linear optics (NLO) applications, amino acids display specific features of interest such as (i) molecular chirality, which secures acentric crystallographic structures; (ii) absence of strongly conjugated bonds, leading to wide transparency ranges in the visible and UV spectral regions; (iii) zwitterionic nature of the molecule, which favours crystal hardness and also the chiral carbon atoms directs the crystallization in noncentrosymmetry space [10]. L-Arginine and L - Histidine are found to be potential NLO material with good optical, mechanical properties and also the SHG efficiency of these complexes was greater than that of KHP [11, 12].

No reports were available on optical properties of L-Arginine doped KHP and L-Histidine doped KHP. Hence, present investigation deals the detailed estimation of optical band gap, extinction coefficient, refractive index. It is observed that the dopant doesn't disturb the transparency of the KHP crystal. Also LA-KHP, LH-KHP possesses frequency conversion efficiency equal to that of KDP.

II. EXPERIMENT

2.1 Growth

L-Arginine doped potassium hydrogen phthalate and L-Histidine doped potassium hydrogen phthalate single crystals were grown by slow evaporation method. Pure KHP (99.95%) single crystals were harvested from commercially available KHP salt by adopting slow evaporation method and the photograph of the grown crystal is presented in figure.1 (a). Calculated quantity of commercially available Potassium Hydrogen Phthalate salt was dissolved using millipore water. 0.1 m% of L-Arginine (≥98%) (LA) is added into a beaker and the solution was stirrered well for an hour and the pH is determined as 3.91 The solution was filtered using whatman filter paper, the filtered

solution is transferred to petridish and covered with perforated sheet. The solution was allowed to evaporate at room temperature, bantam, lucid seeds were observed within a few days. The crystals were gleaned after 10 days. L-Histidine (≥99%) doped KHP (LH-KHP), (figure.1(c) single crystal was obtained by following the same procedure.

2.1 Solubility and metastable zonewidth

Solubility of pure and doped KHP was analyzed gravimetrically over different saturation temperature and the obtained curved was presented in figure.1. Metastable zone width was observed by adopting polythermal method and the and the nucleation curve was drawn (Figure.1).

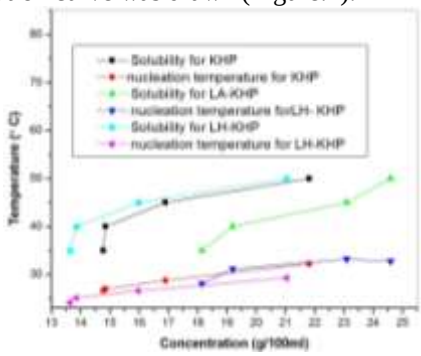

Figure.1 Nucleation curve of pure and doped KHP crystal

2.3 Bulk growth

Based on the solubility diagram, saturated solution of KHP, LA-KHP and LH-KHP was prepared at 40°C using constant temperature water bath. After the achievement of supersaturation, transparent seed crystal tied in a nylon thread was introduced into the solution. The temperature of the bath was reduced by 0.1°C per day and bulk crystals of KHP, LA-KHP and LH-KHP were harvested after 15 days. The photograph of the grown crystals were presented in figure 2 (a - c).

