Effect of Indian Gooseberry doping on Potassium Dihydrogen Phosphate Crystals (KDP)

Usha Rani Pisipaty, S. Balaji

Abstract— Potassium dihydrogen phosphate (KDP) crystal is an interesting non linear optical inorganic material. In this present work, KDP crystal and Indian Gooseberry 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 have 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 Indian Gooseberry extract has been determined by Thermo-Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA). Using Vicker's micro hardness test the mechanical property of KDP crystal and Indian Gooseberry 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 useful to all [1-2]. *Phyllanthus emblica*, also known as emblica ,emblic myrobalan, myrobalan, Indian gooseberry, Malacca tree or amla from Sanskrit *amalaki* is a deciduous tree of the family Phyllanthaceae. It is known for its edible fruit of the same name.

Amla, the Indian Gooseberry belongs to the Euphorbiaceae family. The fruit is very nourishing, but it tastes sour. Both dried and fresh fruits can be consumed for their health benefits. It provides remedies for many diseases.

In the present study KDP has been doped with Indian Gooseberry doped extract in 1 % ratio and grown by slow evaporation aqueous solution growth technique. The grown pure KDP and Indian Gooseberry extract doped KDP crystal has been subjected to 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/DTA), Vicker's microhardness Test. Dopant is added to occupy the interstitial positions in the lattice and in turn this may lead to distinctive changes in the physical properties[3].

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Inspite of having all good factors, the organic crystals could not been employed satisfactorily in devices because of their poor mechanical and thermal stability [4]. So, semi organic crystals having the properties of both inorganic and organic species, are expected to have good optical, thermal and mechanical properties.

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. Within four days the nucleation takes place and a seed crystal in Petri dish has been obtained [5-6]. To obtain Indian Gooseberry extract doped crystal, Gooseberry extract was added to saturated solution. Highly Transparent and full faced crystals were obtained within three weeks. After completion of growth , 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 (TGA/DTA), 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 Indian Gooseberry extract in KDP crystal has been strongly verified by spectral analysis. The FTIR spectrum for transmittance % has been shown in figure 1and 2. The FTIR analysis provides information about the chemical bonding or molecular structure of materials. O-H stretching due to water of crystallization arises at frequencies of 3440 cm-1 in Potassium Dihydrogen Phosphate (KDP) crystal. P-O-H stretching of H2PO4 arises at 2719 cm-1& 2458 cm-1 in KDP spectrum. Whereas in Indian Gooseberry extract doped KDP the bond arise at frequency of 2721cm-1 & at 2441cm-1. At frequency of 1655 cm-1carboxylic acid bond arise in Indian Gooseberry extract doped KDP crystal, where C-O, C-O-H, O-H are highly characteristics.

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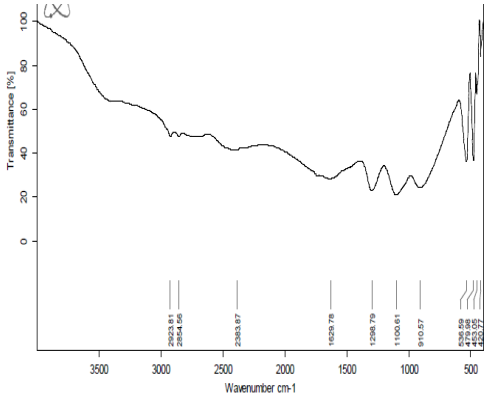

