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Growth and Characterization of Di-Ammonium Hydrogen Phospho Tartrate (DAHPT) – A Semiorganic NLO Crystal

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Abstract: *A new semiorganic non-linear optical crystal of Di-Ammonium Hydrogen Phospho Tartrate (DAHPT) was grown successfully by slow evaporation technique. The grown crystal was subjected to different characterization in order to test its suitability for device fabrication. The lattice parameters of the grown crystals were determined by single crystal X-ray diffraction technique and the crystalline nature of the grown crystal was confirmed by powder XRD analysis. The presence of the functional groups in the crystal lattice was confirmed by FTIR spectral analysis. The elements present in the grown crystal was confirmed by EDAX. The UV-Vis-NIR spectrum of DAHPT shows zero absorbance in the entire visible region which enables it to be suitable for optical applications. Thermal stability of DAHPT was determined from TG/DTA curves. The SHG activity of the grown crystal was confirmed by Kurtz-Perry powder technique. The mechanical strength of the crystal was determined by Vickers hardness test.*

Keywords: *L-Tartaric acid, Crystal growth, EDAX, Optical properties, Thermo-gravimetric analysis*

I. Introduction

In recent years, several studies dealing with organic, inorganic and semiorganic materials for Non Linear Optics (NLO) have been reported, due to the increasing necessitate of cheap and easily processable materials for applications in photonics. Second order nonlinear optical materials have attracted much attention because of their potential applications in emerging optoelectronic technologies[1, 2]. Among these, semiorganic nonlinear materials will be the key elements for future photonic technologies. In semiorganic materials the organic ligand is ionically bonded with inorganic host, because of this, the new semiorganic crystals are having higher mechanical strength and chemical stability. The semiorganic crystals possess several attractive properties such as high damage threshold, wide transparency region and high nonlinear coefficient[3]. The contribution from the delocalized π- electrons belonging to the organic ligand results in wide optical transmittance and high nonlinear electro-optic coefficients. Many device applications of NLO require single crystals in bulk form. This is achieved with the semiorganic crystals, which exhibit wide transparency, large and bulky crystal morphologies. L-Tartaric acid and its compounds form an important class of materials[4] as they exhibit interesting electrical and optical properties. Molecular salts composed of L-Tartaric acid and basic compounds have been synthesized[5, 6]. Some of the reported L-Tartaric acid compound crystals are urea-tartaric acid[7], L-cysteine tartrate[8], cobalt tartrate[9], holmium tartrate[10], calcium tartrate[11], etc. An attempt has been made to form a new compound DAHPT which has not been reported in the literature. The aim of this paper is to grow DAHPT single crystals and characterize it through X-ray diffraction studies, EDAX, SHG, UV-visible transmittance studies, themal studies and microhardness studies.

II. Experimental

2.1 Synthesis and Solubility

Di-Ammonium Hydrogen Phospho Tartrate(DAHPT) was synthesized by dissolving AR grade L-Tartaric acid and Di-ammonium Hydrogen Phosphte in the ratio 1:1 in de-ionized water. The salt was formed in accordance with the following equation.

$$C_4H_6O_6 + (NH_4)_2HPO_4 \rightarrow C_4H_6O_6.(NH_4)_2HPO_4$$

The salt was purified by repeated recrystallization. The solubility of the sample at various temperatures was tested using Gravimetrical method[12]. The solubility curve is shown in Fig.1. From the graph it is observed that the solubility of DAHPT in water increases linearly with temperature. This shows a high solubility gradient and positive temperature coefficient, which ensures that slow evaporation technique is suitable for growing single crystals of DAHPT.

