

GROWTH AND CHARACTERISATION OF SUCCINIC ACID DOPED POTTASSIUM DIHYDROGEN PHOSPHATE CRYSTALS

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Abstract:

Potassium dihydrogen phosphate is a material rich in NLO property with wide range of industrial applications. Certain dicarboxylic acids are also rich in NLO properties so they are used as dopants. In the present work Succinic acid is added in the ratio 1:1 molar percentage to KDP. Single crystals were grown by slow evaporation method. The grown crystals were characterized by powder X-ray diffraction, Single crystal X-Ray diffraction, UV-vis. -spectroscopy, Fourier transform infrared spectroscopy (FTIR).SHG efficiency, Dielectric studies and micro hardness studies. The single crystal X-ray diffraction studies reveal the structure and space group of the crystal. The powder X-ray diffraction study shows that the crystalline perfection of grown crystal is good. Fourier transform infrared studies confirm the functional groups of the crystals. It is seen from UV-vis studies that the optical transparency is found to increase much by adding chlorides. SHG efficiency of KDP is found to be slightly increasing with doping of Succinic acid. Dielectric studies show the conductivity and electrical behaviour of the crystal. Micro hardness studies show the mechanical stability of the crystal.

Keywords —KDP, FTIR, UV-Vis, NLO, XRD, SHG, Microhardness

1. INTRODUCTION

Semi-organic nonlinear optical (NLO) materials have excellent nonlinear and fluorescent properties. They are significantly used in tele communication, optical computing, optical data storage, light emitting diodes, optical information processing etc.[1,2]. As KDP is being widely used in NLO applications and demands to modify its properties, the research work on the modifications of the optical, thermal, mechanical and NLO properties and the growth rate of the KDP crystal by using different dopants is still going on[3-5].

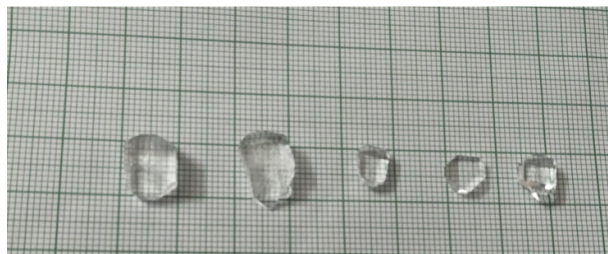
In the present study an effort has been made in growing KDP doped with Succinic acid in the ratio 1:1 by slow evaporation growth technique. The grown crystals are subjected to various spectral analysis like FTIR, UV-Visible, single crystal XRD,

powder XRD, Dielectric and Vickers's micro hardness studies.

A.EXPERIMENTAL PROCEDURE:

Pure KDP AR grade E-Merck and Succinic acid doped crystals were grown by slow evaporation growth technique at room temperature. The saturated solution is prepared by dissolving the solute of KDP in 30g per 100ml in Millipore water. The doping of Succinic Acid was carried out by adding 0.1 weight percentage powder form of Succinic acid into 1 molar 100 ml solution of KDP in millipore water. The mixtures were well stirred for 8 hrs for homogenization. Then it was double times filtered with whatt man filter paper and poured into Petri dishes and covered with perforated polyethylene. The prepared solution was allowed to dry at room temperature and the crystals were obtained by slow evaporation method. In the

period of 10-15 days, the crystal had formed as shown in Fig. 1. Then the grown crystals has been subjected various spectral studies to analyze its characteristics .Grown crystals were found to be colour-less and transparent. Figure 1 shows a photograph of 0.1 wt. Succinic acid doped KDP



Fig(1) As grown crystals of Succinic acid doped KDP

B.Characterization:

The grown Succinic acid doped KDP crystals were subjected to various characterizations .Single crystal X-ray diffraction studies were carried out using single crystal diffractometer ENRAF NONIUS Cad4 and its lattice parameter volume structure and space group is analysed in given in table. Powder X-ray diffraction studies were carried out using powder X-ray diffraction instrument D8 advanced BRUKER Spectrometer using $\text{CuK}\alpha$ radiation source and its wave length ($\lambda=1.54\text{\AA}$), data collected from the 2θ range from 10° to 90° in steps of 0.020 and count time 0.2S.The obtained results are in Fig.2 .Identification of functional groups were carried out by FTIR analysis using JASCO 4100 shown in Fig 3.UV-Visible spectral study is carried out using SHIMADZU 2600 in the range 200-1200nm as shown in Fig.4(a) and the results were compared with that of pure KDP and a comparative studies are made between the Succinic acid doped KDP Crystals. The NLO property of the doped crystal is evaluated by the Krutz and Perry (1968) powder technique using a Q-switched, mode locked Nd:YAG laser. Dielectric property of the crystal is carried out for various temperatures using HIOKI MODEL 3532_50 LCR High Tester. The Vickers micro hardness studies are carried out using Futuretech FM 800 type E series.

