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International Journal of ChemTech Research

CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.6, pp 2691-2696, 2014-2015

Effect of Doping on the Morphology of KAP Nonlinear Optical Single Crystal

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Abstract: Single crystals of potassium acid phthalate (KAP) were grown by the slow evaporation technique at room temperature. The cell parameters were determined by single crystal X-ray diffraction technique. The FTIR studies confirm the presence of functional group in the grown crystal. The optical transmittance studies show that the crystal has transparence in the entire visible and IR region with a lower cutoff of wavelength 300 nm. The TG/DTA analyze reveals the thermal stability of the grown single crystal and the melting point is 297°C. The Vicker's hardness test was used to analyze the mechanical property of the grown crystal. The second harmonic generation (SHG) of KAP is confirmed by Kurtz and Perry powder technique using Nd:YAG laser. The effect of L-histidine doping on the morphology of the KAP single crystal has been studied.
Key Words: Single crystal, XRD, mechanical property, melting point, SHG.

1. Introduction

Nonlinear optical (NLO) material plays a vital role in optical modulation, fiber optic communication and optoelectronics, since they are capable of producing high values of original laser frequency [1, 2]. A continuous effort is made on the organic, inorganic and semiorganic materials with high damage threshold, wide transparency range and high nonlinear coefficient which make them suitable for device fabrication [3, 4]. The organic NLO materials have low thermal and mechanical property and high laser damage threshold for optical application [5, 6]. Inorganic NLO materials have excellent mechanical and thermal properties but possess low laser damage threshold and low optical nonlinearities [7, 8]. A typical semiorganic NLO material is formed by combining of organic ion and an inorganic counter ion to have a favorable high optical nonlinearity, high damage threshold, excellent mechanical and thermal properties [9, 10]. The KAP crystals are playing an important role in the field of nonlinear optics, and they are known second harmonic generating materials that have long stability in devices due to their electro- optical properties and exhibit interesting piezoelectric and elastic properties that are useful in many application [11]. In the present work, the KAP single crystals were grown by slow evaporation technique at room temperature. The grown crystals were subjected to single crystal and powder XRD, UV-Vis, FTIR, Vicker's hardness test and SHG studies. Due to the doping of L-histidine in KAP, a remarkable morphology changes has been observed but there is no change in the structural properties.

2. Experimental Techniques

2.1 Growth of KAP crystal

One mole of KAP was dissolved in the 150 ml of distilled water. The solution was stirred using magnetite stirrer thoroughly to ensure homogeneous concentration of the solution. The solution was filtered to remove suspended impurities in the solution. The solution was kept at room temperature for slow evaporation to crystallize the compound. After three weeks a clear transparent regular shape good quality KAP single crystal with size of 24× 19× 3 mm^3 have been harvested from the mother solution. The grown KAP single crystal is shown in Fig.1.

Simultaneously 1 wt % of L-Histidine was doped in the KAP solution (L-HKAP) and single crystal with size of 11× 8× 5 $mm^3$was obtained within three weeks. The grown crystal shown in Fig.2.

Fig .1 Grown single crystal of KAP.

Fig .2 Grown single crystal of L-HKAP.

3. Result and Discussion

3.1. X-ray powder diffraction

The fine powder of pure and L-histidine doped potassium acid phthalate was subjected to X-ray powder diffraction using a XPERT_PRO diffractometer with CuKα (λ=1.5418 Å) radiation. The sample was scanned for 2θ range and at a scan rate of 2°/min. The recorded X-ray diffraction pattern of pure and L-histidine doped potassium acid phthalate is shown in Figs 3&4. The well defined peak in the XRD pattern revealed the crystalline nature of the crystal.

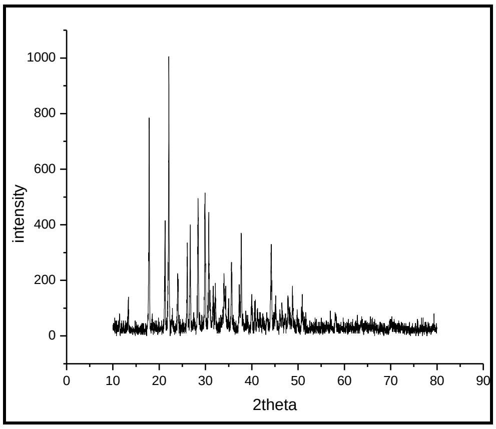

Fig.3. XRD Pattern of KAP.

