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RESEARCH ARTICLE

SYNTHESIS, GROWTH AND CHARACTERIZATION OF SEMI-ORGANIC CRYSTAL: POTASSIUM HYDROGEN OXALATE DIHYDRATE

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ABSTRACT

Potassium Hydrogen Oxalate Dihydrate (PHODH) is a semi-organic nonlinear optical (NLO) material. They are synthesized by chemical method. Crystals of PHODH are successfully grown by slow evaporation solution growth technique using deionized water as a solvent. The grown crystals are analyzed by Single crystal XRD, FT-IR, UV-Vis, TG/DTA, Vicker's micro hardness test and NLO studies. The structure of PHODH as obtained from the XRD analysis is triclinic with space group P1.The single crystal XRD analysis reveals the extended framework architecture of PHODH 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. PHODH crystals are optically transparent in the UV-Visible region and a maximum transparency of 80% is witnessed. The UV cut-off wavelength of PHODH is found to be 256nm. The thermal studies reveal that PHODH is stable up to 288˚C.

INTRODUCTION

In the area of coordination polymers or metalorganic frameworks (MOFs), Yaghi and co-workers [1–5] have introduced the concept of secondary building units (SBUs) such as polycarboxylates, where di or tetrameric carboxylate units on one hand, and H-bond networks on the other hand, play key roles in solid-state building. These two components govern the extended framework architecture through self-assembly process, involving short range and directional bonds among many other different interactions.

Hamzakherfi *et al*. have shown that a large number of oxalate-based metal structures can be generated from polymeric metallic dicarboxylates because dicarboxilic acid can give rise to wide variety of connectivity [6]. These materials have wide applications based on their electrical conductivity and ferroicity [7-9]. In this paper, the synthesis, crystal growth and physical properties of Oxalato-bridge compound Potassium Hydrogen Oxalate Dihydrate ($KHC_2O_4.C_2H_2O_4.2H_2O$) is reported.

Experimental

Synthesis and crystal growth

Oxalic acid and Potassium Hydroxide were taken in the ratio 2:1 and dissolved in deionized water and the solution was left undisturbed. After few days, Potassium Hydrogen Oxalate Dihydrate raw material was collected from the bottom of the beaker.

$$2(C_2H_2O_4) + KOH + H_2O \longrightarrow KHC_2O_4.C_2H_2O_4.2H_2O$$

Saturated solution of Potassium Hydrogen Oxalate Dihydrate (PHODH) was prepared at room temperature and the solution was filtered twice using Wattmann 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. Recrystallization was carried out thrice to improve the purity of the crystals. Good, optically transparent crystals were obtained. Picture of a grown PHODH crystal is shown in Figure 1.

Figure 1 Potassium Hydrogen Oxalate Dihydrate crystal

Characterization

Crystals of Potassium Hydrogen Oxalate Dihydrate (PHODH), obtained from third recrystallization process, were subjected to various characterization studies. The crystal structure and cell parameters have been calculated by Single crystal X-ray diffraction technique using Bruker X8 KAPPA APEX II X-Ray

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diffractometer. The functional groups of the sample were confirmed by FT-IR spectroscopy using PERKIN ELMER FTIR spectrometer. The optical transmission range of the Potassium Hydrogen Oxalate Dihydrate crystals was determined by UV-Vis-NIR spectroscopic analysis using Perkin Elmer make Lambda 35 UV-Visible Spectrometer. The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a CNST thermal analyzer in nitrogen atmosphere. A Q-switched Nd: YAG laser beam of wavelength 1064 nm was used for Second harmonic generation efficiency studies. The mechanical properties of the crystals were studied by making indentation on the selected (001) plane using MMT-X MATSUZAWA hardness tester fitted with a diamond pyramidal indenter.

Single Crystal X-Ray Diffraction Analysis

From the data obtained, the unit-cell parameters were determined using SHELX programme. It is found that Potassium Hydrogen Oxalate Dihydrate has triclinic system with non-centrosymmertric space group P1. The calculated unit-cell parameter values are a=6.3522 (Å), b=7.0164(Å),
c= 10.5850(Å), α=93.829° γ= 101.372°and β = 100.115° and the unit cell volume is 452.8(Å)^3. The XRD pattern of PHODH is shown in the figure 2.

