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Synthesis, Growth, Investigation of Structural, Spectral and Optical Properties of Solution Grown Dipotassium Fumarate Dihydrate Crystal

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Abstract— Single crystals of dipotassium fumarate dihydrate (DKFD) have been grown by slow solvent evaporation method. The structural characteristics of the grown crystals was studied from single crystal and powder X-ray diffraction analysis. The crystal system of the grown crystal was found to be monoclinic. The lower cut-off wavelength of DKFD was found at 300 nm and good transparency window was observed from 300 to 1100 nm. The existence of various functional groups was established from FTIR and FT Raman spectroscopy. The study of the molecule is established using NMR spectroscopy. The thermal stability and decomposition behaviour of the grown crystal is analysed using TGA/DTA analyses. Third order nonlinear susceptibility χ^3 of the crystal was measured at the wavelength of 532 nm by z-scan technique. The observed high value of χ^3 is attributed to the hydrogen bond present in the structure of the crystal.

Keywords— *Dipotassium fumarate dihydrate, Single crystal XRD, Powder XRD, NMR analysis, Z-Scan technique.*

I. INTRODUCTION

The motive of the research is to synthesis a new compound in order to fulfil the requirements for the technological development in various fields. Organic crystals produce large nonlinear optical response, low UV cut off wavelength, but have poor mechanical and thermal stability. Inorganic crystals have high melting point, high mechanical strength but possess poor optical nonlinearity. The combination of organic and inorganic compounds that are easily grown from solution growth technique leads to find a material suitable for device applications. The semiorganic crystals are grown due to their stable physiochemical properties, that are essential for fabrication of devices and in applied research [1,2,3]. Semiorganic crystals are of great interest and found its applications in the field of optical computing, data storage, optical information processing and light emitting diodes [4,5]. Semiorganic materials with hydrogen bonding interactions between cations and anions possess large nonlinearity, low angular sensitivity, large polarizability, better transmittance in UV-Vis region, good mechanical and thermal stability [6-9]. Ionic salt materials provide an important and intense flexible approach for the material development that are used over a broad range of frequencies [10].

II. RELATED WORK

The structure of the title crystal was already reported [11]. In this work the semiorganic DKFD crystals were grown using low temperature solution growth method. The grown crystals were characterized using single crystal X-ray and powder X-ray diffraction method, UV-Vis-NIR spectroscopy, FT-IR and FT-Raman spectroscopy, NMR spectroscopy, Thermal analysis and Z-Scan analysis.

III. MATERIALS AND METHODS

DKFD crystals was obtained from solvent evaporation technique by reacting potassium carbonate and fumaric acid in a molar ratio of 1:1. The weighed reactants were dissolved in deionised water and stirred continuously with magnetic stirrer for about 3hours, and then filtered using Whatman filter paper. The filtered solution was kept in a crystal growth vessel, and covered with polythene paper. Few holes were made in the polythene paper to achieve slow evaporation. After a period of 70 days colourless crystals were grown. Figure 1, shows the reaction scheme of DKFD crystal.

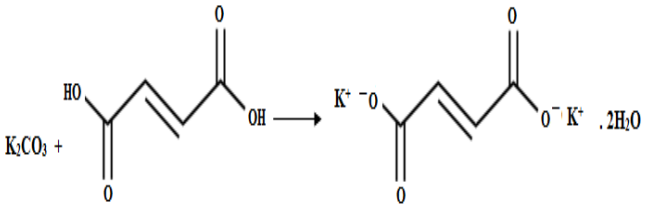

Figure 1. Chemical reaction scheme of DKFD crystal

IV. Results and Discussion

4.1. Single crystal XRD analysis

The lattice parameter of DKFD crystal was determined using NONIUS CAD4 single crystal X-ray diffractometer with MoKα (λ = 0.71069 Å) radiation. The grown crystal belongs to centrosymmetric $P2_1/c$ space group of monoclinic system. The observed lattice parameter matches with the previous reported values [11] and are given in Table 1

4.2. Powder XRD analysis

The crystallinity and structural property of DKFD crystal has been studied from powder X-ray diffraction technique. The crushed powder sample was analysed using Rich Seifert diffractometer with CuKα (λ = 1.54060 Å) radiation. The sample is scanned for 2θ values from 10° to 90° at a rate of 2°/min. Figure 2, shows the Powder XRD pattern of the DKFD crystal. The diffraction pattern was indexed by Rietveld software package. The lattice parameter values were calculated by Rietveld unit cell software package and was matched with single crystal XRD data. The comparison of lattice parameter of single crystal and powder XRD analysis with reported values are given in Table 1.