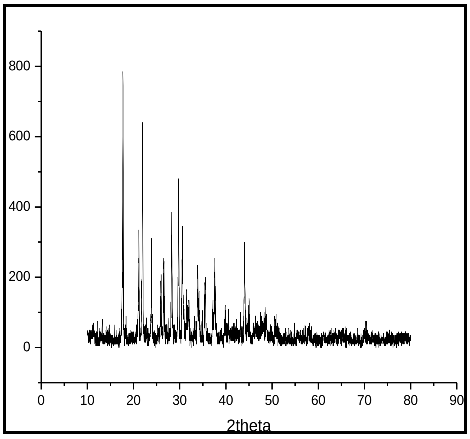

Fig.4. XRD Pattern of L-HKAP.

3.2 Single crystal XRD analysis

` The single crystal XRD analysis for KAP and L-HKAP crystals were carried out using ENRAF NONIUS CAD-4 single crystal X-ray diffractometer with $M_0K\alpha$ (λ= 0.717 Å) radiation. From the XRD data, it was observed that the KAP and L-HKAP belongs to orthorhombic system. The cell dimensions are presented in table 1. The plane (0 $\bar{3}$ 1) is emerged newly in the L-HKAP. The prominent planes are assigned in the morphology shown in Figs. 5&6. There is no remarkable change in the cell parameter for L-histidine doped KAP single crystal but surface morphology changes has been observed.

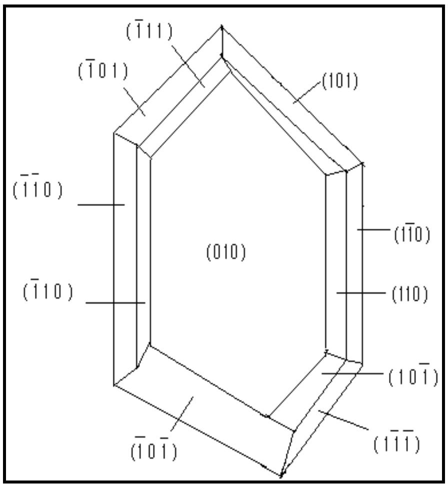

Fig.5. Morphology of KAP.

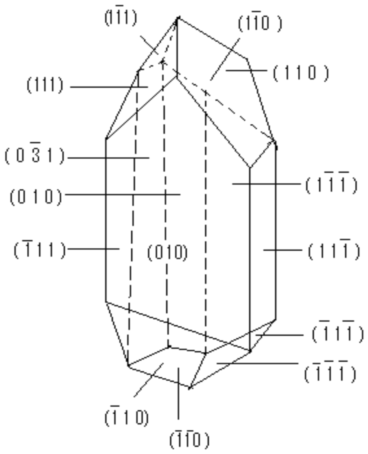

Fig.6. Morphology of L-HKAP.

Table1. Cell parameters of KAP and L-HKAP

Crystal	a (Å)	b (Å)	c (Å)	V (Å)^3	α =β=γ	Crystal system
KAP	9.6047	13.2751	6.5106	830	90°	orthorhombic
L-HKAP	9.605	13.2316	6.446	819.17	90°	orthorhombic

3.3. UV-Vis Spectral Studies

The UV-vis spectral transmittance of KAP single crystal of 2 mm thickness was studied using a Lamda UV-vis Spectrophotometer in the range of 190-1100 nm (Fig.7). The crystal has transmission in the entire visible and IR region. The lower cut off wavelength for KAP is 300 nm and the transmittance percentage of pure KAP is 50 %. The optical transmittance window (300-1100 nm) in the visible and IR regions enables good optical transmission for second harmonic frequencies of Nd:YAG lasers. The direct optical band gap of KAP was determined as 4 eV using Tauc's plot as shown in Fig. 8.

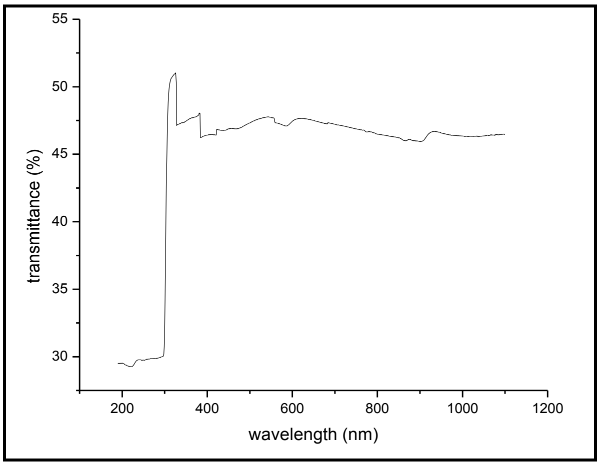

Fig.7. UV-Vis transmittance spectrum of KAP.

