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Growth and Characterization of KDP doped single crystal

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Abstract

Several NLO materials have been used for a large number of technological applications like solid state laser sources. The potassium dihydrogen phosphate (KDP), one of the materials having superior nonlinear optical properties has been employed for a large range of applications. In the present work KDP crystal grown from aqueous solution with Adipic acid which has an organic nonlinear optical material. The crystal system and cell parameters of grown crystal were determined by single crystal X-ray diffraction analysis. The optical absorption and transmission were examined by UV- Vis analysis which was carried out for the grown crystal. Fourier transform infrared spectroscopy (FTIR) used to confirm the functional group of the crystal. The second harmonic generation (SHG) was tested by Kurtz Perry powder test. Thermal stability was confirmed by TGA/DTA analysis. The mechanical properties of the grown crystal were analyzed and elastic stiffness of a crystal was found by Wooster empirical relation.

Keywords: Adipic acid, elastic stiffness, SHG

INTRODUCTION

The single crystals with advanced properties play a significant role in the growth of modern scientific world of advanced technology. Crystal growth is one of the significant fields with controlled phase transformation. The interest in crystal growth process has been increased particularly in the field of technological application [1-3]. Recent research is focused on the search for suitable materials displaying excellent second order nonlinear optical properties for potential application in optoelectronics, telecommunication, and optical storage device [4]. Materials can be classified as single crystals, polycrystals and amorphous materials depending upon the arrangement of constituent molecules, atoms or ions. The single crystals are solids in the most uniform condition that forms the basis for most of the applications of crystals [5].The semi-organic crystals attract great attention in the field of nonlinear optics due to their optical nonlinearity. The most important dicarboxylic acid is an Adipic acid having good optical, thermal and mechanical properties [6]. Improvising the stability of the crystal is attained using KDP as the dopant. Potassium dihydrogen phosphate (KDP) is a well-known inorganic NLO material, having good ferroelectric, piezoelectric and electro-optic properties. KDP favors for its crystal growth in a bulk size suitable for device applications.

SAMPLE PREPARATION

Analytical reagent grade (AR) samples of potassium dihydrogen phosphate and Adipic acid were used for the single crystal of KDP Adipic acid (KDPAP) along with double distilled water has been the convenient solvent by solution evaporation method at constant temperature [7]. The equimolar adipic acid and KDP supersaturated solution were blended well to attain the homogenous solution. The solution was kept for evaporation to dry at room temperature. The purity of crystal was elevated by successive recrystallization process which was free from macro defects by self-nucleation of saturated solution. Single crystals of KDP Adipic acid have been harvested within three weeks were shown in figure 1.

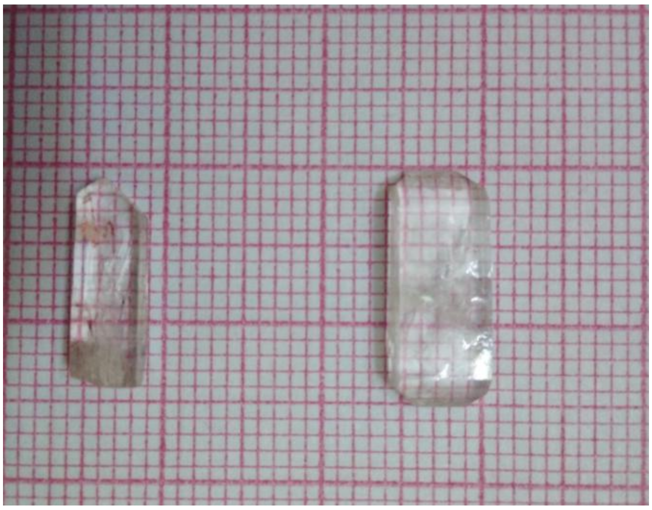

Figure 1. Grown crystal of KDPAP Single crystal

RESULTS AND DISCUSSION

XRD Analysis

To confirm the crystallinity of the grown crystals and the unit cell parameters of potassium dihydrogen phosphate adipic acid was carried out by X-Ray diffraction analysis. It was found that KDP doped Adipic acid having a triclinic system. The lattice parameter values were found to be: a = 6.281Å, b= 6.299Å, c = 6.299Å and α = 107.64º, β = 108.00º, γ =112.79º.The cell parameters were good agreement with reported values of pure adipic and KDP [8, 9].

