

Synthesis, Growth and Characterization of Nonlinear Optical Semi Organic Potassium Formate Dihydrate Single Crystal by Slow Evaporation Method

C. Sudhakar

Department of Physics,
Salem Sowdeswari College,
Salem - 636 010, India.

L. Jothi

Research Department of Physics, Namakkal
Kavignar Ramalingam Government Arts College for Women,
Namakkal - 637 001, India.

Abstract - Good optical quality single crystal PFDH was grown by slow evaporation technique using water as solvent. The grown crystal is analyzed by Powder XRD, FTIR, UV – vis, NLO studies, Vickers microhardness test and TG/DTA. The crystal system and lattice parameters determined X-ray diffraction. The single crystal XRD analysis reveals the extended framework architecture of PFDH through self - assembly process, involving short range and directional bonds among many other different interactions. Fourier transform infrared analysis has confirmed the various functional groups present in the grown crystals. The optical quality and percentage of transmission of grown crystal was assessed using UV- vis analysis. The thermal studies reveal that PFDH is stable up to 280°C.

Keywords: Semi organic, slow evaporation, FT- IR, TGA, Microhardness, NLO

1. INTRODUCTION

Nonlinear optical (NLO) applications demand good quality single crystals, which inherit large NLO coefficient [1], coupled with improved physical parameters one potentially attractive system, where there is a potential for realizing very large second order nonlinear coefficient based on organic crystals. Organic materials have been of particular interest because the nonlinear optical responses in this broad class of materials is microscopic in origin, offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials. In parallel to discover the new NLO materials, it is also very important to modify the physical, optical, and electrical, mechanical properties of these materials either by adding functional groups or by incorporation of dopants for tailor made applications [2,3].

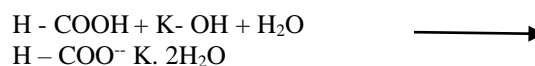
In the presence of dopants, growth promoting factors like growth rate and many of the useful physical properties like optical transparency, Second Harmonic Generation (SHG) efficiency and mechanical stability get enhanced [4]. The growth crystals and powder X-ray analysis and UV spectral analysis, thermal analysis, microhardness, SHG

measurements results of these studies have been discussed in this paper detail [5].

2. EXPERIMENTAL

2.1. Synthesis and Crystal growth

Formic acid and Potassium Hydroxide were taken in the ratio 1:1 and dissolved in water and the solution was left undisturbed, after few days PFDH raw material was collected from the bottom of the beaker.



Saturated solution of Potassium Formate Dihydrate (PFDH) was prepared at room temperature and the solution was filtered twice using wattman filter paper. The pure solution was allowed to crystallize by slow evaporation at room temperature. Small crystals were harvested after a growth period of three weeks. Good optically transparent crystals were obtained. Picture of a grown PFDH crystal is shown in Figure 1.



Figure 1 Photograph of as grown PFDH.

3. RESULTS AND DISCUSSION

3.1. Single Crystal X-Ray Diffraction Analysis

Crystal system and lattice parameters of PFDH single crystal were identified by using ENRAF - NONIUS CAD - 4 single crystal x - ray diffractometer with an incident MoK α ($\lambda = 0.7107\text{\AA}$) radiation source. The crystal structure of the compound has been solved by the single crystal X - ray analysis. It is revealed from the analysis that the PFDH crystal belongs to orthorhombic crystal system with Pnc2

non – centro symmetric space group. The unit cell parameters of the grown crystal were listed in Table 1.

TABLE 1: SINGLE CRYSTAL DATA OF PFDH

Cell Parameter	PFDH
a	8.0734 Å
b	8.1456 Å
c	9.5632 Å
$\alpha=\beta=\gamma$	90°
Volume	629 Å ³
Crystal System	Orthorhombic
Space group	Pnc2

16.043	5.882	0.113	10.667
23.743	4.825	0.126	10.077
25.464	4.033	0.225	9.233
30.739	3.636	0.404	10.575
35.423	4.834	0.402	9.832
Average			10.0768

3.2. Powder X – Ray diffraction

The powder X – Ray diffraction analysis was carried out to confirm the crystallinity and also the purity of the grown PFDH crystal. Powder XRD pattern was recorded by scanning the sample over the range 0 – 90° at a scan speed of 0.02/min. The recorded XRD pattern of PFDH is shown in Figure 2 and the planes were indexed. The appearance of sharp and strong peaks good crystallinity of the grown PFDH crystal. The crystal was identified by comparing the inter planar spacing and intensities of the powder pattern with the JCPDS data of this crystal [6,7].

