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Studies on Various Properties of Undoped and L–Tryptophan Doped Potassium Hydrogen Phthalate Crystals

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Abstract: Potassium Hydrogen Phthalate crystals doped with amino acid L-Tryptophan (0.05mol %) were grown by slow evaporation technique. The characterization of grown crystal was made by powder XRD diffraction, Fourier Transform Infrared spectroscopy (FTIR), UV-Visible spectroscopy, TG/DTA, Vicker's Micro hardness, Dielectric measurements, Second Harmonic and Photoluminescence studies. Structural difference between undoped and doped crystal has been studied by XRD method. Functional groups were identified by FTIR spectroscopy. The transmittance of doped KHP crystal has been used to calculate the optical band gap between the crystals. The TG-DTA results establish the good thermal stability of the material. Mechanical strength of the grown crystal was estimated by Vicker's hardness test. The dielectric constant and dielectric loss has been studied as a function of frequency of the doped KHP crystals. The second harmonic generation has been confirmed by the Kurtz powder method. It was observed to be greater than that of KDP. The photoluminescence study also observed.
Keywords: Dielectric constant, FTIR, Micro hardness, PL studies, SHG studies, TG/DTA, UV, XRD.

I. INTRODUCTION

Potassium Hydrogen Phthalate (KHP) crystal, with the chemical formula K [(C_6H_4COOH-COO)], it belongs to the series of alkali acid phthalates which crystallizes in the orthorhombic structure [1]. It is also well known for its Piezoelectric, Pyroelectric, elastic and optical properties [2, 3]. KHP is chosen as a model compound because of its well developed surface pattern of the (0 1 0) face consisting of high and very low growth steps which can be relatively easily observed by means of optical microscopy [4, 5]. KHP is well known for its application for the production of crystal analyzers for long wave spectrometers [6]. The crystals have excellent physical properties and have a good record for long term stability in devices. KHP crystals are used as the second, third and fourth harmonic generators for Nd: YAG and Nd: YLF lasers. Recently, KHP crystals are used as substrate for the deposition of thin film of non – linear optical materials [7]. Most of the amino acids and their complexes belong to the family of organic and semi-organic nonlinear optical (NLO) materials that have potential applications in second harmonic generation (SHG), optical storage, optical communication, photonics, electro-optic modulation, optical parametric amplification, optical image processing, etc.[8-13]. Amino acid family crystals have over the years be subjected to extensive investigation by several researchers for their nonlinear optical properties [14-17]. Since KHP is a semi organic material, the addition of amino acids might enhance the NLO properties. Other researcher also reported the limited work in the literature on the KHP crystals with the amino acid L-Tryptophan as a dopant in 1mol% and 2 mol% (J. bhuvana and G. Madurambal) [18] and various characterization has not been studied in detail. It is with this intention; the present work in amino acid L-Tryptophan (LT) were added as an impurity in to the parent KHP and the effect of these impurities on the structure, optical, thermal and mechanical properties have been studied and reported. However, various characterizations such as NLO, Photoluminescence studies and laser damage threshold have been evaluated.

II. EXPERIMENTAL METHOD

The amino acid L-Tryptophan doped KHP crystals were grown by the slow evaporation method. The KHP salt was dissolved in de ionized water. The solution was stirred well for three hours constantly using magnetic stirrer. With this solution, 0.05 mol % of L-Tryptophan was added as a dopant. After homogeneous mixing solutions, it was kept in dust free area for slow evaporation. After a period of timing a good quality transparent single crystals of undoped and L-Tryptophan doped KHP crystals were grown. Photographs of doped and undoped grown crystal are shown in Fig.1.

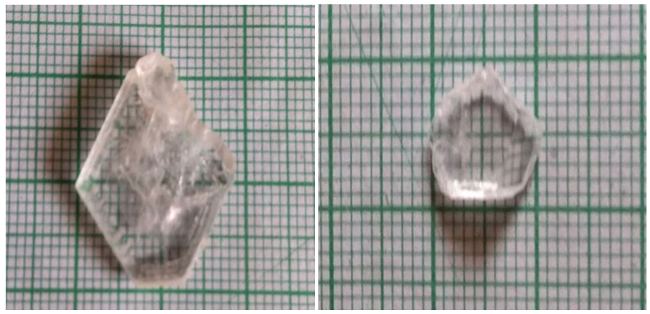

Fig.1.Grown crystals of undoped and 0.05 mol % L-Tryptophan doped crystals.