FTIR Analysis

The sample of KDP adipic acid was characterized by FTIR spectroscopy in order to identify the functional groups and detect the vibrational modes of molecules in the sample. The measurement was done with KBr pellet method for the wavelength range 400-4000cm^{-1} and the spectra of KDPAP shown in figure 2.[8] The bands observed in the spectra were 2385 cm^{-1} and 2301 cm^{-1} confirms that P-H stretching , the peak 1708cm^{-1} due to C=O Stretching ,3221 cm^{-1} broader peak due to hydrogen bonded O-H stretching, 2761 cm^{-1} confirm the C-H stretching, 675 cm^{-1} due to O-C=O bending and C-C-CHO bending due to dopant , 585 cm^{-1} due to P-O-H stretching of the grown crystal,980 cm^{-1} due to P-O antisymmetric stretch and 756 cm^{-1} C-H out of plane deformation.[9]

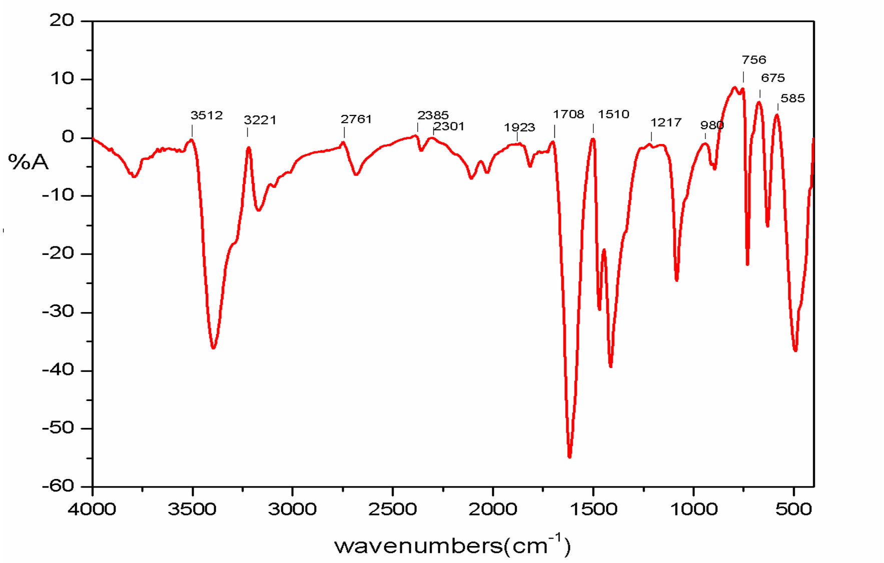

Figure 2. FTIR spectrum of KDPAP Single crystal

Optical Studies

The absorption and transmission spectra of KDP Adipic acid are recorded using UV-Vis spectrometer (BERKIN ELMEP LAMBDA 35) in the wavelength range between 200nm and 1100nm are shown in figure 3 & 4. [10] The spectrum was recorded at near IR, Visible and UV regions. The absorbance is not enrolled in the wavelength range starting from 354nm to 916nm and this is an advantage for materials having NLO properties.[11] The sharp fall of the transmittance was observed in 354nm which indicates the single crystal have the transmission in UV region and their no transmission in the visible region. From that the cut-off wavelength the optical band gap is found as 3.50eV using the relation (1).

