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GROWTH AND CHARACTERIZATION OF PURE AND DL-ALANINE DOPED KDP CRYSTALS BY GEL METHOD

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Abstract

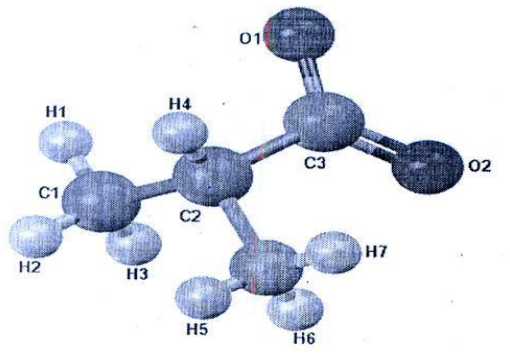
Optically good quality pure and DL-Alanine doped KDP crystals have been grown by GEL method at constant temperature and their characterization has been studied. GEL method is very simple method and be utilized to synthesize crystals which are having low solubility if the optimum condition obtained properly. 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 DL-Alanine doped KDP crystals were characterized by UV-Visble spectroscopy. The Stability and decomposition of pure and DL-Alanine 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 DL-Alanine doped KDP crystals was higher than the pure KDP crystals. The dielectric behaviour of DL-Alanine 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), DL-Alanine, FTIR , XRD study, UV-Visible spectroscopy, Dielectric studies, TG/DTA , SHG, SEM,EDAX

I.INTRODUTION

In the last decade, second order nonlinear optical (NLO) crystals have attracted much attention because of their potential applications in many fields. Advanced laser-based imaging, optical communication and data storage systems require improved nonlinear optical materials. Coherent blue and green light are important for many applications such as display, high-resolution printing, and signal processing [1-3]. A number of such crystals, especially from the amino acid family, have recently been reported [4-8]. DL-Alanine is one among the rare amino acid, crystallizing in a non- centrosymmetric space group. The structure of DL-Alanine was elucidated by Subha Nandini et al. [9]. The crystal structure is stabilized by a network of characteristic head-to-tail hydrogen-bond sequences.The structure contains three types of such sequences; straight sequence along the c-axis with O2 of the carboxylate as acceptor, zigzag sequence along

the 21 screw axis with O1 of the same carboxylate group as acceptor and zigzag DL-sequence among the glide-related molecules with O2 of the carboxylate group as acceptor. Figure.1 shows the molecular structural arrangement (head-to-tail hydrogen-bond sequence) and the occurrence of -the π-π* transition in the carboxylate group account for the nonlinearity in this crystal.



Solution crystallization is a key technique for separation and purification in pharmaceutical and many other specialty chemicals industries. It is of treat interest to control crystal growth kinetics and habit [10] as they exert a great impact on crystallization and the subsequent downstream processing (e.g. filtration and drying) of the product crystals. Furthermore, alteration of crystal growth kinetics by tailor-made-additives or solvents can offer a means for polymorph control,[11-13] which is of paramount importance in solid drug dosage forms. Even through great efforts have been made, precise control of crystals habit and polymorphs remains challenging both academically and industrially, as the fundamental understanding of solution crystallization is still insufficient [14-18]. Polar crystals, non centrosymmetric in structure, possess a polar axis, with different functional groups at the opposing ends of the polar axis [19]. Because of the characteristic packing arrangement, polar crystals generally have salient properties such as optical activity, electrical activity, and chemical reactivity. The importance of polar crystals in organic solid state chemistry has been previously demonstrated by their applications in nonlinear optics [20,21]. In order to obtain desirable polar crystals for their characterization and application, it is essential to understand the growth mechanisms of polar crystals, especially the effect of solvents on crystals growth and morphology[22]. DL-Alanine are typical organic polar crystals. The molecular structure of glycine and DL-alanine are very similar, with an alanine molecule ($CH_3CH(NH_2)$ - COOH) having and additional methyl group, compared to a glycine molecule (NH_2CH_2COOH). As simple α-amino acids, they are substantially water-soluble [23]. In aqueous solution, glycine and DL-Alanine exist as zwitterion [24] (e.g., glycine zwitterions, NH_3 $+CH_2COO$) and are packed in zwitterionic from in their crystal structure [25]. In the present investigation, single crystals of Pure and DL-Alanine doped KDP crystals were grown and characterized by Single Crystal X-ray diffraction, fourier transform infrared (FTIR) spectroscopic studies, thermo gravimetric analysis (TGA/DTA), SEM, EDAX, UV - Vis spectral analysis and second harmonic generation (SHG) studies were also carried out for the first time, on these useful method for the growth of pure and metal doped KDP crystals.

