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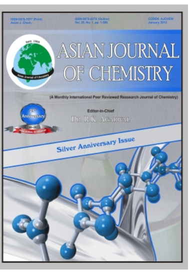

Growth and Characterization of Pure and L-Alanine Sodium Nitrate doped Potassium Dihydrogen Phosphate Single Crystals

FERNANDO LORETTA[1,*], S. PERUMAL[2] and S. RAMALINGOM[3]

[1]Department of Physics, Holy Cross College, Nagercoil-629 004, India
[2]Physics Research Centre, S.T. Hindu College, Nagercoil-629 002, India
[3]Department of Physics, Vivekananda College, Agasteeswaram-629 701, India

*Corresponding author: E-mail: lorettajosep@gmail.com

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Single crystals of pure and L-alanine sodium nitrate (LASN) doped potassium dihydrogen phosphate (KDP) were grown from aqueous solution by slow evaporation technique at room temperature. The grown crystals were colourless and transparent. The grown crystals were subjected to single crystal X-ray diffraction studies and powder X-ray diffraction studies to study their structural characteristics. The functional groups present in the grown crystals were identified using FTIR spectral analysis. EDAX analysis confirms the presence of L-alanine sodium nitrate in the doped potassium dihydrogen phosphate crystal. UV-Visible transmission spectral studies and non-linear optical studies indicate that the optical transparency and second harmonic generation efficiency of potassium dihydrogen phosphate crystals are enhanced due to L-alanine sodium nitrate doping. Microhardness studies show that the L-alanine sodium nitrate doped potassium dihydrogen phosphate crystal is harder than pure potassium dihydrogen phosphate.

Key Words: Potassium dihydrogen phosphate, Doping, Crystal growth, Nonlinear optical material, Characterization.

INTRODUCTION

Potassium dihydrogen phosphate (KDP) crystal exhibits excellent electro-optical and non-linear optical (NLO) properties and is commonly used in several applications such as frequency conversion, laser fusion and electro-optical modulation. The easy growth of large single crystals, a high optical damage threshold and a relatively low production cost are the qualities that makes this phosphate crystal attractive for a variety of optical applications[1,2]. This classical material belongs to the scalenohedral class of tetragonal crystal systems having tetramolecular unit cell with lattice parameters a = b = 7.448 Å and c = 6.977Å[3,4]. The rapid growth of good quality potassium dihydrogen phosphate crystals, the newly developed techniques and the beneficial effect of organic and inorganic impurities on the properties of potassium dihydrogen phosphate crystals have been reported by various investigators[1,5-9]. It has been reported in the literature that doping non-linear optical crystals with various dopants can alter the physical and chemical properties of the crystals and doped-non-linear optical crystals find wide applications in opto-electronic devices compared to undoped non-linear optical crystals[10,11].

Amino acid family crystals are playing an important role in the field of non-linear optical organic molecular crystal. They are interesting materials for non-linear optical application as they contain proton donor carboxyl acid (-COO) group and the proton acceptor amino (NH_2) group in them[12]. Some amino acids like L-arginine, L-lysine, L-alanine and γ-glycine are evidently showing non-linear optical activity because they have a donor NH_2 group and acceptor COOH group and also intermediate charge transfer is possible[13]. L-alanine (LA) is the smallest, naturally occurring chiral amino acid with a non-reactive hydrophobic methyl group ($-CH_3$) as a side chain. L-alanine has the zwitterionic form ($^+NH_3-C_2H_4-COO^-$) both in crystal and in aqueous solution over a wide range of pH, which favours crystal hardness for device application[14,15]. Improvement in the non-linear optical property of the potassium dihydrogen phosphate crystal and modifications in the structural, optical, mechanical and electrical properties and thermal properties have been identified by doping potassium dihydrogen phosphate with a variety of amino acids[16-19]. Kumaresan *et al.*[20] have also reported the effect of metal ion and amino acid doping on the optical properties of potassium dihydrogen phosphate crystal. Muley *et al.*[21] have studied thermal, non-linear optical properties of potassium dihydrogen phosphate crystal doped with L-arginine and L-alanine and have reported that L-alanine doped potassium dihydrogen phosphate crystal may be used for second harmonic generation purpose with improved second harmonic generation efficiency and optical transparency at the place of pure potassium dihydrogen phosphate crystals, also L-alanine doped potassium dihydrogen phosphate crystals highlight their prospects of application as non-linear optical materials[14]. The dielectric constant and the dielectric loss values of L-alanine doped potassium dihydrogen phosphate crystals were lower than the pure potassium dihydrogen phosphate crystals and found to be more useful for high speed electro-optic modulations as compared to pure potassium dihydrogen phosphate crystal[22].

