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Growth, Thermal, Mechanical and Dielectric Studies of Glycine Doped Potassium Acid Phthalate Single Crystals

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ABSTRACT

Single crystals of glycine doped potassium acid phthalate (KAP) have been grown from low temperature solution growth method by employing slow evaporation of the solvent at room temperature. The grown crystal was subjected to various studies such as X-ray diffraction (XRD), Fourier Transform Infrared (FTIR), UV-visible and Second Harmonic Generation (SHG) studies. The thermal stability, mechanical strength and dielectric constant were also measured. The various studies revealed the influence of the glycine on KAP and the investigations indicated that glycine played an important role in the changes of the spectral, optical and mechanical properties of KAP crystals.

***Keywords**: nonlinear optics; growth from solution; X-ray diffraction; dielectric constant*

1. INTRODUCTION

Second order nonlinear optical (SONLO) materials have recently attracted much attention because of their potential applications in emerging optoelectronic technologies [1,2]. It has been reported that organic crystals have very large nonlinear susceptibility compared with inorganic crystals, but their use is impeded by low optical transparency, poor mechanical strength, low laser damage threshold and inability to produce and process large crystals [3,4]. The inorganic NLO materials have excellent mechanical and thermal properties with optical nonlinearities because of the lack of extended π-electron delocalization. The semiorganic NLO materials combine good qualities of both organic and inorganic materials. Hence, in recent years much attention has been paid to semiorganic NLO materials. Crystals of phthalic acid derivatives are potential candidates for NLO and electro-optic processes [5]. KAP, a semiorganic material, is one of the well- studied important NLO crystals in the alkali metal acid phthalate (MAP) family [6-8]. MAP crystals are well known for their applications in the long-wave X-ray spectrometers [9]. Recently MAP crystals were used as substrates for a deposition of thin films of organic nonlinear materials [10]. KAP crystallizes in the orthorhombic system with a=6.46Å, b=9.60Å and c=13.85Å and space group $Pca2_1$ [11]. The influence of metal ion impurities like sodium, lithium and rubidium on the physical, chemical and mechanical properties of KAP single crystals have been reported [12]. The amino acids play an important role in the field of nonlinear optical crystals [13, 14]. Amino acid may be used as dopant in order to enhance the material property such as nonlinear optical [15]. On the basis of the above considerations, in the present investigation we report the growth and characterization of glycine doped KAP single crystals.

2. CRYSTAL GROWTH

Commercially available KAP salt (AR grade) was dissolved gradually in deionized water until a saturated solution was obtained. The calculated amount of 3mol% glycine was added to the solution with stirring. Then the solution was filtered and crystallization was allowed to take place by slow evaporation under room temperature. Optically transparent crystal of size $7x5x2mm^3$ was obtained in a period of 45 days. The as-grown crystal is shown in Fig. 1.