II. Experimental Procedure:

Crystal Growth

AR grade of KH_2PO_4 , DL–Alanine and D.M. water were used. All the growth process were carried out in a room temperature. The growth of Pure and DL-Alanine doped KDP crystals has been carried out using single diffusion gel growth technique. Glass test tube of 21cm length and 4.5cm 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 4.8 cm diameter and allowed to get into the gel diameter were used as crystal growth apparatus. Sodium meta silicate solution of 1.06 g/cm3 was used and the PH was maintained at 4.8. 2.5M KDP for pure and 10% of DL-Alanine of dopants were used separately formation. After the gel was set, the gel is kept for one more day for proper gel set. Then 30ml of alcohol was added to set gel. When alcohol diffuses into the set gel, it reduces the solubility of the impregnated to KDP and DL-Alanine doped KDP in the gel [25-29]. This induces nucleation and the nuclei grew into single crystals. The good transparent crystals harvested within a period of 3 weeks. The pure and DL- Alanine doped KDP crystal growing in gel medium shown in figure: 2.1

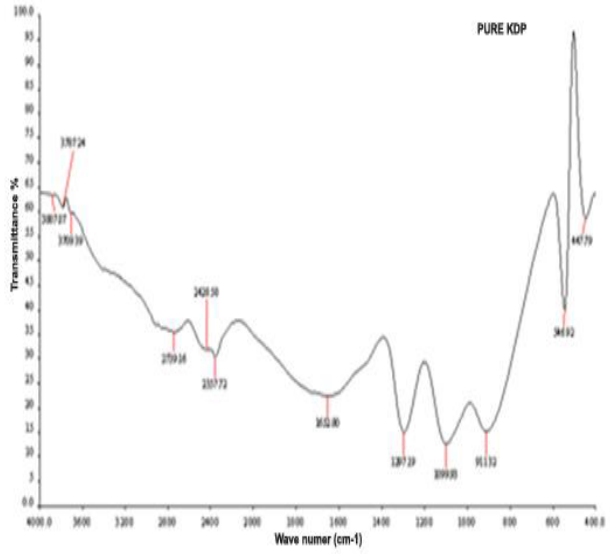
Figure:2.1

Figure: 2.2. Pure KDP Crystals

Figure: 2.3. DL-Alanine doped KDP Crystals

III RESULT AND DISCUSSION

Fourier transform infra-red spectroscope (FTIR) analysis: The FTIR spectra of pure and DL-Alanine doped KDP samples were recorded using thermo-Nicolet Aviator 370 spectrophotometer in the range of 400-4000cm^{-1} with KBr pellet method of resolution 0.9cm^{-1}. The recorded spectrum reveals the presence of all functional groups occurring in KDP were confirmed. The Spectrum of DL-Alanine doped KDP crystals indicates an appreciable shift of peak positions to lower and higher values suggesting incorporation of dopants in the crystal lattice.