The calculated lattice parameter values are found to change as seen from table mixing changes the cell axes and hence cell volume. At maximum intensity the various structure parameters like the crystalline size, micro strain and dislocation density has been calculated by Debye – Scherrer's formula.

$$D = \frac{K\lambda}{\beta \cos\theta} \text{ ----- (1)}$$

Where,

D is the grain size (nm)

K is the shape factor or Scherrer constant (0.9)

λ is the X – ray wavelength (1.5418 Å)

β is the broadening of diffraction line measured at half of its maximum intensity

θ is the Bragg's angle

The crystalline size (D) was calculated using Scherrer's formula from the full width at half maximum and the size was found to be 10.0768 nm as given in the Table 2.

TABLE 2: CRYSTALLINE SIZE OF PFDH

2 θ (deg)	d spacing(Å)	FWHM (deg)	Crystalline size (nm)
16.043	5.882	0.113	10.667
23.743	4.825	0.126	10.077
25.464	4.033	0.225	9.233
30.739	3.636	0.404	10.575
35.423	4.834	0.402	9.832
Average			10.0768

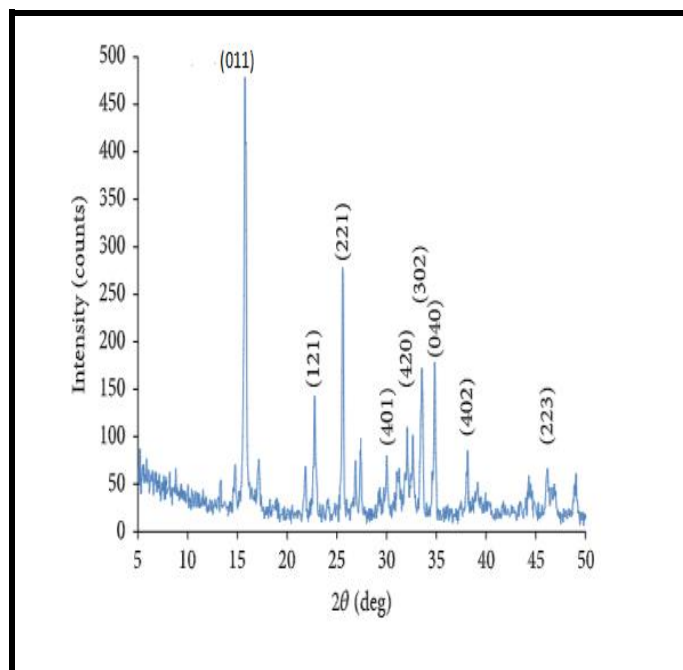


Figure 2 Powder X - Ray spectrum of PFDH.

3.3. Fourier Transform Infrared (FTIR) Spectral Analysis

Vibrational Spectroscopy is effectively used to identify the functional groups and determine molecular structure of the synthesized compounds, and this information is of immense help to organic chemists because it can be directly related to molecular structure. The infrared assignment was made in the range from 400 to 4000 cm⁻¹ with the help of spectrum recorded on PERKIN ELMER FTIR Spectrometer. The complexity of infrared spectra in 1440 to 660 cm⁻¹ region makes it difficult to assign all the absorption bands, because of the unique patterns found there, it is often called the fingerprint region.

Absorption bands in the 4000 – 1450 cm⁻¹ region are usually due to stretching vibrations of diatomic units and this is sometimes called group frequency region. FTIR Spectrum of PFDH is shown in Figure.3. The broad band at 3470 cm⁻¹ and the band at 3313 cm⁻¹ are due to OH stretching vibrations. The band 2836 cm⁻¹ is due to CH vibrations. CH bending vibrations are found at 1350 cm⁻¹. The band at 1229 cm⁻¹ is due to CO stretching vibrations. The peak at 661 cm⁻¹ is due to COH has been assigned twist band. [8,9]. The other peaks of PFDH crystal are assigned and compared with similar compounds in the Table 3.

