Growth and Characterization of Pure and Neem Leaves Extract Doped Potassium Dihydrogen Phosphate (KDP) Crystal

R.Kayalvizhi, G.Meenakshi

Abstract*— Potassium dihydrogen phosphate (KDP) crystal is an interesting non linear optical inorganic material. In this present work, KDP crystal and neem leaves extract doped KDP crystal has been grown by slow evaporation aqueous solution growth technique. The grown crystals have been investigated through various techniques viz. Fourier Transform Infrared Spectroscopy has been used for spectral analysis of grown crystals. The grown crystal has been subjected to X-ray diffraction for structural analysis. Using Energy Dispersive X-ray Spectroscopy, presence of element with weight percentage has been calculated. Nonlinear optic measurement has been used to find the SHG efficiency. Increase in KDP crystal thermal stability by an organic additive of neem leaves extract has been determined by Thermo-Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA). The conductivity and capacitance of KDP crystal and neem leaves extract doped KDP has been analyzed. Using Vicker's micro hardness test the mechanical property of KDP crystal and neem leaves extract doped KDP has been studied.

Keywords: KDP-Potassium Dihydrogen Phosphate, slow evaporation technique, organic impurity, NLO.

I. INTRODUCTION

KDP crystal has aroused considerable interest amongst several research workers because of its wide frequency conversion, high efficiency of frequency conversion, good UV transmission, high damage threshold against high power laser and high birefringence, though its NLO coefficients are relatively low. It is more fashionable to all [1-2]. Neem is a natural antibiotic, which kill or stop the growth of microorganisms including both bacteria and fungi. With advances in medical chemistry, most of today's antibacterial is chemically semi synthetic modifications of various natural compounds [3-4]. In the present study the organic neem leaves extract has been doped with KDP in 1 % ratio and grown by slow evaporation aqueous solution growth technique.

The grown pure KDP and neem leaves extract doped KDP crystal has been subjected Fourier Transform Infrared Spectroscopy (FTIR), UV Spectroscopy, Photoluminescence Spectroscopy, X-ray Diffraction (XRD), Energy Dispersive X-ray Spectroscopy (EDX), Nonlinear optic measurement, Thermo gravimetric and differential thermal analysis (TA/DSC), Dielectric test, Vicker's micro hardness test.

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II. EXPERIMENTAL PROCEDURE AND CHARACTERISATION

Potassium Dihydrogen Phosphate (KDP) is a well known inorganic salt, which has been purified by repeated recrystallization using the method of dissolving in distilled water. Then the solution of KDP salts have been prepared in a slightly under saturation condition by stirring well for five hours constantly using magnetic stirrer, till the salts have been dissolved in water. Then the prepared solution has been transferred into two clean Petri dishes and kept for crystallization at room temperature in a quiet place. Within four days the nucleation takes place and a seed crystal in Petri dish has been obtained [5-6].

A supersaturated solution of pure KDP and 1% of neem leaves extract doped KDP at room temperature has been prepared by same processes and then filtered into 1 lit beaker. The good quality seed has been suspended in respective beakers with the help of nylon thread. A slow evaporation method has been employed to grow KDP and neem leaves extract doped crystal [7]. After completion of growth run, the crystals have been harvested and subjected to various characterization viz. Fourier Transform Infrared Spectroscopy (FTIR), UV Spectroscopy, Photoluminescence Spectroscopy, X-ray Diffraction (XRD), Energy Dispersive X-ray Spectroscopy (EDX), Nonlinear optic measurement, Thermo gravimetric and differential thermal analysis (TA/DSC), Dielectric test, Vicker's micro hardness test and the corresponding results have been compared with pure KDP crystal.

III. RESULTS AND DISCUSSION

A. Fourier transforms infrared

The qualitative aspects of infrared spectroscopy are one of the most powerful attributes of this diverse and versatile analytical technique. The Fourier Transform Infrared Analysis has been carried out between 4000 - 400cm^{-1} by recording the spectrum using KBr pellet technique. The incorporation of neem leaves extract in KDP crystal has been strongly verified by spectral analysis. The FTIR spectrum for transmittance % has been shown in figure 1and 2.

The complexity of infrared spectra in 1450 to 600 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 to 1450 cm^{-1} region are usually due to stretching vibrations of diatomic units, and this is sometimes called the group frequency region.

