Growth And Characterisation Of Pure And Methyl Violet Dye Doped Potassium Dihydrogen Phosphate (KDP) Crystal

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Abstract: An inorganic single crystal Potassium Dihydrogen Phosphate (KDP) and an additive of organic methyl violet dye doped KDP crystal has been grown by slow evaporation solution growth technique. In order to characterize the changes in KDP behavior due to an organic additive - spectral analysis has been carried out to confirm the functional groups in the crystals by Fourier Transform Infrared Spectroscopy. The grown crystal has been subjected to X-ray diffraction analysis for structural analysis. Presence of element with weight percentage has been identified and calculated by Energy Dispersive X-ray Spectroscopy. Nonlinear optic measurement has been used to find the SHG efficiency. Thermo gravimetric and differential thermal analysis helps to find the thermal stability of the grown crystal. To determine the electrical property, the grown crystal has been subjected to conductivity and capacitance analysis. And the mechanical property has been determined by Vicker's micro hardness test.

Keyword: KDP-Potassium Dihydrogen Phosphate, slow evaporation technique, methyl violet dye, NLO.

INTRODUCTION

Present day advanced technologies heavily relay on one particular class of matter, i.e. the crystals. Crystals are the unacknowledged pillars of modern technology and has prominent role to play in the era with immense technological excellence attributing to the usefulness of many crystals in important areas of service to the humanity namely science, medicine, engineering, technology, strategic areas of defense and space science. Without crystals, there would be no electronic industry, no photonic industry, no fiber optic communications, which depend on crystals such as semiconductors, superconductors, polarizer, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries [1-3].

Methyl violet is a pH indicator. Depending on the amount of attached methyl groups, the color of dye can be altered [4-5]. In the present investigation the organic additive of methyl violet dye has been doped with KDP in 0.1 % ratio by molecular calculation and grown by slow evaporation technique. The grown pure KDP and methyl violet dye doped KDP crystal has been subjected to various characterizations to analysis its spectral, structural, chemical, NLO, thermal, electrical and mechanical properties [6-7].

EXPERIMENTAL PROCEDURE

The inorganic potassium dihydrogen phosphate (KDP) salts have 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. A supersaturated solution of pure KDP and 0.1% of methyl violet dye doped KDP at room temperature has been prepared by same processes and then filtered into 1 lit beakers. 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 methyl violet dye doped crystal. After completion of growth run, the crystals have been harvested and subjected to various characterization viz. Fourier Transform Infrared Spectroscopy (FTIR), UV Spectroscopy, Photolumine scence 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.

RESULTS AND DISCUSSION

Fourier transforms infrared

A non-destructive technique of FTIR spectrometer has been made for pure KDP and methyl violet dye doped KDP crystal for around 3mg of sample mixed with KBr powder in the range of 4000 - 400cm-1. The incorporation of methyl violet dye in KDP crystal has been strongly verified by spectral analysis. The FTIR spectrum for transmittance % has been shown in figure 1 and 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.

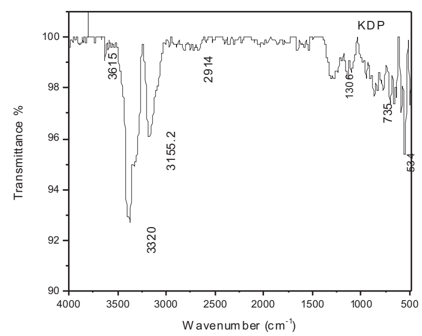

Figure 1 shows the transmittance % peak of pure KDP crystal

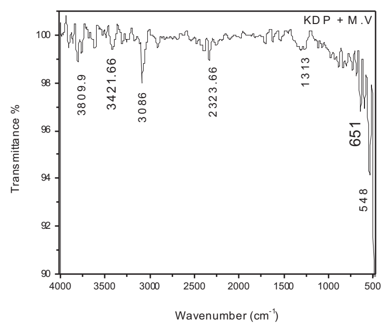

Figure 2 shows the transmittance % peak of methyl violet dye doped KDP crystal

Table 1 shows the functional group assignments for KDP and methyl violet dye doped KDP frequency.

