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### RESEARCH ARTICLE

## INFLUENCE OF AMINO ACID DOPANTS ON THE GROWTH AND PROPERTIES OF POTASSIUM HYDROGEN PHTHALATE SINGLE CRYSTALS FOR NONLINEAR OPTICAL APPLICATIONS

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#### Abstract

Undoped and the impact of amino acid dopants such as L-Glutamic acid (LGA), L-Asparagine (LAS) and L-Serine (LS) on the growth process and properties of potassium hydrogen phthalate (KHP) single crystal by slow evaporation solution growth technique have been examined. The unit cell parameters of the grown crystals have been affirmed by means of single crystal X-ray diffraction analysis. The crystallinity of the title materials was examined by powder X-ray diffraction. The FT-IR spectral studies identify the presence of expected functional groups of the grown crystals. The optical transmission of the grown crystals has been recorded using UV-Vis spectral analysis. The thermal stability of the grown crystals has been analyzed by TG-DTA studies. Microhardness mechanical studies show that hardness number increases with the load for the grown crystals by Vickers microhardness method. The nonlinear optical (NLO) properties were analyzed utilizing Kurtz and Perry powder technique.

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#### Introduction:-

Alkali metal hydrogen phthalate crystals which includes Potassium hydrogen phthalate (KHP) or Potassium acid phthalate (KAP), Sodium hydrogen phthalate (NaHP) or Sodium acid phthalate (NaAP), Rubidium acid phthalate (RbAP), Cesium acid phthalate (CsAP) and Lithium acid phthalate (LiAP) are semi-organic materials extensively recognized for their utility in the long-wave X-ray spectrometers and requirements within the volumetric analysis [1].

Currently, for a deposition of thin films of organic nonlinear materials, alkali metal hydrogen phthalate crystals have been hired as substrates. Specifically, a single orientation of thin poly (diacetylene) films is prepared by epitaxial growth on organic crystals consisting of alkali metal salts of phthalate and having a lower degree of symmetry than alkali halides [2] and those crystals are crystallized as noncentrosymmetric rhombic structures. Crystals of alkali metal hydrogen phthalates have covalent (intramolecular), ionic (cation-anion), Van-der Waals (among neighboring molecules) and intermolecular hydrogen bonds O-H...O (H-bonds among anions in chains) and for this reason they may be ascribed to strong H-bonds for which might be feasible the fermi-resonance interactions of stretching vibrations  $\nu(\text{O-H})$  with combinations of bending in-plane ( $\beta(\text{O-H})$ ) and out-of-plane ( $\gamma(\text{O-H})$ ) vibrations due to intraanionic anharmonicities.

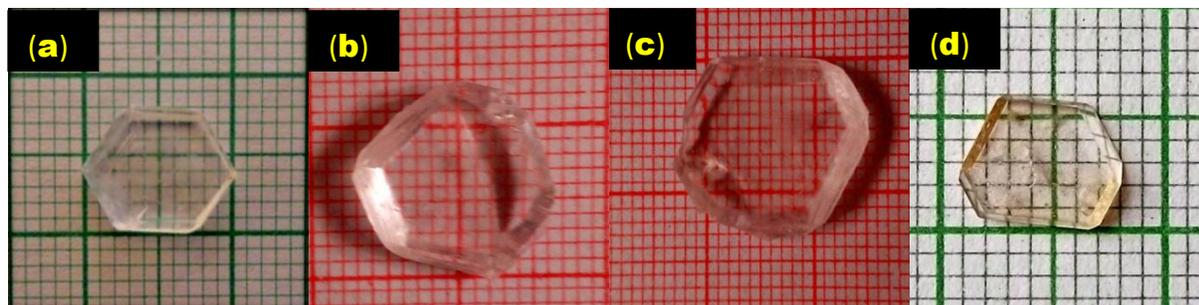
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Potassium hydrogen phthalate (KHP) are widely hired in the subject of x-ray spectroscopy as a monochromator and additionally as an analyzer. KHP exhibits pyroelectric, piezoelectric, elastic, nonlinear optical (NLO) properties, elasto-optic [3] and electro-optical studies on a sequence of alkali substituted hydrogen phthalate crystals which included it [4] and it crystallizes in an orthorhombic crystal structure with space group  $Pca2_1$  [5]. KHP has platelet morphology with perfect cleavages alongside the (010) plane. The usage of the periodic bond chain evaluation, the morphology of KHP has been decided [6]. Presently, for the growth of highly oriented thin films of conjugated polymers with nonlinear optical susceptibility, KHP crystals have been hired as substrates [7,8]. KHP is taken as the model compound due to its well-evolved surface pattern on the (010) face inclusive of high and very low growth steps which can be distinct without difficulty located by using optical microscopy [9,10] and it is extensively hired as Q-switches for Nd:YAG, Nd:YLF, Ti:Sapphire and Alexandrite lasers. In view of this, a series of crystalline salts of amino acids doped KHP have been investigated [11-15]. In this manuscript, single crystals of amino acids doped KHP were successfully obtained by introducing additives inclusive of LGA, LAS and LS adding in pure KHP solution. The crystal structure of the grown crystals has been confirmed by single crystal X-ray diffraction analysis and the grown crystals were characterized by various instrumentation techniques such as powder X-ray diffraction (PXRD) analysis, spectral, optical, thermal, mechanical and NLO analysis in order to check its suitability for device fabrications. An attempt was made to impact of amino acids dopant single crystals in the pure KHP and their characterizations.