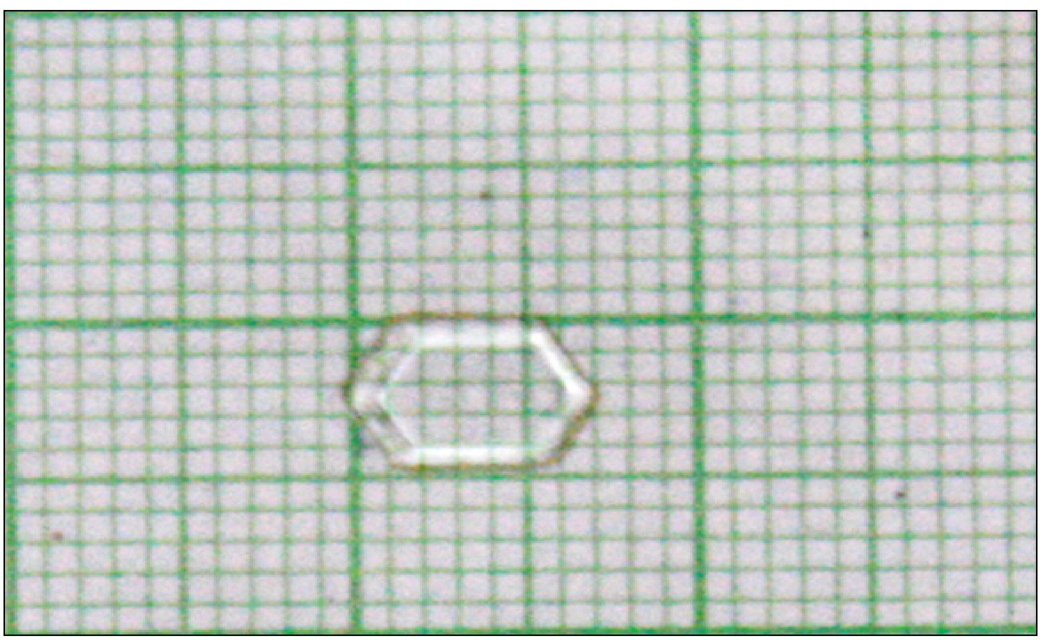

Fig. 1. Grown crystal of glycine doped KAP

3. CHARACTERIZATION

Single crystal X-ray diffraction analysis was carried out using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK_{α} (λ=0.1770 Å) to identify the structure and to determine the lattice parameter values. X-ray powder pattern of the crystal was recorded on a SIEFERT X-ray diffractometer using CuK_{α} (1.5406Å) radiation. The sample was scanned over the range 10 to 50° at a scan rate $1^{\circ}min^{-1}$. To measure the SHG efficiency, Kurtz powder technique was performed on the grown crystals. The FTIR spectrum was recorded in the range 400-4000cm^{-1} employing a Perkin-Elmer spectrometer by KBr pellet method to analyse the incorporation of glycine into KAP. To study the linear optical properties, the optical absorption spectra was measured in the range 200 to 1100nm using the instrument Lambda-35 UV-Vis-NIR spectrophotometer. The microhardness measurements for the grown crystals were made using Leitz-Wetzlar microhardness tester fitted with a Vicker's diamond pyramidal indentor attached to an incident light microscope. The dielectric measurements on the grown crystals were carried out using the instrument HIOCKI 3532-50 LCR HITESTER.

4. RESULTS AND DISCUSSION

4.1. Single Crystal X-ray Diffraction Analysis

Single crystals of glycine doped KAP crystallized in the orthorhombic system with space group $Pca2_1$. The lattice parameters were found to be: a=6.50Å, b=9.65Å, c=13.36Å and $\alpha=\beta=\gamma=90^{\circ}$. This analysis revealed that the incorporation of glycine in the KAP crystal does not change the crystal structure though there is a small change in the lattice parameters.

4.2. Powder X-ray Diffraction Analysis

The powder XRD pattern was recorded and the peaks were indexed using single crystal XRD data. The recorded diffractogram pattern is shown in Fig. 2. From this analysis, it is observed that the indexed peaks were slightly shifted when compared to that of pure KAP [16] indicating the incorporation of glycine into KAP.