Frequency (cm^{-1})		Functional group assignments
KDP	Methyl violet dye doped KDP	
-	3809	Free O-H stretching
3615	3620	O-H stretching
-	3421	O-H stretching hydrogen bonded
3320	3325	O-H stretching
3155	-	O-H stretching
-	3086	NH stretching
2914	2911	P-O-H stretching
2329	2323	P-O-H bending
1306	1313	P=O stretching
-	651	CH_2 Rocking
531	548	HO-P-OH bending

O-H stretching due to water of crystallization arises at frequencies of 3809 cm^{-1} 3615 cm-1, 3620 cm^{-1}, 3421 cm^{-1}, 3320 cm^{-1}, 3325 cm^{-1} and at 3155 cm^{-1} in KDP and methyl violet dye doped KDP crystal spectrum respectively.

NH stretching bond arise at 3086 cm^{-1} in methyl violet dye doped KDP crystal. P-O-H stretching and bending arise at 2914 cm^{-1} and 2329 cm^{-1} in KDP spectrum. Whereas in methyl violet dye doped KDP the bond arise at frequency of 2911 cm^{-1} and at 2323 cm^{-1}.

At a frequency of 1306 cm^{-1} and 1313 cm^{-1} P=O stretching occurs in KDP and methyl violet dye doped KDP respectively. CH_2 rocking peaks arise in methyl violet dye doped KDP crystal at a frequency of 651 cm-1. HO-P-OH bending compound frequency arises at 531 cm-1 and at 548cm-1 in both KDP and methyl violet dye doped KDP crystals [8].

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.

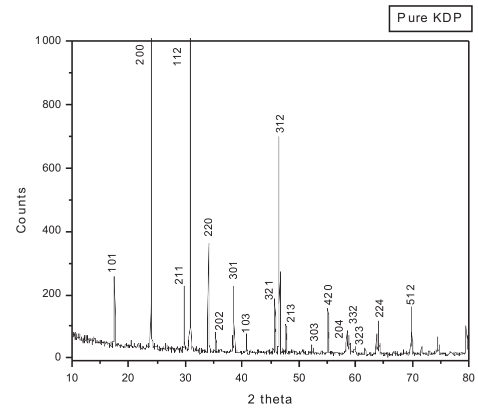

Figure 3 shows the powder XRD pattern of pure KDP crystal

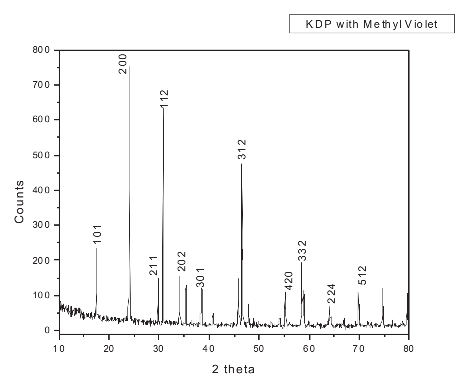

Figure 4 shows the powder XRD pattern of methyl violet doped KDP

The hkl planes 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 [9-10].

Table 2 shows the calculated structural parameters of KDP crystal, methyl violet dye doped KDP crystal.

Sample	2θ value (deg)	d- spacing (A°)	FWHM (deg)	Crystalline size (nm)	Micro strain ($\times 10^{-3}$lines^{-2}/m^4)	Dislocation density ($\times 10^{14}$ lines/m^2)
KDP	30.79	2.90	0.07	119.80	0.29	6.97
KDP+M.V	24.00	3.704	0.09	88.66	0.39	1.27

The crystalline size of KDP crystal has been reduced by an organic additive of methyl violet dye. This executes that the additive is perfectly incorporated into the KDP crystal lattice.

Energy Dispersive X-ray

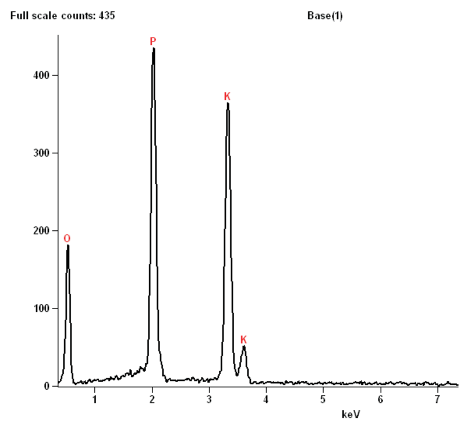

Figure 5 shows the EDX spectrum of pure KDP crystal

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 methyl violet dye 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

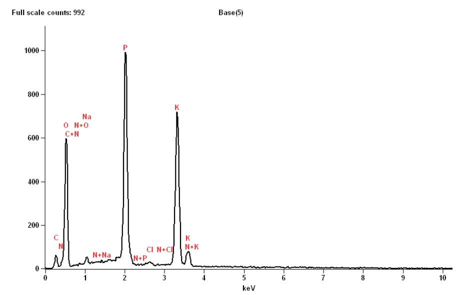

Figure 6 shows the EDX spectrum of methyl violet dye doped KDP crystal

Table 4 shows the estimated weight % of methyl violet dye doped KDP crystal.