### Experimental details:-

All high-purity commercially available reagents have been purchased and used without in addition purification. The commercially obtainable raw material of Potassium hydrogen phthalate (E-Merck) and L-Glutamic acid (E-Merck), L-Asparagine (E-Merck) and L-Serine (E-Merck) were used to synthesize the grown crystals. The double distilled water was used to prepare the aqueous solution of the grown crystals. The calculated amount of pure KHP is first dissolved in double distilled water and stirred continuously for 4 hours to yield a homogenous solution. After filter the solution by Whatman filter paper, it was kept in temperature controlled water bath (accuracy  $\pm 0.1^\circ\text{C}$ ) by means of slow evaporation at ambient temperature. After a span of 21 days, the crystal with good transparency and well-defined shape were harvested shown in the Fig. 1a.



**Figure 1:-** As grown crystals of (a) Undoped KHP (b) LGA doped KHP crystal (c) LAS doped KHP crystal (d) LS doped KHP crystal

Amino acids doped KHP crystals were obtained by the calculated amount of 0.5 mole % of LGA, LAS and LS were slowly dissolved separately using different beakers in the pure KHP solution. The reactants have been stirred continuously for 4 hours to yield a homogenous mixture of the solution. The prepared solutions were filtered through Whatman filter paper. To grow the crystal of high quality, the prepared solutions were kept in the temperature controlled water bath. In the course of the slow evaporation, well-defined, colourless single crystals of LGA doped KHP, LAS doped KHP and LS doped KHP with good transparency were obtained in the duration of 32 days, 34 days and 37 days respectively. The photograph of the as-grown crystals is shown in Fig. 1b, Fig. 1c and Fig. 1d.

### Results and Discussion:-

#### Single crystal X-ray diffraction:-

The single crystal XRD data of the grown crystals have acquired using an ENRAF NONIUS CAD 4 diffractometer with  $\text{MoK}\alpha$  radiation ( $\lambda=0.71073 \text{ \AA}$ ) to identify the unit cell parameters. The grown crystals crystallize in an orthorhombic symmetry with a space group of  $Pca2_1$ . The obtained unit cell parameters for undoped and amino

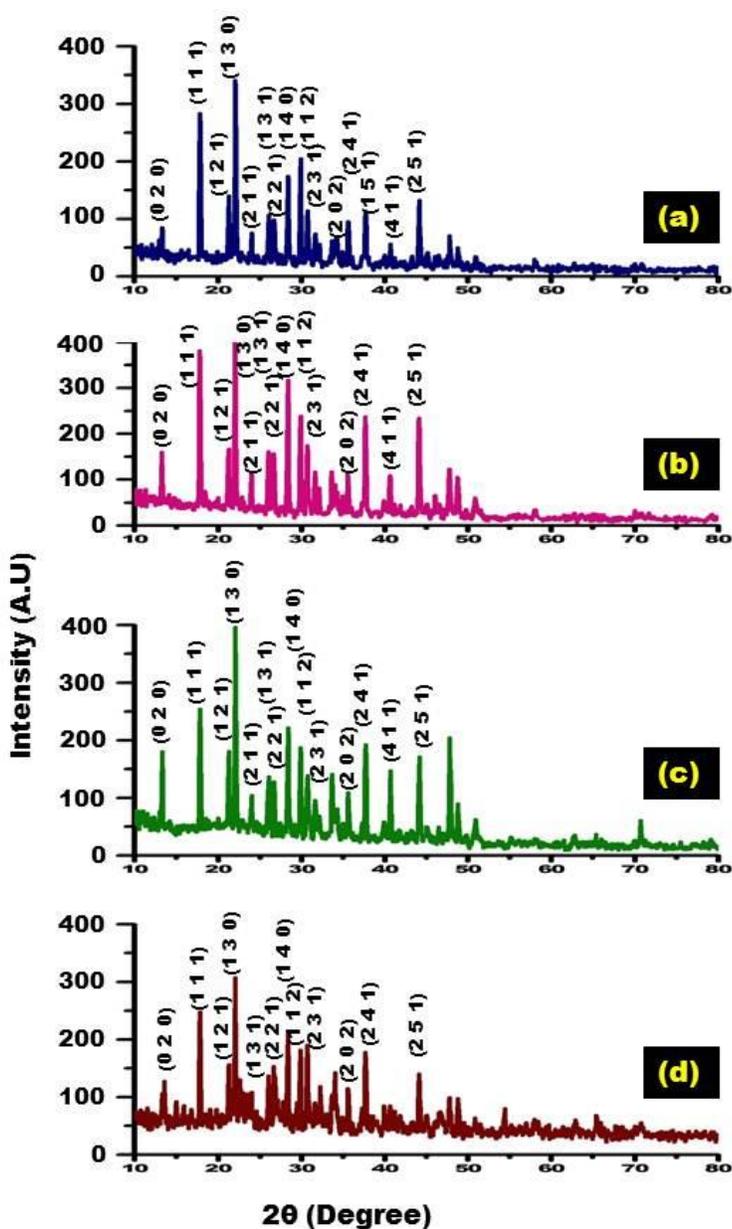
acids doped KHP crystals are presented in Table 1. From Table 1, the grown crystals have been confirmed by examining the presently calculated lattice parameters values with already reported values [16] which give the close agreement.