Recent interest is focused on the development of new non-linear optical (NLO) semiorganic materials which posses the advantage of both organic and inorganic materials. Complexes of amino acids with inorganic salts are considered to be novel materials for second harmonic generation properties and they are found most of the times as promising as potassium dihydrogen phosphate or even better than it. The effect of the metal ions and organic material present in the semiorganic material L-arginine hydrochloride[2] and copper thiourea complex[23] on the non-linear optical property of potassium dihydrogen phosphate crystals has been so far reported. Complexes of L-alanine have been recently crystallized to form semi-organic non-linear optical (NLO) materials such as L-alanine hydrogen chloride, L-alanine acetate, L-alanine sodium nitrate, L-alanine aluminium nitrate, *etc.* that have potential applications in second harmonic generation and have been investigated by many researchers[24-28]. The second harmonic generation efficiency of L-alanine sodium nitrate was determined to be about two times that of potassium dihydrogen phosphate crystal[27].

Improvement in optical and non-linear optical properties of potassium dihydrogen phosphate is proposed by doping it with semiorganic non-linear optical material L-alanine sodium nitrate in different molar ratios. In the present work, we report the growth of single crystals of pure and 1 mol % L-alanine sodium nitrate doped potassium dihydrogen phosphate crystals by slow solvent evaporation technique and the characterization of the grown crystals by single crystal and powder XRD studies, FTIR, EDAX analysis, UV-VIS transmission studies, microhardness studies and second harmonic generation efficiency measurements. The results are discussed in this paper.

EXPERIMENTAL

Crystal growth: Single crystals of pure and 1 mol % L-alanine sodium nitrate doped potassium dihydrogen phosphate were grown by solution growth employing slow evaporation technique at room temperature. Using pure potassium dihydrogen phosphate salt (G.R. Merck) and deionized water, the saturated solution of potassium dihydrogen phosphate was prepared in accordance with the solubility data. The solution was thoroughly stirred for homogenization and then filtered into a borosil beaker using Whatmann filter paper. The pH of the solution was noted as 3.8. The beaker containing the saturated solution (200 mL) was closed with perforated cover and kept in a dust free atmosphere to allow slow evaporation of the solvent. Transparent, good quality potassium dihydrogen phosphate crystals were harvested within 20-30 days. For the growth of L-alanine sodium nitrate doped potassium dihydrogen phosphate crystals initially the semiorganic dopant L-alanine sodium nitrate was synthesized using AR grade L-alanine and sodium nitrate in the molar ratio 1:1. The calculated amount of L-alanine and sodium nitrate salts were very well dissolved in deionized water and thoroughly mixed using a magnetic stirrer, small transparent colourless single crystals of L-alanine sodium nitrate were grown within 30-40 days employing slow evaporation technique at constant room temperature. The identity of the grown L-alanine sodium nitrate crystals were confirmed by FTIR analysis[28]. These crystals were further purified by recrystallization and powdered. Potassium dihydrogen phosphate salt was added to the powdered crystalline sample of L-alanine sodium nitrate in the molar ratio 1:0.01 to form a saturated solution. The solution was thoroughly stirred for homogenization and then filtered into a borosil beaker using Whatmann filter paper. The pH of the solution was noted as 3.8. The beaker containing the saturated solution (200 mL) was closed with perforated cover and kept in a dust free atmosphere to allow slow evaporation of the solvent. Single colourless, transparent crystals of L-alanine sodium nitrate doped potassium dihydrogen phosphate were harvested within 20-30 days. The photograph of pure and 1 mol % L-alanine sodium nitrate doped potassium dihydrogen phosphate crystals are shown in Fig. 1(a-b), respectively.