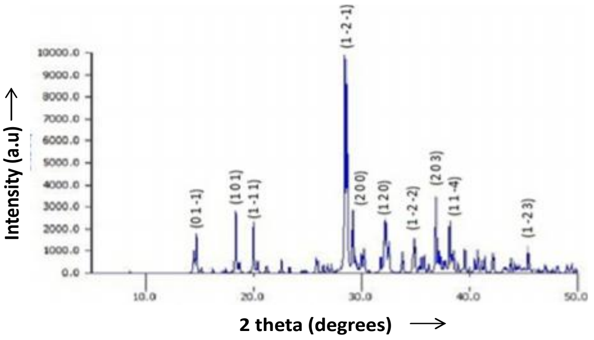

Figure 2 XRD pattern of PHODH crystal

Crystal structure reveals that the material is Potassium (hydrogenoxalato) (dihydrogenoxalato) dihydrate complex: $K(HC_2O_4)(H_2C_2O_4)(H_2O)_2$ (Fig. 3). It is closely related to the family of dihydrates known as trihydrogen oxalate [10] and has metal (Potassium) analog. The localization of all H atoms brings out its one dimensional polymeric structure that can be affiliated to coordination polymers.

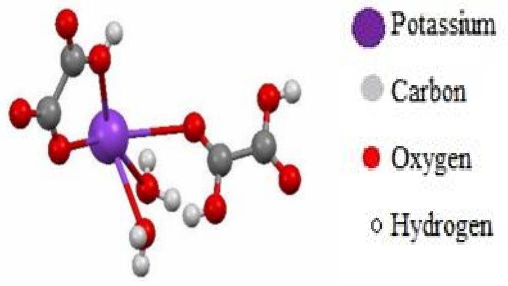

Figure 3 Potassium Hydrogen Oxalate Dihydrate molecules

The asymmetric unit contains one potassium cation, one partially deprotonated ligand (HL), two half oxalic acid molecules (H_2L) and two water molecules. The potassium atom is coordinated with seven oxygen atoms, five oxygen atoms from two HL and two H_2L, and two oxygen atoms from two independent aqua ligands (Fig. 4). The crystal is seen to consist of layers of anions alternating with cationic layers. The anionic layers consist of infinite chain of hydrogen bonded hydrogen oxalate ions. The framework is built from isolated $KO_7(H_2O)_2$ polyhedra, bridged by four carboxylate ligands (two HL and two H_2L).

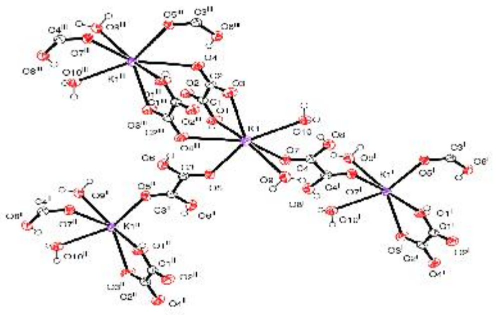

Figure 4 Packing of Potassium Hydrogen Oxalate Dihydrate

In this polymeric packing, the framework stability is maintained by an extensive hydrogen bond network involving all O atom of hydrogen oxalate anion, unionized oxalic acid molecules and water molecules. The found atomic positions clearly show that the $HC_2O_4^{--}$ ion and $H_2C_2O_4^{--}$ ion in potassium Hydrogen Oxalate Dihydrate is non-planar. In these structures the hydrogen bonds to the anions are probably responsible for the deviation from planarity. The hydrogen bonding scheme in $KHC_2O_4.C_2H_2O_4.2H_2O$ is responsible for the lack of a center of symmetry in the potassium hydrogen oxalate dihydrate as the two oxygens engaged in hydrogen bonding are situated trans relative to one another. The K-O bond lengths vary between 2.8639 and 3.2492(Å)(Table 1). These values are slightly more than that reported for Potassium hydrogen oxalate [10].

