Growth and Characterization of Pure and Urea, Thiourea Doped KDP Crystals by Gel Method

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***Abstract* - Optically good quality pure and urea, thiourea doped KDP crystals have been grown by GEL method at constant temperature and their characterization has been studied. GEL method is very simple method and be utilized to synthesize crystals which are having low solubility if the optimum condition obtained properly. The presence of functional groups of crystals is qualitatively analyzed from FTIR spectra. X-ray diffraction study has been carried out in order to see the effect of dopants on the structural parameters of KDP. The powdered X-ray diffraction analysis revealed the tetragonal structure of KDP and doped crystals. Single crystal X-ray diffraction revealed the lattice parameter values. The grown urea, thiourea doped KDP crystals were characterized by UV-Visble spectroscopy. The Stability and decomposition of pure and urea, thiourea doped KDP Crystals are determined by TG/DTA Analysis. The second harmonic generation (SHG) was measured by using ND-YAG laser. The relative second harmonic generation (SHG) efficiency of Urea & ThioUrea doped KDP crystals was higher than the pure KDP crystals. The dielectric behavior of urea, thiourea doped KDP crystals were lower than pure KDP crystals and has been studied in the frequency range from 100Hz to 100 KHz. SEM study was performed to indicate the influence of dopants on surface morphology of KDP crystals..EDAX study was used to know the idea about the elements present in the crystals.**

Keywords: Single crystal growth, growth from GEL Method , non-linear optic, Potassium dihydrogen phosphate (KDP), Urea, Thiourea, FTIR , XRD study, UV-Visible spectroscopy, Dielectric studies, TG/DTA , SHG, SEM, EDAX.

I. INTRODUCTION

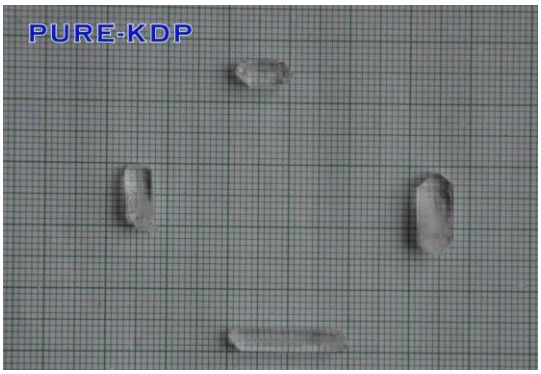
Nucleation process is the initial and most important phenomenon in liquid-solid phase transition[1]. Recently, nonlinear optics (NLO) is at the foremost of prevalent research due to its applications in frequency shifting, optical switching, optical memory and optical modulation for the technological areas such as telecommunications, optical interconnection and signal processing [2]. Urea (N_2H_4CO) and Thiourea (N_2H_4CS) are simple organic molecules with immense dipolemoment and have the ability to from a large scale network of hydrogen bonds. 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]. Inspite of having all good factors, the organic crystals could not be 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, Pooder[5] has reported that the addition of urea to KDP crystal enhances the second harmonic generation of KDP and also its mechanical strength. The KDP crystals doped with metal ion impurities have better non-linear optical property than pure KDP crystals. Potassium dihydrogen orthophosphate (KDP) KH_2PO_4 is an interesting material and, due to that fact, several research workers have shown considerable interest on it (Varma et al [6]; Henisch [7]; Rashkovich [8]; Udupa et al [9]; A research programme on the growth and physical properties of pure and impurtity added KDP crystals is being carried out in this laboratory. As a part of the programme, we have studied the effect of organic impurities urea, a non-linear optical material, and thiourea, a ferroelectric material, added heavily. Urea ($NH_2 – CO – NH_2$) belongs to the tetragonal crystal system. The unit cell has the dimensions given as a=b=5.645 A and c = 4.704 A and two molecules . Urea is highly soluble in water and its solubility at 17^0C is 100 parts by weight per 100 parts by weight of water. Its molecular weight and density are 60.06 and 1.335g/cc respectively (John 1979). Thiourea (NH_2-CS-NH_2) belongs to the orthorhombic crystal system. The unit cell has the dimensions given as a=5.50 b=7.68 and c=8.57 A and four molecules . Thiourea is soluble in water and its solubility at 13^0C is 9.2 parts by weight per 100 parts by weight of water. Its molecular weight and density are 76.12 and 1.405g/cc respectively (John 1979). The grown crystals were characterized using XRD, TG/DTA, UV-Vis, FTIR, SEM, EDAX and Vickers microhardness to reveal the structure, thermal properties, optical transmittance, functional groups, atomic arrangements, elements present and mechanical strength for pure, urea and thiourea dopoed KDP crystal.