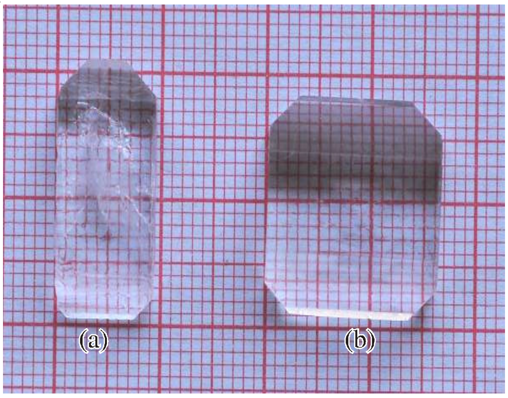

Fig. 1. Photograph of (a) pure potassium dihydrogen phosphate (b) 1 mol % L-alanine sodium nitrate doped potassium dihydrogen phosphate

RESULTS AND DISCUSSION

X-Ray diffraction studies: Single crystal X-ray diffraction analysis has been carried out to confirm the crystallinity and to find the lattice parameters of the grown crystals. Single crystals of pure and L-alanine sodium nitrate doped potassium dihydrogen phosphate crystals were subjected to single crystal X-ray diffraction studies using BRUKER NONIUS CAD4 single crystal x-ray diffractometer to obtain the unit cell parameters. The obtained results show that the lattice parameters for pure potassium dihydrogen phosphate crystals are $a = b = 7.441$ Å, $c = 6.987$Å, $\alpha = \beta = \gamma = 90^\circ$ and volume = 386.859 $(\text{Å})^3$ and for L-alanine sodium nitrate doped potassium dihydrogen phosphate crystals $a = b = 7.454$ Å, $c = 6.993$ Å, $\alpha = \beta = \gamma = 90^\circ$ and volume = 388.545 $(\text{Å})^3$. The results confirm that the L-alanine sodium nitrate doped potassium dihydrogen phosphate crystals are crystalline and crystallize in the same tetragonal structure as that of pure potassium dihydrogen phosphate. The unit cell parameters of the pure potassium dihydrogen phosphate crystal obtained in this work are observed to have close agreement with the reported work[3,4] and slight change of lattice parameters is observed for the L-alanine sodium nitrate doped sample compared to pure potassium dihydrogen phosphate crystal. The changes in the lattice parameters may be attributed to the presence of L-alanine sodium nitrate in the lattice of the potassium dihydrogen phosphate crystal. The presence of dopant in the potassium dihydrogen phosphate crystal may produce lattice strain, which leads to a change in unit cell parameters. To confirm the values of lattice parameters obtained from single crystal XRD studies, powder XRD studies were also carried out and the XRD patterns of pure and L-alanine sodium nitrate-doped potassium dihydrogen phosphate crystals are presented in Figs. 2 and 3, respectively. Well-defined peaks at specific 2θ values show high crystallinity of the grown crystals. All the reflections of the powder XRD patterns of this work were indexed using the INDEXING and TREOR software packages. It is noticed that there are slight shifts in reflection peaks and change in intensity in the powder XRD pattern of the L-alanine sodium nitrate-doped sample compared to that of the pure potassium dihydrogen phosphate sample. The lattice parameters obtained from the indexed XRD patterns using the UNIT CELL software package are observed to be comparable with the values obtained from single crystal XRD studies. The incorporation of L-alanine sodium nitrate into the lattice of potassium dihydrogen phosphate crystal has resulted in changes in the lattice parameters of doped potassium dihydrogen phosphate without changing its basic structure.