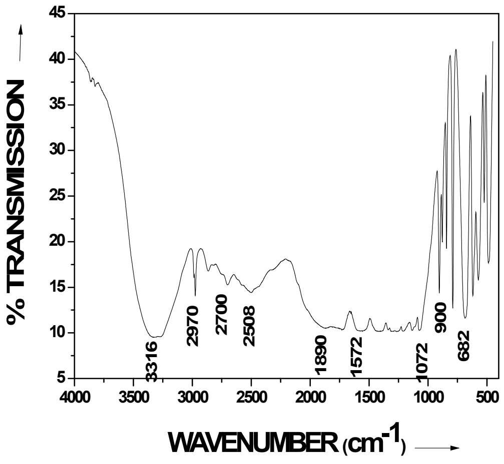

Figure 5 FTIR spectrum of PHODH

The molecule seems to possess the characterististics of both the oxalate ions and the oxalic acid molecule. The C-O bonds not engaged in hydrogen bonding are short (1.2068 to 1.2281 Å)whereas the other bonds are longer (1.2830 to 1.2987 Å). The bond lengths indicates O(4) to carry the negative charge, and O(1) to carry the hydrogen atom, as 1.26 Å is commonly observed for CO distances in oxalate ions, whereas 1.30 Å has been found for corresponding distances in oxalic acid. The hydrogen bonding pattern shows strong and linear bonds, where the two oxalic acid molecules, as well as the single anion, act as donors involving, each of the three, one protonated oxygen atom in the shortest hydrogen bonds, between 2.4818 (Å) and 2.5233(Å) (Table 2).

The moderate hydrogen bonds concern one water molecule as donor, the acceptor being the ionized ligand, which involves the two deprotonated oxygen atoms not implied in the precedent strongest H-bonds. The O-C-O angles in $KHC_2O_4.C_2H_2O_4.2H_2O$ are greater than 120^o in accordance with earlier observations. The two O-C-O angles determined in KHC_2O_4 are significantly different, the difference being 3.07^o, which is in agreement with the earlier reported value 2.9^o[10].