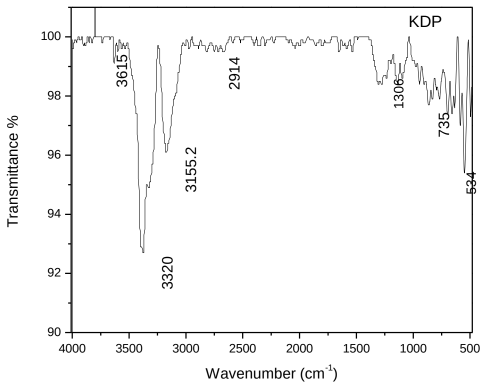

Figure 1 shows the transmittance % peak of pure KDP crystal

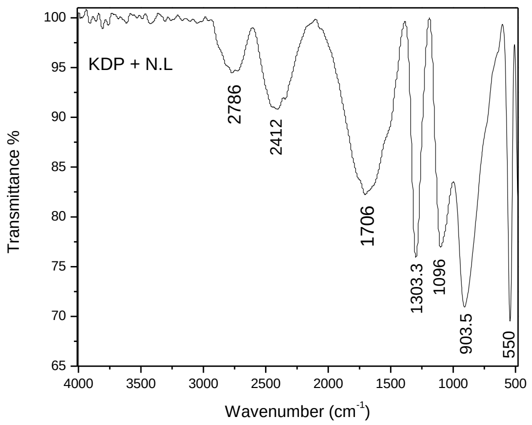

Figure 2 shows the transmittance % peak of neem leaves extract doped KDP crystal

O-H stretching due to water of crystallization arises at frequencies of 3615 cm^{-1}, 3320 cm^{-1} and at 3155 cm^{-1} in Potassium Dihydrogen Phosphate (KDP) crystal. P-O-H stretching of H_2PO_4 arises at 2914 cm^{-1} in KDP spectrum. Whereas in neem leaves extract doped KDP the bond arise at frequency of 2786 cm^{-1}. At 2329 cm^{-1} and 2412 cm^{-1} P-O-H bending occurs in KDP and neem leaves extract doped KDP crystal. At frequency of 1706 cm^{-1} carboxylic acid bond arise in neem leaves extract doped KDP crystal, where C-O, C-O-H, O-H are highly characteristics.

At a frequency of 1306 cm^{-1} and 1303 cm^{-1} P=O stretching occurs in KDP and neem leaves extract doped KDP respectively. P-O stretching arises at a frequency of 1096 cm^{-1} in neem leaves extract doped KDP. And at 903 cm^{-1}, P-O-H stretching arises in neem leaves extract doped KDP crystal. C-C deformation bond arises at 550 cm^{-1} in neem leaves extract doped KDP crystal. HO-P-OH bending compound frequency arises at 531 cm^{-1} in KDP crystal [8-9]. Table 1 shows the functional group assignments for KDP and neem leaves extract doped KDP frequency.

Frequency (cm^{-1})		Functional group assignments
KDP	Neem leaves extract doped KDP	
3615	-	O-H stretching hydrogen bonded
3320	-	O-H stretching
3155	-	O-H stretching
2914	2786	P-O-H stretching
2329	2412	P-O-H bending
-	1706	Carboxylic acid
1306	1303	P=O stretching
-	1096	P-O stretching
-	903	P-O-H stretching
-	550	C-C deformation
531	-	HO-P-OH bending

B. X-ray Diffraction (XRD)

The powder X-ray Diffractometer analysis (XPERT-PRO) has been carried out for the rapid identification and quantification of grown crystal at 2 theta position of 10° to 80°. The obtained results have been shown in figure 3 and 4.

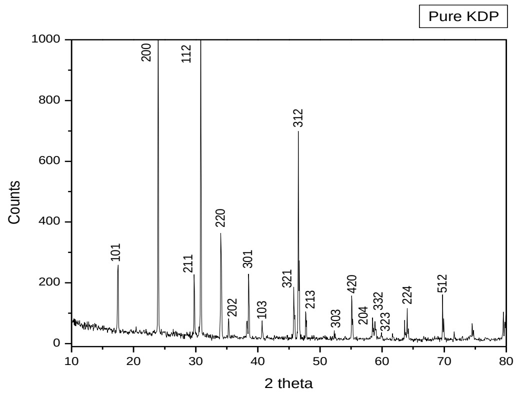

Figure 3 shows the powder XRD pattern of pure KDP crystal

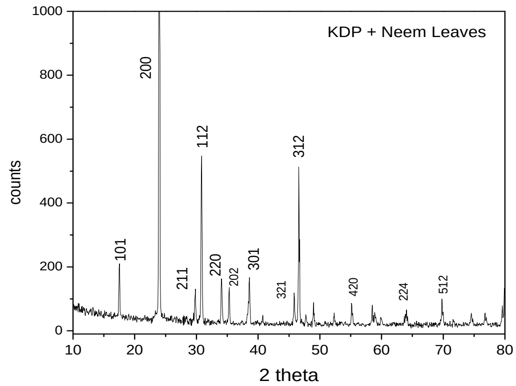

Figure 4 shows the powder XRD pattern of neem leaves extract doped KDP

The hkl plane values have been determined by JCPDS file. At maximum intensity the various structure parameters like the crystalline size, micro strain and dislocation density has been calculated by Debye – Scherer's formula and tabulated below [10-11].