II EXPERIMENTAL

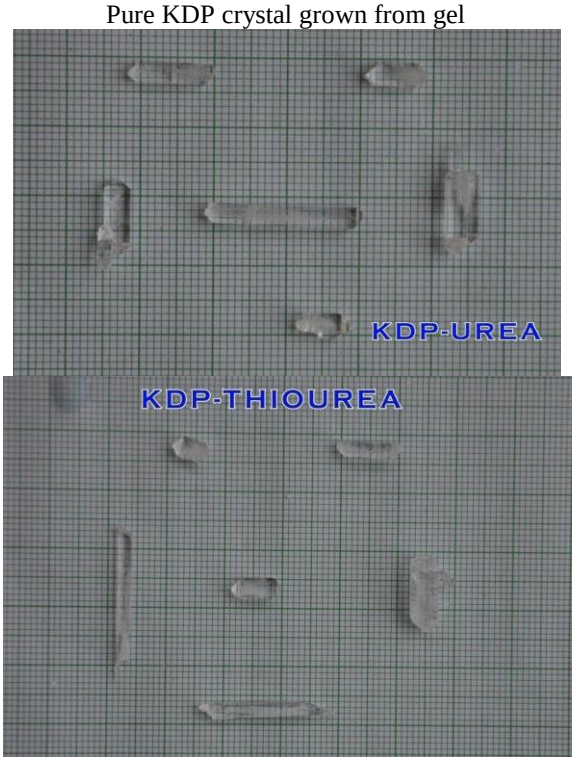
AR grade of KH_2PO_4 , Urea , Thiourea and D.M. water were used. All the growth process were carried out in a room temperature. The growth of Pure, urea and thiourea doped KDP crystals has been carried out using single diffusion gel growth technique. Glass test tube of 21cm length and 4.5cm diameter were used as crystal growth apparatus. Sodium meta silicate solution of 1.06 g/cm^3 was used and the PH was maintained at 4.8. 2.5M KDP for pure and 10% of dopants were used separately in 50ml D.M. water with sodium meta silicate stock solution until the PH

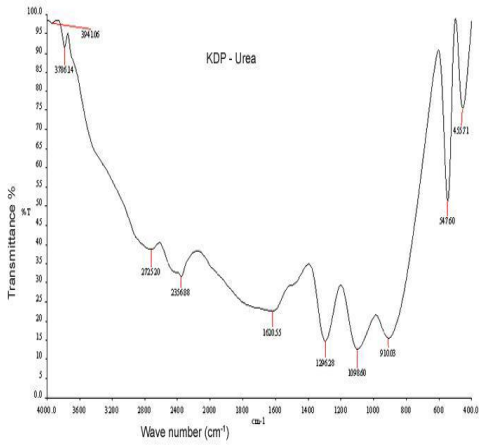
was set to 4.8. This was transferred into different test tubes of 21cm length and 4.5 cm diameter and allowed to get into the gel formation. After the gel was set. It is kept for one more day for proper gel set.Then 30ml of alcohol was added. When alcohol diffuses into the set gel, it reduces the solubility of the impregnated pure KDP, urea and thiourea doped KDP in the gel [10]. This induces nucleation and the nuclei grew into single crystals. The good transparent crystals harvested within a period of 3 weeks. The crystal growing in gel media are shown in figure

Figure.1.1: Pure, urea and thiourea doped KDP crystals near the interface and inside the gel.