Fourier transform infrared spectral studies: The Fourier transform infrared spectrum was recorded for powdered samples of pure and 1 mol % L-alanine sodium nitrate doped potassium dihydrogen phosphate crystals using Perkin- Elmer FTIR spectrometer by KBr pellet technique in the range 4000-400 cm^{-1}. The spectra of pure and L-alanine sodium nitrate doped potassium dihydrogen phosphate crystals are shown in Figs. 4 and 5, respectively. The effect of L-alanine sodium nitrate on the vibrational frequencies of the functional groups of pure potassium dihydrogen phosphate crystal has been identified in the spectra and Table-1 presents the frequency assignments of the grown crystals. The deviation in the frequencies, the missing and additional peaks clearly indicate the interaction and entry of the dopant into the lattice sites of potassium dihydrogen phosphate crystal.

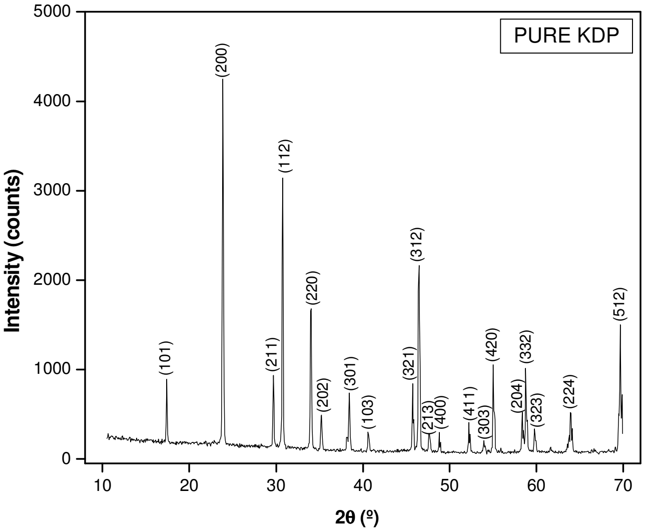

Fig. 2. Powder XRD pattern of pure potassium dihydrogen phosphate

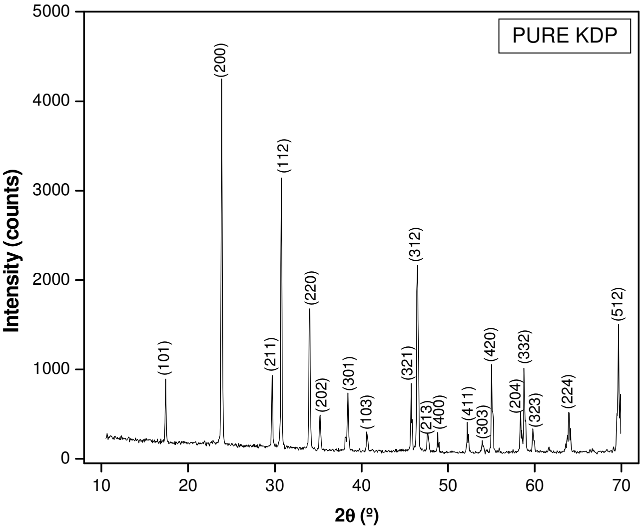

Fig. 3. Powder XRD pattern of L-alanine sodium nitrate doped potassium dihydrogen phosphate

