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Growth, Spectral Studies, Thermal and NLO Aspects of L-Asparagine Doped KHP Crystals

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Abstract: **Potassium Hydrogen Phthalate (KHP) crystals doped with Amino acid L-Asparagine (0.1 & 0.15mol %) were grown by slow evaporation technique. Structural characterizations of the grown crystals were carried out by powder X-ray diffraction method. It reveals that the grown crystals of undoped and doped KHP crystals are in orthorhombic structure. The functional groups were identified by Fourier Transform Infrared Spectroscopy. The enhancement of optical transparency in the doped KHP crystal was recorded using UV-Visible spectrophotometer. Mechanical strength of the grown crystal was estimated by Vickers hardness test. The TG-DTA results establish the good thermal stability of the material. 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: **FTIR, Micro hardness, LDT, PL, SHG, UV, XRD.**

I. INTRODUCTION

In recent years, the search of NLO materials with good transparency has lead to the development of photonic and optoelectronic technologies [1]. Potassium Hydrogen Phthalate, often called simply KHP is an interesting analyzer material in X-Ray spectroscopy [2, 3]. KHP possesses piezoelectric, pyroelectric, elastic and non linear optical properties. KHP crystallizes into orthorhombic system with the non-centro symmetric space group Pca_{21} and the lattice parameters are found to be a= $9.605A^0$, b=$13.331A^0$, c= $6.473A^0$. The perfect cleavages (010) plane of KHP is more suitable for surface morphological studies like etching and SEM. Recently KHP crystals have been used as substrate materials for the growth of a highly oriented film of conjugated polymers with high non linear susceptibility [4]. Now amino acid family crystals are also playing an important role in the field of non-linear optics. Other researcher also performed similar studies such as growth and characterization of KHP with the amino acid L-Asparagine as a dopant in 0.5 mol% (S. Shek Dhavud and J. Thomas Joseph Prakash) [5]. It is with this intention; the present work in amino acid L-Asparagine (LA) (0.1 & 0.15mol%) were added as an impurity in to the parent KHP and the effect of these impurities on the structure, optical, thermal, mechanical, NLO and Photoluminescence properties have been studied and reported.

II. EXPERIMENTAL METHOD

The amino acid L-Asparagine 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, 0.1 & 0.15mol% of L-Asparagine was added as a dopant. After homogeneous mixing solutions, it was kept in dust free area for slow evaporation. After a period of time a good quality transparent single crystals of undoped and L-Asparagine doped KHP crystals were grown. Photographs of doped and undoped grown crystal are shown in Figure.1.

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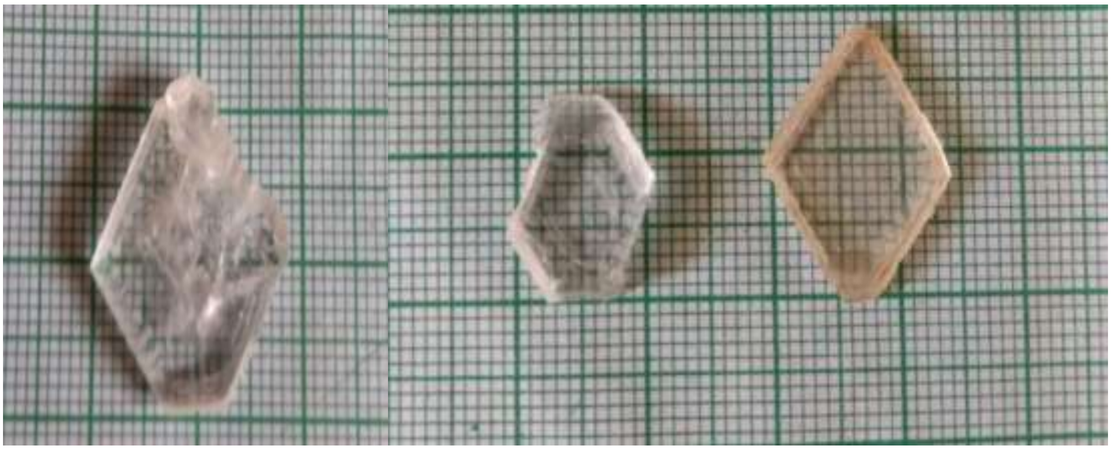

Fig 1: Grown crystals of Undoped and (0.1&0.15 mol %) L-Asparagine doped crystals

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 Pca_{21}, which is in good agreement with the standard JCPDS data (31-1855). The XRD pattern of LA doped KHP shows slight changes in peak intensities and peak positions, when compared to the undoped KHP [6]. The cell parameters and volume of undoped and doped KHP crystals were calculated and the values are match with the reported values [7]. 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.