**Table 1:-** Unit cell parameters of undoped and amino acids doped KHP crystals

Unit cell parameters	Reported value KHP [16]	Undoped KHP Present work	LGA doped KHP	LAS doped KHP	LS doped KHP
a	6.48 Å	6.56 Å	6.53 Å	6.44 Å	6.51 Å
b	9.61 Å	9.60 Å	9.52 Å	9.58 Å	9.48 Å
c	13.37 Å	13.38 Å	13.42 Å	13.48 Å	13.41 Å
$\alpha = \beta = \gamma$	90°	90°	90°	90°	90°
Volume (Å) <sup>3</sup>	832.58	842.61	834.26	831.65	827.59

**Powder x-ray diffraction:-**

The grown crystals were finely powdered and subjected to powder XRD analysis with a X'pert PRO powder X-ray diffraction (40 kV) using Cu-K $\alpha$  radiation of wavelength  $\lambda = 1.5406$  Å. The powder XRD patterns of undoped KHP, LGA doped KHP, LAS doped KHP and LS doped KHP crystals are shown in Fig. 2a, Fig. 2b, Fig. 2c and Fig. 2d. All the detectable peaks could be indexed by using standard reference data (JCPDS card no: 31-1855 for pure KHP).



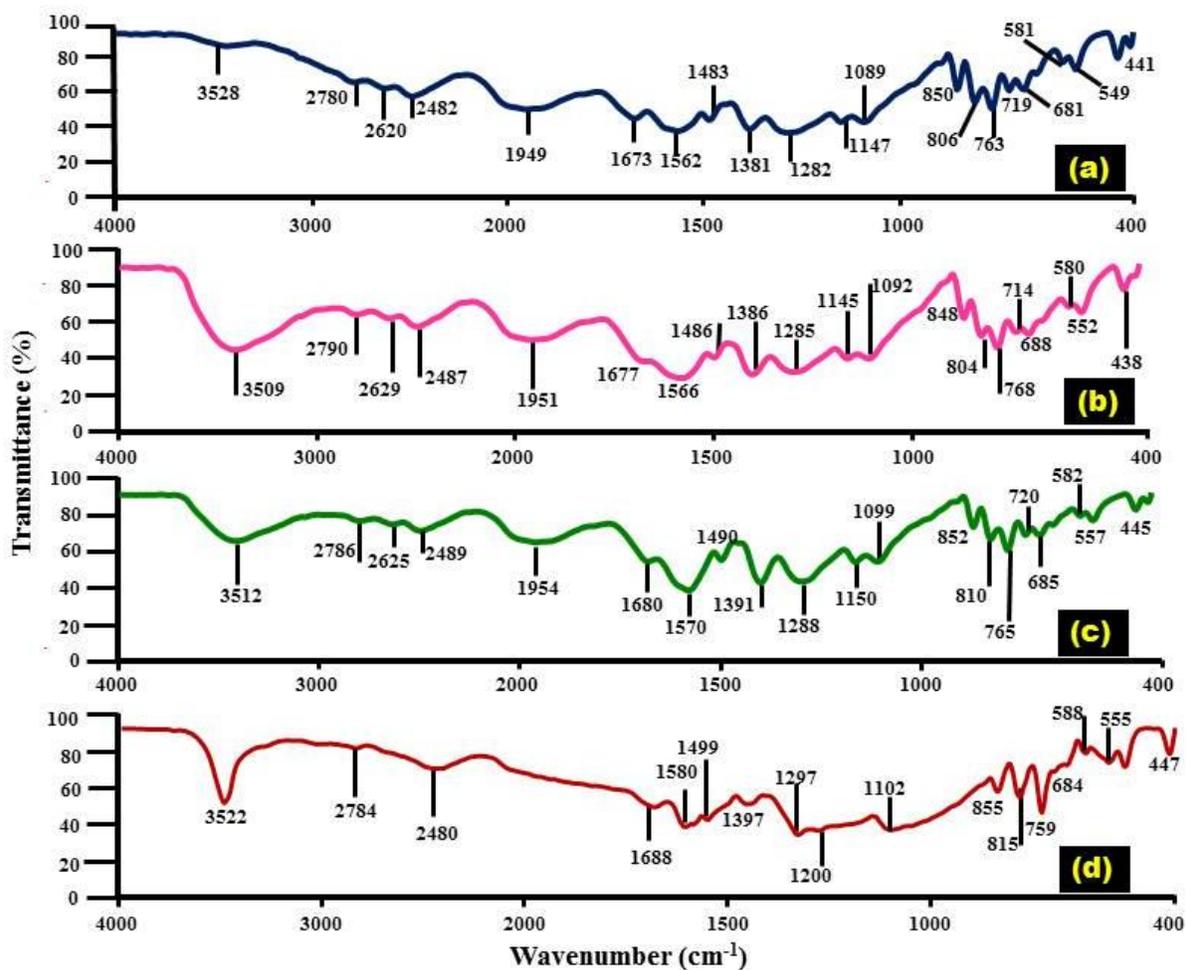
**Figure 2:-** Powder XRD pattern of (a) Undoped KHP (b) LGA doped KHP crystal (c) LAS doped KHP crystal (d) LS doped KHP crystal