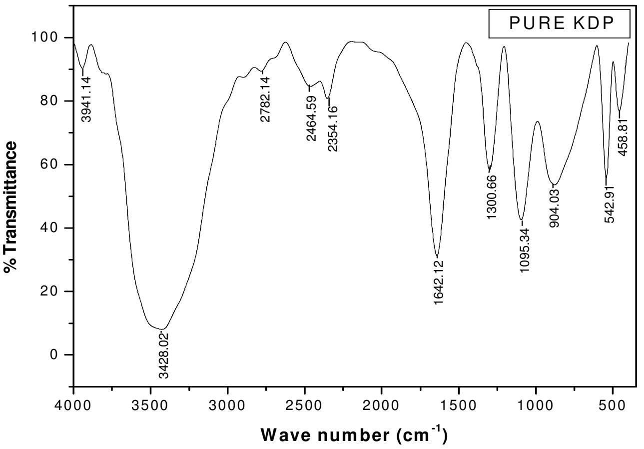

Fig. 4. FTIR spectrum of pure potassium dihydrogen phosphate crystal

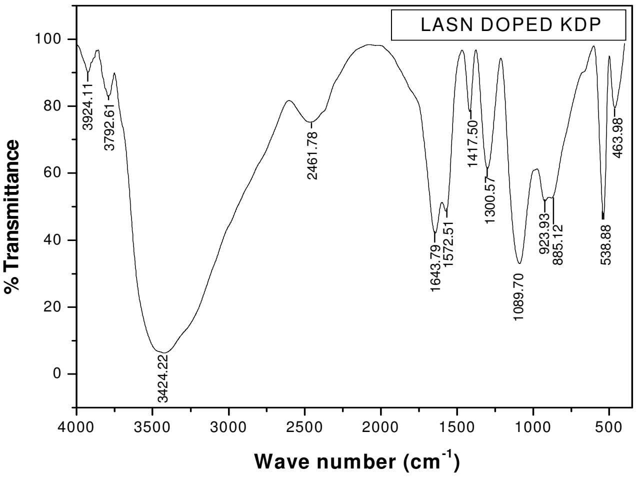

Fig. 5. FTIR spectrum of L-alanine sodium nitrate doped potassium dihydrogen phosphate crystal

TABLE-1
FTIR ASSIGNMENTS FOR PURE AND LASN DOPED KDP CRYSTALS

Pure KDP Wavenumber (cm^{-1})	LASN doped KDP wavenumber (cm^{-1})	Assignment
3941.14	3924.11	O-H stretching due to water of crystallization
–	3792.61	Free O-H stretching hydrogen bonded KDP
3428.02	3424.22	O-H hydrogen bond stretching
2782.14	–	P-O-H asymmetric stretching
2464.59	2461.78	O = P-OH stretching
2354.16	–	P-O-H bending
1642.12	1643.79	O ‖ P-OH stretching
–	1572.51	NH_3 bending
–	1417.50	C = H bending
1300.66	1300.57	P = O stretching
1095.34	1089.70	P-O stretching
904.03	923.93	P-O-H stretching
–	885.12	COO^- stretching
542.91	538.88	HO-P-OH bending
458.81	463.98	P-O H distortion

Optical transmission spectral studies: Pure and L-alanine sodium nitrate doped potassium dihydrogen phosphate crystal plates with a thickness of 2 mm without any antireflection coating were cut and used for optical measurements. The UV-visible-near infrared transmission spectrum was recorded using Perkin-Elmer Lambda 35 UV-visible spectrometer in the range 190-1100 nm. From the spectra, it is observed that both the pure and L-alanine sodium nitrate doped potassium dihydrogen phosphate crystals show good transmittance in the entire visible and near infrared regions. The pure potassium dihydrogen phosphate crystal has 76 % and 1 mol % L-alanine sodium nitrate doped potassium dihydrogen phosphate crystal has 80 % transmittance. Thus the addition of and L-alanine sodium nitrate has increased the transmittance of pure potassium dihydrogen phosphate. The UV-visible-near infrared transmission spectra of pure potassium dihydrogen phosphate and L-alanine sodium nitrate doped potassium dihydrogen phosphate are shown in Fig. 6. A complex formed of L-alanine with potassium have progressively improved the optical quality of potassium dihydrogen phosphate crystals with higher transparency[2]. It could be concluded that the L-alanine doping plays a key role in improving the optical quality of potassium dihydrogen phosphate crystals. This is the most desirable property of materials possessing non-linear optical activity[14].