TABLE 3: VIBRATIONAL BAND ASSIGNMENTS OF PFDH CRYSTAL

Wave number (cm ⁻¹)	Bond Assignments
3470	O - H stretching
2836	C – H stretching
1350	C – H bending, in plane
1229	C – O stretch
1048	C – H bending, out of plane
661	C – O – H twist plane

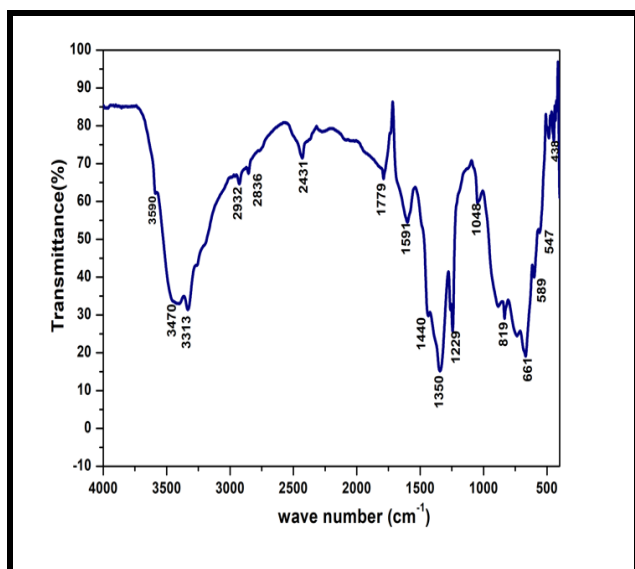


Figure 3 FTIR spectrum of PFDH crystal.

3.4. UV – Visible Spectral Analysis

A good optical transmission is desirable for NLO crystal and determine the optical transmittance range and hence the suitability for the application of optical device, the grown transmission spectrum of PFDH crystal was recorded using PERKIN ELMER make Lambda 35 UV – visible spectrometer in the range 200 nm to 1200 nm and the

observed spectrum of PFDH crystal is shown in Figure 4 and Figure 5.

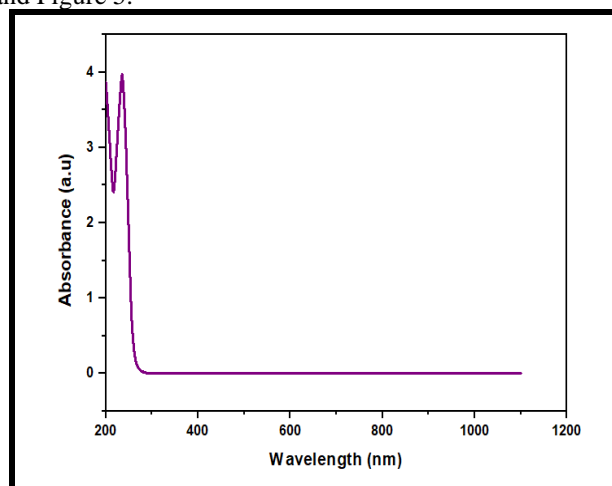


Figure 4 UV-Visible Absorption Spectrum of PFDH.

The absence of absorption of light in the visible range of the electromagnetic spectrum is an intrinsic property of all the amino acids. The dependence of optical absorption coefficient on photon energy helps to study the band structure and type of transition of electrons. The optical absorption coefficient (α) was calculated from transmittance using the following relation.

Absorption coefficient

$$\alpha = \frac{1}{d} \log\left(\frac{1}{T}\right) \text{ ----- (2)}$$

Where T is the transmittance and d is the thickness of the crystal. As a direct band gap material, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies (hv).

Bandgap energy

$$E_g = \frac{1240}{\lambda} \text{ (eV) ----- (3)}$$

Where E_g is the optical band gap and λ is the lower cut – off wavelength of the sample and where h is Plank’s constant. Bandgap energy was the difference in energy between the valence band and the conduction band of a solid material it is simply the energy of forbidden electrons movement in the material it is simply the energy was governed by the structural disorder, an imperfection in stoichiometric and passivation at the surface and the disorder of phonon states. It is inversely proportional to the bandgap energy. From the UV – VIS spectrum, lower cut - off wavelength was observed at 218 nm this is due to interbond electronic transitions. Using the lower cut – off wavelength bandgap energy value was calculated as 4.6 eV which is shown in Figure 5. The high transmission of the grown crystal in the entire visible region with a wide bandgap indicates the low defect concentration in the grown material [10,11]. It is seen from the spectrum that the crystal is transparent in the entire range without any absorption peak, which is an essential parameter for the NLO crystals.