Table 1 Bond lengths [Å] and angles [deg] for PHODH

C(1)-O(2)	**1.2091(17)**	**O(2)-C(1)-O(1)**	**124.89(13)**	**O(1)-K(1)-O(3)**	**54.63(3)**
C(1)-O(1)	1.2987(17)	O(2)-C(1)-C(2)	121.86(13)	O(1)-K(1)-O(5)	69.88(3)
C(1)-C(2)	1.5491(19)	O(1)-C(1)-C(2)	113.24(12)	O(3)-K(1)-O(5)	118.47(3)
C(2)-O(3)	1.2281(17)	O(3)-C(2)-O(4)	127.96(13)	O(1)-K(1)-O(2)#6	137.51(3)
C(2)-O(4)	1.2556(17)	O(3)-C(2)-C(1)	117.30(12)	O(3)-K(1)-O(2)#6	84.03(3)
C(3)-O(5)	1.2136(17)	O(4)-C(2)-C(1)	114.73(12)	O(5)-K(1)-O(2)#6	135.55(3)
C(3)-O(6)	1.2830(17)	O(5)-C(3)-O(6)	126.52(12)	O(1)-K(1)-O(10)	108.71(3)
C(3)-C(3)#1	1.552(3)	O(5)-C(3)-C(3)#1	120.65(15)	O(3)-K(1)-O(10)	81.17(3)
C(4)-O(7)	1.2068(17)	O(6)-C(3)-C(3)#1	112.83(14)	O(5)-K(1)-O(10)	146.15(3)
C(4)-O(8)	1.2932(17)	O(7)-C(4)-O(8)	126.54(13)	O(2)#6-K(1)-O(10)	69.26(3)
C(4)-C(4)#2	1.539(3)	O(7)-C(4)-C(4)#2	121.79(15)	O(1)-K(1)-O(7)	89.28(3)
O(1)-K(1)	2.8639(11)	O(8)-C(4)-C(4)#2	111.67(15)	O(3)-K(1)-O(7)	121.02(4)
O(1)-H(1A)	0.8200	C(1)-O(1)-K(1)	126.01(8)	O(5)-K(1)-O(7)	78.65(3)
O(2)-K(1)#3	2.8886(11)	C(1)-O(1)-H(1A)	109.5	O(2)#6-K(1)-O(7)	124.38(3)
O(3)-K(1)	2.8662(11)	K(1)-O(1)-H(1A)	124.5	O(10)-K(1)-O(7)	67.51(3)
O(4)-K(1)#4	3.0396(12)	C(1)-O(2)-K(1)#3	137.41(9)	O(1)-K(1)-O(9)	156.15(3)
O(5)-K(1)	2.8741(10)	C(2)-O(3)-K(1)	125.50(9)	O(3)-K(1)-O(9)	146.70(3)
O(6)-H(6A)	0.8200	C(2)-O(4)-K(1)#4	122.79(9)	O(5)-K(1)-O(9)	93.97(3)
O(7)-K(1)	2.9075(11)	C(3)-O(5)-K(1)	134.03(9)	O(2)#6-K(1)-O(9)	66.24(3)
O(8)-K(1)#5	3.2492(12)	C(3)-O(6)-H(6A)	109.5	O(10)-K(1)-O(9)	74.68(3)
O(8)-H(8A)	0.8200	C(4)-O(7)-K(1)	132.95(9)	O(7)-K(1)-O(9)	69.87(3)
O(9)-K(1)	2.9203(12)	C(4)-O(8)-K(1)#5	114.15(9)	O(1)-K(1)-O(4)#4	72.18(3)
O(9)-H(9B)	0.889(15)	C(4)-O(8)-H(8A)	109.5	O(3)-K(1)-O(4)#4	71.83(3)
O(9)-H(9A)	0.884(16)	K(1)#5-O(8)-H(8A)	98.1	O(5)-K(1)-O(4)#4	67.54(3)
O(10)-K(1)	2.8943(12)	K(1)-O(9)-H(9B)	120.4(15)	O(2)#6-K(1)-O(4)#4	87.09(3)
O(10)-H(10A)	0.885(15)	K(1)-O(9)-H(9A)	97.7(16)	O(10)-K(1)-O(4)#4	145.82(3)
O(10)-H(10B)	0.881(15)	H(9B)-O(9)-H(9A)	107.4(17)	O(7)-K(1)-O(4)#4	145.25(3)
K(1)-O(2)#6	2.8885(11)	K(1)-O(10)-H(10A)	122.1(14)	O(9)-K(1)-O(4)#4	118.83(3)
K(1)-O(4)#4	3.0396(12)	K(1)-O(10)-H(10B)	110.5(14)	O(1)-K(1)-O(8)#7	127.11(3)
K(1)-O(8)#7	3.2492(12)	H(10A)-O(10)-H(10B)	106.2(17)	O(3)-K(1)-O(8)#7	130.20(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+2 #2 -x+2,-y+2,-z+2 #3 x,y-1,z #4 -x,-y+1,-z+1 #5 x+1,y,z #6 x,y+1,z #7 x-1,y,z

Table 2 Hydrogen bonds for PHODH [Å and deg]

D-H...A	d(D-H)	d(H...A)	d(D...A	<(DHA)
O(1)-H(1A)...O(9)#3	0.82	1.70	2.5233(14)	175.7
O(6)-H(6A)...O(4)#4	0.82	1.68	2.4999(14)	173.4
O(8)-H(8A)...O(10)	0.82	1.66	2.4818(14)	176.3
O(10)-H(10A)...O(3)#8	0.885(15)	1.845(16)	2.7056(14)	163.6(19)
O(10)-H(10B)...O(2)#9	0.881(15)	1.867(16)	2.7362(15)	169(2)
O(10)-H(10B)...O(4)#9	0.881(15)	2.578(19)	3.0747(16)	116.6(17)
O(9)-H(9B)...O(5)#10	0.889(15)	2.018(18)	2.8367(14)	152.5(19)
O(9)-H(9B)...O(6)#11	0.889(15)	2.239(18)	2.8901(15)	129.9(18)
O(9)-H(9A)...O(7)#10	0.884(16)	1.933(17)	2.7866(15)	162(2)
O(9)-H(9A)...O(8)#7	0.884(16)	2.35(2)	2.8350(15)	114.5(18)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+2 #2 -x+2,-y+2,-z+2 #3 x,y-1,z #4 -x,-y+1,-z+1 #5 x+1,y,z #6 x,y+1,z #7 x-1,y,z
#8 -x+1,-y+2,-z+1 #9 -x+1,-y+1,-z+1 #10 -x+1,-y+2,-z+2 #11 x+1,y+1,z