Pure KDP crystal grown from gel

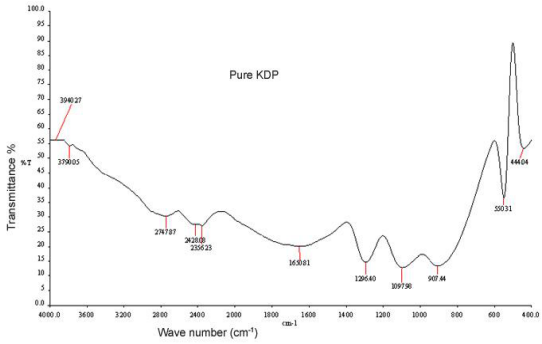




Urea and Thiourea doped KDP crystal grown from gel

III RESULT AND DISCUSSION

A. Fourier transform infra-red spectroscope (FTIR) analysis:



The FTIR spectrum of Pure and doped were recorded using thermo-Nicolet Avatar 370 spectrophotometer in the range of 400-4000 cm^{-1} with KBr pellet method of resolution 0.9cm^{-1}. The recorded spectrum of pure, urea and thiourea doped KDP crystals are shown in figure 2.1 & 2.2. The spectrum reveals the presence of all functional groups occuring in pure, urea and thiourea KDP crystal were confirmed. FTIR analysis also provides information about the chemical bonds and molecular structure of a material. The spectrum of Pure, Urea and Thiourea doped crystals indicates an appreciable shift of peak positions to lower and higher values which signifies the incroporation of dopants in the crystal lattice For example: The broad band which appears in the range 3940 to 2783 cm^{-1} is due to free OH stretching of KDP. The FTIR analysis of pure and doped crystals confirms the fundamental functional groups and their vibration modes of KDP crystals. In the spectra of KDP crystals, some bands of H_2PO_4 overlap with urea and thiourea vibrations. Hence few bands of dihydrogen phosphate ion become broader and some of the frequencies are slightly shifted. Some of them overlap with the OH stretching vibrations of dihydrogen phosphate ion, the symmetric deformation of NH3+ ion. The CH3 bending vibrations of pure, urea and thiourea appear around 1450cm^{-1}. These vibrations of urea and thiourea present in

the spectra of doped KDP crystals reveals the incorporation of impurities in the crystals

Figure:2.1:FTIR Spectrum of pure KDP

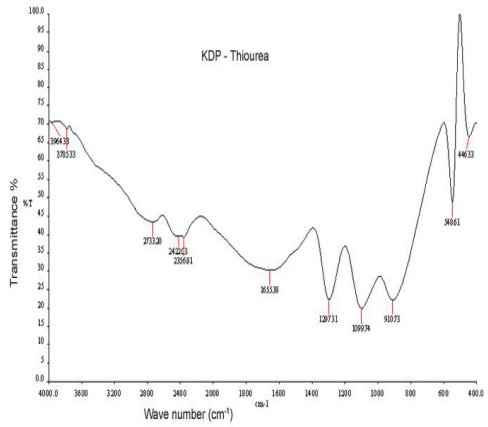


Figure:2.2:FTIR Spectrum of urea and Thiourea doped with KDP

The band of medium intensity 450cm^{-1} is due to the tensional oscillation of NH3 +. The vibration band at 900cm^{-1} is an out of plane bending of N-CO-N group. The band at 1090cm^{-1} is due to NH2 rocking. The strong band at 2500 and 2920cm^{-1} denote the stretching of hydrogen banded O-H groups. The broadening of the peak indicates the transfer of proton from KDP to urea and thiourea. Hence these spectral clearly should the incorporation of urea and thiourea in KDP.

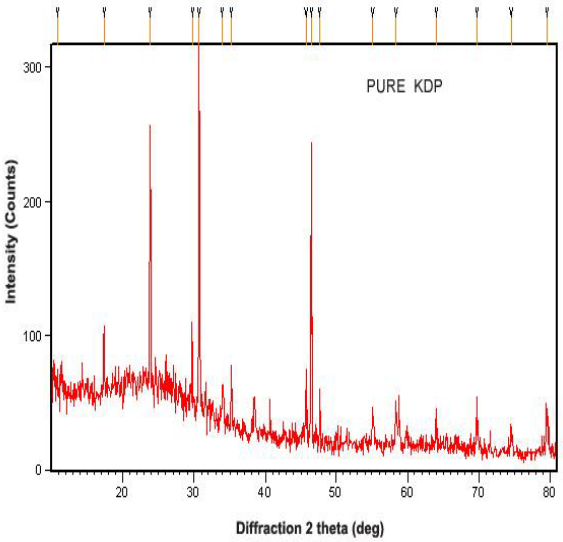
Table I: Observed FTIR Frequencies (Cm-1) and intensities of Pure,Urea,Thiourea doped KDP Crystals.