Figure 1 - Transmittance % peak of pure KDP crystal

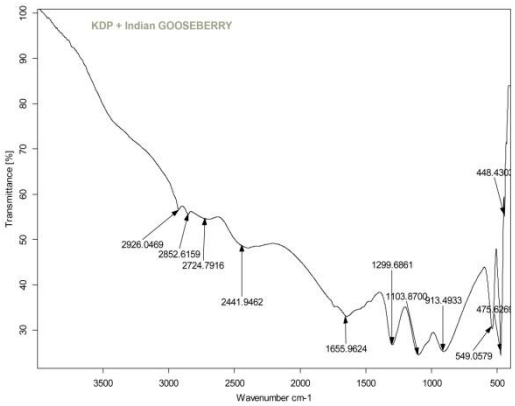

Figure 2 - Transmittance % peak of Indian Gooseberry extract doped KDP crystal

At a frequency of 1103 cm-1 P-O-H stretching occurs in KDP and Indian Gooseberry extract doped KDP [7-8]. N-H stretching arises at a frequency of 920 cm-1 &913 cm-1 in KDP and in Gooseberry extract doped KDP respectively. Table 1 shows the functional group assignments for KDP and Indian Gooseberry extract doped KDP frequency.

Table 1 - Functional group assignments for KDP and Indian Gooseberry extract doped KDP frequency

Frequency (cm-1)		Functional group assignments
KDP	Indian Gooseberry doped KDP	
3440	-	O-H streching
2719	2721	P-O-H Symmetric Streching
2458	2441	P-O-H streching
1761	------	NH_3^+ anti symmetric bending
1623	1655	C=C stretching
1103	1103	P-O-H stretching of KDP
920	913	N-H stretching
538	544	PO_4^{3-} bending
483	475	N-H Torsional
446	448	N-HTorsional
421	-	N-H Torsional

B. X-ray Diffraction (XRD)

Powder X-ray diffraction analysis

Powder X-ray diffraction analysis was performed to confirm the quality of crystals and to indentify the cell dimensions using bruker A X3D8 PERT–PRO advance model powder diffractometer with cuKα radiations(I=1-5405984).It is also used to confirm the physical phase of crystal. X-ray diffraction study is used to identify the reflection planes. The XRD pattern of KDP & Indian Gooseberry extract doped KDP is shown in figure 3 & 4. The crystalline size of KDP crystal has been reduced by an organic additive of Indian Gooseberry extract. This executes that the additive is perfectly incorporated into the KDP crystal lattice.

The sharp and specific Bragg angle confirms the crystalline nature of the pure and Indian Gooseberry doped KDP. It is interesting to note the there is a small shift in 2θ position and change in intensity, which is clearly shown in the XRD spectrum. This indicates the entering of the impurity molecules into the KDP lattice, resulting in a change in the internal structure of the crystal (bond length).

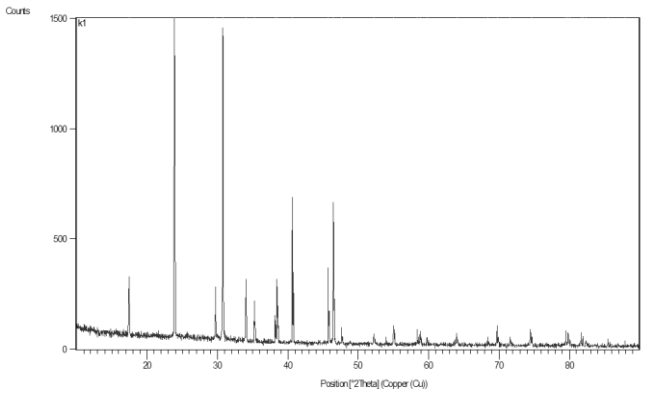

Figure 3 - Powder XRD pattern of pure KDP crystal

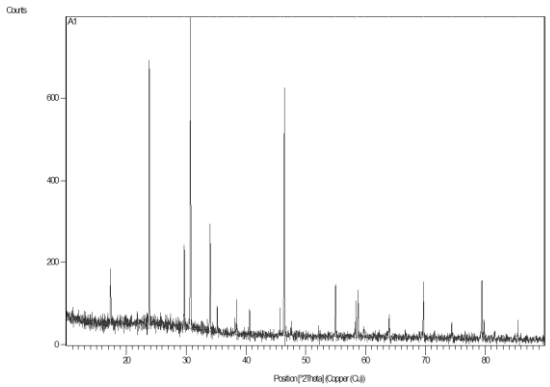

Figure 4 - Powder XRD pattern of Indian Gooseberry extract doped KDP

Single crystal X-rd studies

Single crystal X-ray diffraction data were recorded using MACH 3 Nonius CAD-4. X-ray diffractometer with CuKα radiation. (I = 1.540598Å) for the grown crystals. It is confirmed from that study that pure and Indian Gooseberry doped KDP crystals are Tetragonal in structure.