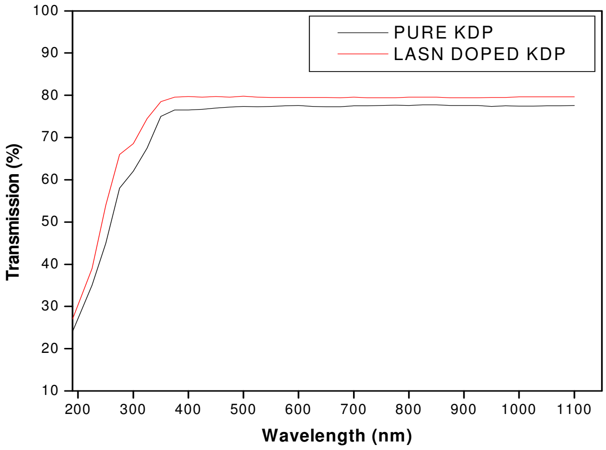

Fig. 6. UV-Visible transmission spectra of pure potassium dihydrogen phosphate and L-alanine sodium nitrate doped potassium dihydrogen phosphate

Second harmonic generation (SHG) test: Kurtz and Perry powder technique[29] is extremely useful for the initial testing of materials for second harmonic generation (SHG). The fundamental beam of wavelength 1064 nm, from a Q-switched Nd:YAG laser was used. The pure and L-alanine sodium nitrate doped potassium dihydrogen phosphate crystals were ground into fine powder and packed in micro capillary tubes mounted in the path of laser pulses with pulse width 6 ns and repetition rate 10 HZ, having an input energy of 0.68 J/pulse. The second harmonic generation was confirmed by the green emission of wavelength 532 nm from the samples. The output energy for pure and 1 mol % L-alanine sodium nitrate doped potassium dihydrogen phosphate samples was measured to be 8.9 mJ/pulse and 12.58 mJ/pulse for pure and L-alanine sodium nitrate doped potassium dihydrogen phosphate, respectively. The second harmonic generation efficiency of 1 mol % L-alanine sodium nitrate doped potassium dihydrogen phosphate was calculated to be 1.413 times that of pure potassium dihydrogen phosphate. The L-alanine doping is beneficial for second harmonic generation efficiency. Lin *et al.*[30] studied the mechanism of the optical behaviour of potassium dihydrogen phosphate crystals theoretically by the plane wave pseudo-potential total energy software package. The origin of non-linear effects has been explained through the real space atom cutting analysis for potassium dihydrogen phosphate. The contribution of PO_4 group to the second harmonic generation effect is dominant and the hydrogen bonds contribute much for birefringence. The possibility of hydrogen bonding between O of phosphate unit of potassium dihydrogen phosphate and amino group of L-alanine may lead to increase contribution of PO_4 to second harmonic generation effect. Moreover, in the amino acid second harmonic generation efficiency is due to the contribution of carbonyl group and hydrogen bond, by adding amino acid the hydrogen bond as well as the carbonyl group are introduced in the potassium dihydrogen phosphate, which may give contribution to give rise in second harmonic generation property. Increase in second harmonic generation may also be due to central ion in metal organic complex which offers a certain anisotropic field to keep non-linear optical active chromopores and vary the hyper polarizibility value[13,31].

Energy dispersive X-ray analysis: In order to confirm the presence of the elements of L-alanine sodium nitrate into pure potassium dihydrogen phosphate crystals, the sample of grown crystals were subjected to energy dispersive X-ray analysis. The grown 1 mol % L-alanine sodium nitrate doped potassium dihydrogen phosphate crystal was analyzed using EDAX detector (model-Thermoelectron Corporation with superdry/II) equipped in Hitachi model S-3000H scanning electron microscope. The obtained spectrum (Fig. 7) confirms the presence of the elements of L-alanine sodium nitrate in pure potassium dihydrogen phosphate crystals.