: Figure:3.1.FTIR Spectrum of pure KDP Crystal

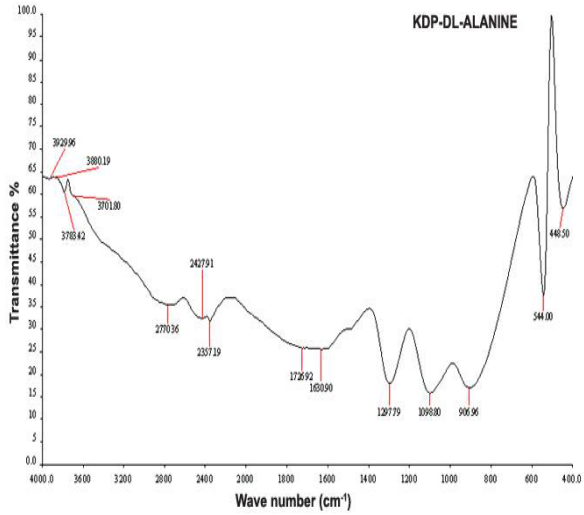


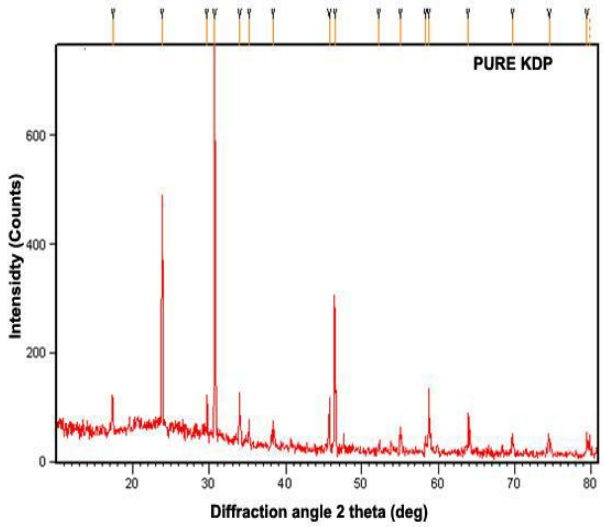
Figure:3.2.FTIR Spectrum of DL-Alanine doped KDP crystal.

Table: Observed FTIR Frequencies (Cm^{-1}) and intensities of pure and DL-Alanine doped KDP crystals

Pure KDP	KDP+DL-Alanine	Assignment
	3929	O-H Stretching vibration
3887	3890	O-H Stretching vibration
3787	3783	N-H Stretching
3709	3701	H_2O asym. Stretching
2739	2770	P-O-H sym. Stretching C=O Stretching
2428	2427	NH_3+ anti asym. Bonding P-O-H stretching
2357	2357	P-O-H Bonding of KDP C=O stretching
	1726	NH_3+ anti asym. Bonding
1652	1630	NH_3 asym.bending
1297	1297	CH_2 Wagging
1099	1098	NH_3 rocking
911	906	C-C-N sym.stretching
546	544	PO_4^{3-} bending
447	448	N-H Torsional oscillations

Using the characteristic frequency values and infrared structural correlation chart, the following vibration assignments are made. For Pure KDP crystal, frequency observed at 3701-3923cm^{-1} is due to O-H stretching hydrogen bonded of KDP. The band observed at 2700 – 2800 cm^{-1} is due to P-O-H-Sym stretching. The band observed at the wave numbers 556cm^{-1} corresponds to the vibration of the PO_4^{3-}. In frequency, probably involved in hydrogen bonding the O-P-O symmetric stretching is found at 911cm-1, the bands below 1300cm^{-1} are due to framework vibrations of dihydrogen phosphate. The asymmetric modes are observed at 1100cm^{-1} 300cm^{-1}. P=O stretching is observed at 1620 cm^{-1}. The peaks at 2928 and 3421cm^{-1} are due to the hydrogen bonded P-O-H stretch of KDP. The carboxylic acid group present in the molecule of DL-Alanine [30,31] donates its proton to the amino group to form the structure; $NH_3^+CHCH^3COO^-$. Thus in the solid state, DL-Alanine exists as a dipolar ion in which carboxyl group is present as a carboxylate ion and amino group is present as an ammonium ion. Due to

this dipolar nature, DL-Alanine has a high melting point (280^0C). The bands due to hydrogen bonding modes appear just below 3000 cm^{-1}. The bands at 2800 and 2600 cm^{-1} are assigned to C – H stretching. The C-O stretching of COO^- gets overlapped with the NH_3^+ asymmetric stretching mode. The C – COO^{-1} vibrations produce strong peaks at 1652 and 1726 cm^{-1}.



X-ray analysis :

X-ray powder diffraction studies

The XRD profiles shown figure that the samples were of single phase without detectable impurities. There are some variations in peak intensified of pure KDP crystals and slight shifts in peak position as a result of DL-Alanine doped KDP crystals. These observations could be attributed to strains in the lattice. The powder X-rd pattern. are given in figure 3.3 & 3.4.

