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Growth and Characterization of Adipic Acid Doped Potassium Hydrogen Phthalate: A Nonlinear Optical Single Crystal

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Adipic acid doped potassium hydrogen phthalate (AAKHP) and pure potassium hydrogen phthalate single crystals were grown by slow evaporation method. Single crystal X-ray diffraction analysis was carried out to determine the lattice parameters in a = 6.47 Å, b = 9.59 Å, c = 13.25 Å and space group of $Pca2_1$. This confirms the grown AAKHP belongs to the orthorhombic system. Various diffracting planes of the grown crystal were indexed using powder X-ray diffraction study. Fourier-transform infrared studies confirm the presence of various functional groups in the grown crystal. The transmittance spectrum shows that the lower cutoff wavelength is around 290 nm. The nonlinear optical property of the grown crystal has been studied by Kurtz powder second harmonic generation (SHG) analysis. EDAX analysis confirms the presence of various elements in the AAKHP crystal. Vickers micro-hardness studies are used for the analysis of mechanical behaviour of the grown crystal. The paramagnetic nature of the grown crystal was confirmed by vibration spectrum magnetometer technique.

Keywords: Potassium hydrogen phthalate, Adipic acid, Crystal, X-Ray diffraction, Optical materials, Mechanical properties.

INTRODUCTION

In the last few decades, researchers have aimed at finding some high quality materials for the crystal family. The nonlinear optical (NLO) materials have a significant impact on optical communication, laser technology and storage technology. Nonlinear optics (NLO) have received greater attention because of new frequency conversion materials over the past decade has led to the discovery of semiorganic crystals, because of their large non-linearity, high resistance to laser irradiation, high stability and good mechanical properties. Their inadequate transparencies, optical quality, low laser damage threshold and inability to grow in big size have impeded in the use of single crystal semiorganic materials for practical device applications. A strong need continues to exist for lower cost, more efficient, higher average power materials for optical parametric amplification and second harmonic generation (SHG) throughout the blue and near UV spectral regions [1-5].

Potassium hydrogen phthalate (KHP) with chemical formula $C_8H_5KO_4$, also known as the potassium acid phthalate (KAP) is an interesting material as an analyzer in X-ray spectroscopy. Potassium hydrogen phthalate (KHP) is a semi-organic compound and it crystallizes from the aqueous solution in orthorhombic system with space group of $Pca2_1$ [6,7]. Potassium hydrogen phthalate crystals are easily grown by using the slow evaporation solution growth technique with water as a solvent. Thilagavathy *et al*. [8] studied the structure of pure KHP and L-Lysine doped KHP single crystals. The structural, thermal, mechanical and optical properties of KHP have also reported [9]. The literature shows that most of the KHP crystals are grown using melt growth in which the crystal or the solution from which it is growing are in motion during growth, having probability of defects. Adipic acid is used as an important substance in chemical industries with high solubility. It can be used as an organic solvent. The adipic acid is recognized as a promising compound to explore the co-crystal formation with imidazole-ring containing molecules [10,11]. Santhi *et al*. [12] have reported on urea adipic acid crystal which possesses very good mechanical properties [12]. In present work reporting result on the growth and characterization of pure KHP and adipic acid doped KHP (AAKHP) crystals. In solution grown method, it has been observed that certain dopants are playing vital role to enhance the physical properties of single crystal. The presence of very low concentration of certain dopant enhances crystalline perfection [13-15]. In this article, the effect of adipic acid on crystalline perfection, NLO, optical, mechanical properties of KHP are analyzed and also elemental analysis of the grown crystal was carried out [16-20].

EXPERIMENTAL

Synthesis: The single crystal of pure KHP and adipic acid doped KHP was grown by slow evaporation method. An AAKHP single crystal was synthesized by using potassium hydrogen phthalate (GR) and adipic acid (AR). The saturated solution of potassium hydrogen phthalate was prepared using double distilled water. Adipic acid (1 mol %) is added with the solution, then the mixture was thoroughly stirred and using magnetic stirrer for homogenization. Repeated recrystallization was carried out in order to eliminate the impurities in AAKHP crystal. The nucleation was observed in the solution of crystallization. After 2 weeks, a good quality single crystals have been gleaned with dimension up to 12 mm × 8 mm × 4 mm. The grown pure KHP and doped AAKHP crystals are shown in Fig. 1.