**Spectral analysis:-**

FTIR spectra of the grown crystals were recorded in the range  $400 - 4000 \text{ cm}^{-1}$  using KBr pellet in a Perkin-Elmer spectrometer. The FTIR spectra of undoped KHP, LGA doped KHP, LAS doped KHP and LS doped KHP are shown in Fig. 3a, Fig. 3b, Fig. 3c and Fig. 3d.

**Figure 3:-** FTIR spectrum of (a) Undoped KHP (b) LGA doped KHP crystal (c) LAS doped KHP crystal (d) LS doped KHP crystal

To establish the presence of amino acids within the lattice of undoped KHP, the O-H stretching vibration of KHP is considered because the O-H stretching vibration is greater touchy to hydrogen bonding interaction with the doped



amino acids. The band assignments of the grown crystals are given in Table 2.

**Table 2:-** Vibrational Assignments of undoped and amino acids doped KHP crystals

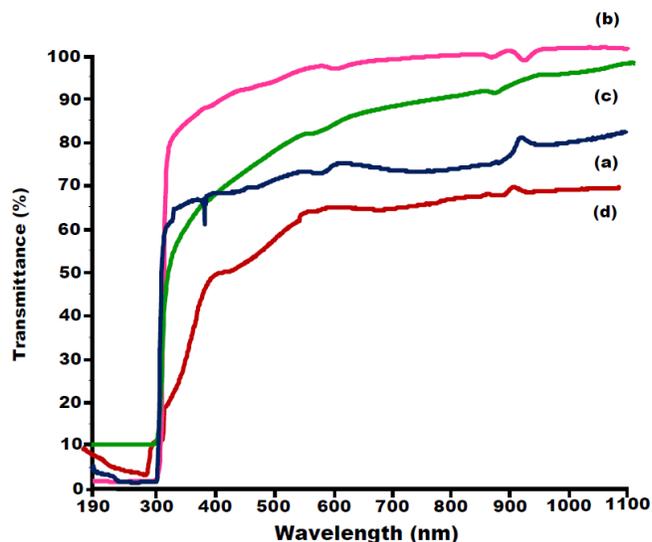
Wavenumbers (cm <sup>-1</sup> )				Tentative Assignments
Pure KHP	LGA-KHP	LAS-KHP	LS-KHP	
3528	3509	3512	3522	O-H stretching hydrogen bond
2482	2487	2489	2480	C-H aromatic stretching
1949	1951	1954	1957	C=C asymmetric stretching
1673	1677	1680	1688	Carboxylic acid C=O symmetric stretch
1562	1566	1570	1580	C=O carboxylate ion asymmetric stretching
1483	1486	1490	1499	C=C ring stretching
1381	1386	1391	1397	C=O carboxylate ion symmetric stretching
1282	1285	1288	1297	C-O stretching
1147	1145	1150	1155	C-C stretching
1089	1092	1099	1102	C-C-O stretching
850,806	848,804	852,810	855,815	C-H out of plane bending
763	768	765	759	C-C stretching
719	714	720	711	=C-H out of plane deformation
681	688	685	684	C-O wagging
549	552	557	555	C=C-C out of plane ring deformation
441	438	445	447	C=C out of plane ring bending

Considering the phenyl ring vibrations, there's no change observed due to doping in C-C stretching, C-H stretching, C-C skeletal aromatic ring vibrations, C-H aromatic stretching, C-H in-plane bending and C-H out of plane bending for the grown crystals. Considering the carboxylic acid vibrations, a small change is observed due to doping in C=O bending, C-O stretching and O-H stretching. Further, a small change is observed in C=O symmetric stretching in the case of doped crystals. The carboxylate ion (COO<sup>-</sup>) vibrations (C-O and C=O bond symmetric and asymmetric stretching) are modified slightly due to doping. So, the results imply that the dopant molecules have entered into undoped KHP crystals matrix. Also, the amino acid can be present at the O-H stretching of the carboxylic acid due to the fact there is no shift in the phenyl ring. The obtained FT-IR spectra are in excellent agreement with that pronounced in the literature for undoped KHP crystals [17].