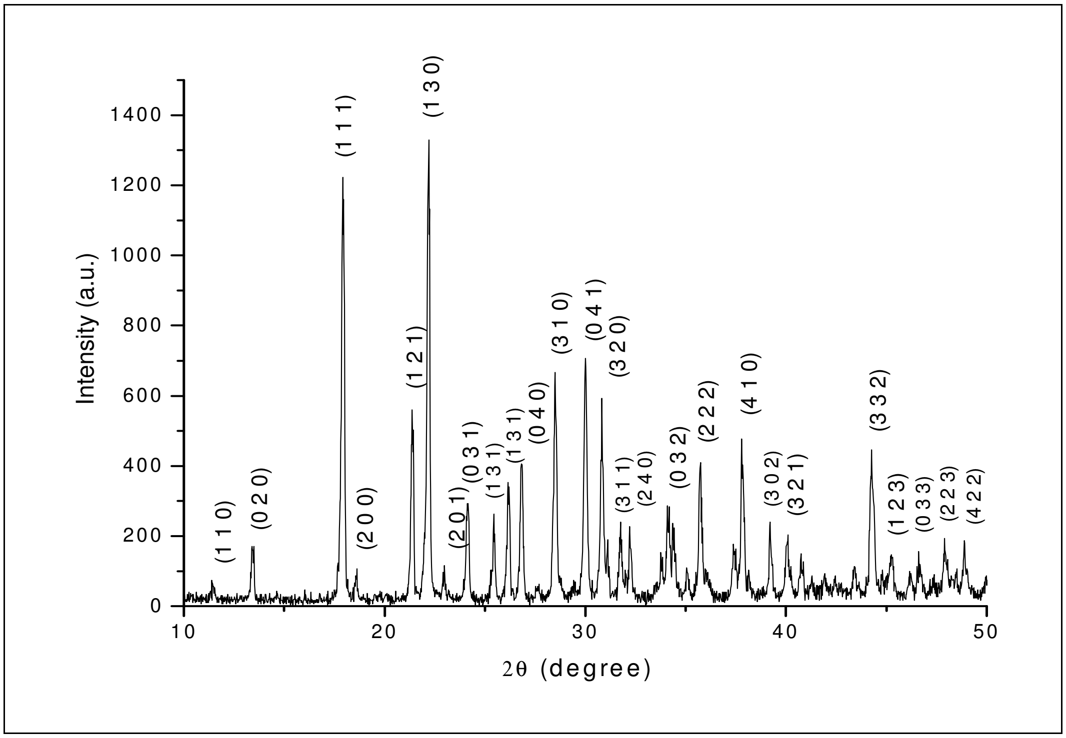

Fig. 2. Powder XRD pattern of glycine doped KAP

4.3. FTIR Spectral Analysis

The FTIR spectrum of glycine doped KAP is shown in Fig. 3. The vibrational frequencies obtained for glycine doped KAP and pure KAP are presented in Table 1. The presence of glycine in the lattice of KAP has been found from the O-H stretching vibration of KAP, as the O-H stretching vibration is more sensitive to hydrogen bonding interaction with the doped amino acids [17]. The characteristic O-H stretching peaks at 3415 and 2478cm^{-1} are shifted to 3466 and 2486cm^{-1}**,** indicating the substitution of glycine on the hydrogen site rather than on the potassium site. The asymmetric stretching vibration of the carboxylate ion is shifted to higher energy (1569cm^{-1}) compared to pure KAP (1562cm^{-1}).