C.RESULT AND DISCUSSION:

KDP crystal is a promising NLO material with high transparency and frequency doubling property when doped with Succinic acid shows some changes in its Characteristics when subjected to Single crystal X-ray diffraction , powder X-Ray diffraction , Fourier transform Infra red Spectroscopy ,UV Spectroscopy, SHG measurements, Dielectric measurements and Hardness studies.

1. Single crystal xrd studies:

Single crystal X-ray diffraction analysis was carried out using ENRAF NONIUS Cad4 diffractometer to identify the lattice parameters. The single crystal X-ray diffraction studies confirm the tetragonal structure with the space group of I-42d .The lattice parameters of Succinic acid doped are; $a=b=7.3129\text{\AA}$, $c=7.001\text{\AA}$, with volume $V=386\text{\AA}^3$. The crystal parameters and cell volume were found to be well in agreement with reported values [6] as shown in table (1).From the grown doped crystal lattice parameters and space group it is clear that the basic structural property and space group of KDP is not altered by the dopant[7].

Compound	Crystal system	Space group	Unit cell parameters
KDP	Tetragonal	I-42d	$a=b=7.455\text{\AA}$, $c=6.975\text{\AA}$. $\alpha=\beta=\gamma=90^\circ$
KDP doped with Succinic acid	Tetragonal	I-42d	$a=b=7.3119\text{\AA}$, $c=7.010\text{\AA}$. $\alpha=\beta=\gamma=90^\circ$

Table-1 Lattice parameters for pure KDP and Succinic acid doped KDP

2. Powder XRD Studies:

The Succinic acid doped KDP crystals when subjected to X-ray diffraction shows pattern as in fig 2 .While comparing with the powder xrd pattern of pure KDP it is found that 2θ values shifted and this suggests that the structure of KDP is slightly disturbed by of Succinic acid which tries to change the transparency.

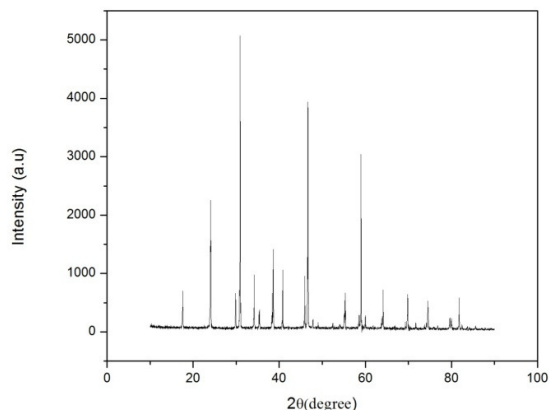


Fig:2 Powder XRD Pattern of succinic acid doped KDP

3. Fourier-Transform Infrared Spectroscopy Studies:

FTIR is a technique which is used to obtain an infrared spectrum of absorption, emission or photoconductivity of a solid, liquid or gas. It collects high spectral resolution data over a wide spectral range. This analysis has been carried out by recording the spectrum in the range 4000 – 400 cm⁻¹ using KBr pellet method. The spectrum of Succinic acid doped KDP is shown in fig 3. The presence of O-H stretching frequency at 1664 confirms the presence of Succinic acid. The appearance of medium O-H bending frequency at 1380. IR spectra in 1450-600 are called the fingerprint region so it is difficult to assign all absorption bands this region. The already reported Succinic acid showed peaks of corresponding functional group such as peaks due to C=O, P=O, Phosphonic acid (O=P-OH) and -OH. In the present study of Succinic acid doped KDP crystal grown by slow evaporation method given in Table-2 shows the functional group and their frequencies, which is in coordination with previous study [8].

