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Comparative Study of Mechanical, Dielectric and Thermal Properties of Solution Grown NLO Crystal Potassium Acid Phthalate Doped with L-Phenylalanine and L- Tryptophan

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ABSTRACT

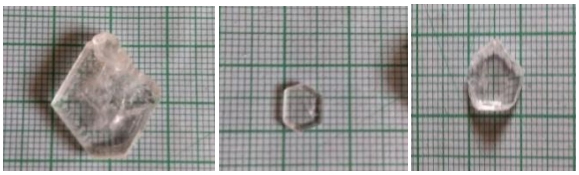
Potassium Hydrogen Phthalate crystal doped with amino acids L-Phenylalanine and L-Tryptophan (0.05mol %) were grown by slow evaporation solution growth technique. Structural difference between undoped and doped crystal has been studied by XRD method. Functional groups were identified by FTIR spectroscopy. 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 is 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 on 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 in 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 like urea with high mechanical stability [7]. In recent years, amino acid based non linear optical crystals with better linear optical properties. The wider choice of materials, improved high non-linearity, low transformation temperature, fast response and high transparency make this system [8]. Non linear optical phenomena have got a tremendous interest after the advent of laser sources and then play a vital role in the development of laser technology. Since KHP is a semi organic material, the addition of amino acids might enhance the NLO properties. It is with this intention; the present work is amino acids L-Phenylalanine (LP) and L-Tryptophan (LT) was added as an impurities in to the parent KHP and the effect of these impurities on the structure, optical, thermal and mechanical properties have been studied and reported.

II. EXPERIMENTAL METHOD

Potassium Acid Phthalate (KHP) crystals were grown by the slow evaporation solution growth technique at room temperature with double distilled water as solvent. Initially saturated KHP solution was prepared at room temperature. The amino acids L-Phenylalanine (LP) and L-Tryptophan (LT) were selected as dopant. The dopant concentration in the solution was 0.05mol%. The prepared saturated solutions of undoped, LP and LT doped KHP were well stirred for 4 hours. The homogeneous solution was filtered with a whatman filter paper. The solutions were stored in separated beakers covered with perforated sheets. The crystals were formed by evaporation of solvent with time interval of 25-30 days. The grown crystals were harvested and subjected to characterization studies. Photographs of undoped, LP and LT doped KHP crystals are shown in Figure 1.



(a) (b) (c)

Figure 1. Grown crystals of (a) undoped and (0.05mol %) (b) LP and (c) LT doped crystals

III. RESULTS AND DISCUSSION

3.1 Powder X-Ray Diffraction:

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 in orthorhombic structure with space group $Pca2_1$, which is in good agreement with the standard JCPDS data (31-1855). The XRD pattern of LP & LT doped KHP shows slight changes in peak intensities and peak positions, when compared to the undoped KHP [9]. The cell parameters and volume of undoped and doped KHP crystals were calculated and the values are match with the reported values [10]. There is a slight change in the lattice parameters and volume of the doped crystals. This is may be due to the lattice distortion by doping in the parent compound.

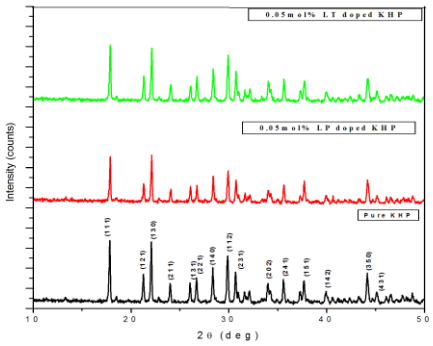


Figure 2. Powder XRD patterns of undoped and doped KHP crystals

Table 1. lattice parameters of undoped, LP & LT doped KHP crystals

Lattice parameters	JCPDS Data	Undoped KHP	0.05 mol% LP doped KHP	0.05mol% LT doped KHP
a(A^o)	9.605	9.625	9.622	9.590
B(A^o)	13.331	13.319	13.303	13.29
C(A^o)	6.472	6.460	6.441	6.45
Volume (A^o)^3	828.83	828.213	824.838	823.34

3.2 FTIR Analysis

FTIR spectrum of undoped, LP and LT 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 observed vibrational frequencies and their assignments are listed in table 2. In the FTIR spectrum, P-O-H asymmetric stretching appears at 2784 cm^{-1} for the undoped and 2794 cm^{-1}, 2777 cm^{-1} for the doped compound. This shift is due to the incorporation of amino acids 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 ring stretching appears at 1489 cm^{-1} for undoped and 1483 cm^{-1}, 1476 cm^{-1} for the dopant .