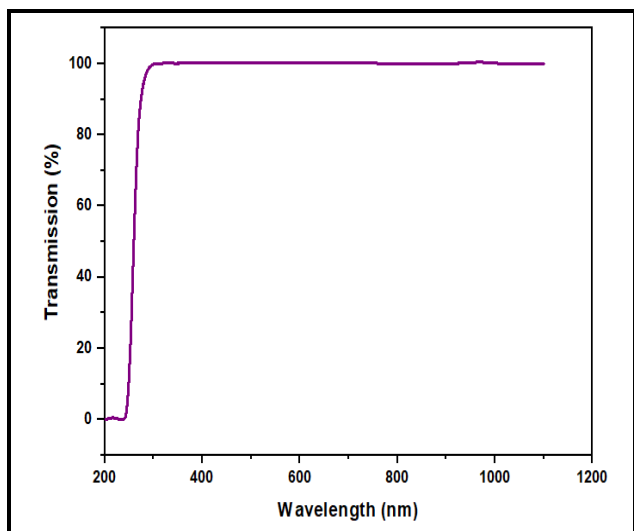


Figure 5 UV-Visible Transmittance Spectrum of PFDH. The PFDH crystal is transparent in the entire UV – visible region. A better transmittance with lower cut – off wavelength in the visible region gives a bandgap energy for PFDH as 4.98 eV. It has an average transparency of about 98% in the visible region with a lower cut – off wavelength occurs at 190 nm. Optically polished single crystals of thickness 3 mm were used for this study Figure5 shows that the absorption spectrum of the grown crystals and the presence of lower cut off wavelength range of the materials possessing NLO activity.

3.5. Fluorescence Analysis

Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiations. The most striking examples of fluorescence occur when the absorbed radiation is in the UV region of the spectrum and thus invisible to the human eye and the emitted light is in the visible region. Fluorescence generally found in compounds containing aromatic functional groups with low energy $\pi \pi^*$ transition levels. Compounds containing aliphatic and alicyclic carbonyl structures or highly conjugated double – bond structure exhibit fluorescence. The emission spectrum of PFDH in the range 260 – 860 nm. The spectrum is given in Figure.6 Which shows a peak at about 490.50 nm indicates that PFDH crystal has a blue fluorescence

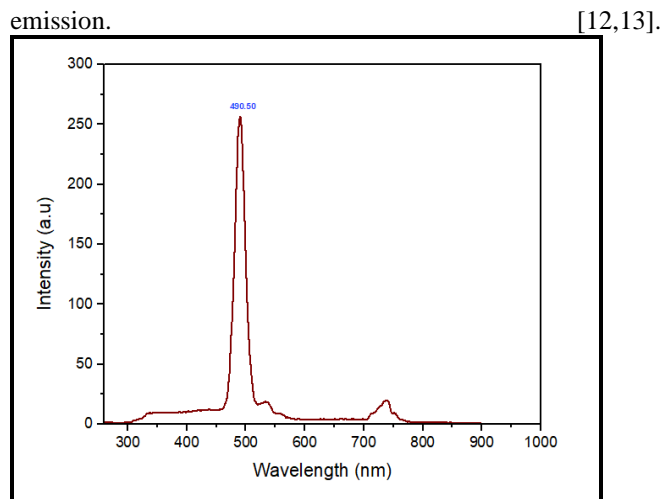


Figure 6 Fluorescence spectrum of PFDH. [12,13].

3.6. Nonlinear Optical Test

The most widely used technique for confirming SHG from prospective second order NLO materials is the Kurtz – Perry powder technique. The fundamental frequency of 1064nm from Q – Switched Nd; YAG laser was used to test the second harmonic generation property of the PFDH crystal by using Kurtz technique. The output from the pulse energy 4ml/pulse and pulse width of 8ns and signal generated in the crystalline sample was confirmed from the emission of green radiation of wavelength 532nm collected a monochromator after separating the 1064 nm pump beam with an IR – blocking filter. A Photomultiplier tube is used as a detector. It is observed that the measure SHG efficiency of PFDH crystals was 1.5 times that of Potassium Dihydrogen Phosphate (KDP) [14].