III. RESULTS AND DISCUSSION

A. Powder XRD Analysis

The grown crystals were subjected to powder XRD analysis using X'pert pro with cu Kα1 radiation (λ = 1.54060 A^0) for the phase analysis. Powder XRD patterns of the grown crystals shown in Fig.2. The results confirmed that all the crystals formed into orthorhombic structure of space group Pca_{21} according to JCPDS data (31-1855). The XRD pattern of L-Tryptophan doped KHP shows slight changes in peak intensities and peak positions, when compared to the undoped KHP [19]. The cell parameters of undoped and doped KHP crystals were calculated and the data are given in table 1.

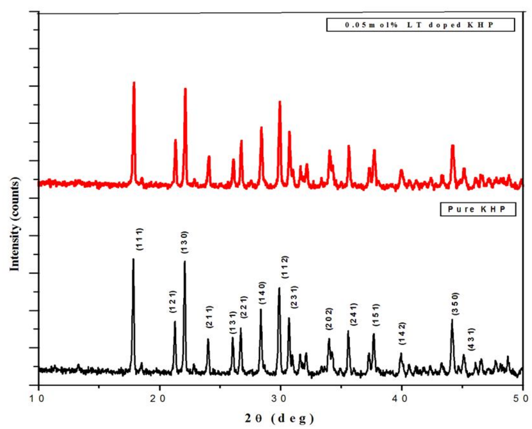

Fig.2. XRD pattern for undoped and 0.05 mol % L-Tryptophan doped KHP crystal

Table.1 Lattice parameters of undoped and LP doped KHP crystals

Lattice parameters	JCPDS Data	Undoped KHP	0.05mol% LT doped KHP
a(A^o)	9.605	9.625	9.590
B(A^o)	13.331	13.319	13.29
C(A^o)	6.472	6.460	6.45
Volume$(A^o)^3$	828.830	828.213	823.34

B. FTIR Analysis

FTIR spectrum of undoped and L-Tryptophan doped KHP crystals were recorded using Perkin Elmer spectrum in the range 400-4000 cm^{-1} by KBr pellet technique. The FTIR spectra of the grown crystals are given in Fig.3. The FTIR spectra of 0.05mol% doped crystals show strong NH symmetric stretching at 2400-2650 cm^{-1}. More NH stretching vibrations is introduced due to doping of L-Tryptophan and the NH absorption peaks become stronger. In the FTIR spectrum, OH^- stretching hydrogen bonds to appeared at 2784 cm^{-1} for the undoped and 2777 cm^{-1} for the doped compound. This shift is due to the incorporation of L-Tryptophan into the

KHP material. This shift may also be due to the free stretching of NH_2 group present in the dopant. In addition to that, C=C rings stretching to appear at 1489 cm^{-1} for undoped and 1476cm^{-1} for the dopant.

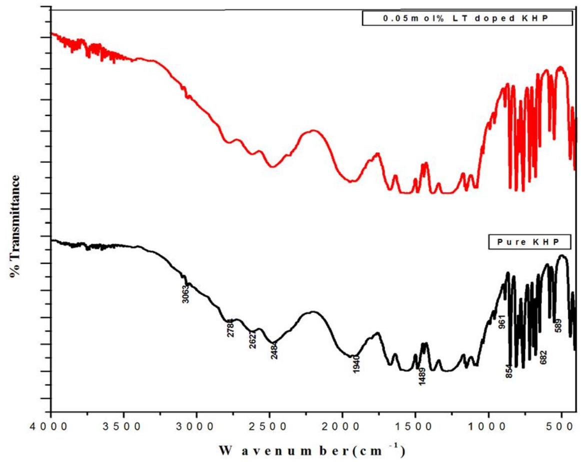

Fig. 3. FTIR analysis for undoped and 0.05 mol % L-Tryptophan doped KHP crystals

C. UV-Visible –NIR –Spectroscopy

The UV-visible – NIR spectroscopy was performed on the samples by using UV-700 SHIMADZU spectrophotometer. The recorded transmittance spectra of undoped and doped crystals in the wavelength range 200-1100 nm. Large absorptions are found at around 300 nm for undoped and doped KHP crystals due to n-π transition to the carbonyl group of the carboxyl functions [20, 21]. There is no absorption observed in the region from 350-1100 nm for the undoped and doped crystals which make the materials suitable for second harmonic generation. From the Tauc's plot, a graph is drawn between hν and $(\alpha h\nu)^2$ and is displayed in Figure 4. The band gap energy of the crystals is evaluated by exploring a straight line of the linear region of the graph at photon energy. The band gap energies for the undoped and doped crystals are almost same and the calculated values are 3.9, 3.88 eV respectively.