Element	Weight %	Atom %
C	15.22	23.65
N	0.78	1.03
O	47.81	55.76
Na	0.80	0.65
P	15.97	9.62
Cl	0.34	0.18
K	19.09	9.11
Total	100.00	100.00

Figure 6 shows Energy Dispersive X-ray spectrum analysis of methyl violet dye 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 methyl violet dye doped with KDP crystal is shown in table 4.

Simple Harmonic Generation

The NLO property of grown KDP crystal and methyl violet dye 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 [11-12]. The SHG was confirmed by the green emission of wavelength 532 nm from the samples. The output energy for pure KDP & methyl violet doped KDP was measured to be

8.5 mJ & 23.45 mJ respectively and its histogram graph has been shown in figure 7. The addition of organic impurity increases the SHG efficiency 3 times greater than KDP crystal efficiency.

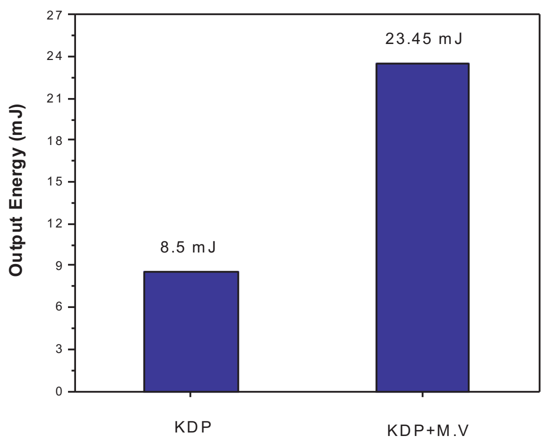

Figure 7 shows the histogram graph of output energy for KDP and methyl violet dye doped KDP crystals

DSC – TGA analysis

Differential thermal analysis & Thermogravimetric analysis has been carried out simultaneously between the temperature ranges of 20℃ to 500℃ at a heating rate of 20℃ 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 methyl violet 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℃ showing the absence of any absorbed water molecules in the sample. In pure KDP crystal the decomposition starts at 215.86℃, 253.18℃ and at about 296.77℃, 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 [13-14]. 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 methyl violet dye doped KDP crystal the decomposition starts at 222℃, 257℃ and at about 309℃ the weight is reduced to about 3%, 2.3 % & 5.4% respectively it appears to be the major stage of decomposition.

The DSC spectrum reveals that the endothermic peaks at 232ºC due to the melting of the crystal. The major decomposition occurs between 222ºC and 309ºC 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 266°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 methyl violet dye doped KDP crystal can retain its texture and the crystal application is restricted up to 232ºC.