RESULTS AND DISCUSSION

Single crystal X-ray diffraction analysis: Single crystal X-ray diffractometers are most often used to determine the molecular structure of the new materials. The unit cell dimensions of the grown crystals were recorded by using BRUKER NONIUS CAD4 single crystal X-ray diffractometer. A good quality crystal was selected for the X-ray diffraction study. The grown crystals crystallize in orthorhombic system with a space group of $Pca2_1$ is shown in Table-1.

TABLE-1
UNIT CELL PARAMETERS OF PURE AND AAKHP CRYSTAL

Parameters	Pure KHP	AAKHP
a (Å)	6.56	6.47
b (Å)	9.61	9.59
c (Å)	13.25	13.25
$\alpha = \beta = \gamma$ (°)	90	90
Volume (Å)^3	842.61	862

Powder X-ray diffraction: The grown crystals were finely powdered and subjected to powder XRD analysis, using Rich-Seifert powder diffractometer with CuKα radiation of wavelength (λ = 1.5405 Å). The powder XRD patterns of pure KHP and AAKHP crystals are shown in Fig. 2. The Miller indices (hkl) of the corresponding planes were indexed. The observed prominent peak of pure and doped KHP is (111) but the intensities of the diffracted peaks are found to be varied [21]. The intensity corresponding to (002) is maximum but it is not varying in the case of AAKHP. But there is variation in intensity of (111) plane. These sharp peaks indicate the indusion of dopant in KHP lattices; and the crystals have good crystallinity. The slight shift in 2θ values of PXRD patterns of the doped crystal values indicate that their lattice constants are slightly changed [22,23].

FTIR analysis: The FTIR spectra of pure KHP and AAKHP grown crystals are given in Fig. 3. In the spectra, the characteristics OH stretching peaks occur at 3422 and 3427 cm^{-1} for synthesized pure and adipic acid doped KHP compound, respectively. The peaks at 1564 and 1559 cm^{-1} are due to the carboxylate (COO$^-$) vibrations, which are shifted slightly due to doping. The results implied that the dopant molecules have entered into KHP crystal matrix. The C-C stretching of 1146