#### Optical analysis:-

The optoelectronic efficiency of the NLO material is typically decided by way of the transparency window in the UV-Visible region. The optical transmission spectra of the grown crystals have been showed within the wavelength region from 190-1100 nm using a Perkin-Elmer Lambda 35 UV-Visible spectrophotometer. The lower cut-off

wavelength is observed at 300 nm for the grown crystals. The transmission percentage of undoped, LGA doped KHP, LAS doped KHP and LS doped KHP crystals are 70%, 94%, 82% and 60% respectively (Fig. 4a, Fig. 4b, Fig. 4c & Fig. 4d).



**Figure 4:-** UV-Visible Transmission spectrum of (a) Undoped KHP (b) LGA doped KHP crystal (c) LAS doped KHP crystal (d) LS doped KHP crystal

Of all the four crystals, LGA doped KHP crystal indicates highest transmission percentage. The enhancement in the optical transmission is the direct outcome of the improvement in the crystal quality in the LGA doped KHP crystal in compared to other three crystals. The obtained results were compared with the reported work [12].

#### Thermal analysis:-

The grown crystals become analyzed by way of subjecting it to TG/DTA analysis in a closed chamber with controlled nitrogen flow atmosphere under 1000 °C at a heating rate of 20 K/min using a Perkin-Elmer thermal analyzer STA 409 PC. The thermal behaviors of a crystal have a significant role in a crystal growth and its applications. Thermal behaviors like thermal expansion, specific heat and thermal conductivity are basic properties for lasers, especially for high power systems. When a beam of laser interacts with a nonlinear optical crystal, a locality of its incident energy is regenerate into thermal energy resulting in a temperature gradient inside the crystal and if the NLO crystal exhibits large specific heat, then the increase in the thermal gradient of the crystal is small. Such a crystal might have large damage threshold and observes application in high power laser systems. TG/DTA curves for undoped, LGA doped KHP, LAS doped KHP and LS doped KHP crystals are shown in Fig. 5a, Fig. 5b, Fig. 5c & Fig. 5d.

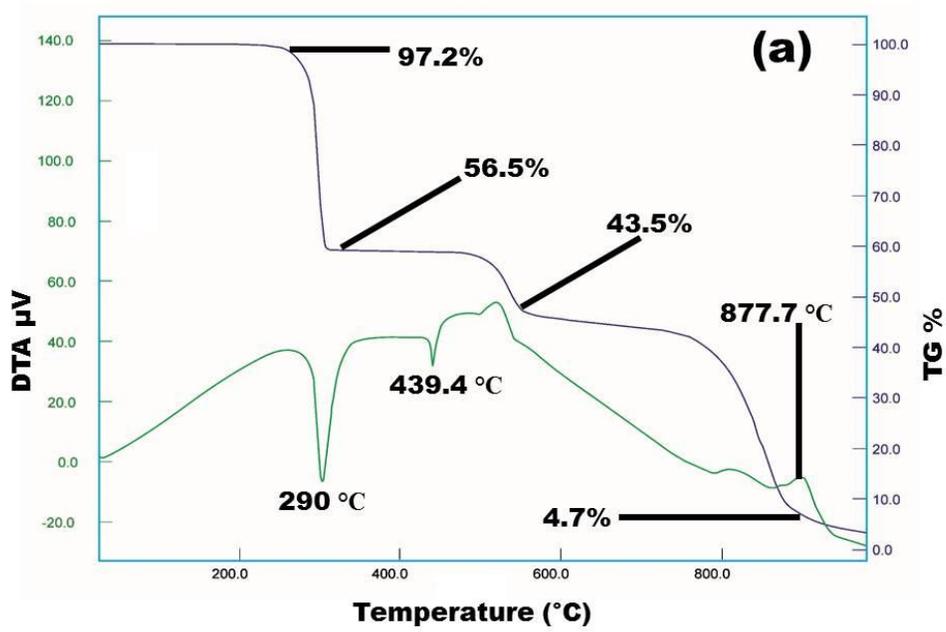


Figure 5:- TG/DTA thermogram of (a) undoped KHP crystal.