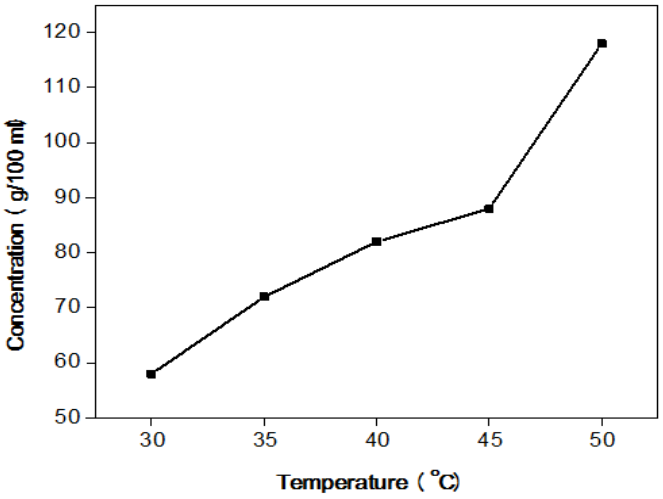

Fig. 1 Solubility curve

2.2 Growth Of DAHPT Crystal

Single crystal of DAHPT was grown by slow evaporation technique at room temperature (30°C). In accordance with the solubility data, the saturated solution of the re-crystallized salt of DAHPT was prepared. To avoid fungus few drops of hydrogen peroxide was added to the solution and it was constantly stirred for about 2 hours using a magnetic stirrer and was filtered using whatmann filter paper. Then the filtered solution was kept in a borosil beaker covered with a porous paper and kept in a dust-free atmosphere for slow evaporation. Transparent, colorless crystals were obtained after a period of about 90 days and is shown in Fig. 2.

Fig. 2 Photograph of DAHPT crystal

III. Material Characterization

In order to ascertain the structure, single crystal X-ray diffraction data were collected using a Brukes-Nonius MACH3/CAD4X-ray diffractometer with MoK_{α} radiation (λ=0.71069Å). Powder X-ray diffraction pattern of the sample was obtained using a powder X-ray diffractometer (PANalytical Model, Nickel filtered Cu K_{α} radiations (λ= 1.54056 Å) at 35 KV, 10mA). The sample was scanned over the required range for 2θ values (10°-70°). The FTIR spectra of the sample were recorded using a SHIMADZU spectrometer by the KBr pellet technique in the range 400 – 4000 cm^{-1}. The infrared spectroscopy is effectively used to identify the functional groups of the grown crystals. The optical transmission spectra of DAHPT crystal was carried out in the region 200 –2200 nm using Lambda 35 model PERKIN ELMER DOUBLE BEAM spectrometer. The thermal characterization was determined by using a NETZSCH STA 409C/CD thermal analyzer in nitrogen atmosphere. The NLO property of the crystal was confirmed by the Kurtz powder SHG test. The microhardness of the grown crystals was measured using a Leitz Weitzier microhardness tester with a diamond indenter.

IV. Results And Discussion

4.1 Crystal Structure and X – Ray Diffraction Analysis

Single crystal X- ray diffraction data for the DAHPT single crystal is presented in Table 1. The DAHPT crystal possess its orthorhombic structure with P222 space group which is recognized as noncentrosymmetric. This noncentrosymmetric nature is an essential requirement for a NLO material.

TABLE 1: Crystal Data Of DAHPT Single Crystal

Molecular Formula	$C_4H_6O_6(NH_4)_2HPO_4$
Molecular Weight	282.16
Unit cell parameters	
a	7.631 (9)Å
b	7.831 (4)Å
c	11.048 (8)Å
α	90^o
β	90^o
γ	90^o
Volume	660.3(8) $Å^3$
Crystal system	Orthorhombic
Z	4
Density	2.837g/cm^3
Space group	P_{222}
Crystal color	Transparent, Colorless
Wavelength	1.54056 Å

The powder XRD pattern of DAHPT is shown in Fig.3. The sharp peaks show high crystallinity of the grown crystal. The diffraction peaks were indexed using the INDEXING software package following the procedure of Lipson and Steeple[13].