The calculated lattice parameters for Indian Gooseberry doped extract are a=b=7.473A^o and c=6.391A^{o}and α =β =γ =90^o

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Table 2 - Lattice Parameter Values for Pure and Indian Gooseberry Doped KDP Crystals

S No	Sample	Lattice parameter		α =β =γ	Cell volumes V(A°)	Structure
		a=b(A°)	c(A°)			
1	Pure KDP	7.448	6.965	90°	316	Tetragonal
2	KDP + Indian Gooseberry	7.473	6.391	90°	300.4	Tetragonal

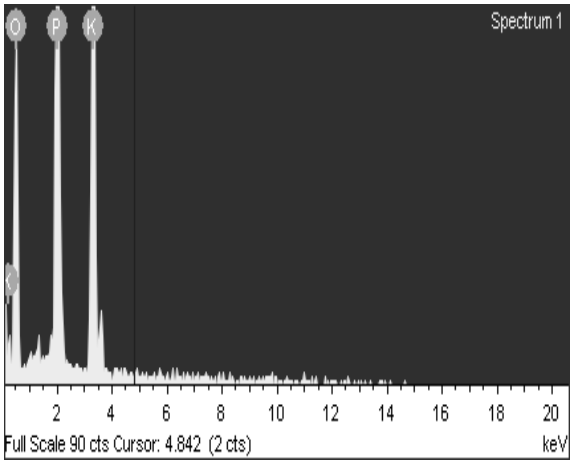

Figure 5 shows the EDX spectrum of pure KDP crystal

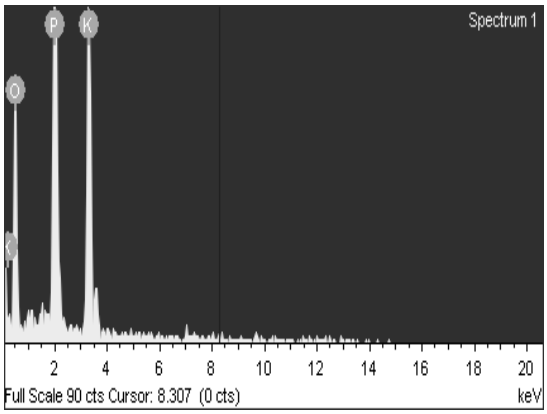

Figure 6 - EDX spectrum of Indian Gooseberry extract doped KDP

Table 3 - Estimated % of K, P, and O in pure KDP crystal

Sl.No.	Sample Code / Name of the Sample	Output Energy (milli joule)	Input Energy (joule)
1	Pure KDP	10.8	0.70
2	Indian Gooseberry doped KDP	12.2	0.70
3	KDP(Reference)	8.94	0.70

C. Energy Dispersive X-ray

The chemical composition weight percentage has been determined from EDX spectrum. EDX is an important tool for characterizing the elements present in crystal. In the present study the grown crystals were analyzed by FEI QUANTA 200F energy dispersive X-ray analyzer. The estimated percentages of K,P and O in pure KDP are reported in Table 3. 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 doped KDP crystal is shown in table 4.

Table 4 - Estimated % of Indian Gooseberry extract doped KDP

Element	Weight%	Atomic%
O	48.66	67.43
P	23.32	16.69
K	28.01	15.88
Total	100.00	100.00

D. Simple Harmonic Generation

The NLO property of grown KDP crystal and Indian Gooseberry 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 [9-10]. The SHG was confirmed by the green emission of wavelength 532 nm from the samples. The output energy for pure KDP & Indian Gooseberry extract doped KDP was measured to be 10.8 mJ & 12.2 mJ respectively. The addition of organic impurity increases the SHG efficiency of Indian Gooseberry doped KDP than KDP crystal efficiency.