Table 2 shows the calculated structural parameters of KDP crystal, neem leaves extract doped KDP crystal.

Sample	Crystalline size (nm)	Micro strain ($\times 10^{-3} lines^{-2}/m^{4}$)	Dislocation density ($\times 10^{14}$ lines/m^2)

KDP	119.80	0.29	6.97
KDP + N.L	67.94	0.51	2.16

The crystalline size of KDP crystal has been reduced by an organic additive of neem leaves extract. This executes that the additive is perfectly incorporated into the KDP crystal lattice.

C. Energy Dispersive X-ray

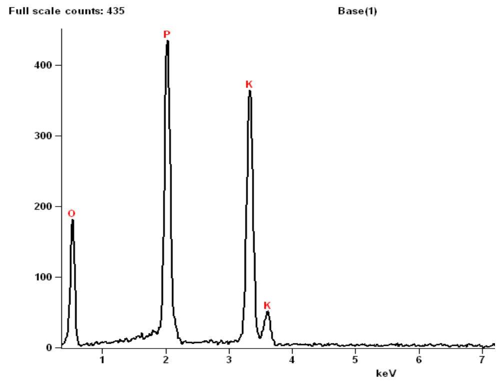

Figure 5 shows the EDX spectrum of pure KDP crystal

Figure 5 shows the Energy Dispersive X-ray spectrum analysis of pure KDP crystal. From EDX spectrum the chemical composition weight has been calculated. The estimated % of K, P, and O in pure KDP crystal is show in table 3.

Table 3 shows the estimated weight % of neem leaves extract doped KDP crystal.

Element	Weight %	Atom %
O	57.29	74.54
P	19.52	13.12
K	23.19	12.34
Total	100.00	100.00

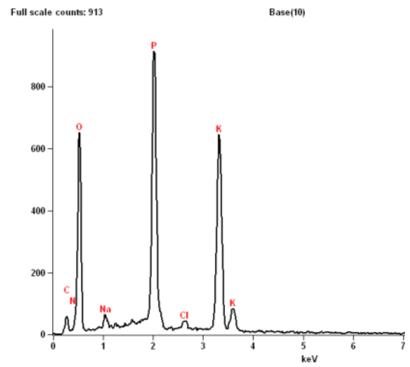

Figure 6 shows the EDX spectrum of neem leaves extract doped KDP crystal

Table 4 shows the estimated weight % of neem leaves extract doped KDP crystal.

Element	Weight %	Atom %
C	15.35	23.59
N	1.15	1.52
O	48.83	56.34
Na	0.84	0.67
P	15.08	8.99
Cl	0.66	0.34
K	18.10	8.55
Total	100.00	100.00

Figure 6 shows Energy Dispersive X-ray spectrum analysis of neem leaves extract doped KDP crystal. The chemical composition weight percentage has been determined from EDX spectrum. The estimated % of C, N, O, Na, P, Cl, and K in organic additive neem leaves extract doped with KDP crystal is shown in table 4.

D. Simple Harmonic Generation

The NLO property of grown KDP crystal and neem leaves extract doped KDP crystals have been confirmed by Kurtz – Perry Powder technique. A Q-switched Nd:YAG laser emitting a fundamental wavelength of 1064nm with a pulse rate of 0.62ns was allowed to strike the sample cell [12-13]. The SHG was confirmed by the green emission of wavelength 532 nm from the samples. The output energy for pure KDP & neem leaves extract doped KDP was measured to be 8.5 mJ & 22.12 mJ respectively and its histogram graph has been shown in figure 7. The addition of organic impurity increases the SHG efficiency nearly 3 times greater than KDP crystal efficiency.