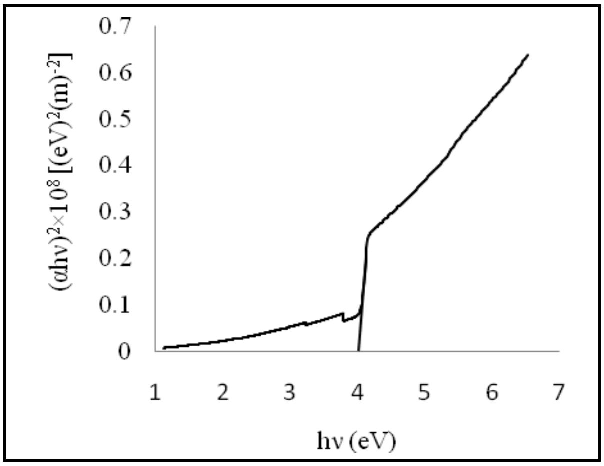

Fig. 8 Tauc's plot of KAP crystal.

3.4 FTIR spectral analysis of KAP

The FTIR spectrum of KAP was recorded in the range of 400-4000 cm^{-1} using KBr pellet technique [Fig.9]. The peak at 2483 cm^{-1} represents the presence of O-H stretching. The symmetric and asymmetric stretching vibrations of carboxylate ion were observed at 1381 cm^{-1} and 1563 cm^{-1} respectively [12]. The C-C-O stretching vibration of KAP was observed at 1089 cm^{-1} [13]. The C-O stretching vibration where observed in KAP at 1285.cm^{-1}. The C-H stretching was observed in KAP at 850 cm^{-1} and C-O wagging was observed in KAP at 682 cm^{-1}.

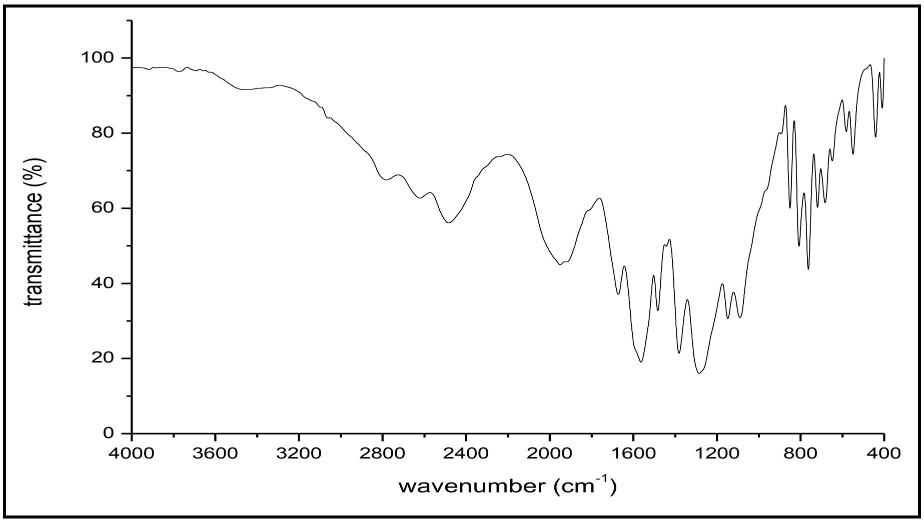

Fig.9. FTIR spectrum of KAP

3.5. TG/DTA analyzes

The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) of KAP were carried out using SII NanoTechnology TG/DTA 6200 for a sample weight of 4.806 mg in the temperature range of 28-800°C at a heating rate of 10°C/min in nitrogen atmosphere (Fig.10). The TGA curve shows that the KAP has good thermal stability up to 296°C as there is no weight loss below that temperature. In the TGA curve, the major weight loss 40.09% occurred in the temperature range 298 - 320°C due to libration of volatile substance in the compound. Further weight loss (16%) is obtained in the temperature range of 490-535°C. The DTA curve shows that the melting point of sample is 297°C, and this melting point value is well agree with melting point measured using conventional method. The material undergoes endothermic transition around 308°C followed by another endothermic peak at 440° C. The sharpness of the peak shows good degree of crystalline of the sample.