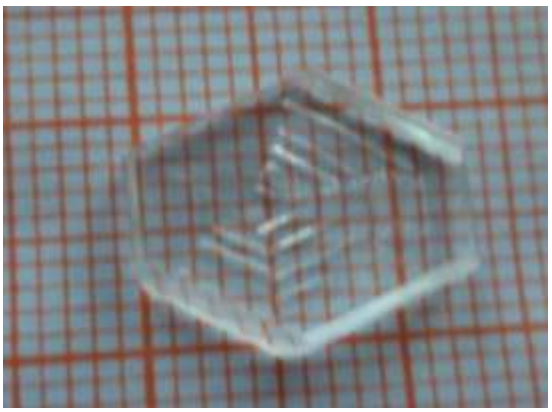

Figure.2 (a) Pure KHP single crystal

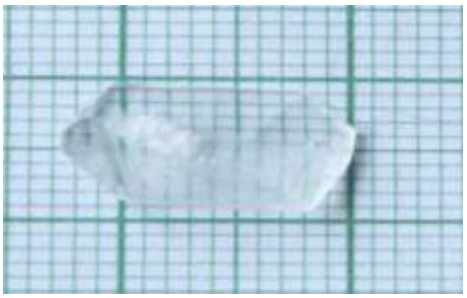

Figure.2 (b) L-Arginine doped KHP (LA-KHP) single crystal

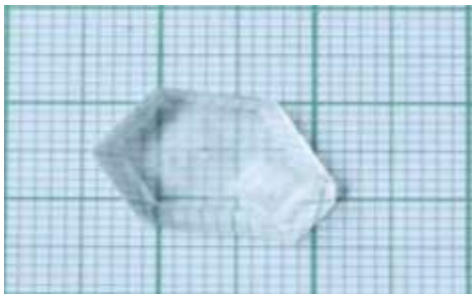

Figure.2(c) L-Histidine doped KHP (LH-KHP) single crystal

III. RESULT AND DISCUSSION

3.1 Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction was carried out using Cu Kα (λ=1.5014 A°) on Bruker Kappa APEXII .The determined lattice parameter is tabulated (Table.1). Pure KHP, LA-KHP and LH-KHP crystals, were crystallized in orthorhombic (P) crystal system in noncentrosymmetry space group $Pca2_1$. There is a slight change in the lattice parameter of the doped crystals. This may be due to the lattice distortion by dopants in the parent compound [6]

Pure KHP	LA-KHP	LH-KHP
a = 6.568 Å	a = 6.47 Å	a = 6.47 Å
b = 9.309 Å	b = 9.60 Å	b = 9.61 Å
c = 12.556 Å	c = 13.28 Å	c = 13.30 Å
α = β = γ = 90°	α = β = γ = 90°	α = β = γ = 90°
V = 767.693 Å^3	V = 825 Å^3	V = 825 Å^3

Table.1 Lattice parameter for the grown crystals

The upshots of doping depends on the concentration of dopant as well as on other defect factors such as its position in the cation sub-lattice, location of cation vacancies, interchangeability of cations, clusters types which arises due to improper alternation of the stoichiometric cations, difference in the ionic radii of host cations and impurity cations, complex structure of the host material, size and concentration of domains, strain in the crystal,

peak shift, growth orientation, variation in peak intensity, strength of bonding, Grain size, Grain boundaries, retarding/driving forces and crystallite alignment. Current investigation shows that the lattice parameter of pure and doped KHP lies close to each other. Thus, it is clear that the doping does not affect the crystal structure but it has great impact on the morphology of the KHP crystals.

3.2 FT-IR STUDIES

FT-IR spectra of KHP, LA-KHP and LH-KHP were recorded with a SHIMADZU MODEL IR Affinity-1 FT-IR spectrophotometer using KBr pellet technique.