Figure 3.3:.X-rd Spectra of Pure KDP Crystal

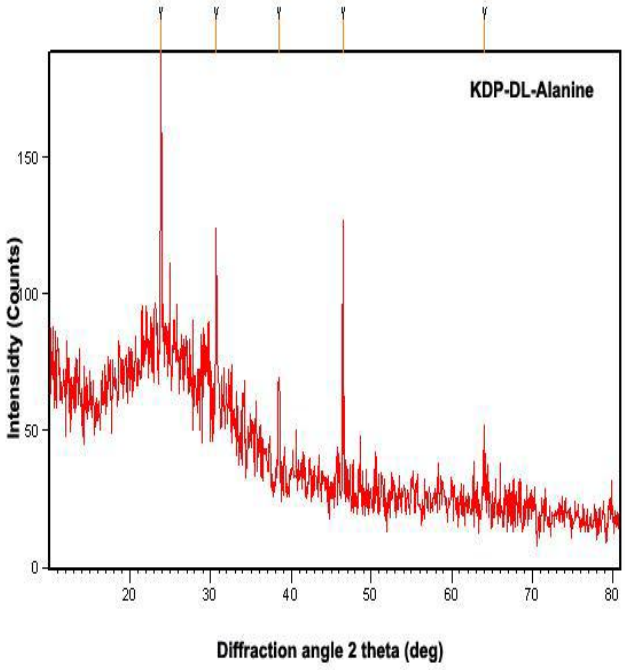


Figure 3.4: Powder X-rd pattern of DL-Alanine doped KDP Crystal

The X-ray powder diffraction analysis was used to confirm the physical phase of the product. Grown crystals were ground using an agate mortar and pestle in order to determine the crystal phases by X-ray diffraction. The XRD analysis (Rigaku, D/maz-2500) was performed with a graphite-monochromated CuKα radiation using a tube voltage and current of 40 kV and 100mA, respectively.

Single Crystal X-rd studies

Single crystal X-ray diffraction data were recorded using MACH3 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 and DL-Alanine doped KDP crystals. The above results are in good agreement with earlier report .

TABLE : LATTICE PARAMETER VALUES FOR PURE AND DL-ALANINE DOPED KDP CRYSTALS

S.No.	Sample	Lattice Parameter		α=β=γ	Cell Volumes V(A_0)	Structure
		a=b(A^0)	C(A^0)			
1	Pure KDP	7.432	6.952	90	384	Tetragonal
2	KDP+DL-Alanine	7.490	7.011	90	393	Tetragonal

Micro hardness:

The hardness of a material is a measure of its resistance to plastic deformation. The Vickers microhardness number (H_V) was calculated using relation

$$H_v = \frac{1.8544P}{d^2} \text{ Kg/mm}^2$$

Where P is the indenter load (kg) and "d" is the diagonal length of the impression (mm). The values are tabulated in table. The plot of Vickers hardness verses load for the pure and DL-Alanine KDP crystals are shown in figure-3.5.

Table-3.2. Microhardness Values of Pure KDP and DL-Alanine doped KDP

S.No.	**Sample**	**25Kg**	**50Kg**	**100Kg**
1	**Pure KDP**	**52.2**	**61.8**	**94.2**
2	**DL-Alanine**	**36.2**	**45.0**	**60.6**