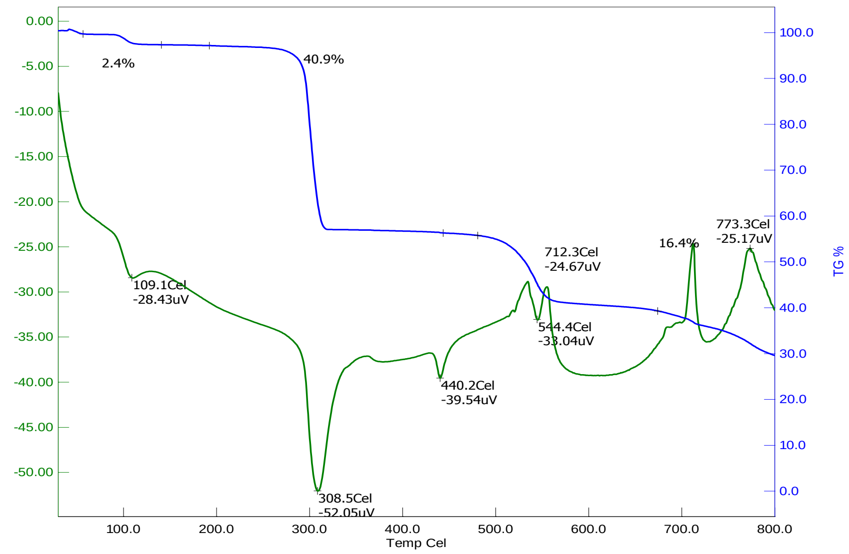

Fig.10. TG/DTA curves of KAP.

3.6 Vicker's Microhardness

Microhardness measurements were carried out using Shimadzu HMV-2 fitted with Vicker's pyramidal indenter and attached to an incident light microscope. The microhardness measurement is commonly used to determine the mechanical strength of the material. The grown crystal with well developed face (010) was selected for microhardness study. Hardness measurements were taken for applied load varying from 25 to 100 gm keeping the indentation constant at 10 sec.

$$Hv=1.8544\ P/d^2\ kg/mm^2$$

Where P is the applied load in kg and d is the diagonal length of the indentation impression in

Millimeter and 1.8544 is a constant of a geometrical factor for the diamond pyramid. A plot between the hardness number and the load [10]. Hardness increases with the increases of load is shown in Fig. 11.

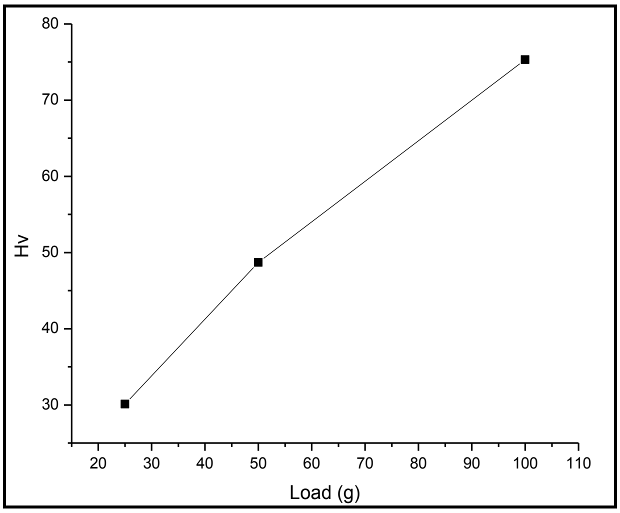

Fig.11.Vickers hardness graph of KAP.

3.7 Measurement of SHG

The second harmonic generation (SHG) test was carried out by Kurtz and Perry powder SHG method [14]. In this method the powdered sample was illuminated using Q-switched Nd: YAG laser with input power of 0.68 J and input wavelength of 1064 nm. The second harmonic generation was confirmed by the emission of green radiation emitted by the sample. The SHG efficiency of the output signal is found to be 0.4 times that of KDP.

4. Conclusion

The single crystals of pure KAP and L-histidine doped KAP (L-HKAP) crystals have been grown by slow evaporation solution growth technique at room temperature. Single crystal XRD analysis confirmed that KAP and L-HKAP crystals were belongs to orthorhombic system and new plane ($0\ \bar{3}\ 1$) were emerged in the L-HKAP crystal. The presences of various functional groups in the KAP have been confirmed by FTIR analysis. The Transmittance spectrum reveals that the crystal has a lower cutoff wavelength of 300 nm and has a 50 % of transmittance. The TG/DTA shows that that the material has good thermal stability. The Vickers hardness measurement shows that the material has good mechanical stability. The SHG efficiency was measured as 0.4 time that of KDP.

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