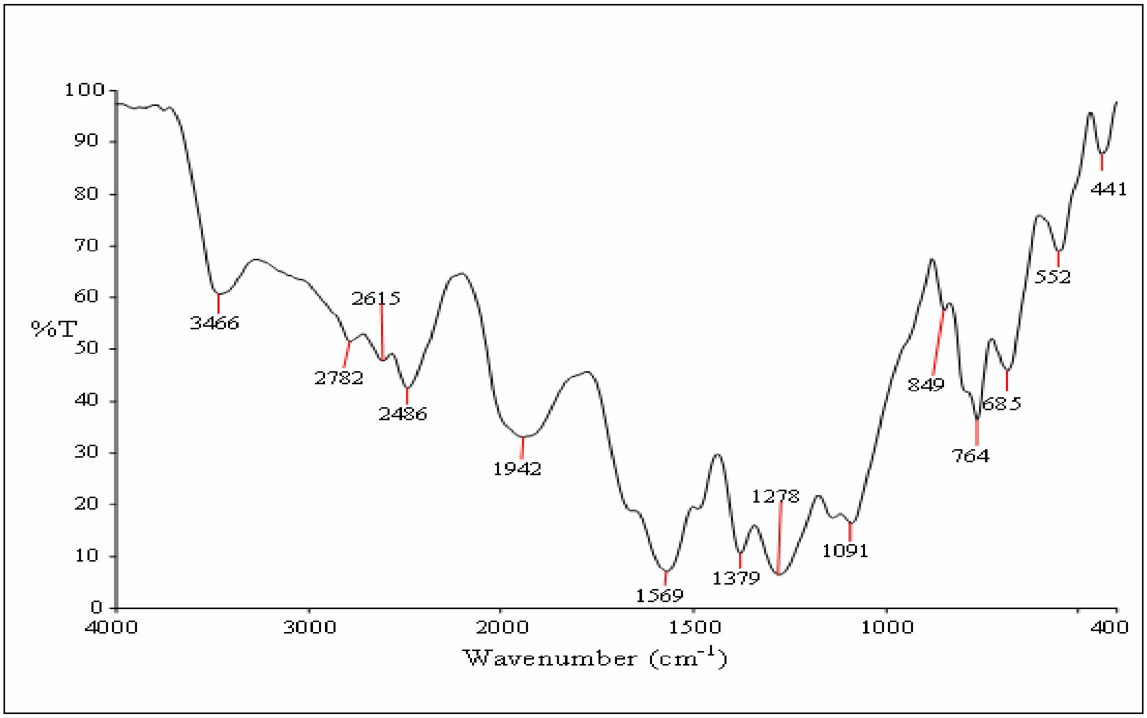

Fig. 3. FTIR spectrum of glycine doped KAP

Table 1. Vibrational frequency assignments for pure and glycine doped KAP

Pure KAP[12] cm^{-1}	glycine doped KAP cm^{-1}[present work]	Assignments
3415	3466	O-H stretching hydrogen bond
1544	1569	-C=O carboxylate ion=O asymmetric stretching
1382	1379	-C=O carboxylate ion=O symmetric stretching
1288	1278	C-O stretching
1087	1091	C-C-O stretching
852	849	C-H out of plane bending
767	764	C-C stretching
684	685	C-O wagging
550	552	C=C-C out of plane ring deformation
450	441	C= plane bending

4.4. Thermal Analyses

The TGA/DTA analyses of glycine doped KAP single crystal were carried out between 50 and 1200˚C at a heating rate of 20k/min in nitrogen atmosphere and are shown in Fig. 4. The TGA curve shows a sharp weight loss at 290˚C without any intermediate stages, which is assigned as melting point of the crystal. There is no weight loss below 290˚C, illustrating the absence of absorbed water in the crystal. It is reported that the melting point of the pure KAP is 290˚C [18]. Hence, we can conclude that there is no change in the melting point of the KAP due to the addition of glycine. From the DTA trace, the endothermic peak observed at 317˚C may be attributed to decomposition of glycine doped KAP. These analyses indicate that the compound could be used for the fabrication of any optical devices below its melting point.