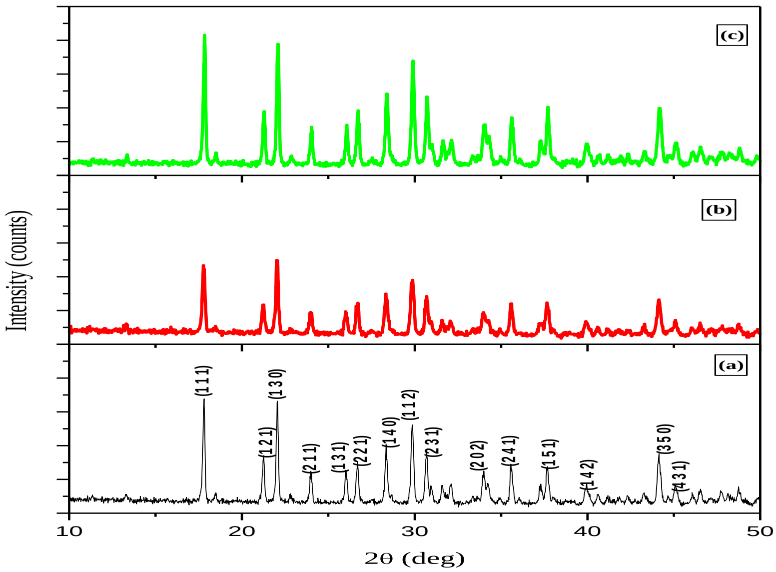

Fig 2: Powder XRD patterns of KHP crystals; (a) Undoped (b) 0.1 & (c) 0.15mol% LA doped KHP

TABLE 1: Lattice parameters of undoped and LA doped KHP crystals

Lattice parameters	Un doped KHP	0.1 mol% LA doped KHP	0.15mol % LA doped KHP
a(A^o)	9.625	9.59	9.61
B(A^o)	13.319	13.31	13.29
C(A^o)	6.460	6.47	6.46
Volume $(A^o)^3$	828.213	827.48	825.94

3.2 FTIR Analysis:

FTIR spectrum of undoped and LA 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 Figure 3. The FTIR spectra of 0.1 and 0.15 mol% doped crystals show strong NH symmetric stretching at 2400-2650 cm^{-1}. More NH stretching vibrations are introduced due to doping of LA and the NH absorption peak become stronger. 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}and 1483 cm^{-1}for the dopant .

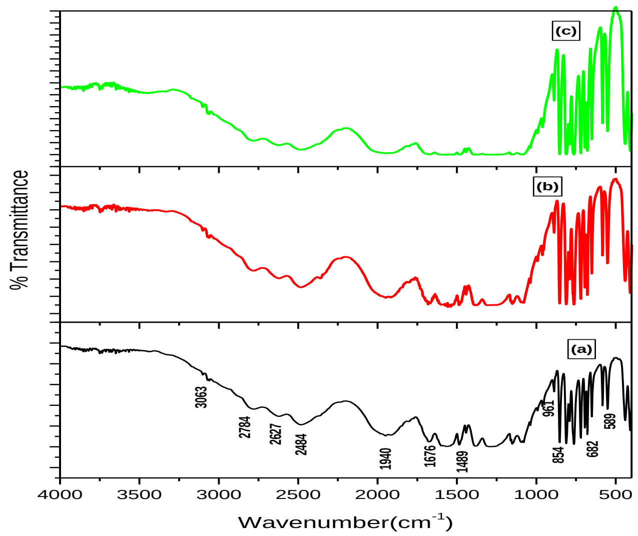

Fig 3: FTIR spectra of KHP crystals; (a) Undoped, (b) 0.1mol% LA (c) 0.15mol% LA

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 Figure 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 [8, 9]. 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.

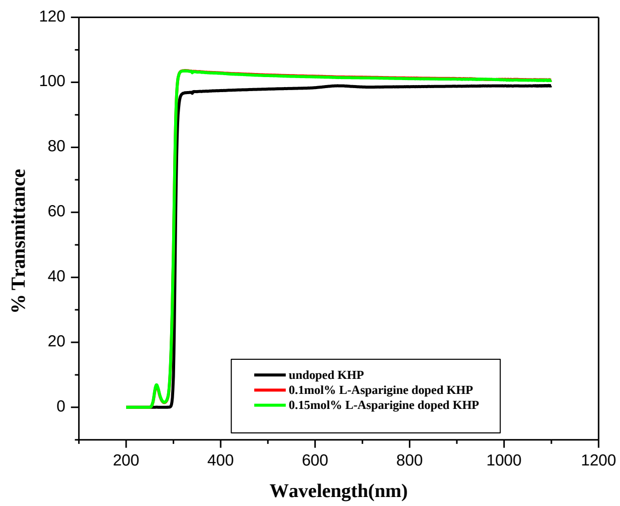

Fig 4: UV-NIR spectra of KHP crystals, (a) Undoped, (b) 0.1mol% LA, (c) 0.15mol% LA

3.4 Micro hardness studies:

Measurement of hardness is a useful non-destructive testing method to determine the hardness of the material [10]. Vicker's micro hardness test was carried out on undoped and LA 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 [11]. 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. Mayer's law [12] relates the load and size indentation as $P= Kd^n$, where k and n are the constants. The value of n is found to be 2.9 for undoped crystal. Onitsch states that the values $1.0<n<1.6$ for hard materials and $n>1.6$ for soft materials [13].