Table 1. Lattice parameter of DKFD crystal

XRD	a Å	b Å	c Å	α deg	β deg	γ deg
Single crystal	6.338(2)	7.2461(3)	18.179(3)	90	98.47(4)	90
Powder	6.336	7.2458	18.172	90	98.34	90
Reported Values [10]	6.35(4)	7.27(2)	18.22(8)	90	98.2	90

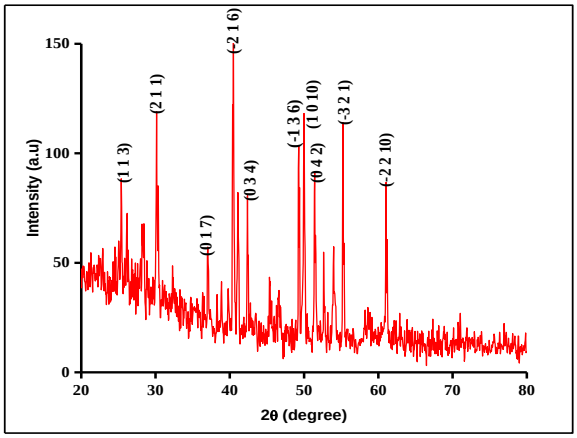

Figure 2. Powder X-ray diffraction pattern of DKFD crystal

4.3. Optical transmission analysis

The optical transparency range was observed from Perkin-Elmer UV-Vis-NIR spectrometer in the range 190 to 1100 nm. The optical transmittance spectrum of DKFD crystal is shown in Figure 3. From the spectrum it is observed that, the lower cut-off wavelength lies at 300 nm. The crystal has wide optical transmission from 300 to 1100 nm. There was no further absorption of the crystal in UV, Vis, and near IR regions. This reveals that the DKFD crystal have good transparency and can be used for optoelectronic applications and also to produce frequency tripling of Nd:YAG laser fundamental wavelength 1064 nm.

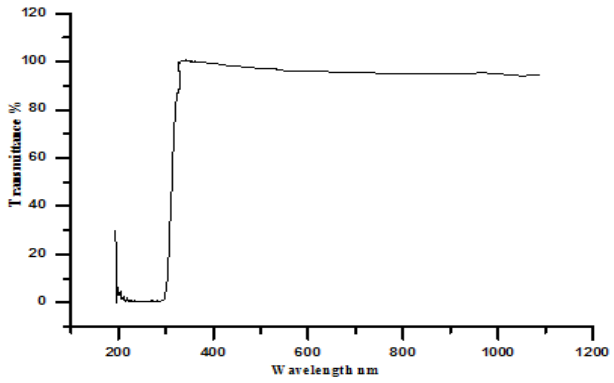

Figure 3. UV-Vis-NIR spectrum of DKFD crystal

4.4. FTIR and FT Raman spectral analyses

Fourier Transform infrared spectrum was recorded by the KBr pellet technique using a SPECTROMRXI FTIR spectrometer and FT Raman spectrum was recorded using BRUKER RFS 27 spectrometer to confirm the functional groups. The FTIR and FT Raman spectra of DKFD crystal are given in Figures 4 and 5 respectively. The vibrational frequencies and their corresponding assignments are given in Table 2. The absorption band in the higher wavenumber region at 3429 cm^{-1} is due to the OH stretching vibration. There was no absorption band found in IR and Raman spectra between 2900 and 1700 cm^{-1}, and it was due to the

metal cation K^+, which replaces the position of hydrogen of carboxylate group, thus forming a bond between metal cation and carboxylate anion (K^+ ^-OOC) [12,13]. The band observed at 1563 cm^{-1} and 1398 cm^{-1} in IR spectrum are attributed to the asymmetric and symmetric vibration of carboxylate group [14]. The difference between two wavenumbers ΔV = 165 cm^{-1} (asymmetric and symmetric vibration of COO^- group) indicates the bridging mode of carboxylate groups with metal cation [15]. Thus, when ΔV is below 200 cm^{-1}, both carboxylate group of fumaric acid binds the metal cation (K^+) forming bidentate bond [16]. The presence of band at 1222 cm^{-1} and 983 cm^{-1} in IR and 1269 cm^{-1} and 977 cm^{-1} in Raman spectra may be due to the asymmetric and symmetric stretching of C-C vibration. The peak at 744 cm^{-1} in IR and 776 cm^{-1} in Raman were assigned to wagging of C-H group.