Pure KDP	KDP +Urea	KDP+ Thiourea	Assignments
3940	3941	3964	O-H Stretching
3790	3786	3785	O-H Stretching
2747	2725	2733	P-O-H sym. Stretching C=O Stretching
2428	2422		NH3+ anti asym. Bonding P-O-H stretching
2356	2356	2356	P-O-H Bonding of KDP C=O stretching
1650	1620	1655	NH3+ anti asym. Bonding
1296	1296	1297	P=O Stret. Of KDP
1097	1098	1099	NH3+ rocking, C-N Stretching
907	911	910	N-H Wagging
550	547	548	PO_4^{-2} – bending Wagging COO^-
444	455	446	S-C-N sym. Pending N-H Torsional osciallation

In doped KDP crystal FTIR spectrum the band observed at the wave numbers of the PO_4^{3-}ion probably involved in hydrogen bonding. The O-P-O symmetric stretching is found at 900cm^{-1}. The bands below 1300cm^{-1} are due to the frame work vibrations of dihydrogen phosphate. The asymmetric modes are observed at 1100 and 1300cm^{-1}. P = 0 stretching is observed 1640 cm^{-1}. It is seen that these are very weak bonds. The peak at 2700 cm^{-1} range is due to P-O-H symmetric stretching. The strong intensity band at 2420cm^{-1} is due one of the P-O-H bending of KDP. The intense bands observed at 540 and 424cm^{-1} are due to P-OH deformation. From the figure the main peak at 900-911 cm^{-1} corresponding to the asymmetric stretching vibration. Vibration of H_2PO_4 aims but the intensity variation was observed at all concentrations.

X-ray diffraction analysis:

Powder X-ray diffraction analysis:



Powder X-ray diffraction analysis was performed to confirm the quality of the crystals and to indentify the cell dimensions using Bruker A X3D8 PERT-PRO, advance model powder diffract meter with Cukα radiations (I=1.5405984). It is also used to confirm the physical phase of the crystal. X-ray diffraction study to identify the reflection planes. Finely crushed powder samples of pure, urea and thiourea doped KDP were subjected to the powder XRD analysis. The powder XRD patterns of pure, urea and thiourea doped KDP crystals were acquired using JEOL-JDX 8030 X-ray diffractometer at a rate of 10 to 90 degree per min. Nickel filtered CuKα(λ=15405Ă) radiation was used. The recorded spectrum is shown in fig 2.3 & 2.4. The sharp and specific Bragg angle confirms the crystalline nature of the pure, urea and thiourea doped KDP.

Figure2.3:Powder X-rd pattern of KDP Crystal

It is interesting to note the there is a small shift in 2θposition 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).

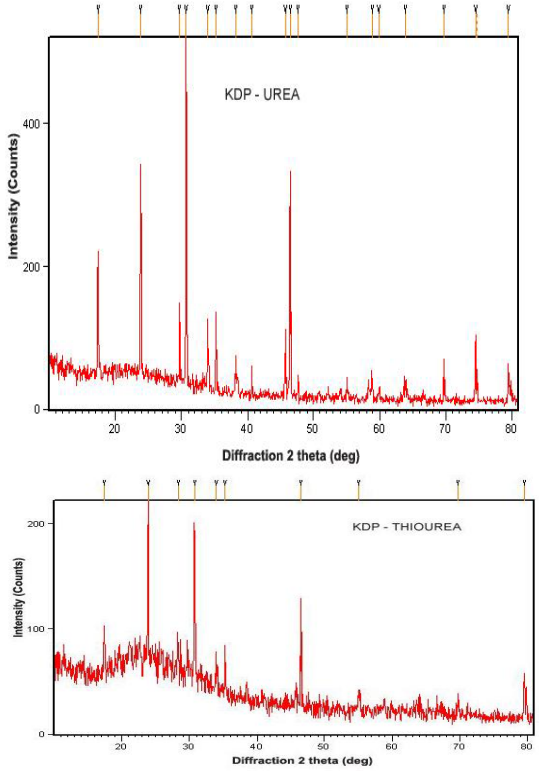


Figure 2.4:Powder X-rd pattern of Urea and Thiourea doped KDP Crystals

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 = 1.540598A^0) for the grown crystals. It is confirmed from that study that pure, urea and thiourea doped KDP crystals. The above results are in good agreement with earlier report