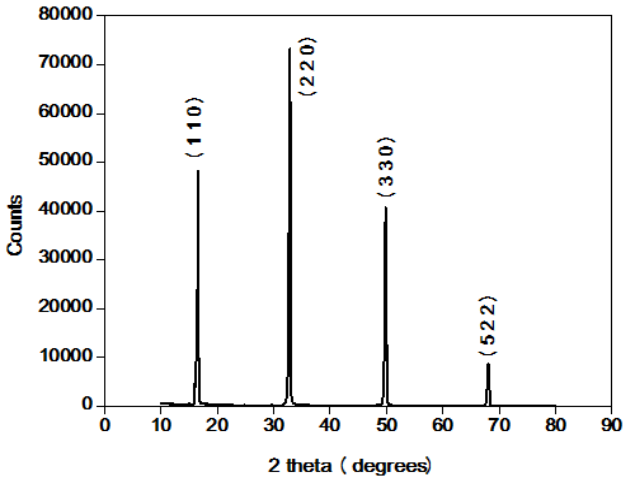

Fig. 3 Powder X-ray diffraction pattern of DAHPT crystal

4.2. Fourier Transform Infrared (FTIR) Analysis

The FTIR spectrum of DAHPT was recorded in the region 400 – 4000 cm^{-1} as shown in Fig 4. The functional groups present in the DAHPT crystal were identified and the assignments are given in Table 2.

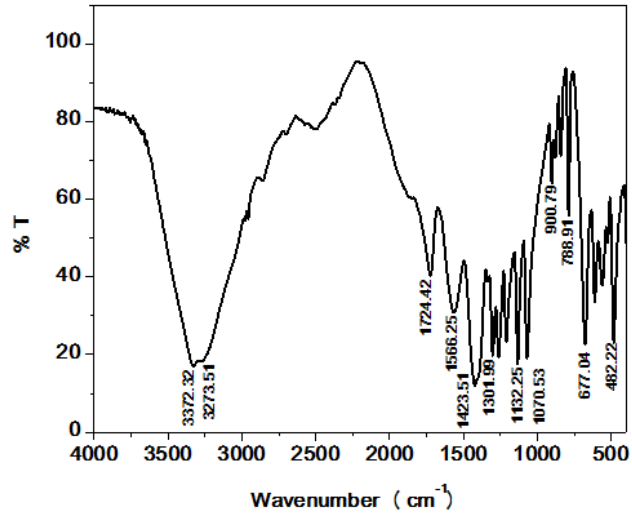

Fig. 4 FTIR spectrum of DAHPT crystal

Table 2. FTIR frequency assignment for DAHPT

Wavenumber (cm^{-1})	Assignment
3327.32	O – H stretching
3273.31	O – H stretching
1724.42	C=O symmetric stretching
1566.25	COO^- asymmetric stretching
1423.51	Bending vibration of Ammonium
1301.99	P-O stretching vibration
1070.53	P-O-H Vibrations
788.91	P-O-H Vibrations
677.04	PO_4 Vibrations
561.30	PO_4 Vibrations
482.22	PO_4 Vibrations

The peaks observed at 3327.32 cm^{-1} and 3273.31 cm^{-1} are due to the presence of O–H stretching vibrations. The symmetric and asymmetric stretching of C=O and COO^- are observed at 1724.42 cm^{-1} and 1566.25 cm^{-1} respectively. The peak at 1423.51 cm^{-1} is due to the bending vibrations of ammonium. The P-O stretching vibration is observed at 1301.99 cm^{-1}. The peaks at 1070.53 cm^{-1} and 788.91 cm^{-1} represent P-O-H vibrations. The peaks at 677.04cm^{-1},561.3 cm^{-1} and 482.22 cm^{-1} are due to the PO_4 vibrations[14].

4.3 EDAX Studies

Energy Dispersive X-ray Analysis (EDAX) is a micro-analytical technique used to identify the elements present in the sample. The EDAX spectrum of the crystal is shown in Fig.5. The atomic and weight percentage of the elements are listed in Table 3.