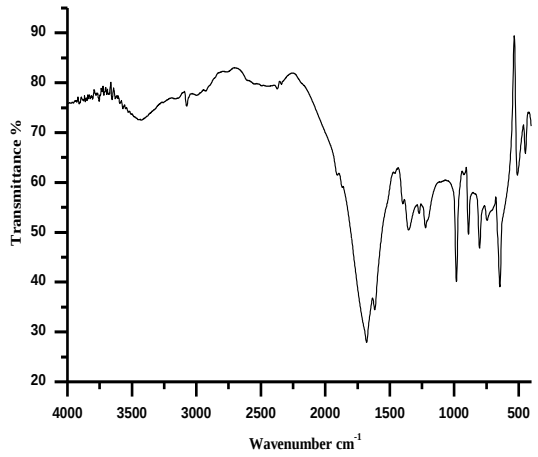

Figure 4. FTIR spectrum of DKFD crystal

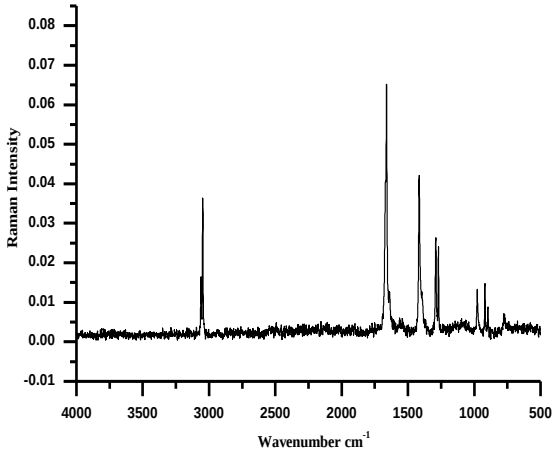

Figure 5. FT Raman spectrum of DKFD crystal

Table 2. Observed vibrational wavenumbers and their assignments

Wavenumber cm^{-1}		Assignments
FTIR	FT Raman	
3429	3374	OH stretching
3074	3060	CH stretching
1563	1542	COO^- asymmetric stretching
1398	1415	COO^- symmetric stretching
1222	1269	C-C asymmetric stretching
983	977	C-C symmetric stretching
889	897	C-O bending
867	876	C=C stretching
744	776	C-H wagging
646	674	COO^- bending

4.5. ^1H and ^{13}C NMR analysis

The ^1H NMR and ^{13}C NMR spectra were recorded using D_2O as solvent at room temperature employing BRUKER instrument operated at 400 MHz for ^1H NMR and 100.6 MHz for ^{13}C NMR for the confirmation of molecular structure. The ^1H NMR spectrum for the DKFD crystal is given in Figure 6. The ^1H NMR peak value for fumaric acid and the DKFD crystal are given in the Table 3. The D_2O solvent peak is observed at δ = 4.692 ppm. The chemical shift of CH proton of fumaric acid in DKFD crystal appeared as a singlet at δ = 6.52 ppm. On comparing this peak value with the corresponding protons of the parent fumaric acid (δ = 6.647 ppm), the values are shifted towards the upfield. Moreover the disappearance of the signal for the acid proton in NMR of the DKFD crystal indicated that the acid proton (-COOH) of the fumaric acid involved in bond formation with the potassium. The shift in value of CH proton and the disappearance of peak for acid proton indicates the intermolecular association between potassium and fumaric acid with the result in formation of crystal.

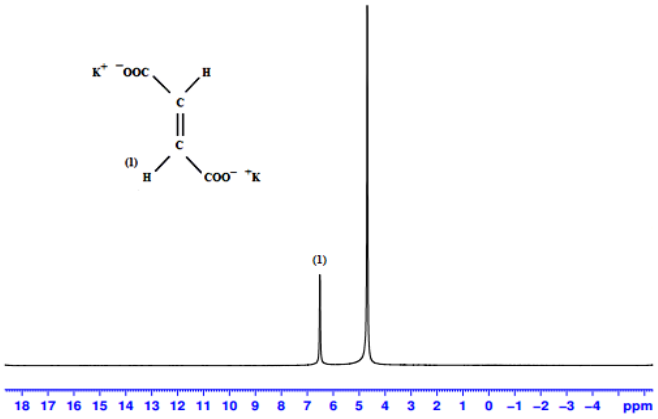

Figure 6. ^1H NMR spectrum of DKFD crystal

Table 3. Chemical shifts in ^{1}H and ^{13}C NMR spectra of DKFD crystal

Chemical shift δ (ppm)			
Spectra	dipotassium fumarate dihydrate crystal	Fumaric acid	Group Identification
^{1}H NMR	6.52	6.647	CH
	4.692	-	D_2O
^{13}C NMR	171.15	177.23	COOH
	133.73	137.95	CH