3.7. Microhardness Studies

Microhardness measurements were carried out using Leitz Weitzler hardness tester fitted with a diamond indenter, studies have been carried out on a selected well transparent single crystal. Analysis of mechanical properties of the grown crystal is also important for the fabrication of electronic and optical devices. The selected surface of the grown crystals was lapped, polished, washed and dried. Hardness measurements were taken for applied load is varying from 25gm to 100gm keeping the indentation constant at 10 sec for all cases.

The Vickers hardness number of grown crystals were calculated using the relation

$$H_v = 1.8544 P/d^2 \text{ kg.mm}^{-2} \text{ ----- (4)}$$

Where H_v is Vickers hardness number, P is the applied load in kg, d is the mean diagonal length of the indenter impression. Figure 7 shows the variation of hardness with applied load. It is observed that the hardness of PFDH increases with the increase of load. This might be due to the release of internal stress generated locally by indentation. [15,16].

The plot of log P and log d shown in Figure 8 is a straight line which is in good agreement with Mayer's law. The slope of the graph gives 'n' and it is determined to be 2.856. 'n' should be between 1 and 1.6 for hard materials and above 1.6 for softer ones. Hence PFDH belongs to soft material category.

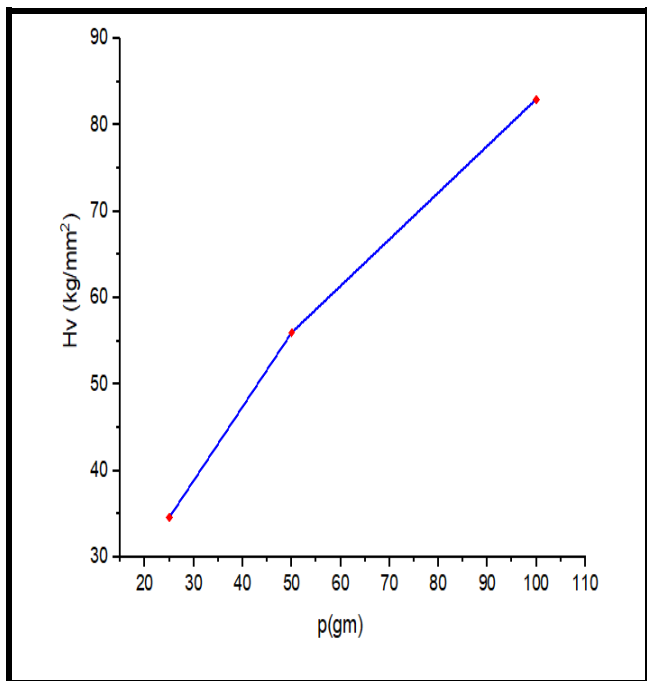


Figure 7 Variation of hardness with applied load of PFDH.

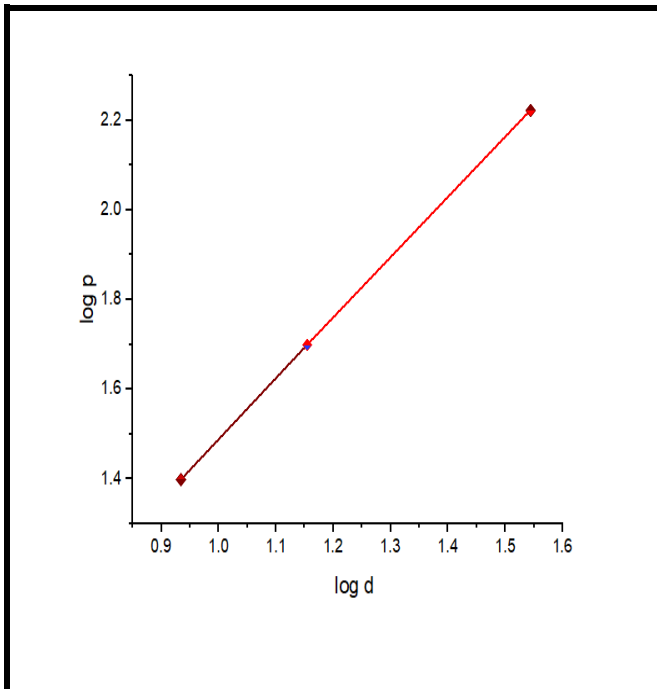


Figure 8 Graph between log p and log d.