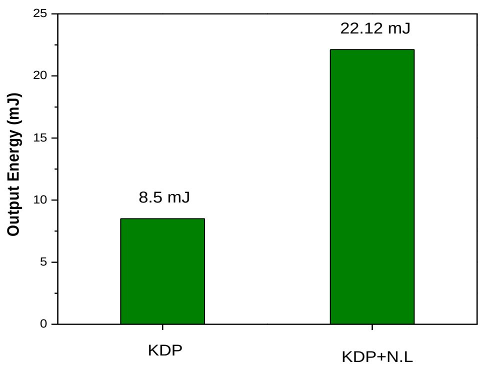

Figure 7 shows the histogram graph of output energy for KDP and neem leaves extract doped KDP crystals

E. DSC – TGA analysis

Differential thermal analysis & Thermogravimetric analysis has been carried out simultaneously between the temperature ranges of 20˚C to 500˚C at a heating rate of 20˚C per minute in nitrogen atmosphere. TA Instrument SDT Q600 and DSC Q20 used to determine the thermal stability of grown crystal. The thermal stability graph of grown KDP crystal and neem leaves extract doped KDP crystal has been shown in figure 8 and 9.

The TGA trace shows the different stages of decomposition. There is no loss of weight observed around 100˚C showing the absence of any absorbed water molecules in the sample. In pure KDP crystal the decomposition starts at 215.86˚C, 253.18˚C and at about 296.77˚C, the weight is reduced to about 3.603 %, 3.54 % & 5.55% respectively it appears to be the major stage of decomposition.

The DSC spectrum reveals that the sharp endothermic peaks at 227ºC due to the melting of the crystal. The sharpness of the endothermic peak shows the good degree of crystallinity of the grown sample [14-15]. The major decomposition occurs between 227ºC and 363ºC with a large weight loss, due to the release of volatile substances in the compound. This weight loss associated with a sharp endothermic peak in DSC trace at 265°C is attributed to the absorption of energy for breaking of bonds during the decomposition of the compound.

In neem leaves extract doped KDP crystal the decomposition starts at 220˚C, 259˚C and at about 307˚C the weight is reduced to about 3.1%, 3.2 % & 3.8% respectively it appears to be the major stage of decomposition.

The DSC spectrum reveals that the endothermic peaks at 234ºC due to the melting of the crystal. The major decomposition occurs between 220ºC and 307ºC with a large weight loss, due to the release of volatile substances in the compound. This weight loss associated with a sharp endothermic peak in DSC trace at 270°C is attributed to the absorption of energy for breaking of bonds during the decomposition of the compound. From these studies, it is concluded that the neem leaves extract doped KDP crystal can retain its texture and the crystal application is restricted up to 234ºC.

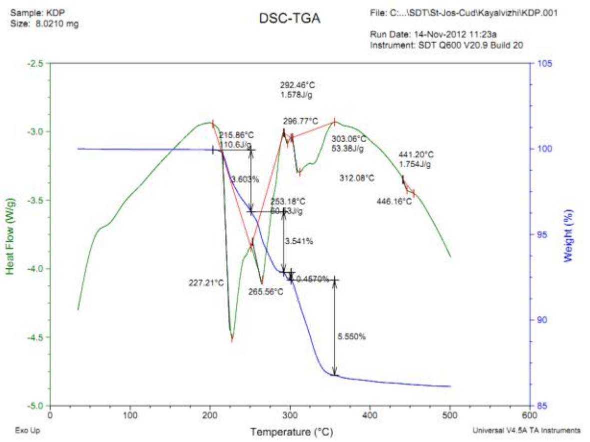

Figure 8 shows the DSC – TGA curves analysis of KDP crystal

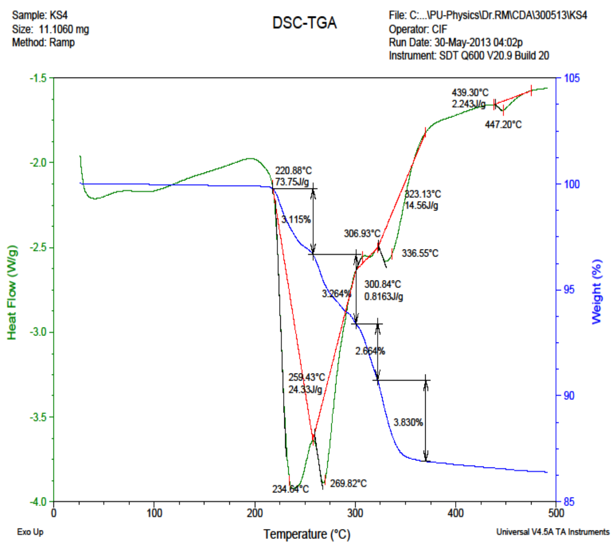

Figure 9 shows the DSC – TGA curves analysis of neem leaves extract doped KDP crystal

F. Electrical studies

The dielectric studies have been carried out to find conductivity & capacitance of grown KDP crystal and neem leaves extract doped KDP crystal. The figure 10 and 11 shows the capacitance & conductivity graph of pure KDP and neem leaves extract doped grown KDP crystal at different frequency. Pure KDP crystal has low capacitance and conductivity range than the neem leaves extract doped KDP crystal. Neem leaves extract additives with KDP increase its dielectric properties than in pure KDP crystal.