TABLE II : LATTICE PARAMETER VALUES FOR PURE, UREA AND THIOUREA DOPED KDP CRYSTALS

S. No.	Sample	Lattice Parameter		α =β =γ	Cell Volumes V(A0)	Structure
		a =b (A^0)	C(A^O)			
1	Pure KDP	7.449	6.968	90	386	Tetragonal
2	KDP+Urea	7.472	6.993	90	390	Tetragonal
3	KDP+Thiourea	7.482	7.001	90	392	Tetragonal

UV - Visible spectroscopy :

The optical properties of material are important as they provide information on the electronic band structure, localised state and types of optical transitions. The UV visible transmission spectrum was recorded using perkin Elmer Model-Lambda 35spectromeler in the range 190-1100mm. It is observed that the pure, urea and thiourea doped KDP crystals showed little absorbance in the entire visible region. The addition of pure, urea and thiourea seems to have increased the crystalline perfection in KDP there by resulting, lesser absorption. The cut off wevelength is around (~ 220 nm) for pure, urea and thiourea doped KDP crystals. The UV Visible data reveals that thiourea dopants improved the optical transparancy and of the crystal confirm the betterment of optical quality. The transmittance comparatively increased when thiourea are doped to KDP crystals fig (2.5 & 2.6)

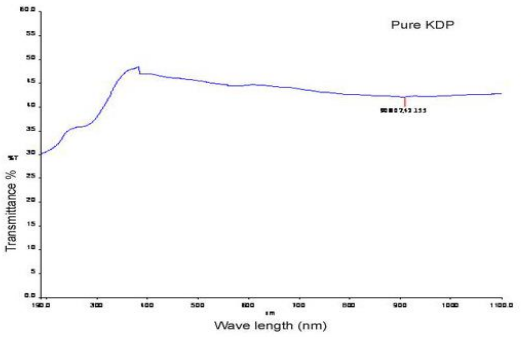


Figure:2.5 - UV Spectrum of Pure KDP Crystal

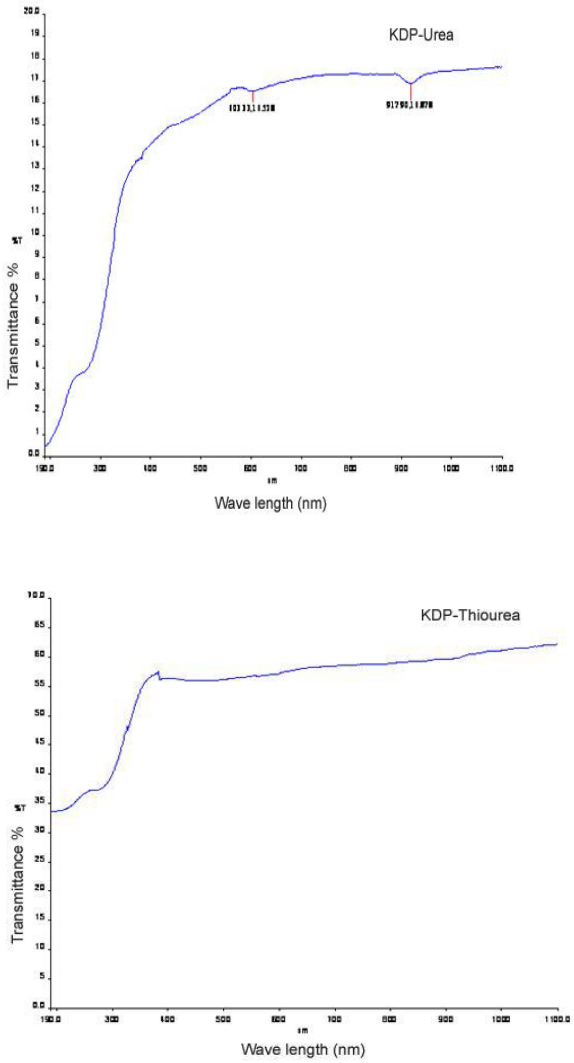


Figure: 2.6- UV Spectrum of Urea and Thiourea doped KDP Crystals

Microhardness study

Hardness test is useful to find the mechanical hardness of the crystal and to estimate the threshold mechanical stress. Vickers hardness measurement of pure, urea and thiourea dpoed KDP crystals were noted by applying loads of 25g, 50g and 100g for a indentation time of 7 sec, for each trial. Repeated trials were performed to ascertain the correctness of the observed results. The collected data is presented on the table 3. The Vickers microcharacters number (Hv) was calculated using the relation.