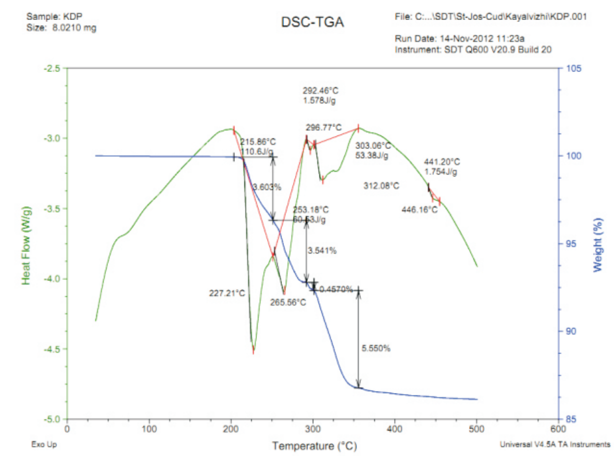

Figure 8 shows the DSC – TGA curves analysis of KDP crystal

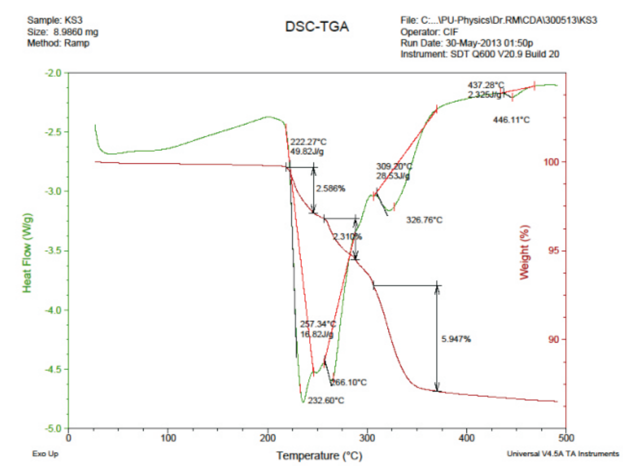

Figure 9 shows the DSC – TGA curves analysis of methyl violet dye doped KDP crystal

Electrical studies

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

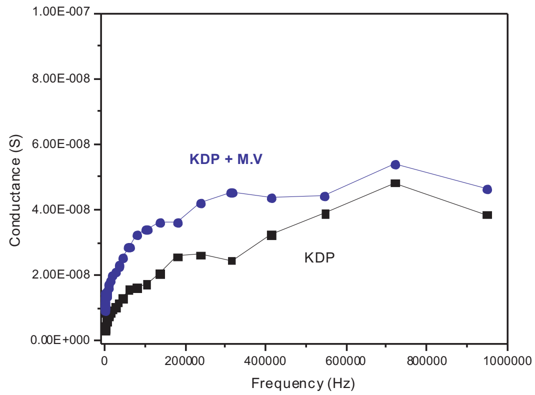

Figure 10 shows the capacitance and conductivity of KDP crystal

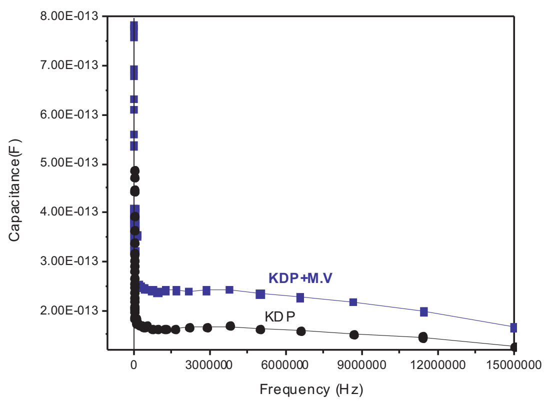

Figure 11 shows the capacitance and conductivity of methyl violet dye doped KDP crystal

Vickers Microhardness

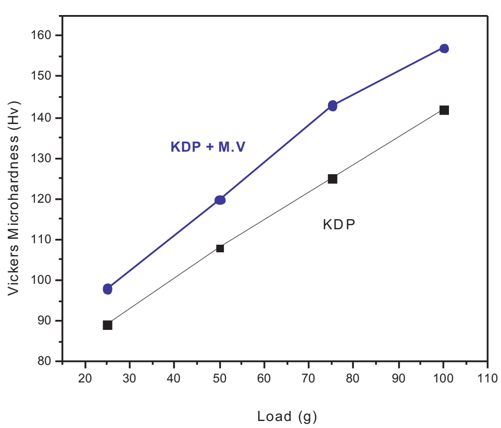

Figure 12 shows the microhardness graph of KDP and methyl violet dye doped KDP crystals

The mechanical property of the grown KDP and methyl violet dye 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/D2) Kg/mm2. Load Vs Hardness number for KDP and methyl violet dye doped KDP crystals shown in figure 12. While comparing the methyl violet dye 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 157Hv respectively. The additive is perfectly located in the KDP crystal lattice and increases the mechanical property.

CONCLUSION

KDP crystal is a queen of all crystals because of its high transparency and best NLO property. Additive of methyl violet dye with KDP gives some changes in its basic character. Here the characteristic properties of pure KDP and methyl violet dye 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 methyl violet dye in potassium dihydrogen phosphate (KDP). The X-ray diffraction analysis determines the incorporation of methyl violet dye 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 methyl violet dye 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 methyl violet dye in KDP crystal. This indicates that the organic impurity methyl violet dye incorporated into KDP crystal lattice and enhances its basic properties.

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