3.8. Thermal analysis

Thermogravimetric and differential thermal analyses were carried out using Perkin Elmer Dia TG/DTA instrument in nitrogen atmosphere at a heating rate of 20°C/min in the

temperature range 40 – 680°C as shown in Figure 8. The spectrum shows that there is small weight loss around 250°C. The material starts decomposing near temperature of 285°C, which is melting point of the PFDH crystal. The weight loss of 73.25% of 7.432 mg of sample was observed in the temperature range from 310°C to 385°C. Thereafter residue remains up to of 680°C. It is clear that the crystal is thermally stable up to 310°C. From the thermal analysis it is concluded that the grown crystal decomposes without melting point at about 310°C and is stable till that temperature, which agrees with the reported value 298° C [17,18]. Thus, it is evident from the TG - DTA curve that the material decomposes before melting and can be used for applications in the field NLO by considering their stability up to 310°C.

The sharp peaks of this endothermic peak show good degree of crystallinity of the grown crystal. The subsequent endothermic peaks that follow this melting point corresponding to the decomposition of the compound. Another important observation is that, there is no phase transition and colour change till the material melts and this enhances the temperature range for the utility of the crystal for NLO applications. It is observed from the literature that the presence of higher decomposing temperature doping increases the thermal stability of the compound [19].

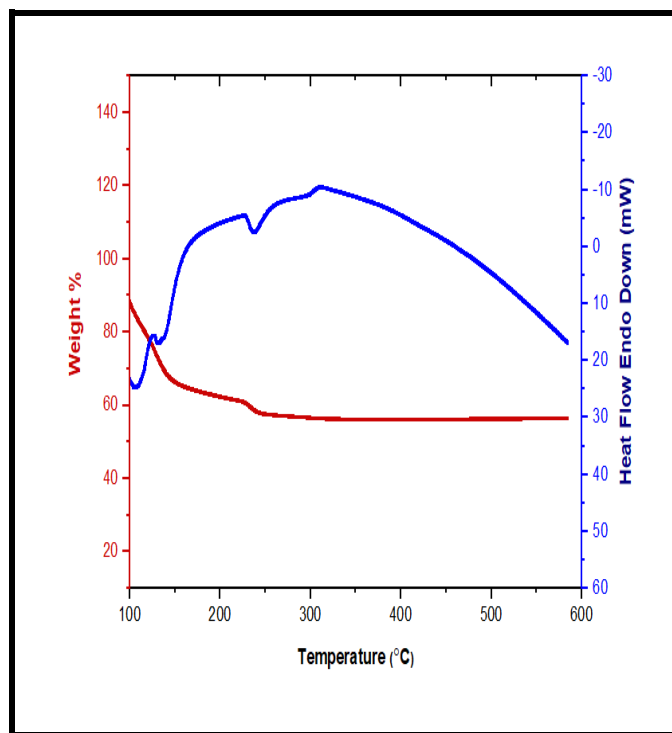


Figure 9 TG - DTA curve for PFDH crystal.

4. CONCLUSION

Potassium Formate Dihydrate crystals are grown by slow evaporation technique. The crystalline nature and purity of grown crystal is confirmed by power XRD technique. We have obtained those crystals possess an orthorhombic arrangement structure. The recorded FTIR spectrum of the

grown crystal PFDH confirms the presence of functional groups in the compound. UV-VIS-NIR spectrum of PFDH shows non-linear optical property which is the essential requirements for any non-linear optical material. The thermal studies of the samples suggest that the thermal stability is better for doped crystals. The fluorescence of the grown sample is confirmed by nonlinear optical property. The SHG efficiency of PFDH crystal is nearly 1.5 times that of standard KDP material. From the overall analysis, it is clear that the synthesized PFDH possess higher efficiency than KDP and can be effectively applied in the optoelectronic field [20,21].

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