Frequency cm-1	Functional group assignments
3491	-OH Stretching H bounded
2934	-CH stretching
2501	-O=P-OH Phosphonic acid
1664	-C=O stretching
1420	C-O-H in plane bending
1321	-OH Stretching
1259	P=O Stretching
910	C=O Stretching
598	-OH-P-OH bending
437	C=O bending

Table:2 Functional groups of Succinic doped KDP grown by slow evaporation method

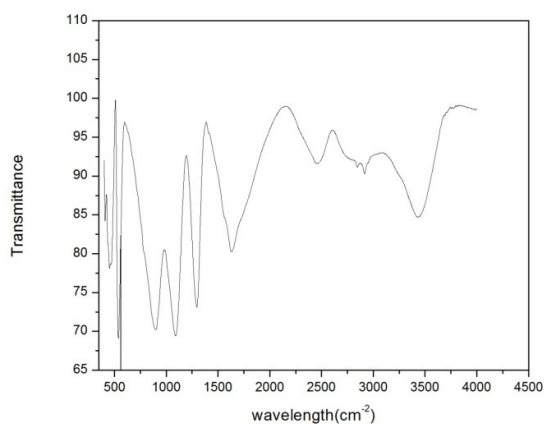


Fig 3. FTIR spectrum of Succinic acid doped KDP crystal

4. UV- Visible Spectral analysis:

The optical transmission spectra has been recorded by using SHIMADZU -2600 spectrometer in the range of 200-1200 nm as shown in fig 4. The crystal is highly transparent in the entire visible region, whereas it has a UV cut off at 301. The transmission is uniformly high (73%) for light in the visible region of electromagnetic spectrum, which is useful for nonlinear device application. The resultant spectrum is shown in Fig. 4(a)

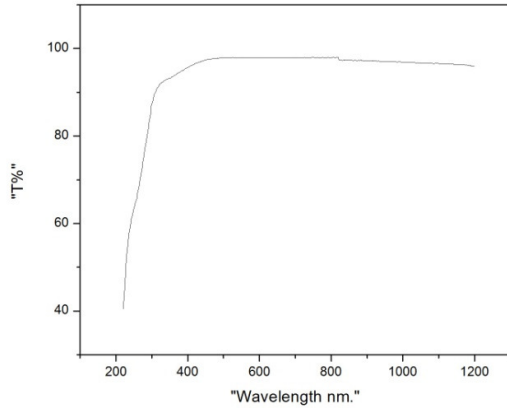


Fig.4(a) UV-Spectrum of Succinic Acid doped KDP

tuning the band gap of the material, one can achieve the desired material.

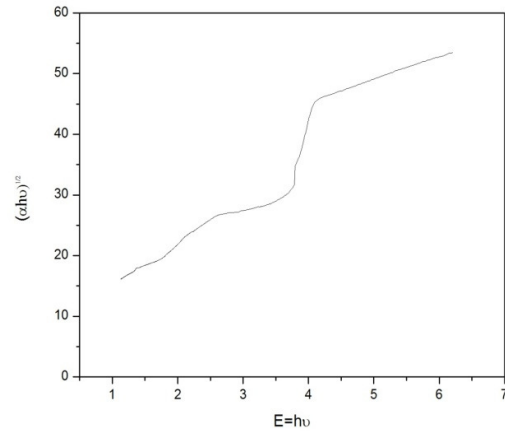


Fig:4(b) plot of $(\alpha h\nu)^{1/2}$ versus photon energy $h\nu$

The measured transmittance (T) was used to calculate the absorption coefficient (α) using the formula:

$$\alpha = \frac{2.303 \log\left(\frac{1}{T}\right)}{t}$$

where t is the thickness of the sample[9].

As in indirect band gap semiconductor, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies ($h\nu$).