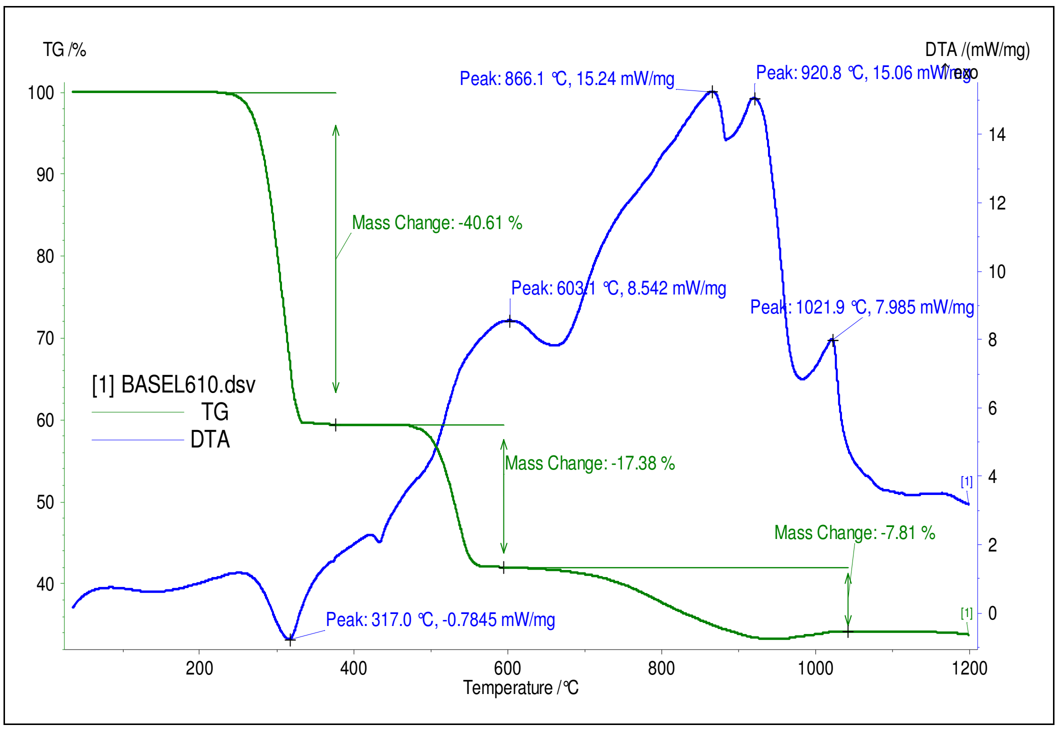

Fig. 4. TGA/DTA trace of glycine doped KAP

4.5. Linear Optical Assessment

UV-visible spectral study is a useful tool to determine the transparency, which is an important requirement for a material to be optically active [19]. Glycine doped KAP crystal of thickness 2mm was employed for this study. The recorded spectrum (Fig. 5) shows that the crystals have very low absorbance in the entire visible and IR region. The UV cut-off wavelength for glycine doped KAP is at 300nm. This results in high percentage of transmission, which is one of the most desired properties for the crystals used for the device fabrication.

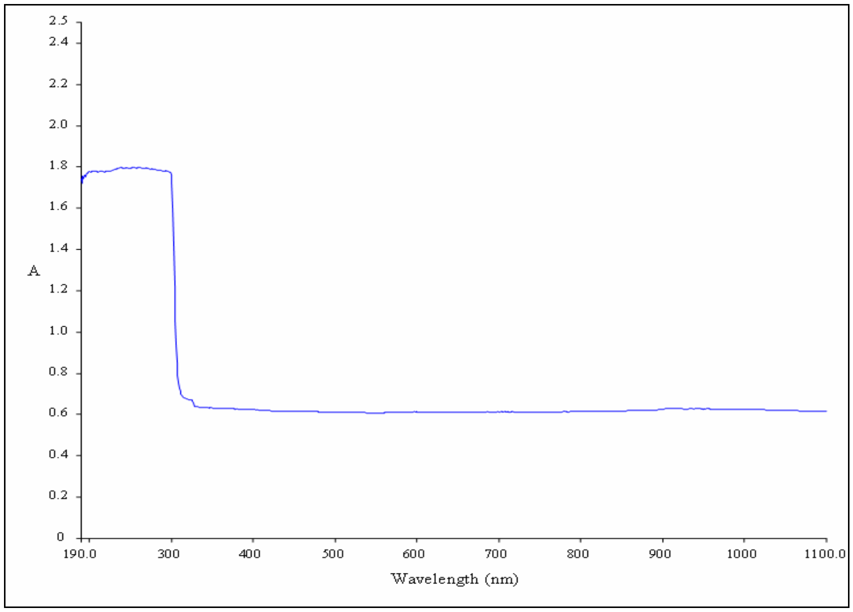

Fig. 5. UV-vis. absorption spectrum of glycine doped KAP

4.6. Second Harmonic Generation Efficiency Measurement

The Kurtz and Perry powder technique remains an extremely valuable tool for initial screening of materials for second harmonic generation. The fundamental beam of wavelength 1064nm from Q-switched Nd: YAG laser (Pro lab 170 Quanta ray) was used to test SHG property of the pure and glycine doped KAP. Pulse energy of 4 mJ/pulse, pulse width of 10 ns and repetition rate of 10 Hz was used in both measurements. The fundamental beam was filtered using an IR filter and photomultiplier tube (Philips photonics) was used as the detector. KDP was used as the reference material and the output power intensity of pure and glycine doped KAP were observed. A second harmonic signal of 35mV and 40mV were obtained from pure and glycine doped KAP respectively, with reference to 62mV of KDP. Thus, the SHG efficiency of pure and glycine doped KAP is roughly 0.6 times that of KDP.