$$E_g=hc/\lambda \tag{1}$$

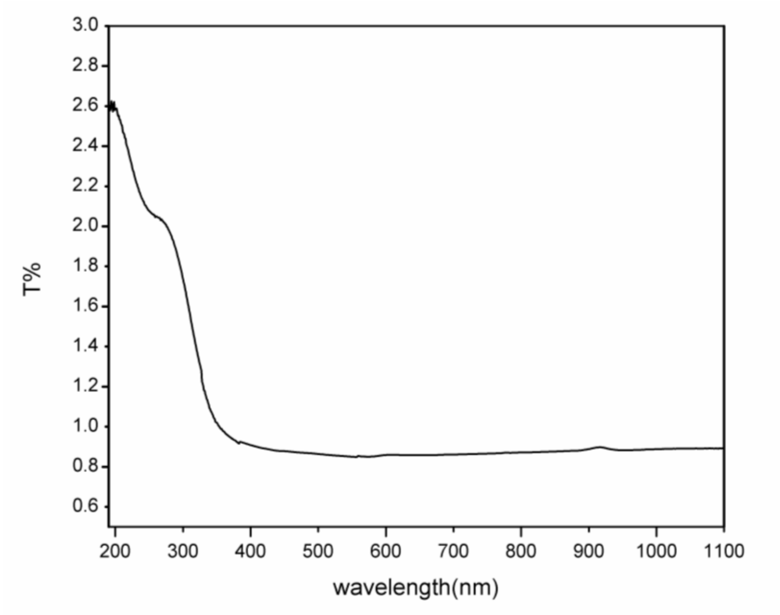

Figure 3. Absorption spectrum of KDPAP single crystal

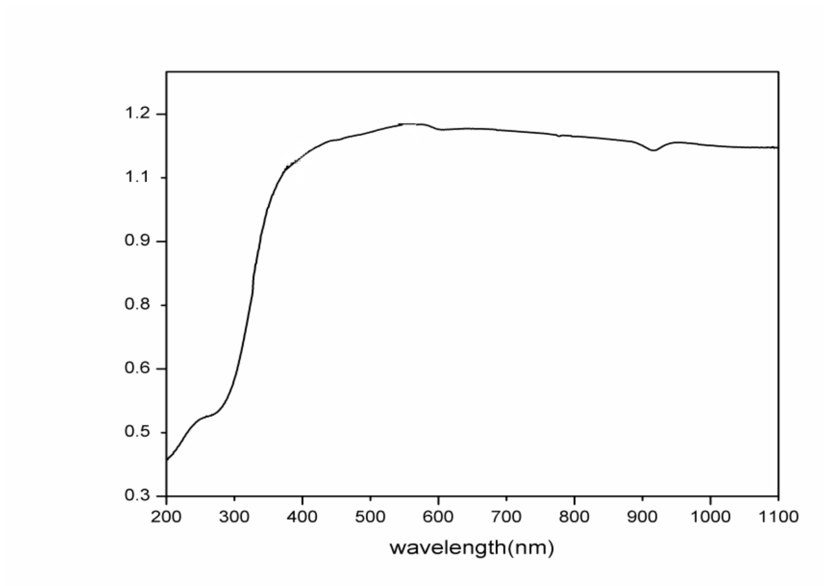

Figure 4. Transmission spectrum of KDPAP single crystal

SHG Efficiency

The NLO property of KDPAP crystal was performed by Kurtz Perry powder technique. The crystal was grained into powder and densely packed in the microcapillary tube of uniform diameter. Quanta-Ray Spectra physics ND:YAG laser producing pulses with a width of 8ns and a repetition rate of 10Hz was used. The laser was focused on falling on the powder sample. SHG was confirmed by the emission of green radiation (532nm) and the optical signal was controlled by a photomultiplier tube (PMT) and converted into voltage output in

CRO [12]. The powder SHG efficiency of KDP Adipic acid was found to be 0.68 times that of the standard KDP crystal.

Microhardness Measurement

Vickers hardness test is a more reliable method of hardness measurement. The Vicker's hardness is the quotient obtained by dividing the kg load by the square mm area of indentation.

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

Hv = Vickers hardness number, P = load in kg, d = arithmetic mean of the two diagonals

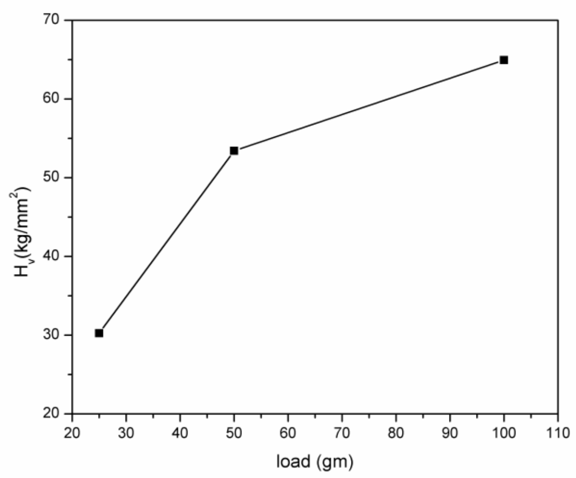

Figure 5. Hardness behavior of KDPAP single crystal

Fig. 5 shows the variation of HV as a function of applied loads, ranging from 25 to 100 g. It is clear from the Fig.5 shows that HV increases with an increase in the load. It reveals that hardness number increases with increasing applied load. This phenomenon is known as reverse indentation size effect (RISE). The Mayer's index number was calculated from the Mayer's law, which relates the load and indentation diagonal length