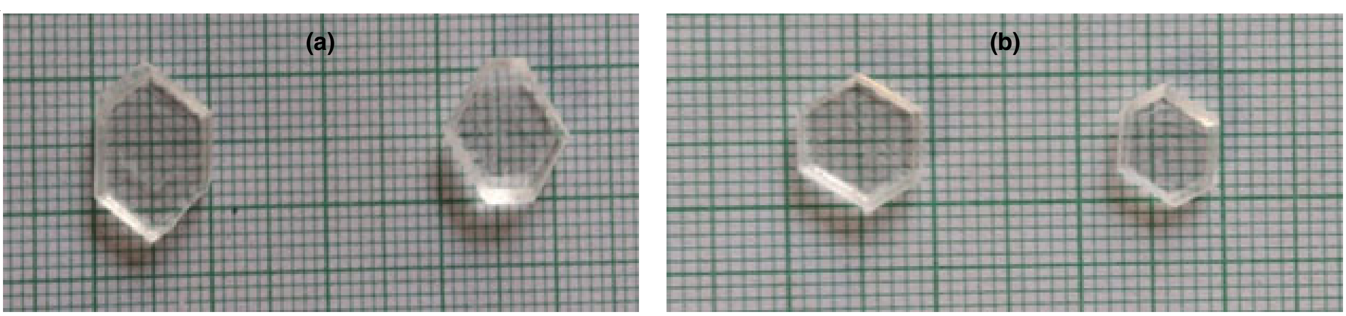

Fig. 1. As grown crystal of (a) pure KHP and (b) AAKHP crystals

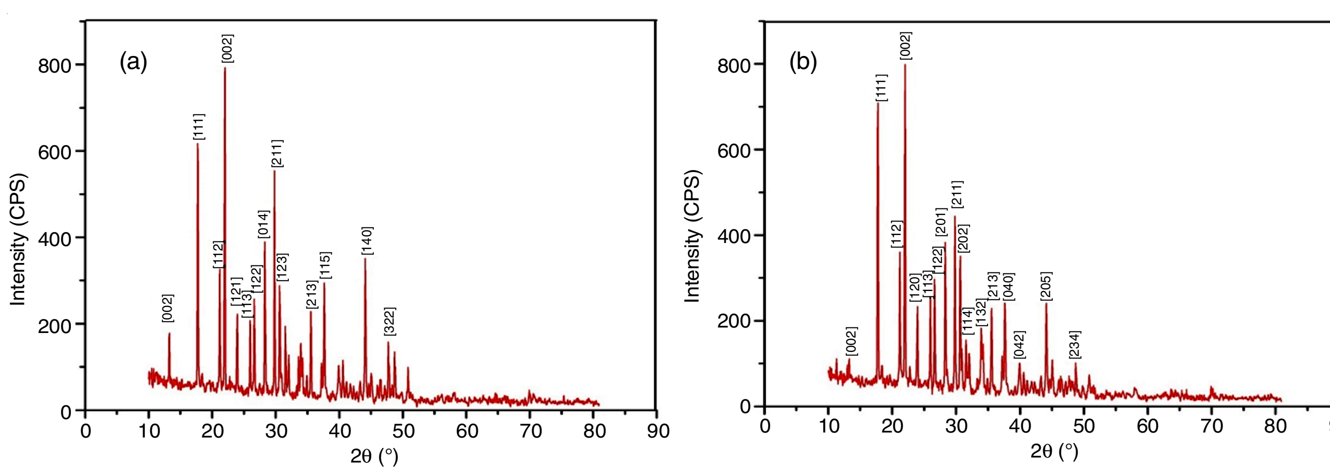

Fig. 2. Powder XRD patterns of (a) KHP crystal and (b) AAKHP crystal

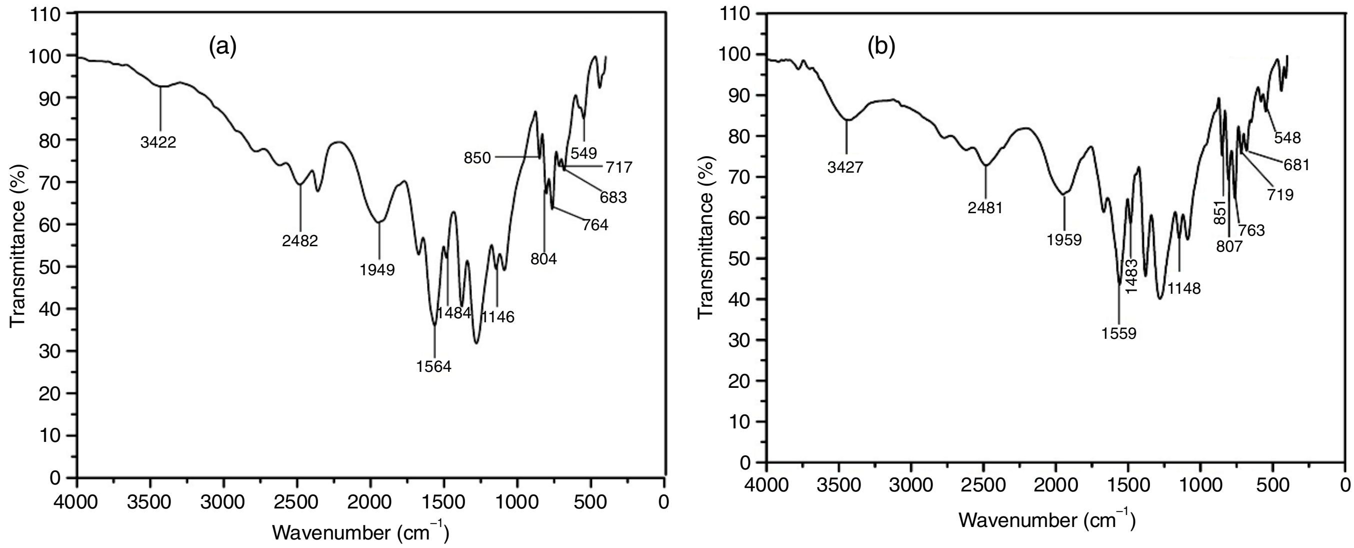

Fig. 3. FT-IR spectra of (a) pure KHP and (b) AAKHP crystals

cm^{-1} is modified slightly to 1148 cm^{-1} again due to doping and the band at 804 cm^{-1} is slightly shift since it appears as a shoulder of the strong CH out-of-plane bending at 807 cm^{-1}. The change in the vibration between 763 and 681 cm^{-1} in the spectrum of adipic acid doped KHP indicates the presence of adipic acid in the lattice of KHP [12-15]. So, the FTIR analysis establishes the presence of adipic acid in the lattice of KHP crystals. Table-2 shows the vibrational band assignments for pure KHP and AAKHP crystal.

Optical analysis: The usage of optoelectronic NLO material is typically decided by the transparent window in the UV-visible region. The optical transmittance spectral analysis was