Fourier Transform Infrared (FTIR) Spectral Analysis

Vibrational spectroscopy gives information on molecular vibrations and this information is of immense help to organic chemists because it can be directly related to molecular structure. To analyze the presence of functional groups in PHODH qualitatively, FTIR spectrum was recorded. The infrared assignments were made in the range from 400 cm^{-1} to 4000 cm^{-1} with the help of spectrum recorded on PERKIN ELMER FTIR spectrometer using KBr pellet.

FTIR spectrum of PHODH is shown in figure 5. The broad band at 3316 cm^{-1} and the band at 2970 cm^{-1} are due to OH stretching vibrations. The band at 2700 cm^{-1} is due to CH vibrations. C=O stretching vibrations are found at 2508 cm^{-1}. The band at 1890 cm^{-1} is due to C=C asymmetric stretching. The peak at 1572 cm^{-1} is due to C=C ring stretching.

The peak at 1072 cm^{-1} is due to C-O bending. $C=H_2$ out of plane bending are found at 900 cm^{-1}.

The peak at 682 cm^{-1} is due to O-H bending vibrations. The assignments confirm the presence of various functional groups in PHODH.

UV-Visible Spectral Analysis

UV–Visible transmission spectrum of PHODH crystal was recorded using Perkin Elmer make Lambda 35 UV-Visible Spectrometer in the range 150 nm to 800nm and the observed spectrum of PHODH crystal is shown in Figure 6. The PHODH crystal is transparent in the entire UV-Visible region. It has an average transparency of about 80% in the Vis region with a lower cut-off wavelength at 256 nm. The wide range transmission is an important requirement for a crystal exhibiting NLO behavior [11]. The band gap PHODH was calculated using the formula $E_g = hc / \lambda$ (eV). The band gap of PHODH was found to be 4.85 eV**.**