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

Where, A is a constant, E_g the optical band gap, h the Planck's constant and ν the frequency of the incident photons. Optical band gap was calculated from the UV-Visible data. The plot between energy ($h\nu$) and $(\alpha h\nu)^{1/2}$ is made as shown in Figure (4.a)

(Where α is the absorption coefficient) and the optical band gap energy

(Ashour et al 1995) is found to be 2.7 eV by extrapolating the slope region (where it cuts the X-axis) which is shown in Figure(4.c)The internal efficiency of the device also depends upon the absorption coefficient. Hence by modifying the absorption coefficient and

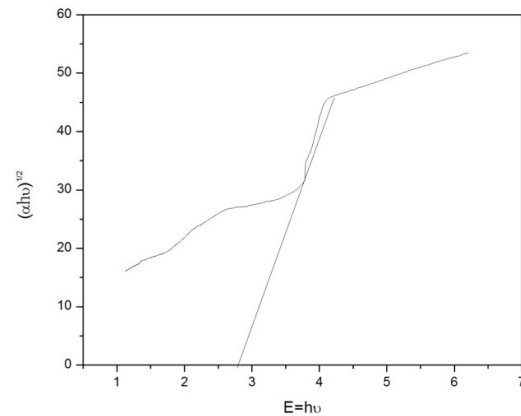


Fig:4(c) plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ showing band gap

which is suitable for fabricating various layers of the optoelectronic device as our requirements.[10].

Extinction coefficient (K) can be obtained from the following equation:

$$k = \frac{\lambda\alpha}{4\pi}$$

The transmittance (T) is given by

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)}$$

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation. Hence,

$$R = \frac{\exp(-at) \pm \sqrt{\exp(-at)T - \exp(-3at)T + \exp(-2at)T^2}}{\exp(-at) + \exp(-2at)T}$$

Refractive index (n) can be determined from reflectance data using the following equation.

$$n = -(R+1) \pm 2 \frac{\sqrt{R}}{(R-1)}$$

5. Simple Harmonic Studies:

The pure and doped KDP crystals were made into fine powders of the size of 10 μm. The micro particles were exposed to 1064 nm laser beam from a pulsed Nd: YAG laser to test the second harmonic generation efficiency. An input pulse of 1.9 mJ/pulse was supplied. Signal amplitude in mill volts on the oscilloscope indicates the efficiency of the sample. The pure KDP crystal gave an output 73 mV whereas the Succinic acid doped KDP crystal showed an increase in the SHG efficiency. The Succinic acid doped KDP crystal gave an output of 77 mV. Thus, the SHG efficiencies of the doped crystals are 1.05 times greater than the standard KDP crystals respectively [11].

6. Dielectric study

The dielectric analysis is an important characteristic that can be used to fetch knowledge based on the electrical properties of a material medium as a function of temperature and frequency. The dielectric studies were measured using **HIOKI MODEL 3532_50 LCR High Tester**. Based on this analysis, the capability of storing electric charges by the material and capability of transferring the electric charge can be assessed.

Dielectric properties are correlated with electro optic property of the crystals, particularly when they are non conducting materials [12]. Microelectronics industry needs low dielectric constant (εr) materials as an interlayer dielectric[13].

The dielectric constant is calculated using the formula

$$\epsilon' = \frac{Ct}{\epsilon_0 A'}$$

where C is capacitance (F), t the thickness (m), A the area(m²), and ε₀ the absolute permittivity in the free space having a value of 8.854 x 10⁻¹² Fm⁻¹.

Figures 5 (a), 5(b) show the variation of dielectric constant and dielectric loss with respect to frequency for all temperatures of Succinic acid doped KDP crystals. Compared to the pure KDP, dielectric constant (εr) value is found to be low for doped KDP[14].

From Figures 5(a) and 5(b), it is clear that dielectric loss is high at low frequency and decreases with high frequencies. The low dielectric loss at high frequency reveals the high optical quality of the crystal with lesser defects, which is a desirable property of NLO applications [15, 16]

dielectric constant and dielectric loss decrease with the increasing frequency. This may be due to the contributions of all the four polarizations such as electronic, ionic, orientation, and space charge, which are predominant in the lower frequency region [17].

The larger value of dielectric constant and dielectric loss at low frequency arises due to the presence of space charge polarization near the grain boundary interfaces, which depends on the purity and perfection of the sample[18].