4.7. Dielectric Study

Dielectric measurement is one of the useful methods for characterization of electrical response in crystalline and ceramic materials. A study of the dielectric properties provides information about electric fields within the solid materials. Frequency dependence of these properties gives great insight into the materials applications. Single crystals of glycine doped KAP cut in the rectangular specimen of thickness 1.2mm and area of cross section $6mm^2$ is subjected to dielectric studies. Silver paste is coated on both the surfaces of the sample to make contact between the crystal and the copper electrodes. The capacitance (C) and dissipation factor (D) of the parallel plate capacitors formed by the copper plate and electrode having the sample as dielectric medium have been measured. The dielectric constant (ε) and dielectric loss ($\tan\delta$) were calculated using the relations, $\varepsilon = Cd/A\varepsilon_0$ and $\tan\delta = D\varepsilon$, Where d is the thickness of the sample, A is the area of the sample and ε_0 is the permittivity of free space. The variation of dielectric constant and dielectric loss with frequency at room temperature are shown in Fig. 6 and 7 respectively. The dielectric constants have high values in the lower frequency region and then it decreases with the applied frequency. The high value of ε at lower frequencies may be due to the presence of all the four polarizations namely, space charge, orientational, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. The low value of dielectric loss at high frequency suggests that the glycine doped KAP crystals possesses enhanced optical quality with lesser defects and this parameter is of vital importance for nonlinear optical materials in their applications.