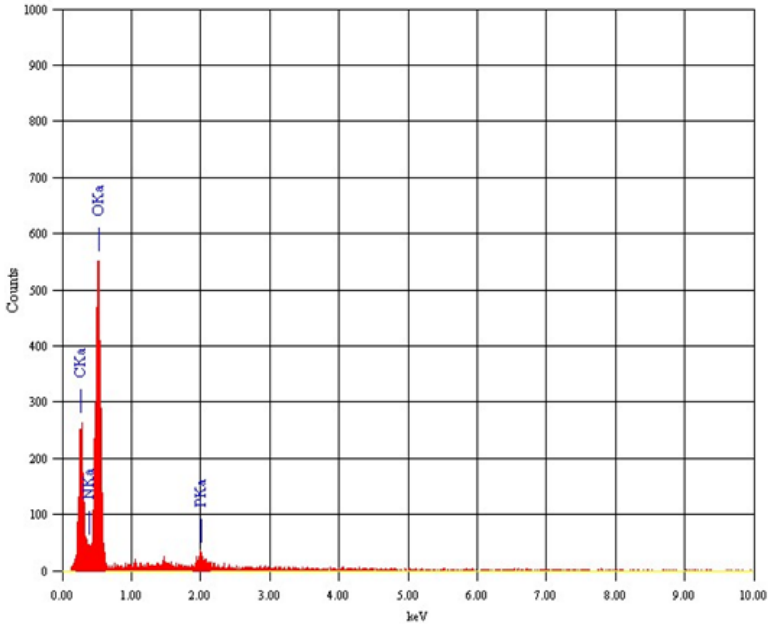

Fig.5 EDAX Spectra of DAHPT crystal

Table 3. Data for atomic and weight percentage of the elements

Element	Weight%	Atomic%
C	52.32	59.76
N	0.63	0.62
O	45.32	38.86
P	1.73	0.76
Total	100	100

4.4 UV-Vis-NIR Spectral studies

A good optical transmittance and less absorption in the UV-Vis-NIR region are the desirable properties for a NLO crystal. The UV-Vis-NIR absorbance spectrum of DAHPT single crystal is shown in Fig. 6. The crystal has zero absorbance in the entire visible-NIR region. The low cut-off wavelength at 220 nm and greater transparency in the visible region make it a suitable material for optoelectronic applications[15]. The absorption coefficient "α" of DAHPT single crystal of thickness 2mm was determined from the optical absorbance measurements.

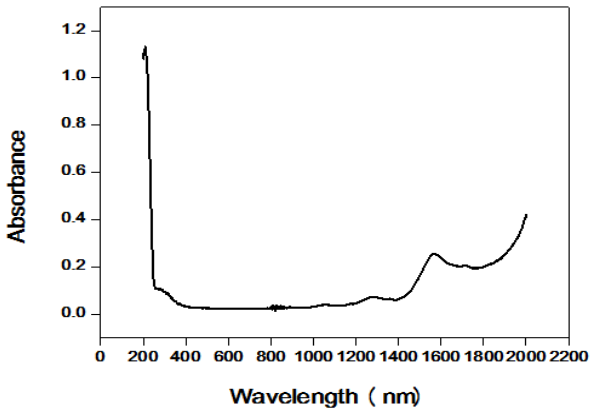

Fig. 6 Optical absorbance of DAHPT

The value of α was calculated using the relation

$$: \alpha = (1/d) \log(1/T) \quad (1)$$

where T is the transmittance and d is the thickness of the crystal. As an indirect band gap material, the crystal under study has an absorption coefficient (α) obeying the following relation[16] for high photon energies (hν)

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

where E_g is optical band gap of the crystal and A is a constant. The value of band gap energy was estimated from the Tauc's plot drawn between hν and $(\alpha h\nu)^{1/2}$ by extrapolating the linear portion of the curve to zero absorption as shown in Fig 7. The band gap energy E_g of DAHPT single crystal is found to be 4.7 eV