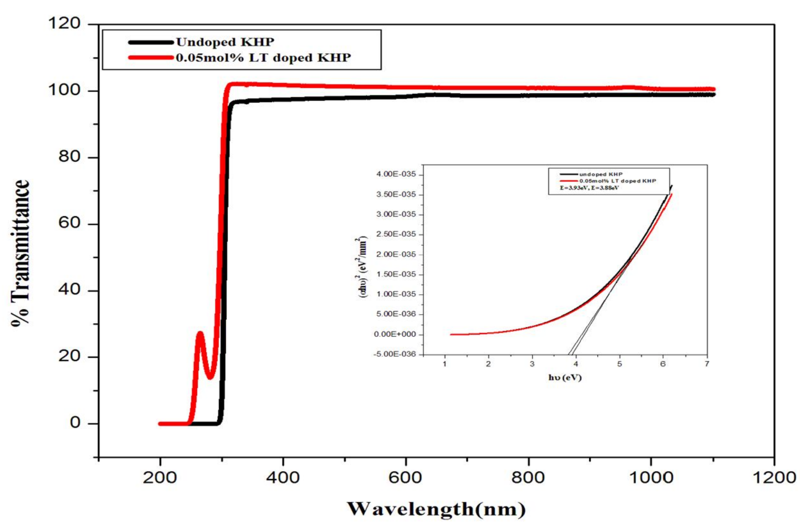

Fig.4. UV Transmittance spectra of undoped and L-Tryptophan doped KHP doped KHP crystals

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. A plot drawn on hardness values and corresponding load is shown in Fig.5

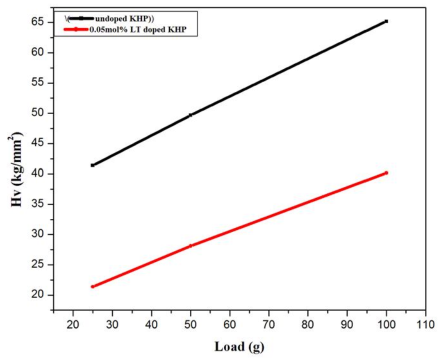

Fig. 5 Micro hardness for undoped and L-Tryptophan doped KHP crystals

The hardness number was calculated using the relation, $Hv=1.8544P/d^2$ Kg/mm^2.Where, Hv is the Vickers hardness numbers, P is the applied load and d is the diagonal length of the indentation impression [22]. It is observed that the hardness numbers increases with increase in load and it reveals that the doped KHP crystal exhibits to reverse indentation effect. The value of the work hardening coefficient is found to be greater than 2 for undoped and doped crystals. The hardness values as a function of loads is shown in Figure 5. Mayer's law [23] relates the load and size indentation as $P= Kd^n$, where k and n are the constants. Onitsch states that the values 1.0<n<1.6 for hard materials and n>1.6 for soft materials. Hence, it is concluded that undoped and doped crystals are also soft materials [24]. The work hardening coefficient of undoped and LT doped KHP values are n= 2.47 and n= 3.71. Hence, it is concluded that doped crystals are also soft materials.

E. Dielectric Studies

The dielectric properties are associated with the electro-optic property of materials, particularly when they are non-conducting materials. The dielectric constant was calculated by using the relation $\varepsilon_r = Ct / \varepsilon_0 A$. Where ε_0 is the permittivity of the free space, C is the capacitance, t is the thickness of the sample and A is the area of the sample. The dielectric constant and dielectric loss for undoped and doped KHP crystals measured for various temperatures at constant frequency 1KHZ are shown in Fig.6. It is obvious from the figures that the values of dielectric constant and dielectric loss increase with increase in temperature for the impurity concentrations considered in the present study. The increase in dielectric constant with temperature is generally attributed to crystal expansion, electronic and ionic polarization, and to presence of impurities and crystal defects [25]. The increase in higher temperatures is mainly attributed to the thermally generated charge carriers and impurity dipoles.