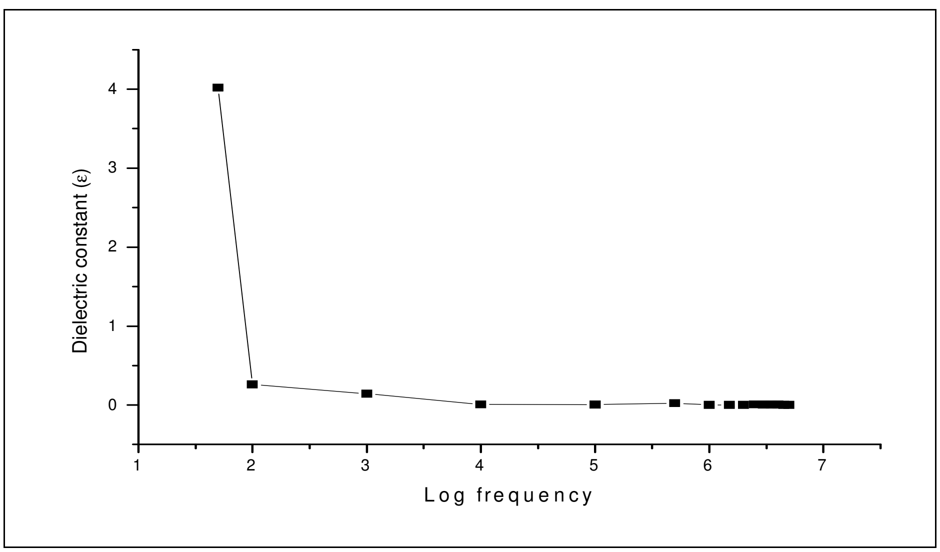

Fig. 6. Variation of dielectric constant with frequency

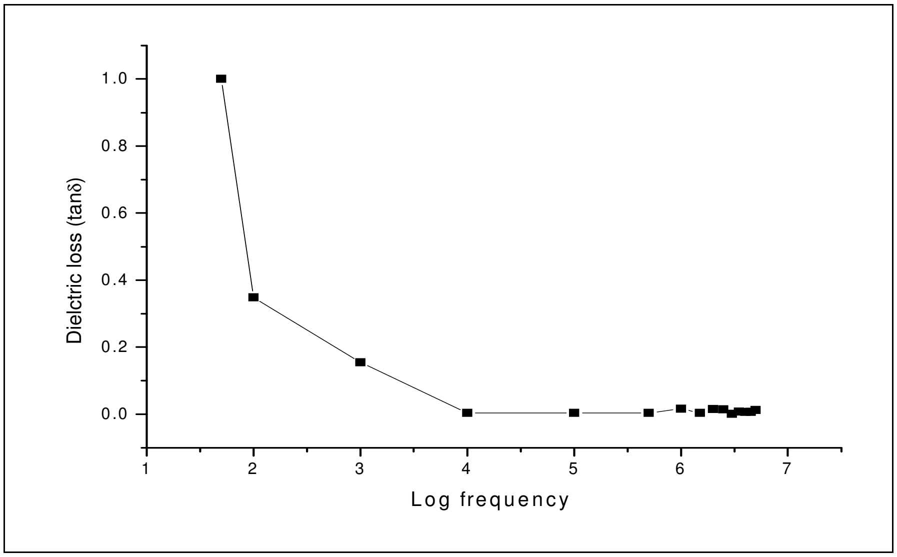

Fig. 7. Variation of dielectric loss with frequency

4.8. Microhardness Studies

The Vicker's microhardness measurement was carried out on the grown crystals to assess the mechanical property. The static indentations were made at room temperature with a constant indentation time of 10s for all indentations. The indentation marks were made on the surfaces by varying the load from 10 to 100g. The Vicker's microhardness number Hv of the pure and glycine doped KAP were calculated using the relation $Hv=1.8544P/d^2 Kgmm^{-2}$. Where P is the applied load in Kg and d is the average diagonal length of the indentation in mm. A graph plotted between hardness number (Hv) and applied load (P) is shown in Fig. 8. At lower load, there is an increase in hardness with load, for both the crystals, which can be attributed to the work hardening of the surface layer. Beyond 100g, significant cracking occurs, which may be due to release of internal stress generated with indentation. The work hardening coefficient of pure and glycine doped KAP is found to be 1.76 and 1.66 respectively. According to Onitsch, $1.0 \leq n \leq 1.6$ for hard material and $n > 1.65$ for soft materials. Hence, it is concluded that pure and glycine doped KAP belongs to soft materials.

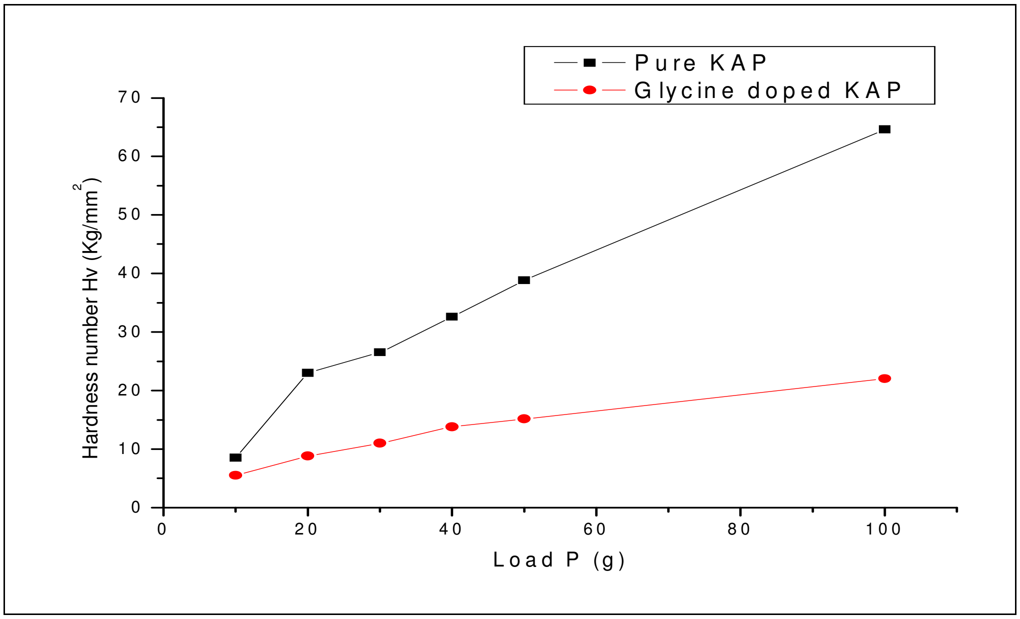

Fig. 8. Vicker's microhardness plot

5. CONCLUSION

Good optical quality single crystals of glycine doped potassium acid phthalate (KAP) have been grown from aqueous solution by slow evaporation technique under room temperature. The grown crystals were characterized by single crystal X-ray diffraction and confirmed that the crystals belong to orthorhombic system. The presence of glycine was confirmed qualitatively using FTIR analysis. The optical absorption study revealed that glycine doped KAP crystals have low absorption in the entire visible region and the UV cut-off wavelength was found at 300nm. The variation of dielectric constant and dielectric loss were studied as a function of frequency. The hardness value of glycine doped KAP is measured to be higher than pure KAP. With promising structural, optical and mechanical properties, glycine doped KAP is a potential material for frequency conversion applications.

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