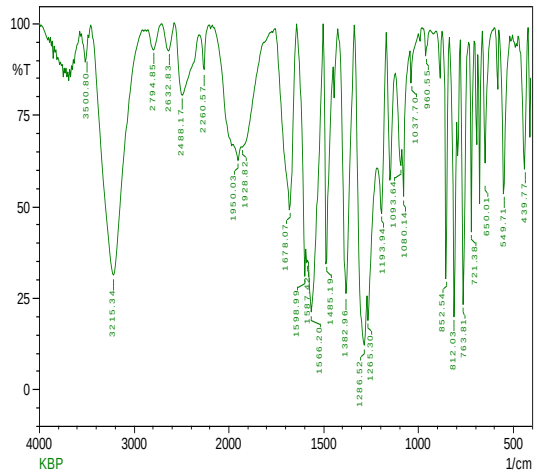

Figure.3 (a) FT-IR for KHP

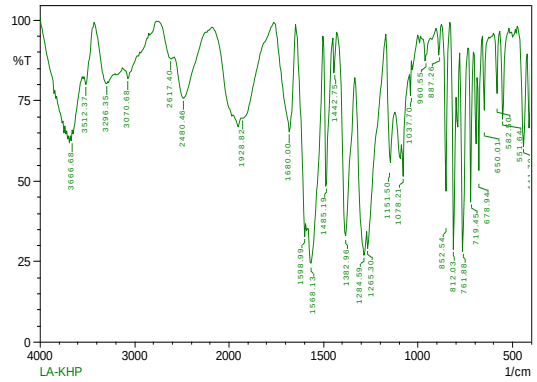

Figure.3 (b) FT-IR for LA-KHP

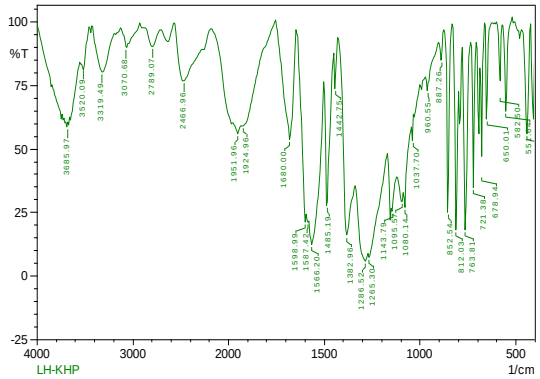

Figure.3 (c) FT-IR for LH-KHP

The spectrum (Figure.3 (a-c)) was recorded in the wave number range of 400–4000cm^{-1} for the identification of functional group of the grown crystal. The identified functional groups and their assigned wave numbers were tabulated (Table.2.)

Wavenumber (cm^{-1})	**Assignments**
< 900	C-H bending vibrations
1568.13&1566.20	asymmetric & symmetric stretching of –C- O
1600-1500	aromatic ring group
1680.00	carbonyl group (C=O)
3070.68-2789.07	C-H stretching
Between 3400 to 2200	Carboxylic O-H
1485.19	N–H asymmetric Bending
1080.14	NH_3^+ rocking
1598.99	asymmetric COO^- stretching

Table.2 FT-IR Wave number assignments for the grown crystals

3.3 Optical studies

It is mandatory that a good optical crystal must possess optical transparency in the UV region. Any absorption near the fundamental or second harmonic leads to loss of conversion frequency. In optical technology, optical transparency of single crystals plays a prominent role. Crystalline defects affect the optical properties [11] such as light absorption, scattering, refractive index and for practical devices crystals free from light scattering and absorbing defects are required [12]. It has been already reported that as density of defect increases, the possibility for the occurrence of the scattering centers also increases [13] and this is responsible for the optical loss into the crystals [14]. UV-Vis spectrum was recorded over the wavelength 200-800 nm using Perkin Elmer Lambda 35. The obtained absorbance spectrum is presented in Figure.4.The dopants does not disturb the transparency of pure KHP single crystal, in all the cases the cut off wavelength is found to be 300 nm. As the pure and doped KHP single crystals possess wide transparency in visible region, it is suitable for optoelectronic application.

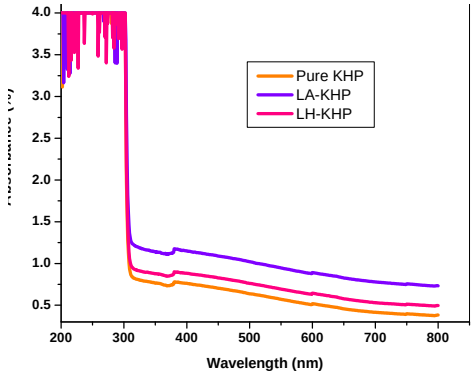

Figure.4 Absorbance spectrum for the grown crystals

3.3.**1 Estimation of optical constants**

The absorption coefficient can be calculated from the tramittance value by using the formula

$$\alpha = {}^{2.303}/_{d}\ log(1/T) \quad (1)$$

Where t is the thickness of the sample. The optical band gap (E_g) can be determined from optical absorption coefficient (α) near the absorption edge by using the relation [15]

$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}} \quad (2)$$

Where

A - Constant

E_g - optical band gap

h – planck constant

ν – Energy of incident photon

For KHP,LA-KHP and LH-KHP the optical band gap was calculated from Tauc's plot (Figure.5).A graph (Figure.5) was plotted between energy of the incident photon vs $(\alpha h\nu)^2$, the energy gap (E_g) is determined by extrapolating the straight line portion of the curve to $(\alpha h\nu)^2 = 0$ and the determined values are tabulated (Table.3). It was observed that the dopant has decreased the optical band gap values of KHP.