The ^{13}C NMR chemical shift for fumaric acid and the DKFD crystal are given in the Table 3. Figure 7, shows the ^{13}C NMR spectrum of DKFD crystal. The ^{13}C NMR spectrum exhibit two signals with respect to two carbon atoms due to different chemical environment. The peaks appearing at δ = 171.15 ppm and δ = 133.73 ppm corresponds to the carbonyl carbon (–CO–) and methylidene carbon (–CH=) of DKFD crystal. On comparing the peak value with the parent fumaric acid (Table 3), the values are shifted towards the upfield. This shift is due to the formation of bond between potassium and fumaric acid and confirms the formation of DKFD crystal.

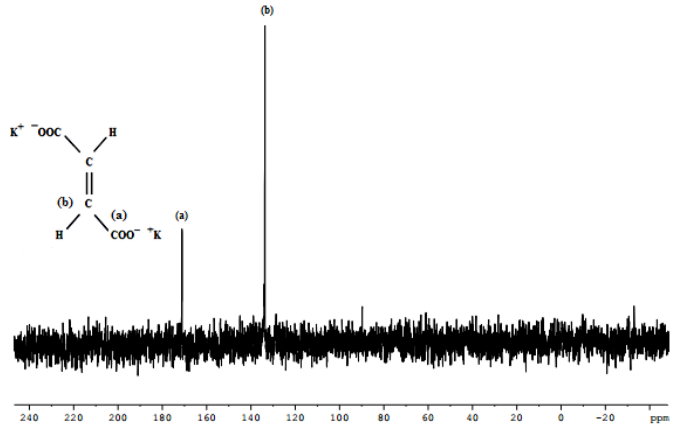

Figure 7. ^{13}C NMR spectrum of DKFD crystal

4.6. Thermal studies

The thermal analysis have been carried out using the instrument NETZSCH SDT Q600 V 8.3 build 101 in nitrogen atmosphere at a heating rate of 20°C/min in the temperature 30-500°C. The TG/DTA curves are shown in Figure 8. The title compound starts to lose the two molecules of water of crystallization in the temperature range 75°C to104°C. The endothermic peak observed near 80°C may correspond to the release of water molecules of crystallisation. From the TGA curve the weight loss (of about 65%) near 188°C was due to the decomposition of the crystal, which was reflected as an endothermic peak in DTA at 189°C. The exothermic peaks above 350°C indicates the further decomposition of the compound. The crystal is stable upto75°C.