$$H_v = 1.8544p/d^2 \ (Kg / mm^2)$$

where p is the indenter load in Kg and d is the diagonal length of the impression in mm. From the fig it is seen that the hardness value of the doped KDP crystal is lower in urea and thiourea compared to the pure KDP crystal. This is because of the incorporation of the urea and thiourea into superfcial crystal lattice and removing defect centres which reduce the weak lattice stresses on the surface.

Table III: MICROHARDNESS VALUES OF PURE, UREA AND THIOUREA
DOPED KDP CRYSTALS

S.No.	Sample	25Kg	50Kg	100Kg
1	Pure KDP	50.2	60.8	73.2
2	KDP+Urea	37.6	42.8	58.4
3	KDP+Thiourea	46.3	58.9	68.1

The plot of Vickers hardness verses load for the pure, urea and thiourea doped KDP crystals are shown in figure 2.7.

Thermal Studies

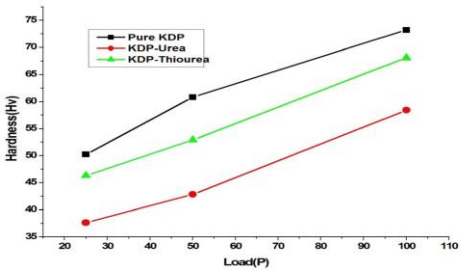


Fig:2.7

Thermal studies gives an idea about the stability and decompostion of crystals TGA and DTA curve for pure, urea and thiourea KDP crystals have been recorded on Perkin Elmer Dimmer TG/DTA at a heating rate 15^0c/mm under argon atmosphere. For pure KDP crystal after temperature about 230^0C the weight loss starts due to the liberation of volatile substances, probably water molecule of decomposed KDP. The weight loss starts at 263^0C and continues upto 350^0C, which is possibly due to decomposition of the KDP.

TGA for pure KDP shows endothermic transition around 263^0C followed by another endothermic peak at 295^0C i.e., midpoint 285.43^0C. TGA shows almost complete weight loss and the residual weight obtained was found to be 13.7%. The total mass loss and saturation occurs at 348.7^0C. They might be attributed to high temperaturs phase transition of KDP. In addition a significant splitting appears in the DTA peak at 285.43^0C. This is possibly indicates the decormposition of KDP in to KPO_3 and water.

$$2KH_2PO_4 \rightarrow 2KPO_3 + 2H_2O$$

The satellite peak might correspond to the low temperature structural phase transition of KDP. In 285.43^0C temperature the liberation of volatile substance such as carbon dioxide and ammonia occurs compare to pure KDP (0.750mg) Weight loss more in urea (0.828mg) and Thiourea(90.786mg) because of inclusion of urea and thiourea into *the* KDP formation and makes crystal soft and free from stress.

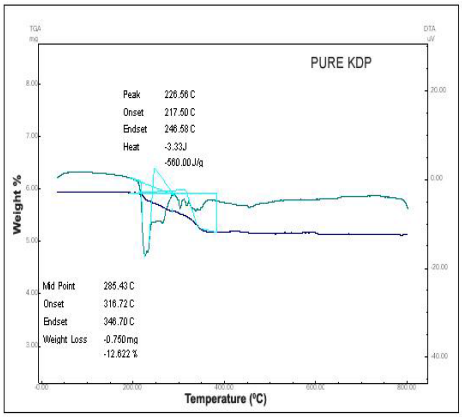
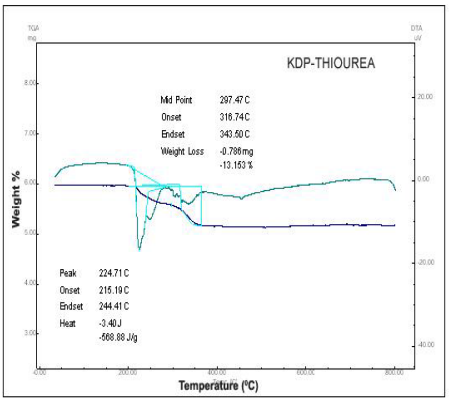