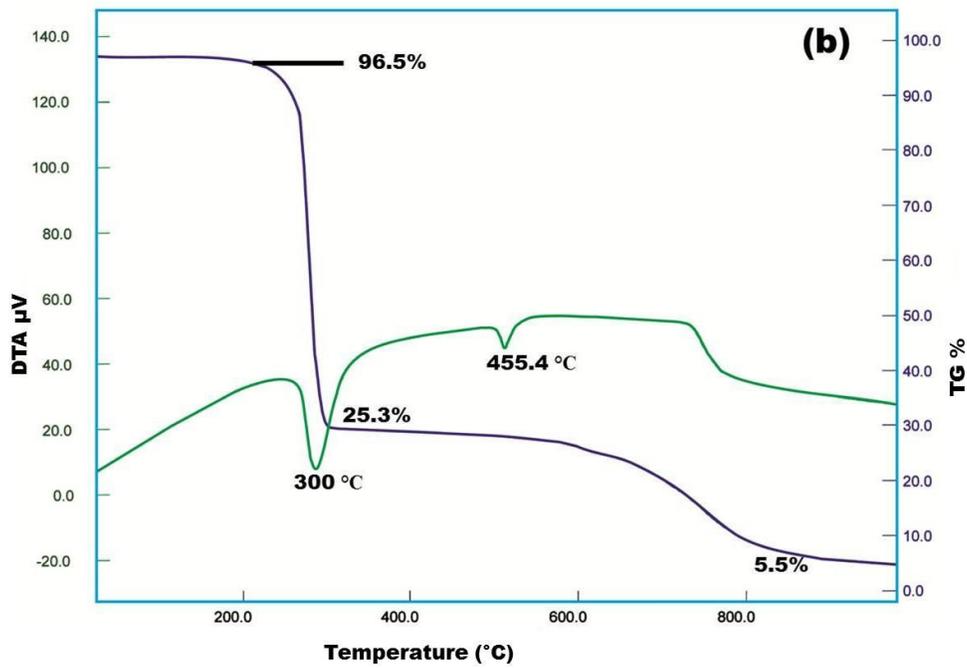


Figure 5:- TG/DTA thermogram of (b) LGA doped KHP crystal

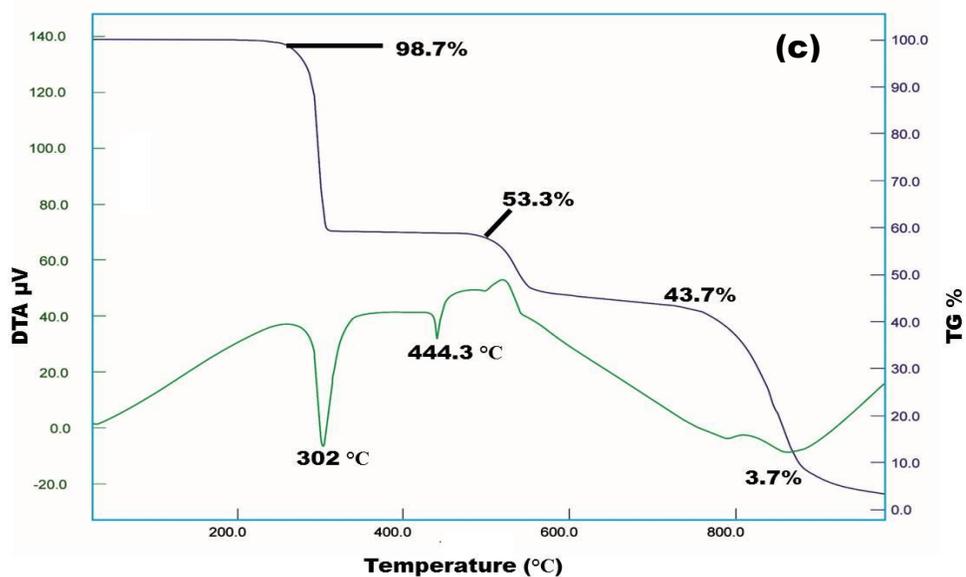


Figure 5:- TG/DTA thermogram of (c) LAS doped KHP crystal

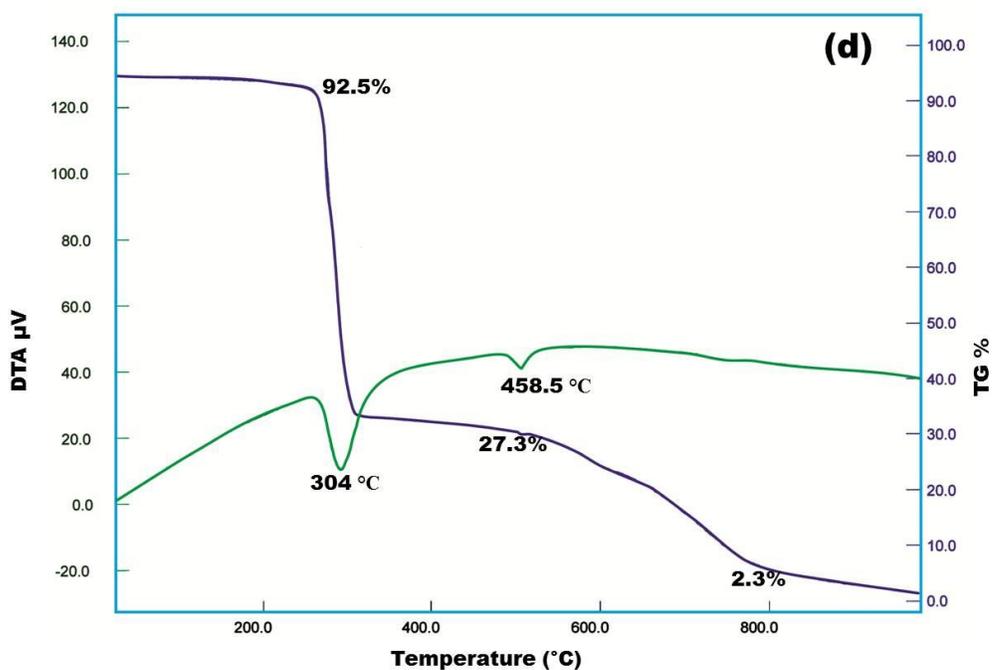


Figure 5:- TG/DTA thermogram of (d) LS doped KHP crystal

From the TG thermogram, undoped KHP crystal showed four stages of weight loss. In undoped KHP crystal, the weight loss starts at around 263.3°C and about 97.2 % of the entire mass loss has come about at some stage in the initial decomposition of undoped KHP crystal. In doped KHP crystals, the weight loss starts at around 265.4°C, 267.6°C and 269.2°C and about 96.5%, 98.7% and 92.5% of the entire mass loss has come about at some stage in their initial decomposition of LGA doped KHP, LAS doped KHP and LS doped KHP respectively. As according to literature survey of Newkirk et al and Belcher et al has reported that the KHP decomposed into  $K_2CO_3$  and char at

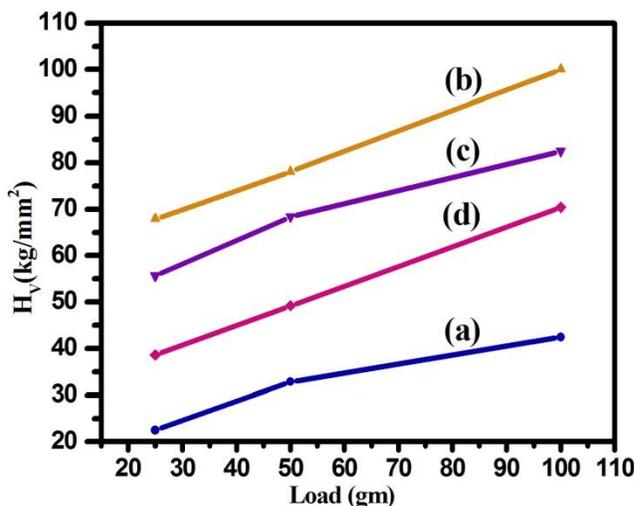
800 °C in the N<sub>2</sub> environment, the prevailing work is of the same opinion properly with these said consequences [18,19]. DTA showed sharp endothermic peak observed at 290°C, 300°C, 302°C and 304°C for undoped, LGA doped KHP, LAS doped KHP and LS doped KHP can be attributed to the decomposition of the grown crystals respectively. Hence, the endothermic peaks above 304.9°C can be due to the formation of volatile fragments. Further, the grown crystals are observed to decompose without melting or phase transformation. As a result, the maximum temperature up to which KHP can be exploited for nonlinear optical applications is limited to 304.9°C.

#### Hardness analysis:-

Vicker's microhardness measurements were carried out the use of Leitz Weitzler hardness tester fitted with a diamond indenter. The mechanical strength of the grown crystals was studied by means of quantifying microhardness because it performs a tremendous position in the fabrication of optoelectronic devices. Vicker's microhardness ( $H_v$ ) is a measure of the hardness of materials calculated from the size of an impact produced under load by the diamond indenter. Hardness value was calculated by the relation

$$H_v = 1.8544 P / d^2 \text{ (Kg/mm}^2\text{)} \quad \text{----- (1)}$$

Where, P (Applied load in Kg), d (Diagonal length of indentation impression in mm) and 1.8544 (Constant of the geometrical factor for the diamond pyramid). The plot of Vicker's hardness ( $H_v$ ) versus load (P) of the grown crystals is shown in Fig. 6a.