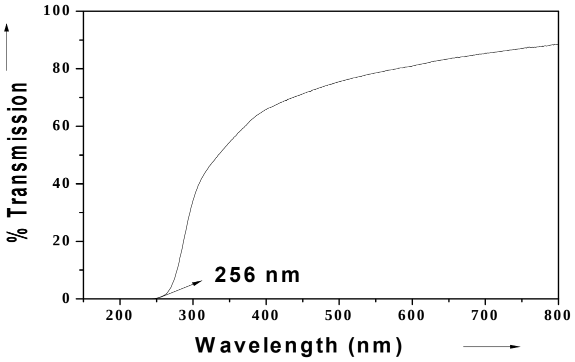

Figure 6UV-Visible Spectrum of PHODH

Thermal Analysis

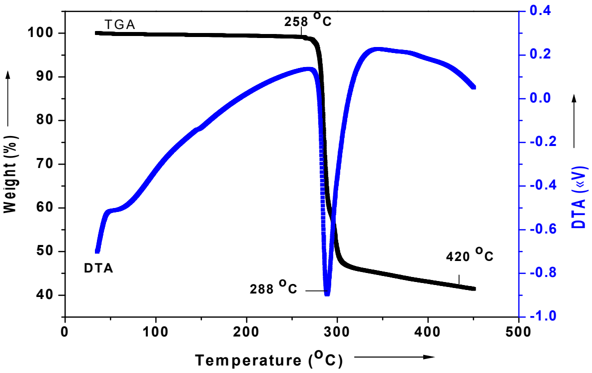

Figure 7 TGA and DTA curves of PHODH

There is no weight loss up to 258 ˚C. The transition occurs between 265 ˚C - 420 ˚C. The endothermic peak observed at 288 ˚ C in DTA in association with a sharp weight loss of about 55% as observed in TGA, may be attributed to the absorption of energy for the breaking of bonds. The major weight loss of 55% indicates that the material undergoes decomposition during melting. The weight loss may be due to the removal of volatile products like K and CO_2 molecules. The sharp endothermic peak at 288°C indicates that the melting point of the substance is 288°C.The high melting point of semi-organic PHODH crystals arises due to the stronger bonding existing between the oxalate molecule and the metal ion .The sharpness of the endothermic peak indicates good crystallinity and purity of the sample.

Microhardness Study

Hardness tests are commonly used to determine the mechanical strength of the grown crystal. Mechanical properties of the PHODH crystal was studied by making indentation on the selected (001) plane using MMT-X MATSUZAWA hardness tester fitted with a diamond pyramidal indenter. Microhardness of PHODH crystal was examined by varying the load and fixing indentation time as 5 sec. Vicker's microhardness number was evaluated from the relation.

$$H_v \;=\; (1.8544 * P) / d^2 \qquad \text{Kg/mm}^2$$

Where,

H_v is the Vicker's microhardness number in Kg/mm^2
P is the applied load in gram
D is the average diagonal length of the indentation in µm.

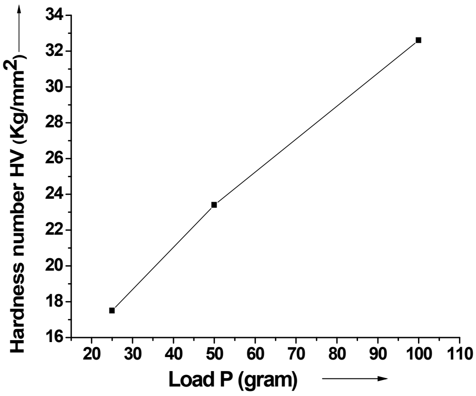

Figure 7 Plot of vicker's microhardness against load for PHODH crystal

Figure 7 Shows the variation of the hardness number (H_v) as the function of applied load for PHODH crystal. It is very clear that the hardness value increases with the applied load. The increase of microhardness with increasing load is in agreement with the reverse indentation size effect (ISE) as observed in similar reports [12, 13]. Beyond the load of 100g, a significant crack developed around the indentation mark, which may be due to the release of internal stresses generated at the corners of the indentation.

Nlo Studies

A Q-switched Nd: YAG laser beam of wavelength 1064 nm (pulse width 8 ns) and the energy of the laser pulse around 0. 68 mJ was allowed to strike the sample cell normally [14]. The beam emerging through the sample was focused on to a Czerny-Turner monochromator using a pair of lenses. The detection was carried out using a Hamamatsu R-928 photomultiplier tube. The signals were captured with an Agilent infinium digital storage oscilloscope interfaced to a computer. NLO signal is captured by the oscilloscope through the photomultiplier tube. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation by the PHODH crystal. The NLO output of PHODH is 5.23 mJ. The second harmonic generation efficiency of PHOHD is found to be nearly equal to 0.5943 times that of KDP (8.8 mJ).

Table 3 Comparison of SHG output of PHODH with KDP

Sample	NLO output
PHODH	5.23 mJ
KDP	8. 8 mJ

CONCLUSIONS

Semi-Organic crystals of PHODH were grown from slow evaporation technique. Single crystal X-ray diffraction study shows that the crystal belongs to triclinic crystal system. The FT-IR spectrum reveals the functional groups of the grown crystals. The thermal studies reveal that melting point of the crystal is 288^{o}C. UV-Visible Spectroscopic studies indicate the average transparency of PHODH in the visible region is about 80% with a lower cut-off wavelength at 256 nm. The band gap of PHODH is found to be 4.85 eV. For a load of 100g, hardness of PHODH crystal is 32.5 Kg/mm^2 the microhardness of the crystal increases with the applied load. That is, the exhibits load dependant hardness. The NLO output of PHODH is 5.23 mJ.

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