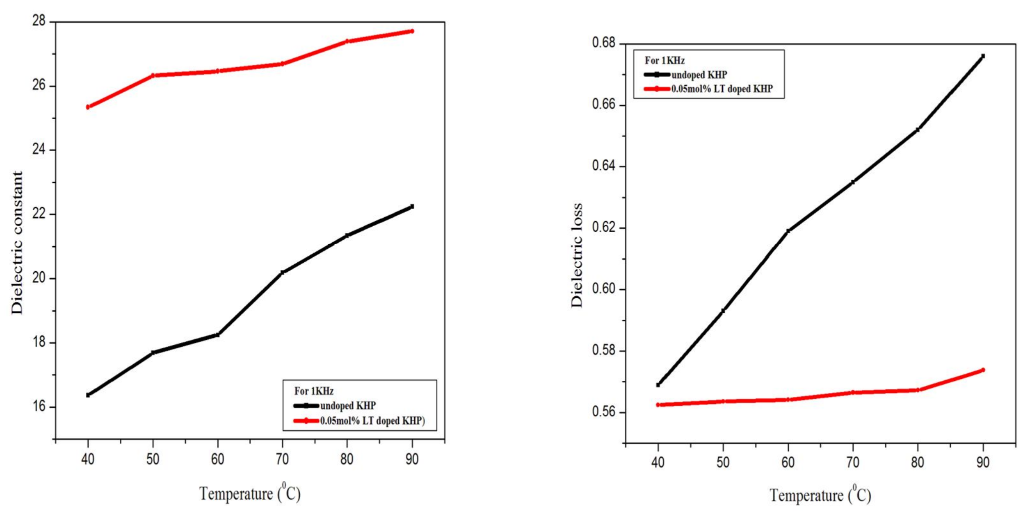

Fig.6. Dielectric constant and Dielectric loss Vs Temperature of undoped and doped KHP Crystals.

F. SHG Measurements

In order to confirm the NLO property of the grown crystals, they were characterized as Nd: YAG laser with the wavelength of about 1064nm. This high intense beam was allowed to be incident on the powdered sample. The emission of green light confirms the second harmonic generation properties of the crystal. The input beam energy was 0.701mJ/pulse and pulse width of 6ns, the repetition rate being 10Hz. The SHG efficiency of undoped KHP crystal was found to be 5.86mJ whereas the LT doped KHP (0.05 mol %) crystal were estimated as 6.45mJ when compared to that of the standard SHG material KDP. Hence the SHG efficiency for 0.05 mol% LT doped crystals was 0.72 times higher than that of the KDP crystal and 1.1 time greater than that of undoped KHP crystal.

G. Photoluminescence Studies

Photoluminescence spectroscopy is a contact less, non-destructive method of probing the electronic structure of materials. The inclusion frees as grown crystals of undoped and LT doped KHP was scanned between 400 and 800nm. The recorded spectrum of the sample is shown in Figure 7. For 347.58 nm is the excitation wavelength, the observed emission bands lies between 450 nm to 600 nm. The results indicate that the grown crystals have a bright emission of the visible region. The high intensity peaks are observed in the region between at 479.6nm and 577.62nm for undoped and LT doped KHP crystals confirm that they emit green fluorescence, which suggest that they are excellent for nonlinear optical applications and scintillators. Then the PL intensity is slowly reduced in the higher wavelength region. It may be attributed to relatively low barrier for rotation of two carboxyl groups of the central c-c bond [26, 27].

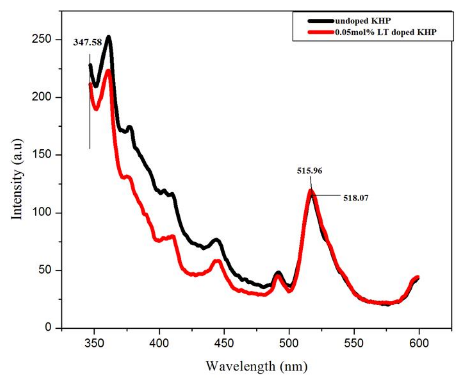

Fig.7 PL intensity Vs wavelength of(a) undoped and 0.05mol% LT doped KHP

H. Laser Damage Threshold Studies

For non linear optical applications, one of the most important considerations and criteria in the choice of material is its tolerance and resistance to laser damage to perform as a device for NLO applications. The laser damage threshold measurement was made on LT doped KHP single crystals using a Q switched Nd: YAG laser for 6 ns laser pulses operating at a wavelength of 1064nm. The lens with the focal length of 15cm was used, which was useful in sett the spot size of the desire value. Apart from the thermal effect, multi photon ionization is an important cause of laser induced damage. The laser damage threshold depends upon the specific heat, thermal conductivity, optical absorption, etc. If the material has high specific heat, the laser damage threshold will be high. If the material has a low laser damage threshold, it has many excellent properties like high optical transmittance and high SHG efficiency [28]. The obtained LDT values and the input energy which made cracks on the surface of crystals are given in the table 3.