Table 2. Vibration assignments of undoped and LP & LT doped KHP single crystals

Undoped KHP	0.05mol % LP doped KHP	0.05mol % LT doped KHP	Assignment of vibrations
3063	3063	3063	C-H stretch aromatics
2784	2794	2777	P-O-H asymmetric stretching
2482	2491	2491	-C-H aromatic stretching
1940	1948	1955	C=C asymmetric stretching
1489	1483	1476	C=C ring stretching
852	847	860	C-H out of plane bending
767	767	767	C-C stretching
694	682	689	=C-H out of plane deformation

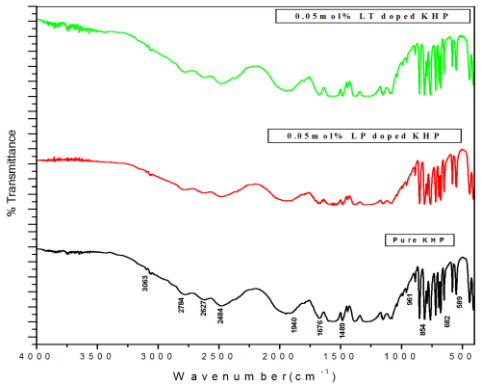


Figure 3. FTIR spectra of KHP crystals: undoped, 0.05mol% LP & LT doped KHP crystals

3.3 Optical Transmittance Studies

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. The recorded spectra are shown in Fig 4. From the graph, it is evident that both undoped and doped KHP crystals have their UV cut off around 300 nm. This is due to n-π transition of the carbonyl group of the carboxyl functions [11, 12]. There is no absorption observed in the region from 350-1100 nm for the undoped and doped crystals which makes the materials suitable for second harmonic generation.

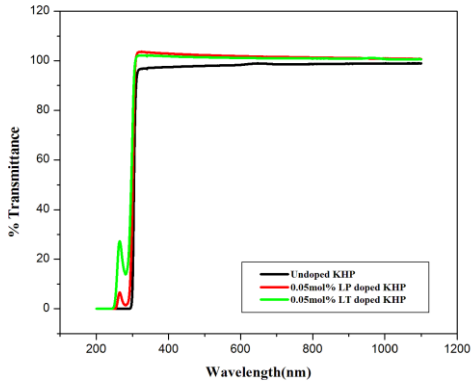


Figure 4. UV-NIR spectra of KHP crystals: undoped, (0.05mol%) LP & LT doped crystals

3.4 Micro hardness studies

Measurement of hardness is a useful non-destructive testing method to determine the hardness of the material [13]. Vicker's micro hardness test was carried out on undoped, LP & LT doped KHP single crystal using micro hardness tester fitted with a diamond indentor. The micro hardness values were calculated from the formula $Hv=1.8544P/d^2$ Kg/mm^2. Where, Hv is the Vickers hardness number, P is the applied load and d is the diagonal length of the indentation impression [14]. It is observed that the hardness number increases with increase in load and it reveals that the doped KHP crystal exhibits reverse indentation effect. The hardness value as a function of loads is shown in Figure 5. The results suggest that 0.05mol% LP doped crystals are preferred for device fabrication than the undoped and 0.05mol% LT doped crystals.

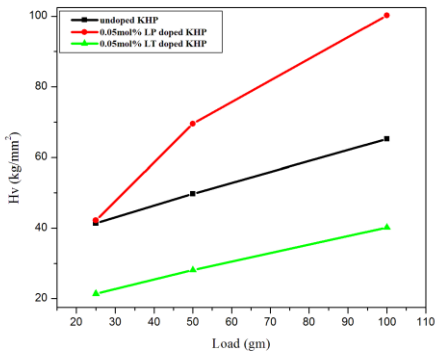


Figure 5. Micro hardness for undoped, LP & LT doped KHP crystals.

3.5 Dielectric Studies

The dielectric constant and the dielectric loss of the undoped, LP & LT doped KHP crystals were studied at 40° c are shown in Figure 6(a) and Figure 6(b) respectively. From the graph, it is clearly seen that dielectric constant decreases as the frequency increases in all cases. The high value of dielectric constant at low-frequency region is attributed to space charge polarization due to charged lattice defects [15]. Further space charge polarization will depend on the purity and perfection of the material. Its influence is large at higher temperatures and is noticeable in the low frequency. Similarly, the dielectric loss decreases with increase in the frequency. This suggests that the dielectric loss is strongly dependent on the frequency of the applied field and very low dielectric loss indicate the high purity of the crystals [16].

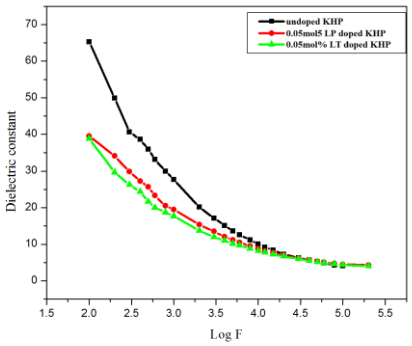


Figure 6a. Variation of dielelctric constant against log frequency for undoped, (0.05mol%) LP & LT doped crystals.