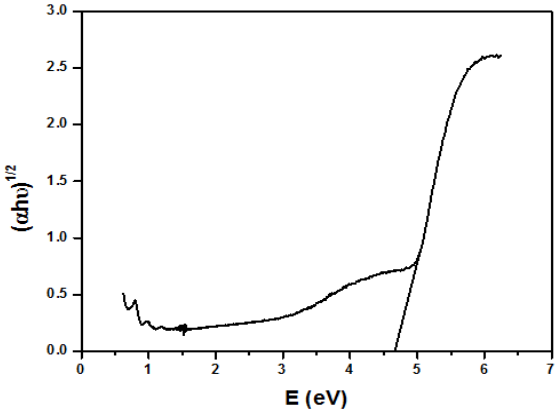

Fig. 7 Tauc's plot

4.5 Thermal studies

The thermal stability of DAHPT was carried out by TG/DTA and is shown in Fig. 8. The sample of weight 3.250mg was subjected to a heating rate of 10°C/min in the nitrogen atmosphere from 40° C to 590° C. The Thermo gram shows a single weight loss around 240° C. Complete decomposition of the sample takes place at 255.46°C with 8% end residue. The absence of endothermic peak at 100°C shows that there is no inclusion of water molecules in the sample. From these results, it is concluded that the crystal is thermally stable upto 210°C. The thermal stability of the crystal is a useful property for its possible NLO applications.

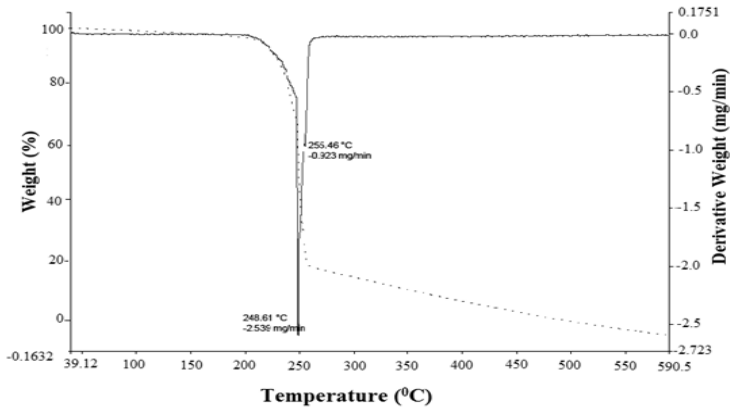

Fig. 8 TG spectrum of DAHPT

4.6 SHG Studies

Kurtz and Perry second harmonic generation test was performed to confirm the NLO property of DAHPT crystal. The powdered sample was illuminated using (Spectra Physics Quanta Ray DHS2. Nd:YAG laser)the first harmonics laser output of 1064nm with pulse width of 8ns and repetition rate 10 Hz. The second harmonics signal, generated in the crystal was confirmed from the emission of green radiation by the crystal. The SHG radiations of 532 nm green light was collected by a photomultiplier tube (PMT-Hamasu R2059) after being monochromated (monochromator-Czerny-Turner) to collect only 532 nm radiation. The optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix – TDS 3052B). Powdered SHG measurements using 1064nm radiation revealed that DAHPT showed SHG efficiency 0.273 times of KDP at a given pulse energy of 2.4mJs^{-1}. The SHG efficiency will vary with the particle size of the powder sample[17].

4.7 Vickers Micro hardness Analysis

Hardness is a measure of resistance of the material to plastic deformation. The hardness of the material plays a significant role in device fabrication. The hardness of the crystal carries information about the mechanical strength and molecular bindings of the material. Microhardness analysis was carried out using Vickers microhardness tester fitted with a diamond indentor. A well polished DAHPT crystal of 2mm thick was placed on the platform on the Vickers microhardness tester and the loads of different magnitude were applied over a fixed interval of time. The hardness was calculated using the relation

$$: H_v = 1.8544\ P/d^2\ (kg/mm^2) \quad (3)$$

where P is the applied load in gram and d is the diagonal length of the indentation in millimeter. The variation of hardness number (H_v) for different loads (P) of DAHPT is shown in Fig. 9. The hardness increases gradually with the increase of load and above 100g cracks were developed on the smooth surface of the crystal due to release of the internal stresses generated locally by indentation. This increase in H_v with load indicates that DAHPT exhibits Reverse Indentation Size effect (RISE).