carried out in the wavelength region from 190-1100 nm, using a Perkin Elmer Lambda 35 UV-Visible spectrophotometer. The lower cut off wavelength is observed at 290 nm for the grown crystal (Fig. 4).

The optical absorption coefficient (α) was calculated from the transmittance data as follows:

$$\alpha = \frac{2.3026 \log (1/T)}{t} \quad (1)$$

TABLE-2
FTIR ASSIGNMENTS OF PURE AND DOPED

Wavenumber (cm^{-1})		Tentative assignments
KHP	AAKHP	
3422	3427	O-H stretching
2482	2481	C-H aromatic stretching
1949	1959	C=C asymmetric stretching
1564	1559	COO^- carboxylate ion asymmetric stretching
1484	1483	C=C ring stretching
1146	1148	C-C stretching
850	851	C-H in-plane bending
804	807	C-H out-of-plane bending
764	763	C-C stretching
717	719	=C-H out-of-plane deformation
683	681	C-O wagging
549	548	C=C- out-of-plane ring deformation

where T is the transmittance and t is the thickness of sample.

$$\alpha h\nu = A (h\nu - E_g)^{1/2} \quad (2)$$

The optical band gap (E_g) of AAKHP was determined as 2.5 eV using Tauc's plot (Fig. 5).