$$P = kd^n \quad (3)$$

$$\log P = \log k + n\log d \quad (4)$$

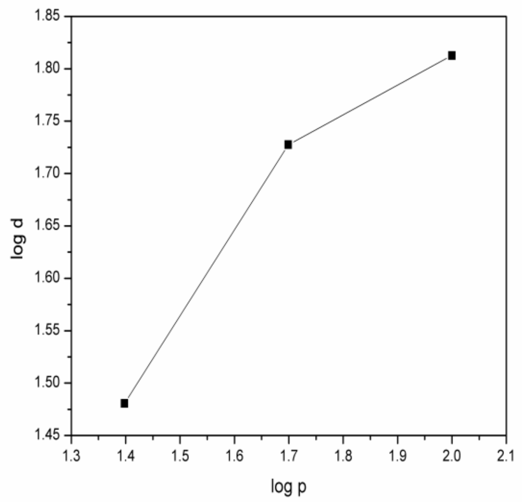

Figure 6. log p VS log d graph of KDPAP crystal

Where k is the material constant and n is the Mayer's index (or work-hardening coefficient). The above relation indicates that H_v should increase with the increase in P if n > 2 and decrease with P when n < 2. The 'n' value was determined from the plot of log P vs log d, as shown in Fig. 6. The slope of the plot of log P versus log d will give the work hardening index (n) which is found to be 2.36. The grown crystal KDP Adipic acid is confirmed with a large amount of mechanical strength which is better for device fabrications. The elastic stiffness constant (C_{11}) was calculated by Wooster's empirical relation. [13] The calculated stiffness constant for different loads was tabulated (Table 1).

$$C_{11}=Hv^{7/4} \qquad (5)$$

Table 1: Stiffness constant of KDP Adipic acid

Load (P) (g)	Hv (kg/mm^2)	C_{11} x 10^{14} (Pa)
25	30.25	3.9
50	53.4	10.54
100	64.95	14.85

Thermal Analysis

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out at heating 20ºC/min in air to determine the thermal stability of the compound and the thermograms are displayed in figure 7. [14] From the TG curves, it is noticed that there is no weight loss up to 220ºC and there is a maximum weight loss in the temperature range 230 ºC to 260 ºC and hence the sample is observed to be thermally stable and suitable for device applications from the DTA curve, it is observed that the KDP Adipic acid crystal shows the first endothermic peak at 184 ºC and the second endothermic peak at 240 ºC which corresponds to the decomposition point of the sample. The broad exothermic peak beyond 350 ºC indicates the liberation of the compounds as gaseous products and the decomposition is completed beyond 400 ºC.

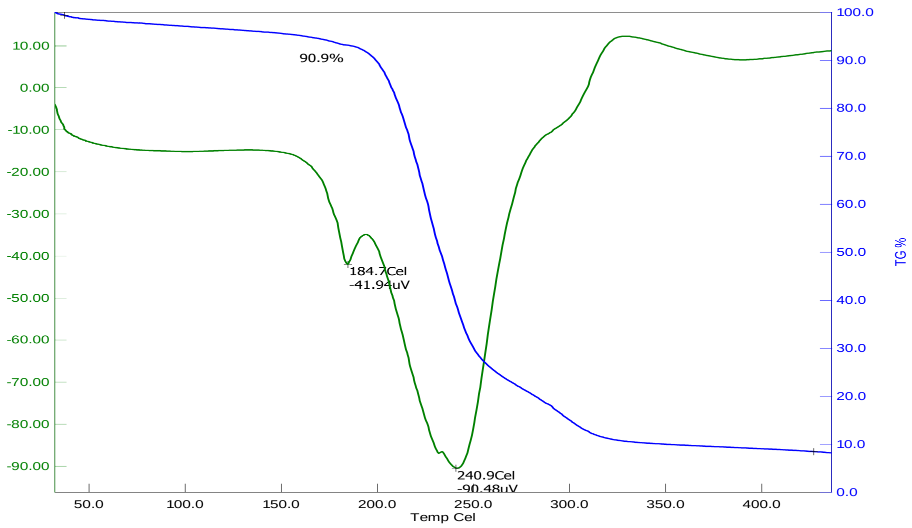

Figure 7 TGA/DTA graph of KDPAP single crystal

CONCLUSION

The KDP Adipic acid crystals were grown by a slow evaporation technique, the FTIR spectrum gives the presence for functional group for the compound and the dopant. The UV-Vis. spectral analysis gives the absorption and transmission of the crystal. The thermal analysis gives the thermal stability of the crystal from the TG curve, in the crystal, there is no weight loss up to 220 ºC. Hence, the crystal is thermally stable for device application. The Second harmonic generations were confirmed by the emission of green radiation. It is a potential material for frequency conversion. The Vickers microhardness test was carried out for the grown crystal the result reveals the mechanical properties of the grown crystal. It is clear that the material suggests that it belongs to hard material category according to Mayer's index number (n).

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