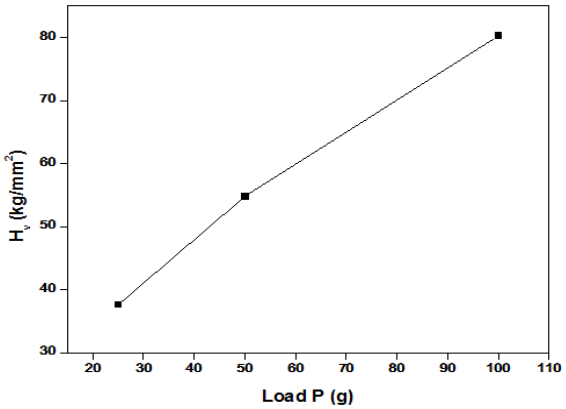

Fig. 9 Plot of load vs H_v

The relation between load P and size d is given by Meyer's law

$$: P = ad^n. \quad (4)$$

Here a is a constant. The workhardening coefficient n was calculated to be 4.47 from the plot of log P versus log d (Fig. 10). According to Onitsch, $1.0 \leq n \leq 1.6$ for hard materials and $n > 1.6$ for soft materials[18]. Hence, it is concluded that DAHPT crystal is a soft material. Elastic stiffness constant is a measure of the ability of the material to resist deformation and it gives an idea about the tightness of bonding with the neighboring atoms. The elastic stiffness constant (C_{11}) for different loads are calculated using Wooster's empirical formula

$$: C_{11} = H_v^{7/4} \quad (5)$$

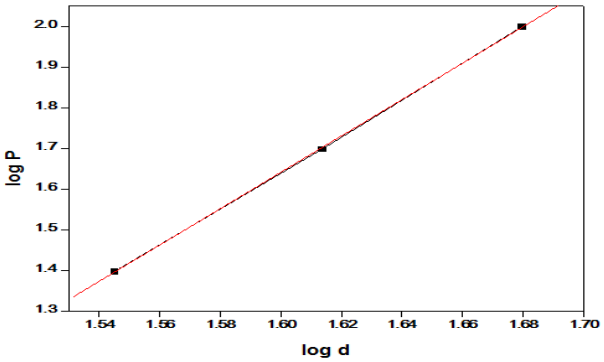

Fig.10 Plot of log d vs log P

In the case of DAHPT crystal, the stiffness constant is found to increase with the applied load. Yield strength is the minimum stress required to resist permanent deformation which is calculated using the relation

$$: \sigma = H_v/3 \quad (6)$$

where σ is the yield strength, H_v is the hardness of the material. The hardness parameters are listed in Table 4.

Table 4. Hardness parameters of DAHPT crystal

S.No	Load(g)	H_v(kg/mm^2)	$C_{11}x10^{14}$ Pa	σ MPa
1	25	37.65	1.7734	122.99
2	50	54.85	3.426	179.1767
3	100	80.3	6.6754	262.3133

V. Conclusions

Di Ammonium Hydrogen Phospho Tartrate (DAHPT) crystals were successfully grown by SEST method and characterized through various characterization techniques. Single crystal XRD studies show that Di Ammonium hydrogen phospho Tartrate crystallizes in orthorhombic structure. The powder XRD pattern was indexed and the crystallinity was confirmed. The functional groups present in the crystal were confirmed by FTIR analysis. The elements present in the grown crystal was confirmed by Energy Dispersive X-ray Analysis (EDAX). The band gap is determined from UV-Vis-NIR studies as E_g = 4.7 eV. Thermal analysis shows that the crystal has thermal stability upto 210^{o}C. Microhardness analysis reveals that DAHPT belongs to soft material category and the hardness parameters are determined. SHG studies show that DAHPT has SHG efficiency of 0.273 times that of the standard KDP crystal.

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