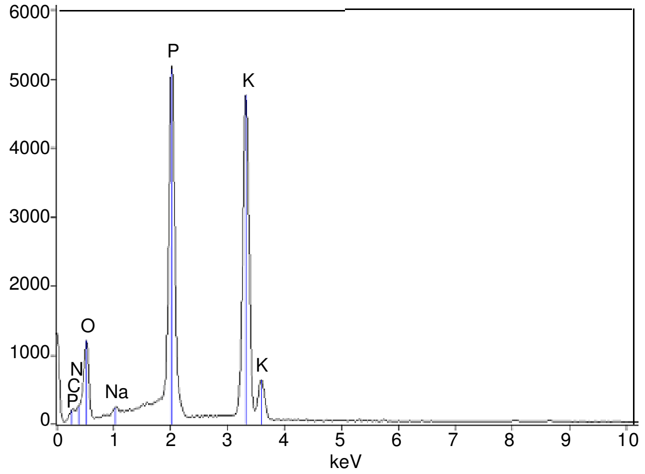

Fig. 7. EDAX spectrum of L-alanine sodium nitrate doped potassium dihydrogen phosphate crystals

Microhardness studies: The microhardness characterization is extremely important as far the fabrication of devices is concerned. Hardness of a material is the resistance it offers to local deformation. Pure and L-alanine sodium nitrate doped potassium dihydrogen phosphate crystals were tested for their microhardness property using Shimadzu HMV-2 Vicker's microhardness tester fitted with a diamond indentor. The measurements were made at room temperature and loads of different magnitude 25-100 g were applied and the indentation time was kept as 5 s for all the loads. The hardness of the crystal is calculated using the relation

$$H_v = \frac{1.8544P}{d^2}$$

where H_v is the Vicker's hardness number, P is the indentation load in kg and d is the diagonal length of the impression in mm. The plot for H_v *verses* P for pure and L-alanine sodium nitrate doped potassium dihydrogen phosphate is shown in Fig. 8. Microhardness studies reveal that the hardness of the doped crystal is higher than the pure sample. The reason may be due to the addition of semiorganic dopant which enhances the strength of bonding with the host material and hence the hardness increases.

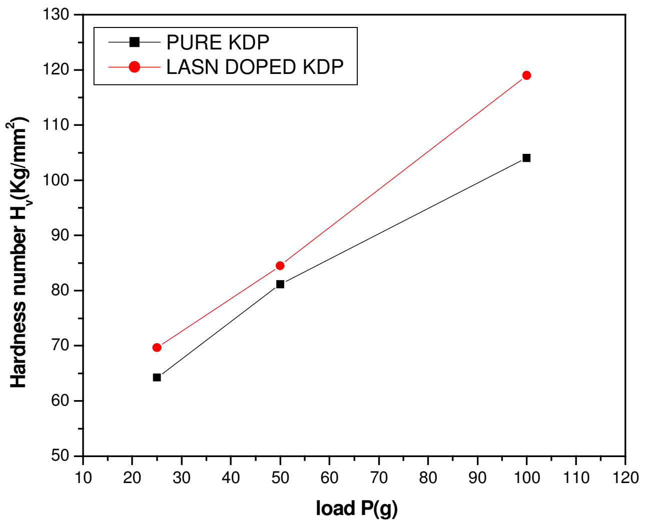

Fig. 8. Variation of H_v with load for pure and L-alanine sodium nitrate doped potassium dihydrogen phosphate

Conclusion

Good quality single crystals of pure and L-alanine sodium nitrate doped potassium dihydrogen phosphate were grown by solution growth technique. The unit cell parameters and structure have been evaluated by XRD studies and the functional groups have been identified from the FTIR spectral analysis for the grown pure and L-alanine sodium nitrate doped potassium dihydrogen phosphate crystals. The optical transmission and the non-linear optical studies show that addition of L-alanine sodium nitrate has enhanced the transmittance and the second harmonic generation efficiency of pure potassium dihydrogen phosphate due to the substitution of L-alanine sodium nitrate into the potassium dihydrogen phosphate crystal lattice. Microhardness measurements reveal that the hardness of potassium dihydrogen phosphate has increased due to doping. From the studies we infer that doping of potassium dihydrogen phosphate with L-alanine sodium nitrate has made potassium dihydrogen phosphate much more efficient with improved qualities and facilitate its application in the field of non-linear optics.

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