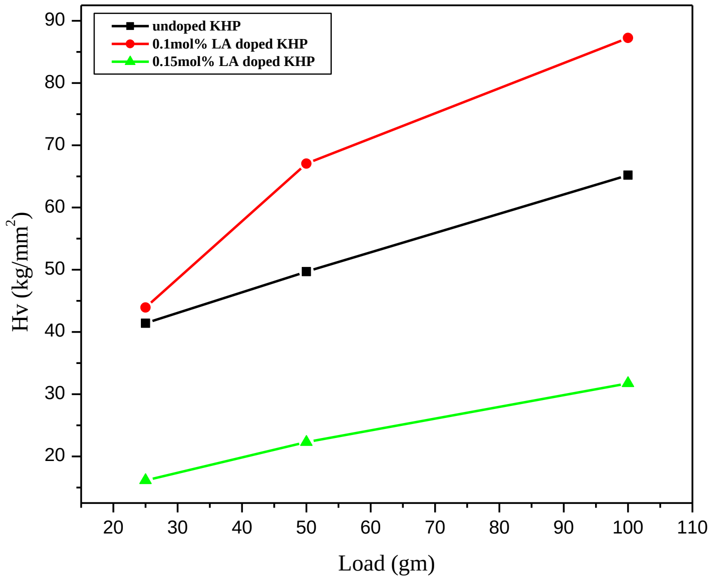

Fig 5: Vickers hardness vs load of Undoped and LA doped KHP crystals

3.5 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 LA doped KHP (0.1 and 0.15mol %) crystal were estimated as 7.16mJ and 8.89mJ when compared to that of the standard SHG material KDP. Hence the SHG efficiency for 0.1, 0.15mol% LA doped crystals were 1.2, 1.5 times that of the undoped KHP crystal.

3.6 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 and LA doped KHP was scanned between 400 and 800nm. The recorded spectrum of the sample is shown in Figure 6. For 345.25 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 observed in the region between at 506nm and 586.6nm for undoped and LA 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 [14, 15, and 16].

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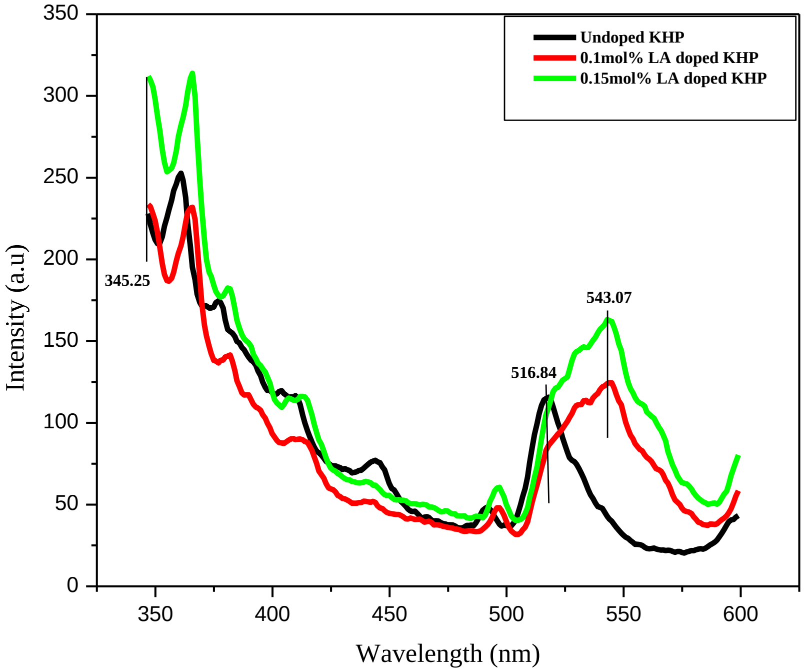

Fig 6: PL intensity vs wavelength of (a) Undoped , (b) 0.1 mol% LA, (c) 0.15mol% LA

3.7 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 LA doped KHP single crystals using a Q switched Nd: YAG laser for 6 ns laser pulses operating at a wavelength of 1064nm. The obtained LDT values and the input energy which made cracks on the surface of crystals are given in the table 2.