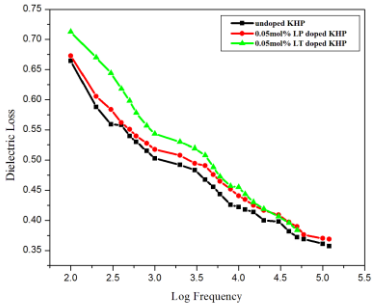


Figure 6b. Variation of dielectric loss against log frequency for undoped, (0.05mol %) LP & LT doped crystals

3.6 SHG Measurements

In order to confirm the NLO property of the grown crystals, they were characterized with 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 LP & LT doped KHP (0.05mol %) crystal were estimated as 6.72mJ and 6.45mJ when compared to that of the standard SHG material KDP. Hence the SHG efficiency for 0.05mol% LP & LT doped crystal was 0.75, 0.72 times that of the KDP crystal and 1.2, 1.1 time greater than that of undoped KHP crystal.

3.7 Photoluminescence studies

Photoluminescence spectroscopy is a contact less, non-destructive method of probing the electronic structure of materials. The inclusion free as grown crystals of undoped, LP & LT doped KHP was scanned between 400 and 800nm. The recorded spectrum of the sample is shown in Figure 7. For 345.79 nm is the excitation wavelength, the observed emission band lies between 450 nm to 600 nm. The results indicate that the grown crystals have a bright emission in the visible region. The high intensity peaks are observe in the region between at 482.6nm and 580.6nm for undoped, LP & 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 group around the central c-c bond [17, 18, and 19].

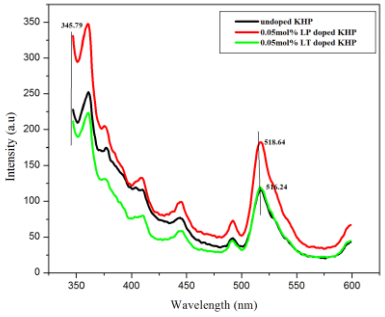


Figure 7. PL intensity vs wavelength of undoped, (0.05mol %) LP & LT doped crystals

3.8 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 LP & 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 5cm was used, which was useful in setting the spot size to the desire value. Apart from the thermal effect, multi photon ionization is an important cause of laser induced damage. The obtained LDT values and the input energy which made cracks on the surface of crystals are given in the table 3.

Table 3. show the LDT values of undoped, LP & LT doped KHP crystals.

Sample	Energy (E) milli joule	LDT Values GW/cm²
Undoped KHP	84	0.347
0.05mol% LP doped KHP	78	0.308
0.05mo% LT doped KHP	61	0.281

3.9 Thermal Analysis

To identify the thermal stability, purity and crystalline nature of solution grown undoped, LP & 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, LP & 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 286.5°C, the melting point of the substance. The second stage of decomposition 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% LP doped KHP at 238.5 ° C and steps to 344.5 ° C as shown in figure 8(a). The decomposition is also accompanied by the melting of the sample at 297.24 ° C as shown by DTA. The second stage of decomposition is from 463.5 ° C to 592.75 ° 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(b). 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

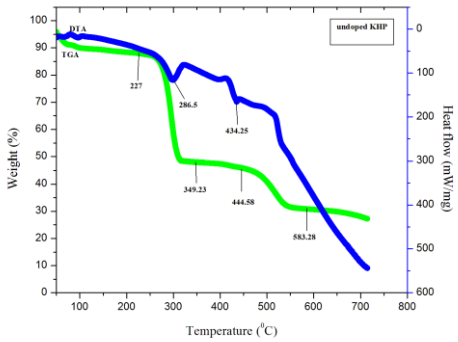


Figure 8. TG- DTA of undoped KHP crystal

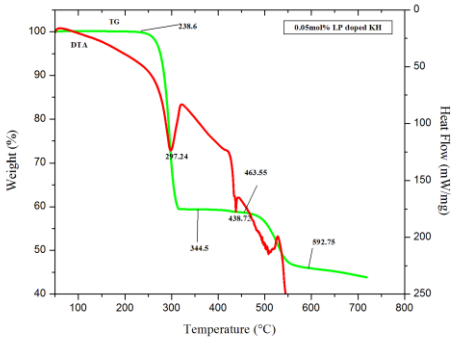


Figure 8a. TG-DTA of 0.05mol% LP doped KHP Crystal

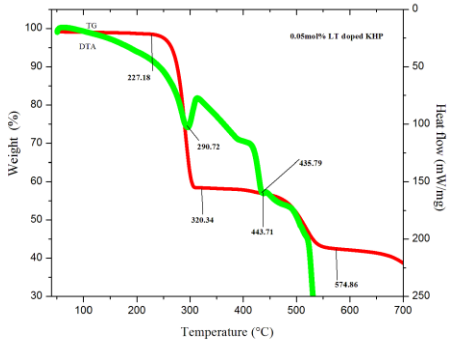


Figure 8b. TG-DTA for 0.05mol% of LT doped KHP crystal

IV. CONCLUSIONS

We have successfully grown good optical quality LP & LT 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 in 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 reveal that the doped KHP crystals come under the soft materials category. From the dielectric study, it is found that both dielectric constant and dielectric loss of the crystal decreases with increasing frequency at constant temperature. 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 LP & LT. TGA studies reveal that the purity of the sample and no decomposition is observed below the melting point. All these properties suggest that LP doped KHP crystal is excellent material for optical applications.

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