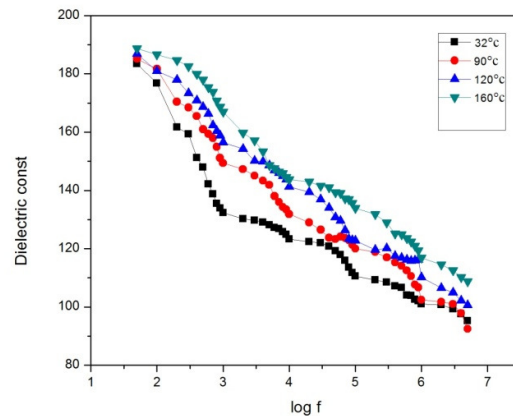


Fig: 5(a) Variation of dielectric constant with log frequency of the electric field of Succinic Acid doped KDP

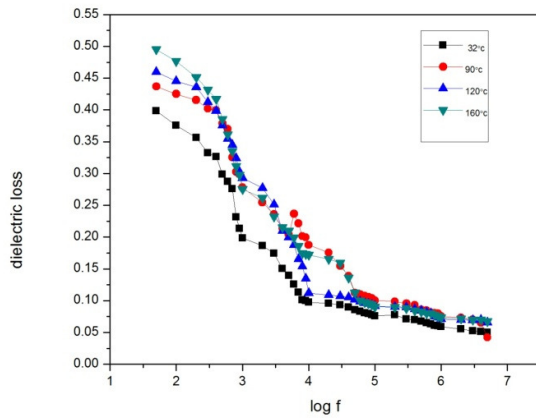


Fig: 5(b) Variation of dielectric loss with log frequency of the electric field of Succinic Acid doped KDP

7. Microhardness studies

Microhardness studies have been carried out on succinic acid doped KDP using Futuretech FM 800 type E series Vicker’s microhardness tester fitted with Vicker’s diamond pyramidal indenter attached to an incident light microscope. The static indentations were made at room temperature with a constant indentation time of 15s for all indentations .The indentation mark were made on the surface by varying the load from 3 to 100g.As micro cracks appeared at higher loads(100g), the load was restricted up to 50gms.The vicker’s microhardness number Hv of the crystal was calculated using the relation $Hv = 1.8554 P/ d^2$ Kg mm⁻² where P is the applied load, d is the diagonal length of the indented impressions in meter.Vicker’s microhardness profile as a function of applied load is shown table 3 and in fig.6.It shows that microhardness value of succinic acid doped KDP decreases with increase in load, while comparing with pure KDP hardness is low[19,20] Vickers micro-hardness value decreases with comparison to pure KDP. It can be conjectured that the doping of Succinic acid softens the KDP crystals.[21]

Load p (gm)	Vicker's Hardness number Hv	
	Pure KDP	Succinic doped KDP
3	101.64719	89.30063
5	130.07932	107.72378
10	139.6869	123.64182
25	146.3166	141.66429
50	152.86302	126.7865

Table-3 Variation of Hv with load applied for pure and succinic doped KDP

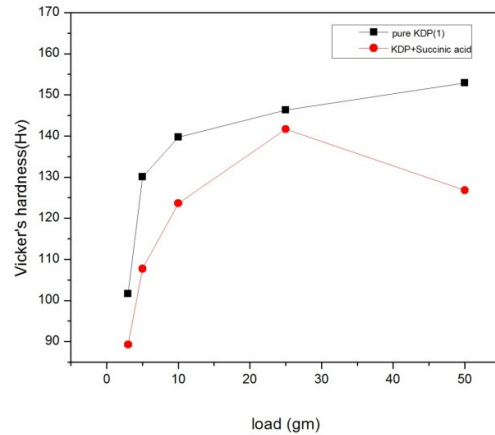


Fig 6 Plot of Hv versus load P for pure Succinic doped KDP crystals.

I. CONCLUSIONS

Single crystals of Succinic acid doped KDP crystals were successfully grown by slow Evaporation method. The Single XRD studies revealed that the crystals are tetragonal and belong to I42d space group. The Powder X-ray diffraction analysis determines the incorporation of Succinic Acid into KDP crystal lattice. The Fourier transform infra-red spectroscopy studies carried out confirms the functional groups of dopant present in the grown crystal. The UV-Vis studies reveals that the grown crystals having transmission in the visible range. Then the grown crystals subjected to Kurtz Perry powder method to test the efficiency of the relative second harmonic generation reveals the moderate NLO property of the grown crystal and the results were compared to standard KDP. From the Dielectric studies of the sample it was noticed that dielectric constant and dielectric loss decreases with increasing frequency. Hardness studies reveals

it is a soft material and Hardness (Hv) was found to decrease by addition of Succinic acid in pure KDP and proves to be good material for photonic device fabrication.

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