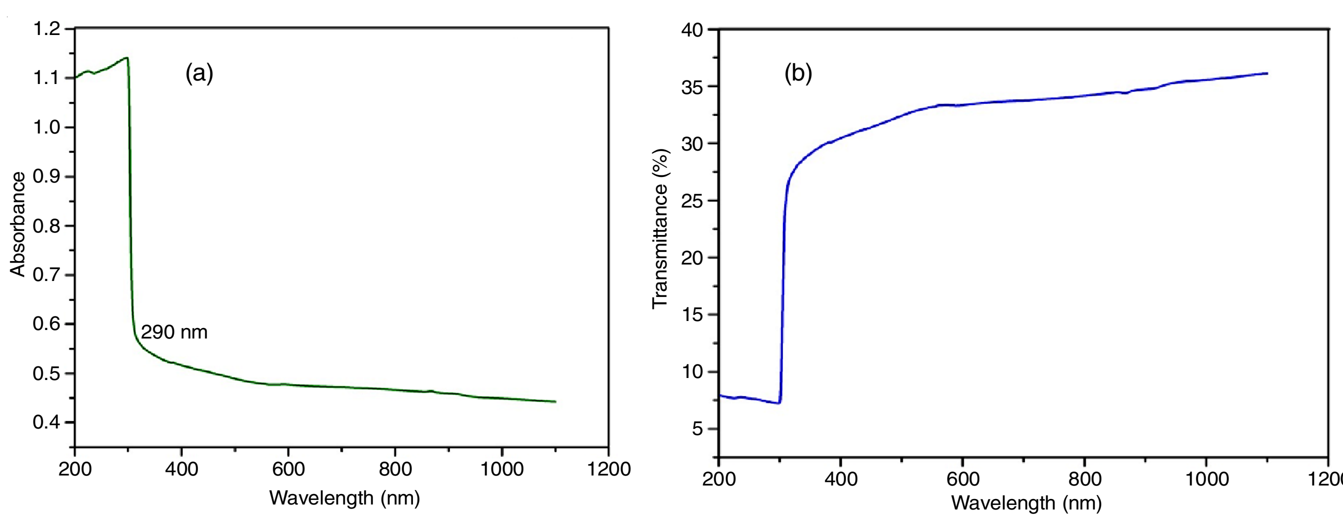

Fig. 4. Optical absorption (a) and optical transmittance (b) spectra of AAKHP crystal

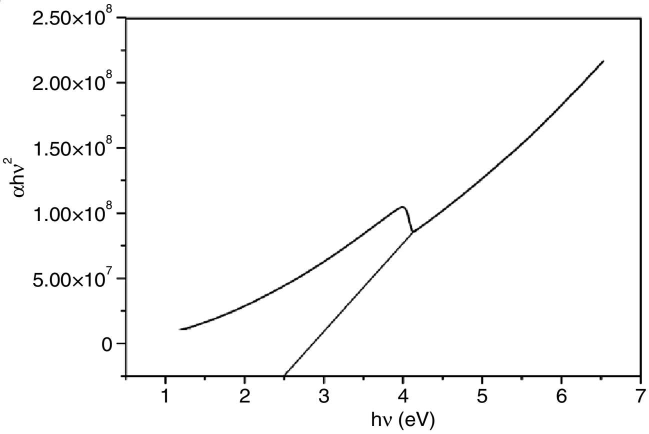

Fig. 5. Tauc's plot of AAKHP crystal

Second harmonic generation (SHG) efficiency: The grown pure KHP crystals and AAKHP crystals are selected for frequency conversion applications. Kurtz and Perry proposed a powder SHG test for the comprehensive analysis of the second order non-linearity. The sample grinded into powder, packed in a tube was irradiated with a laser beam from a Nd:YAG laser source with a wavelength of 1064 nm, hired with an input beam energy of 3.2 mJ, pulse width 8 ns and the repetition rate being 10 Hz. The SHG efficiencies of pure KHP and adipic acid doped KHP crystals are found to be 0.39 times and 0.40 times that of reference material KDP, respectively [5]. This frequency conversion property makes AAKHP crystal a suitable candidate for non-linear optical device applications.

EDAX analysis: Energy dispersive analysis by X-ray (EDAX) was used to analyze the presence of different elements in the grown crystals. To ascertain the presence of various elements in the grown crystal, EDAX analysis was carried out using JEOL-6360 scanning electron microscope and is shown in Fig. 6. The results confirmed that the elements such as C, K and O are present in the AAKHP crystal, which are the constituents of the compound taken for crystal growth (Table-3).

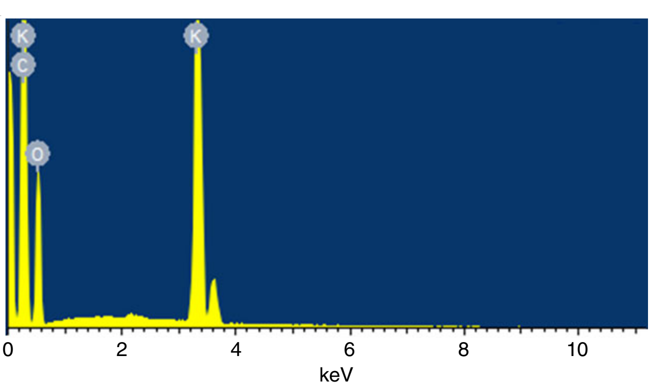

Fig. 6. EDAX spectrum of AAKHP crystal

TABLE-3
ELEMENTAL ANALYSIS OF AA DOPED KHP

Element	Weight (%)	Atomic (%)
C K	49.85	61.50
O K	35.62	32.99
K K	14.54	5.51
Total	100.00	100.00