Table 5 - SHG efficiency of pure KDP & Indian Gooseberry doped KDP

Sl.No.	Sample Code / Name of the Sample	Output Energy (milli joule)	Input Energy (joule)
1	Pure KDP	10.8	0.70
2	Indian Gooseberry doped KDP	12.2	0.70
3	KDP(Reference)	8.94	0.70

E. DTA – 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 argon atmosphere. Thermal studies have been recorded on Perkin Elmer Dimmer.

The TGA curve shows the different stages of decomposition.

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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 DTA spectrum reveals that the sharp endothermic peaks at 190.56 due to the melting of the crystal. The sharpness of the endothermic peak shows the good degree of crystallinity of the grown sample [11-12]. The major decomposition occurs between 161.44ºC and 237.56ºC 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 DTA trace at 237.56°C is attributed to the absorption of energy for breaking of bonds during the decomposition of the compound.

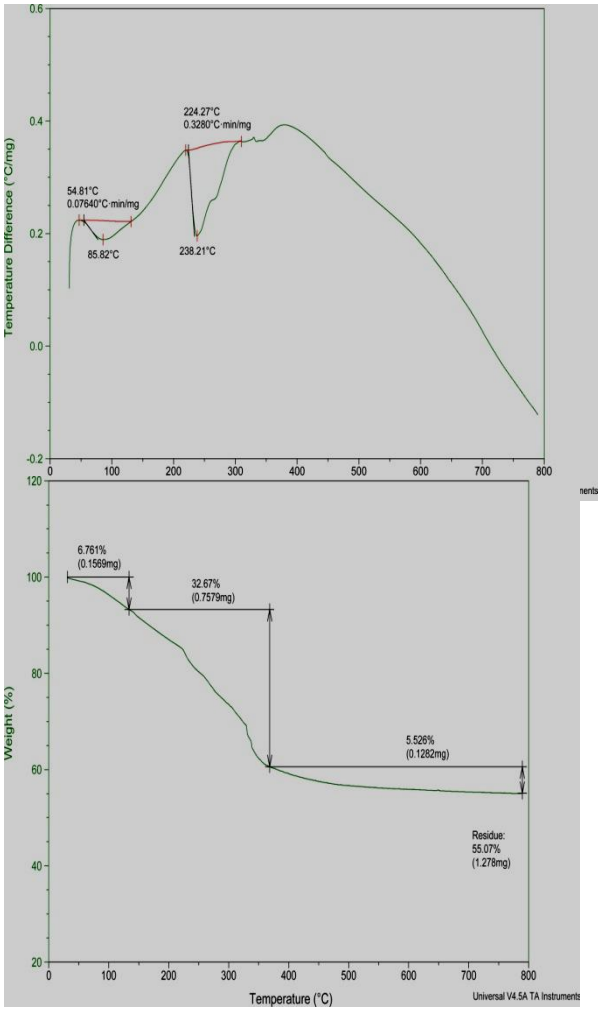

Figure 7 - DTA – TGA curves analysis of KDP crystal

In Indian Gooseberry 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 DTA 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 DTA trace at 238°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 Indian Gooseberry doped KDP crystal can retain its texture and the crystal application is restricted up to 234ºC.