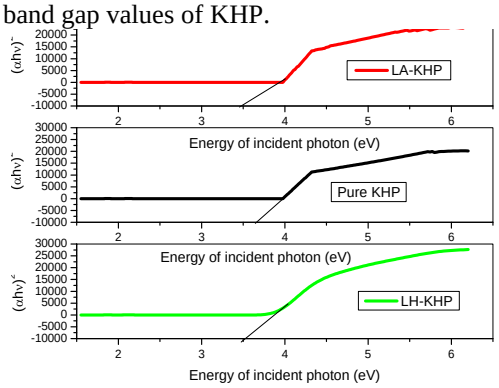

Figure.5 Tauc's plot for pure and doped KHP

Extinction coefficient is the fraction of light lost due to scattering and absorption per unit distance in a participating medium. It can be calculated from the formula

$$k = {}^{\alpha\lambda}/_{4\pi} \quad (3)$$

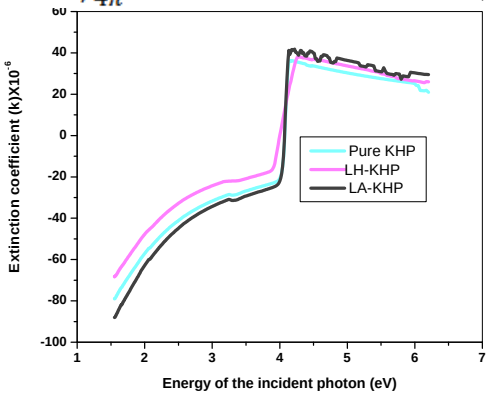

Figure.6 Extinction coefficient for pure and doped KHP

The reflectance can be expressed in terms of absorption coefficient by using the formula

$$R = 1 \pm \frac{\sqrt{1-\exp(-\alpha t)+\exp(\alpha t)}}{1-\exp(-\alpha t)} \quad (4)$$

The variation of extinction coefficient (k) and reflectance (R) as a function of photon energy is shown in figure (6 & 7). From the graphs, it is clear that both the reflectance and extinction coefficient depends on the photon energy. Since the internal energy of the device also depends on the photon energy, by tailoring the photon energy one can achieve the desired material to fabricate the optoelectronic devices.

The refractive index can be calculated by using the given formula and the obtained n values for the crystals 300 nm is tabulated (Table.3)

$$n = {}^{-(R+1) \pm \sqrt{3R^2 + 10R - 3}}/_{2(R-1)} \quad (5)$$

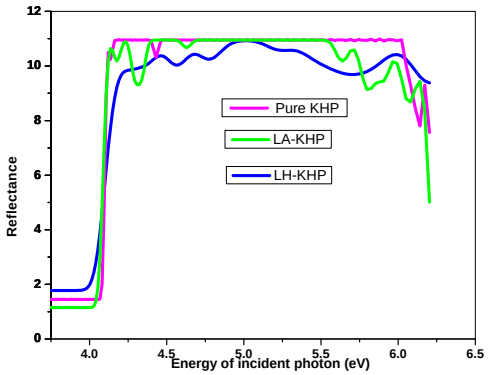

Figure.7 Reflectance for pure and doped KHP single crystals

Table.3 Optical band gap & refractive index values for pure and doped KHP.

Sample	E_g (eV)	Refractive index
KHP	3.6595	1.8436
LA-KHP	3.4797	1.7735
LH-KHP	3.5323	1.8203

3.4 SHG confirmation

The existence of SHG was confirmed by powder Kurtz Perry technique and Q-switched Nd:YAG laser technique. Fine powder of LA-KHP, LH-KHP were used for Kurtz Perry technique and Q-switched Nd:YAG laser technique respectively to confirm the existence of SHG. In Kurtz Perry technique a Q switched Nd: YAG laser beam of wavelength 1064 nm, with an input power of 2.2 mJ/pulse was used. It is found that the conversion efficiency of LA-KHP is equivalent to that of KDP. A Q switched Nd: YAG laser beam of wavelength 1064 nm, with an input power of 0.68J/pulse is passed into LH-KHP and it is observed that the conversion efficiency of LH-KHP is equal to that of KDP.

IV. CONCLUSION

Pure KHP, LA-KHP and LH-KHP single crystals were grown by slow evaporation method at room temperature. After several trails the concentration of the dopants was restricted to 0.1 m%. The grown crystals exhibit positive temperature coefficient of solubility which is suitable for growing bulk crystals. Bulk crystals of pure and doped KHP were grown by slow cooling method. It crystallized in orthorhombic system which is confirmed by single crystal XRD. The presence of functional groups was confirmed by FT-IR analysis. UV-Vis-NIR spectrum reveals that the dopant doesn't disturb the transparency of KHP suitable for optoelectronic applications with cutoff 300 nm. Band gap energy, extinction coefficient and reflectance were computed. By determining the electro-optic coefficients, it can be used for electro-optic modulator. SHG efficiency of doped KHP was found out to be greater than pure KHP.

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