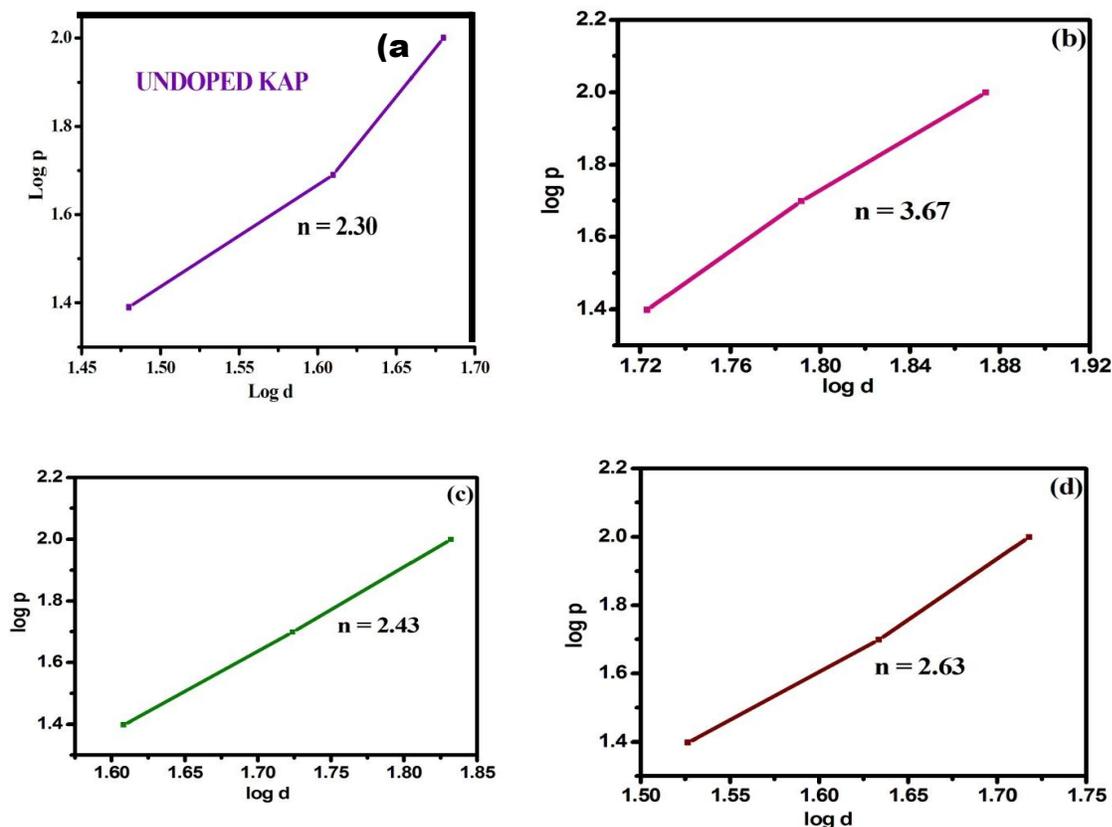


**Figure 6:-** Load P vs  $H_v$  for (a) Undoped KHP (b) LGA doped KHP crystal (c) LAS doped KHP crystal (d) LS doped KHP crystal

From the Fig. 6a, it is seen that hardness value of LGA doped KHP crystal is higher than the hardness value of other three crystals. This is due to the fact the predominant contribution to hardness is ascribed to the high stress required for homogeneous nucleation of dislocation in the small vicinity indented [20]. The presence of cracks shows the decrease in microhardness and it was observed that amino acid doped KHP crystals are highly stable towards the application of mechanical stresses. The noticed changes in the microhardness values of the amino acids doped KHP crystals may be due to the strong interaction of O-H groups of KHP with the COO groups of amino acid [21]. Greater stress is required to form dislocations in an ideal crystal. Hence, the higher hardness value of LGA doped KHP crystal indicates greater stress required to form dislocation which confirms greater crystalline perfection. The work hardening coefficient (n) was estimated by the plot of  $\log p$  vs  $\log d$ . The plot of  $\log d$  vs  $\log p$  for the grown crystals shows a straight line and its slope provides the work hardening coefficient (n)

$$P = K_1 d^n \quad \text{----- (2)}$$

Where  $K_1$  (Standard hardness value which is found from the plot of  $P$  vs  $d^n$ ). The plot of  $\log p$  vs  $\log d$  of undoped KHP (Fig. 7a), LGA doped KHP (Fig. 7b), LAS doped KHP (Fig. 7c) and LS doped KHP (Fig. 7d) depicts that the grown crystals belong to the soft material category.



**Figure 7:-** Log d vs Log p for (a) Undoped KHP (b) LGA doped KHP crystal (c) LAS doped KHP crystal (d) LS doped KHP crystal

#### Second harmonic generation (SHG) analysis:-

The grown crystals have been subjected to a Q-switched Nd:YAG laser beam of wavelength 1064 nm was fired within an input beam energy of 3.2mJ/pulse and pulse width of 8 ns, the repetition rate being 10 Hz. KHP and NaAP crystals are being the phenyl ring and  $\pi$ -electron system that are liable for its NLO efficiency [22]. The estimated SHG efficiencies of undoped, LGA doped KHP, LAS doped KHP and LS doped KHP crystals are found to be 1.5, 1.9, 1.6 and 1.7 times that of the reference material KDP crystal respectively. It genuinely found out that LGA doped KHP crystal which is having SHG efficiency value higher than that of undoped, LAS doped KHP and LS doped KHP crystals.

#### Conclusion:-

Semiorganic single crystals of undoped, LGA doped KHP, LAS doped KHP and LS doped KHP were effectively grown by slow evaporation technique. Single crystal XRD confirmed that the grown crystals have an orthorhombic lattice with  $Pca2_1$  space group for the grown crystals. The powder XRD study confirms that the crystalline perfection of the grown crystals. The presence of functional groups becomes confirmed by means of FTIR spectral analysis. The UV-Visible study implies the optical quality of LGA doped KHP crystal is better than that of undoped, LAS doped KHP and LS doped KHP crystals. The melting and decomposition temperature range of the grown single crystals has been studied by TGA/DTA analysis. In the microhardness analysis, LGA doped KHP crystal has much higher hardness value than undoped, LAS doped KHP and LS doped KHP crystals and it confirms that the grown crystals belong to the soft material. LGA doped KHP crystal is an excellent candidate for SHG applications than LGA doped KHP crystal due to its SHG efficiency value much higher than that of LGA doped KHP. All these properties suggest that LGA doped NaAP crystal may be a promising material for optical applications.

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