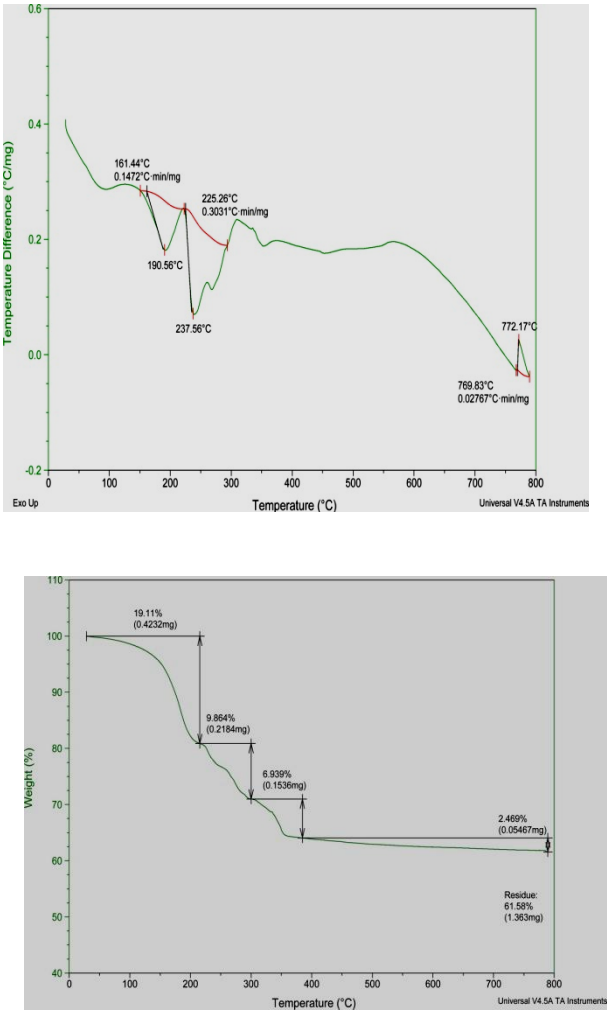

Figure 8 - DTA – TGA curves analysis of Indian Gooseberry doped KDP crystals

F. Vickers Microhardness

The mechanical property of the grown KDP and Indian Gooseberry extract doped KDP crystal has been determined by Vickers Micro hardness test with a diamond indenter at various loads from 25 Kg to 100 Kg.. 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 $H_v=1.854(F/D^2)$ Kg/mm^2. Load Vs Hardness number for KDP and Indian Gooseberry extract doped KDP crystals shown in figure 9.

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While comparing the Indian Gooseberry extract doped KDP crystal with pure KDP, the hardness is high. At 100 Kg the hardness number of KDP and organic impurity doped KDP crystals is $63.5H_v$ and $84.8H_v$ respectively. The additive is perfectly located in the KDP crystal lattice and increases the mechanical property.

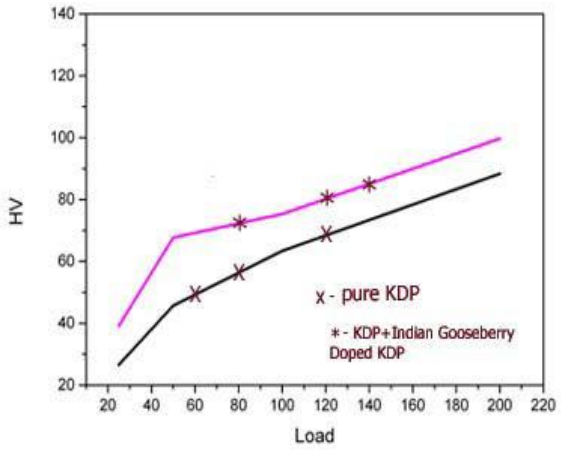

Figure 9 - Microhardness H_v Vs load of pure KDP & Indian Gooseberry doped KDP

Table 6 - Microhardness values of pure KDP & Indian Gooseberry doped KDP

Sample	25Kg	50Kg	100Kg	200Kg
KDP	28.1	45.2	63.5	89.9
KDP + Indian Gooseberry	52.2	60.9	84.8	115

IV. CONCLUSION

Optically good quality crystals of pure KDP and Indian Gooseberry extract doped KDP crystals have been grown by slow evaporation method. Powder X-ray diffraction analysis confirms the crystalline nature of grown crystal. The FTIR spectral analysis confirms the presence of functional groups in the crystals. The SHG test proves the grown crystals are potential candidates for nonlinear applications. The high optical Transparency and SHG prove the optical quality and suitability of the grown KDP with Indian Gooseberry extract doped for optoelectronic device applications. In addition the Mechanical Property has increased by the addition of dopant to KDP.

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