TABLE 2: shows the LDT values of Undoped and LA doped KHP

Sample	Energy (E) milli joule	LDT Values GW/cm^2
Undoped KHP	84	0.347
0.1mol% LA doped KHP	77	0.322
0.15mol% LA doped KHP	73	0.313

3.8 Thermal Analysis:

To identify the thermal stability, purity and crystalline nature of solution grown undoped & LA 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^{o}C/min. TG/DTA curves for undoped & LA doped KHP crystals are shown in Fig 7. The TG curve provides with a quantitative measurement of mass change associated with the transition. The decomposition is accompanied by the melting of the sample at 286.5^{o}C as shown by DTA for undoped KHP in Figure 7. The TG thermo gram reveals that decomposition starts for 0.1mol% LA doped KHP as shown in figure 7(a). The decomposition is accompanied by the melting of the sample at 298.25 ^{o} C as shown by DTA. The TG thermo gram reveals that decomposition starts for 0.15mol% LA doped KHP as shown in Figure 7(b). The decomposition is also accompanied by the melting of the sample at 303.06^{o}C as shown by DTA.

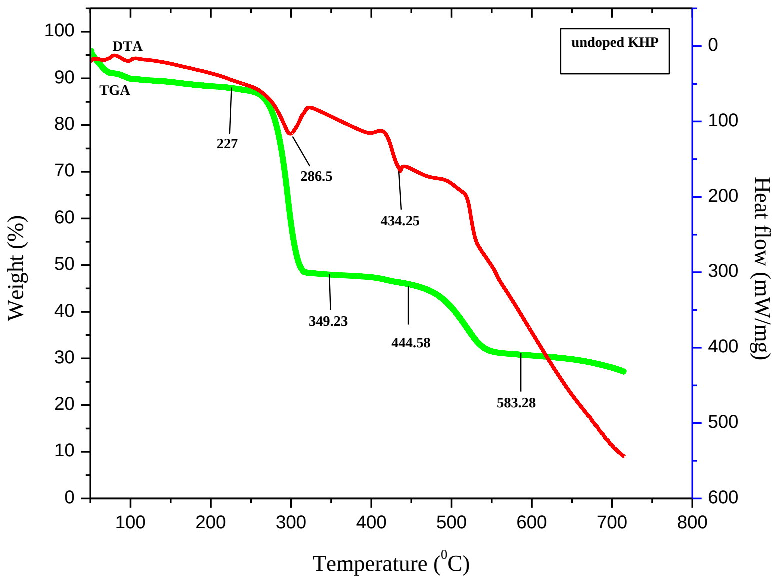

Fig 7: TG- DTA of Undoped KHP crystal

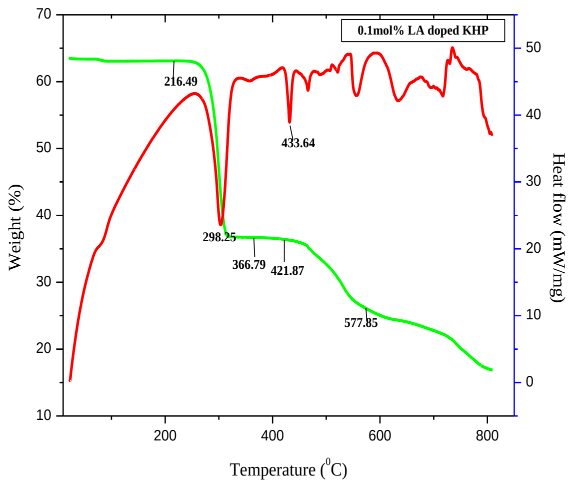

Fig 7(a): TG-DTA of 0.1mol% LA doped KHP crystal

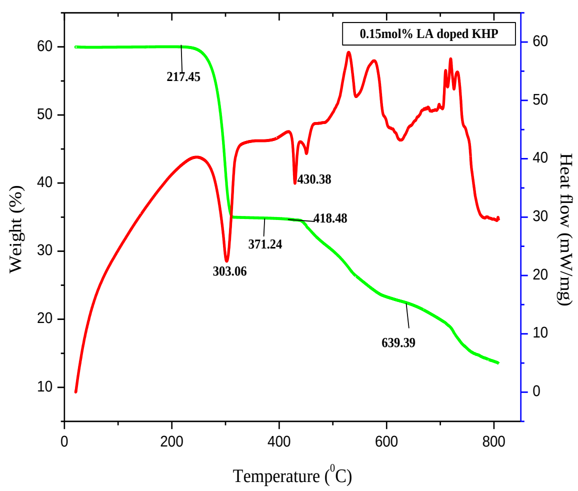

Fig 7(b): TG-DTA of 0.15mol% LA doped KHP crystal

IV. CONCLUSION

We have successfully grown good optical quality L-Asparagine 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. 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-Asparagine.

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