Hardness analysis: The mechanical strength of the grown crystal was studied by means of quantifying microhardness, because it performs a tremendous position in the fabrication of optoelectronic devices. The microhardness analysis of grown crystal was carried out using Shimadzu HMV-2 fitted. Indentations were made on the sample plane with a 25-100 g applied loads. Hardness value was calculated by the relation given as

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

where P is the applied load in kg and d is the diagonal length. The plot of Vickers hardness (H_v) and load (P) shows the increase in microhardness with increase in load and it was also observed that AAKHP crystals are highly stable towards the application of mechanical stress. Hence, the higher hardness value of AAKHP crystal, higher is the stress required to form dislocation which confirms greater crystalline perfection. Using Mayer's law, the Mayer's index (n) is calculated, n = 6 for pure KHP and n = 4.6 for AAKHP, respectively. These values indicate that the grown crystals can be classified as soft material [24,25].

Vibrating sample magnetometer studies: Vibrating sample magnetometer (VSM) is used to analyze the magnetic properties of materials as a function of magnetic field, time and temperature. The powder sample was placed in a glass ampoule mounted in VSM. The moment *versus* field measurements for 20 mg (0.020 g) mass of the sample was taken at room temperature 300 K. The applied filed range is ± 20,000 G. The sample was placed in the field of magnetization B. The magnetic moment per unit volume (M) was induced which related to B. The hysteresis loop traced at room temperature is shown in Fig. 7 for the grown crystal and it exhibits the paramagnetic behaviour.

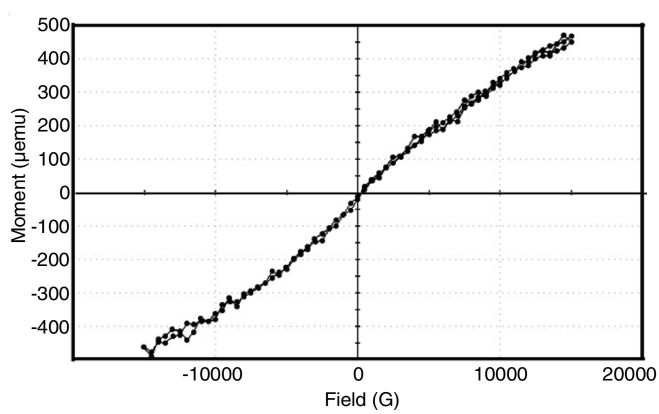

Fig. 7. A plot of typical magnetic moment *vs.* magnetic field

Conclusion

Single crystals of pure potassium hydrogen phthalate (KHP) and adipic acid doped potassium hydrogen phthalate (AAKHP) were effectively grown by the slow evaporation technique. Grown crystals were characterized by XRD and confirmed that the crystals belong to orthorhombic system with space group $Pca2_1$. The presences of functional groups are found out by means of FTIR spectral analysis. The UV-visible study implies the optical quality of AAKHP crystal is better than that of pure KHP. The studies on the NLO property confirmed that SHG efficiency of 1 mol % adipic acid doped crystal is better than that of pure KHP crystal. The UV cutoff wavelength is found to be around 290 nm and the band gap energy 2.5 eV. The powder XRD study confirms that the crystalline nature and purity of the grown crystal. From the indexed peak, it is clear that the (111) plane is the preferred orientation of the grown crystal. The microhardness value is much higher for AAKHP than the pure KHP. The higher micro hardness values established the inclusion of adipic acid into the lattices of KHP. It also confirms that the grown crystal belong to the soft material. The VSM result exhibit the paramagnetic behaviour of the grown crystal. All the properties suggest that adipic acid doped potassium hydrogen phthalate (AAKHP) may be a promising material for optical applications.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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