Figure.2.8:TG/DTA Curve of Pure KDP Crystal



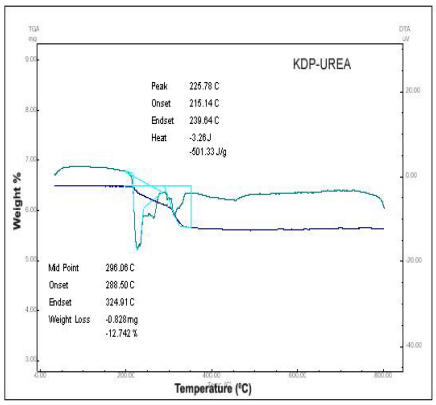


Figure 2.9: TG/DTA curve of Urea and Thiourea doped KDP Crystal

SHG efficiency measurement

The grown crystals were subjected to the NLO study to measure the SHG efficiency pure, urea and thiourea doped KDP crystals. In order to confirm the NLO property the doped KDP crystal has been tested using Nd-YAG laser. Small crystals of pure, urea and thiourea doped KDP was placed on the sample holder and the red colour laser beam was made to pass though the crystal and the incoming beam passing through the crystal converted into the green light. The most widely used technique for confirming the SHG efficiency of NLO materials, to identify the materials with non-centrosymmetric crystal structures, is the Kurtz powder technique. In this method, the powdered sample with an average particle sizes in the range 125-150 □m is filled in micro-capillary tube about 1.5mm diameter, Q-switched Nd: YAG laser emitting a fundamental wavelength of 1064 nm with pulse width 8ns was used. The SHG was confirmed by the emission of green radiation (532nm). The input laser energy incident on the sample was 4.5mj/pulse an energy level optimized not to cause any chemical decomposition of the sample.The SHG efficiency found to be increased with the concentration of urea doped KDP crystals. The SHG efficiency of pure, urea and thiourea doped KDP are shown in Table

TABLE :- SHG EFFICIENCEY OF PURE, UREA AND THIOUREA DOPED KDP CRYSTALS

S.No.	Sample	SHG efficiency (mill joule)
1	Pure KDP	3.05
2	KDP+Urea	3.42
3	KDP+Thiourea	2.76

The measurements of relative SHG efficiency of undoped and doped crystals were done and show non-linear dependence of SHG output on the doping concentration. In the present investigation urea and thiourea doped KDP crystals shows perfection . The increase in NLO efficiency due to the inclusion of urea in KDP crystal

Scanning electron microscope (SEM)studies:
It can be confirmed by SEM images of KDP, that the growth conditions are unconstrained and the crystallites obtained are on the whole as seen in fig.. Due to the different atom interaction among additives, the urea and thiourea doped KDP crystals. The effect of urea and thiourea on the crystal surface morphology influences the volume of crystallites consequently the dopant urea and thiourea affects the expanded capacity of crystallographic plane resulting in various crystallites figure 2.10 & 2.11.

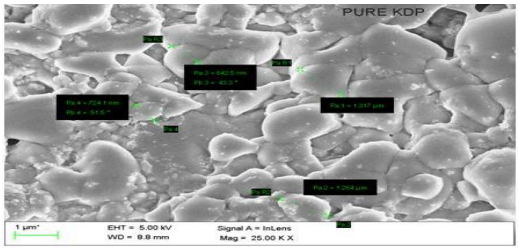


Figure.2.10:Sem pattern of pure KDP

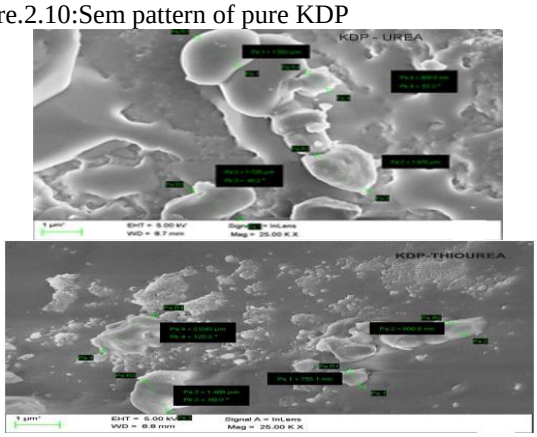


Figure.2.11:Sem pattern of Urea and Thiourea doped KDP Crystal

ENERGY DISPERSIVE X-RAY ANALYSIS (EDAX):
Energy dispersive X-ray analysis (EDAX) used to know the idea about the elements present in the crystals. In the present study, the grown crystals were analyzed by an FEI QUANTA 200F energy dispersive X-ray analyzer. The results obtained in EDAX of the pure, urea and thiourea doped crystal are shown in Fig.2.12 & 2.13. These EDAX spectra confirms the presence of urea and thiourea in the doped KDP samples