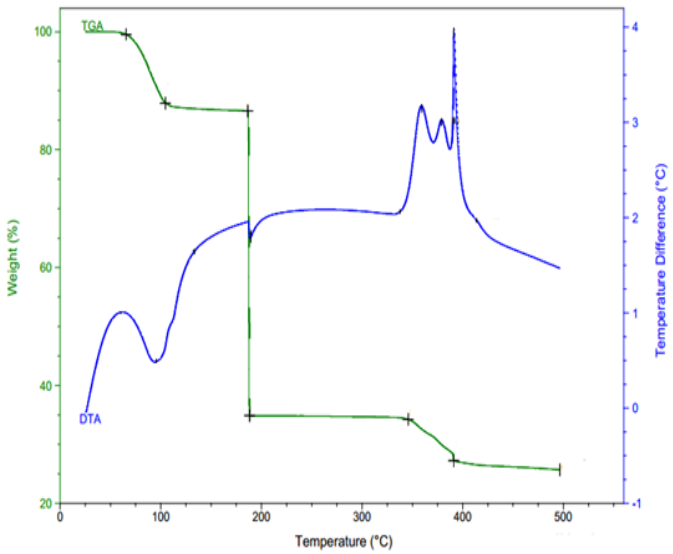

Figure 8. TG/DTA curve of DKFD crystal

4.7. Third order NLO properties

The third order nonlinear optical properties of were determined from z-scan analysis. The z-scan technique employs Nd:YAG laser of intensity 5mW (λ= 532nm), focussed by a lens of 3.5cm focal length in order to measure the optical nonlinearity such as nonlinear refractive index (n_2), absorption co-efficient (β) and third order nonlinear optical susceptibility (χ^3). The optical nonlinear parameters were determined from using standard formulas [17-20] and the values are given in Table 4. The closed and open aperture curves from z-scan measurement are given in Figures 9 and 10 respectively. In the closed aperture curve (Figure 9), the pre focal peak is followed by a post focal valley which indicates that the nonlinear refraction (n_2) is negative for the crystal DKFD. Thus, the peak to valley configuration shows the self defocusing effect of the crystal. From the open aperture curve of dipotassium fumarate dihydrate crystal was shown in Figure 10, and it was concluded that the crystal exhibit saturable absorption property due to an increase in transmittance near the focus (z = 0). The third order susceptibility of the DKFD crystal is high due to the presence of hydrogen bond present in the structure of the crystal[10]. Table 5 shows the χ^3 values of some reported crystals.

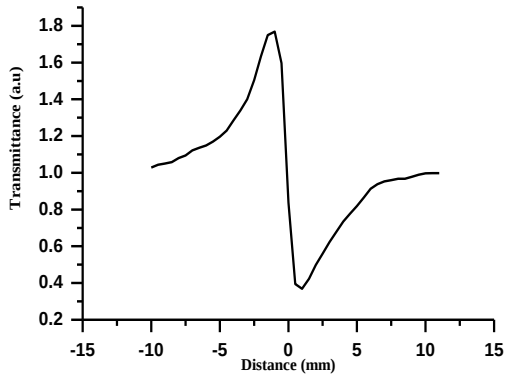

Figure 9. Closed aperture curve of DKFD crystal

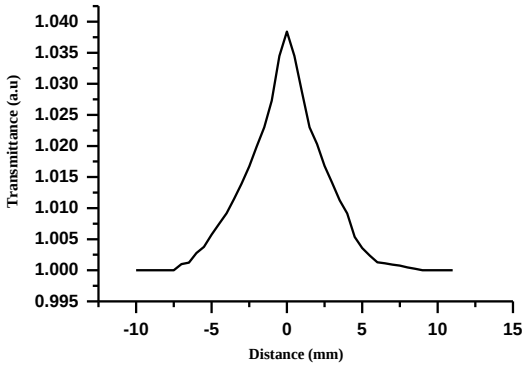

Figure 10. Open aperture curve of DKFD crystal

Table 4. Third order nonlinear optical parameters of DKFD dihydrate crystal

Parameters	Values
Nonlinear refractive index (n_2)	-7.8 x10^{-8} cm^2/W
Nonlinear absorption co-efficient (β)	0.03 x 10^{-4} cm/W
Real part of susceptibility (Re χ^3)	5.84 x 10^{-6} esu
Imaginary part of susceptibility (Im χ^3)	0.19 x 10^{-6} esu
Third order susceptibility (χ^3)	5.85 x 10^{-6} esu

Table 5. (χ^3) values of DKFD with some third order nonlinear optical crystal

Crystal name	Third order susceptibility (χ^3) esu	References
DKFD	5.85 x 10^{-6}	Present work
$LiRbB_4O_7$	2.719 x 10^{-7}	[21]
BCBA	4.853 x 10^{-7}	[22]
4BPTS	4.162 x 10^{-8}	[23]
$LiKB_4O_7$	4.85 x 10^{-9}	[24]
DSHS	2.432 x 10^{-7}	[25]
KDP	1.5 x 10^{-14}	[26]

V. CONCLUSION AND FUTURE SCOPE

Single crystals of DKFD were grown from solvent evaporation method. The single crystal and powder XRD studies measures the lattice parameter of the grown crystal. The UV-Vis-NIR spectrum showed that the crystal has good transparency from 300 to 1100 nm. The FTIR and FTRaman analyses confirms the presence of functional groups in the crystal. The NMR analysis finds the position of hydrogen and carbon atoms present in the structure of grown crystal. The thermal stability and decomposition temperature were investigated from TG/DTA experiments. From the z-scan measurement, the crystal exhibit negative nonlinear refractive index and self-defocussing effect. By growing a bulk crystal and further it can be used in optoelectronic applications.

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