Table 3: LDT values for undoped and LT doped KHP crystals

Sample	Energy (E) milli joule	LDT Values
Undoped KHP	84	0.347 GW/cm^2
0.05mol% LT doped KHP	61	0.281 GW/cm^2

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I. Thermal Analysis

To identify the thermal stability, purity and crystalline nature of solution grown undoped and LT doped KHP crystals; they were subjected to thermal analysis**.** The grown crystals were placed in a closed chamber with controlled nitrogen flow atmosphere at heating rate of 5°C/min. TG/DTA curves for undoped and LT doped KHP crystals are shown in Figure 8. The TG curve provides with a quantitative measurement of mass change associated with the transition. It indicates that on melting the material decomposes and loses mass. From the TG diagram, undoped KHP crystal showed two stages of weight loss. Thus the curve shows a gradual mass loss. From this graph, the weight loss starts at around 227°C and steps at 349.9 °C. The decomposition is also accompanied by the melting of the sample at 286.5 °C as shown by DTA. It is observed that the material is stable up to 298°C, the melting point of the substance. The second stage of decompositions is from 444.58 °C to 583.2 °C. The residue at the end is at 714.8 °C. The TG thermo gram reveals that decomposition starts for 0.05mol% LT doped KHP at 227.18 °C and steps to 320.34 °C as shown in figure 8(a). The decomposition is also accompanied by the melting of the sample at 290.72 °C as shown by DTA. The second stage of decompositions is from 443.71 °C to 574.86 °C. The residue at the end is at 716.8 °C

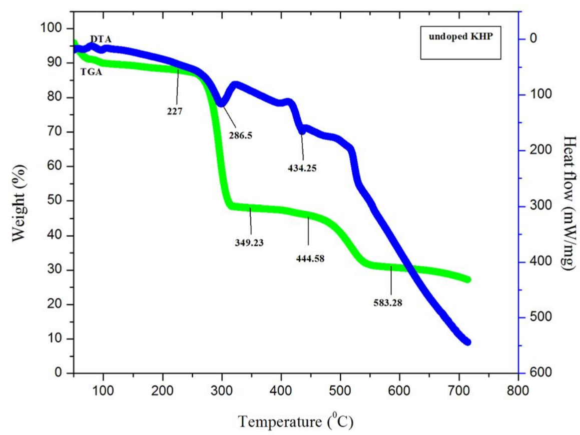

Fig (8) TG-DTA for undoped KHP crystal

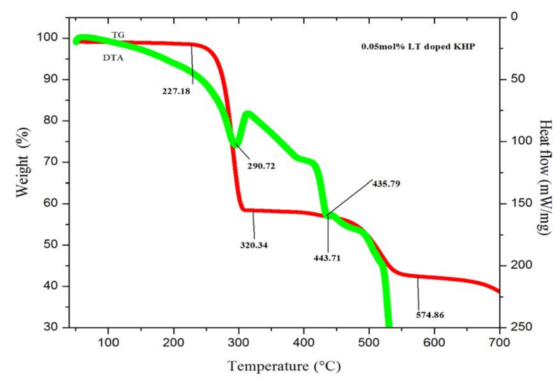

Fig 8 (a) TG-DTA for 0.05mol% of LT doped KHP crystal

IV. CONCLUSION

We have successfully grown good optical quality L-Tryptophan doped KHP single crystals from aqueous solution by slow evaporation technique under room temperature. Powder X-ray diffraction results confirmed that all the doped crystals are crystallized in the orthorhombic structure. The FTIR spectrum confirmed the presence of functional groups of the undoped and doped compounds. Optical transmittance studies revealed that the undoped and doped KHP crystals have transmittance in the entire visible region, which is essential for optical device applications. Micro hardness studies to reveal that the doped KHP crystals come under the soft materials category. From the dielectric study, it is found that both dielectric constants and dielectric loss of the crystal increases with increasing temperatures at constant frequency. The fluorescence studies indicate that the crystals have green fluorescence emission. Interestingly, second harmonic generation efficiency of KHP is dramatically improved by doping with small quantities of L-Tryptophan. TG-DTA studies to reveal that the purity of the sample and no decomposition is observed below the melting point.

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