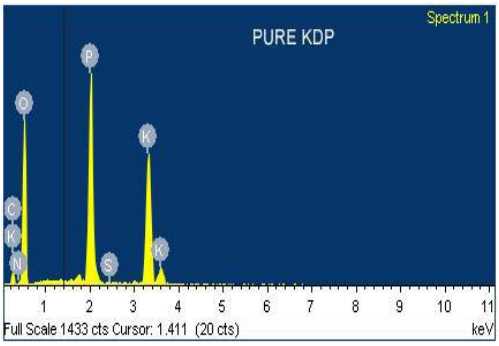


Figure:2.12-EDAX Spectrum of Pure KDP

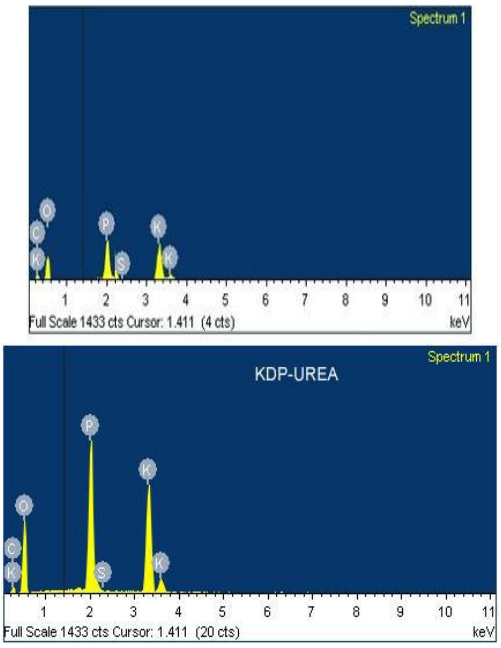


Figure: 2.13- EDAX Spectrum of Urea and Thiourea doped KDP Crystals

SUMMARY:

Transparent colourless crystals of pure, urea and thiourea doped KDP crystals were grown by gel method at room temperature. In gel method the microbial growth can be controlled due to the three dimensinal structure of the gel formation. Gel method is very simple method and be utilized to synthesize crystals which are having low solubility, if the optimum condition should be obtained properly. In the present investigation pure, urea and thiourea doped KDP crystals successfully grown by gel method. If the crystals were grown at constant temperature, it is established that the transparency and size of the grown crystals are increased. FTIR spectroscopy of pure, urea and thiourea doped KDP crystals proved the doping of pure, urea and thiourea in the doped crystals. The functional groups and some expected frequency matched with the previous literature values. The frequency confirmed the pure urea and thiourea doped KDP crystals. Powder X-ray diffraction confirmed the structure of pure, urea and thiourea doped KDP crystals All crystal belong to the tetragonal system. X-ray diffraction studies, revealed the lattice parameters and density measurements were confirmed that the dopants have gone into the lattice of crystals. This study showed that slight distortion in unit cell with a decrease in volume in all doped crystals. Single X-rd revealed the lattice parameter values, which are matched with the reported values. The values revealed the tetragonal system UV-Visible gave the idea about the quality, colour transparency of the pure, Urea and Thiourea doped KDP crystals. The urea and thiourea doped crystals showed the improved transmittance. Microhardness studies revealed the hardness of crystals. The urea and thiourea doped KDP crystals showed the little hardness due to the incorporation of urea and thiourea into the pure KDP crystals and make the crystal soften. Thermal studies generally gave the idea about the stability and decomposition of crystals. The urea and thiourea doped KDP crystals showed high and comparable stability than pure KDP crystals, this is due to the liberation of ammonia, carbonioxide and water. The residue weight loss also increased in urea.

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