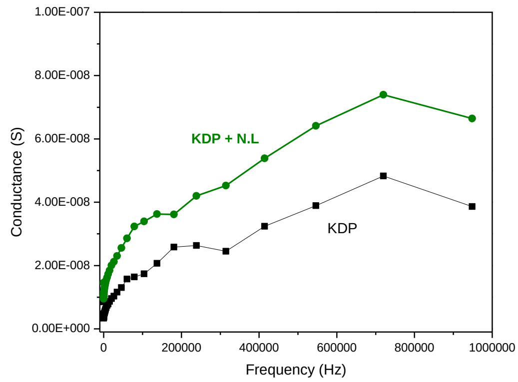

Figure 10 shows the capacitance and conductivity of KDP crystal

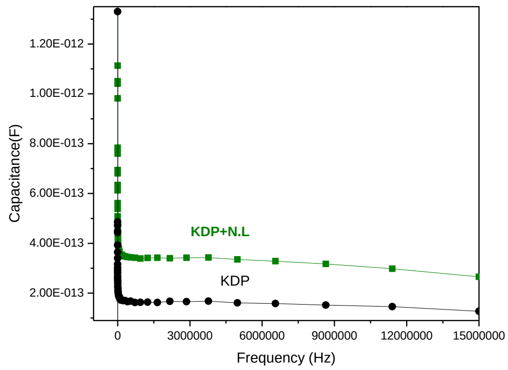

Figure 11 shows the capacitance and conductivity of neem leaves extract doped KDP crystal

G. Vickers Microhardness

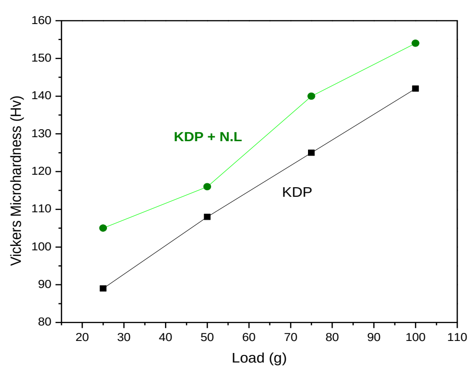

Figure 12 shows the microhardness graph of KDP and neem leaves extract doped KDP crystals

The mechanical property of the grown KDP and neem leaves extract doped KDP crystal has been determined by Vickers Micro hardness test with a diamond indenter at various loads from 25g to 100g. The static indentation has been made on the surface of the crystal and the size of the impression is measured with the aid of a calibrated microscope.

The Vickers Microhardness has been calculated using the formula $Hv=1.854(F/D^2)$ Kg/mm^2. Load Vs Hardness number for KDP and neem leaves extract doped KDP crystals shown in figure 12. While comparing the neem leaves extract doped KDP crystal with pure KDP, the hardness is high.

At 100g the hardness number of KDP and organic impurity doped KDP crystals is 142Hv and 154Hv respectively. The additive is perfectly located in the KDP crystal lattice and increases the mechanical property.

IV. CONCLUSION

Single inorganic grown KDP crystal and organic impurity neem leaves extract doped KDP crystal has been investigated through Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Energy Dispersive X-ray Spectroscopy (EDX), Nonlinear optic measurement, Thermo gravimetric and differential thermal analysis (TA/DSC), Dielectric test and Vicker's micro hardness test has been studied.

Fourier Transform Infrared Spectroscopy (FTIR) confirms the presence of organic additive neem leaves extract in potassium dihydrogen phosphate (KDP). The X-ray diffraction analysis determines the incorporation of neem leaves extract into KDP crystal lattice. The presence of chemical composition has been identified by Energy Dispersive X-ray Spectroscopy and its weight percentage has been calculated for pure KDP and doped KDP crystal. The SHG efficiency has been increased three times in neem leaves extract doped KDP crystal. The addition of organic impurity increased the thermal stability of KDP crystal. The electrical and mechanical property has been increased in addition of neem leaves extract in KDP crystal. This indicates that the organic impurity neem leaves extract incorporated into KDP crystal lattice and enhances its basic properties.

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