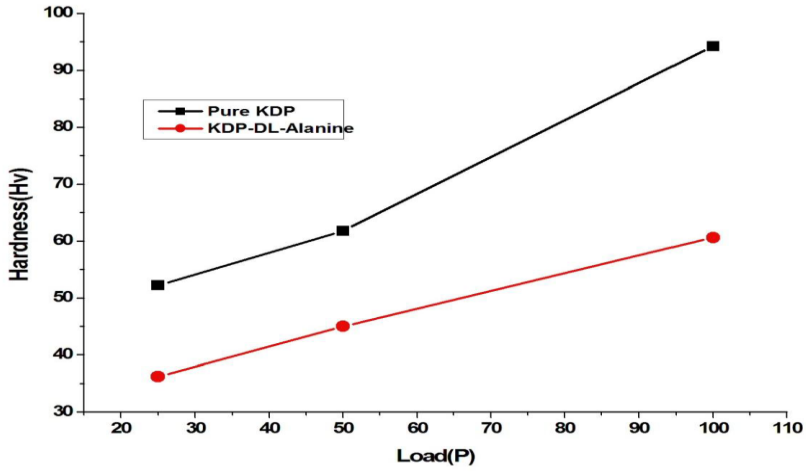
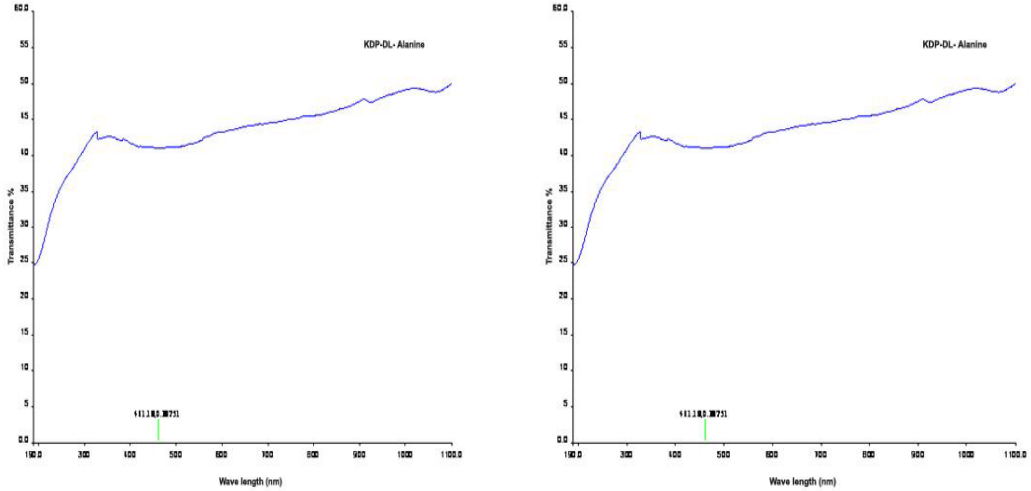


Figure 3.5:- The plot of Vickers hardness verses load for the pure and DL-Alanine KDP crystals
Pure KDP crystals are harder than DL-Alanine doped KDP. This in difference is due to the incorporation of DL-Alanine in to the pure KDP domain.

Optical Property Studies (UV - Visible)

The recorded transmittance spectra of pure and 10% DL-Alanine doped KDP crystals in the Wavelength 200-1200mm are shown in figures. It can be seen that the crystals have sufficient transmission in the entire visible and near infrared region. The DL-Alanine doped KDP crystal showed the improved transmittance compared to pure KDP crystal. The absorbance is very less for the DL-alanine doped crystals. The DL-Alanine doped KDP crystals showed high transmission due to the DL-Alanine incorporated into the KDP domain and make the crystal soft and less strees.

Figure 3.6: UV –Visible spectrum pure and DL-Alanine doped KDP Crystals



Non Linear Optics (NLO):

The most widely used technique for confirming the SHG efficiency of NLO materials, to identify the materials with noncentrosymmetric crystal structures, is the Kurtz powder technique. In this method, the powdered sample with an average particle sizes in the range 125-150 μm 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 of pure KDP and doped KDP are shown in Table.

Table : Non Linear Optics (NLO)

S.No.	Sample	SHG efficiency
1	**Pure KDP**	**3.07**
2	**KDP –DL-Alanine**	**3.77**

The DL-Alanine doped KDP crystals showed the enhanced NLO efficiency. This is due to the incorporation DL-Alanine into the pure KDP crystals.

Thermal analysis (TG/DTA)

The thermal analysis gives the stability and thermal decomposition of pure and DL-Alanine doped KDP Crystals. The curves of TG/DTA for pure and DL-Alanine doped KDP systems recorded in nitrogen ambient in the temperature range between 30 and 500^0C at a heating 15^0C/min. are given in the figure. To analyze the thermal stability and to confirm the melting point of the material, the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using PL-STA 1500 Thermal analyzer at a heating rate of 20^0C min^{-1} in air is shown in the figure. 3.7

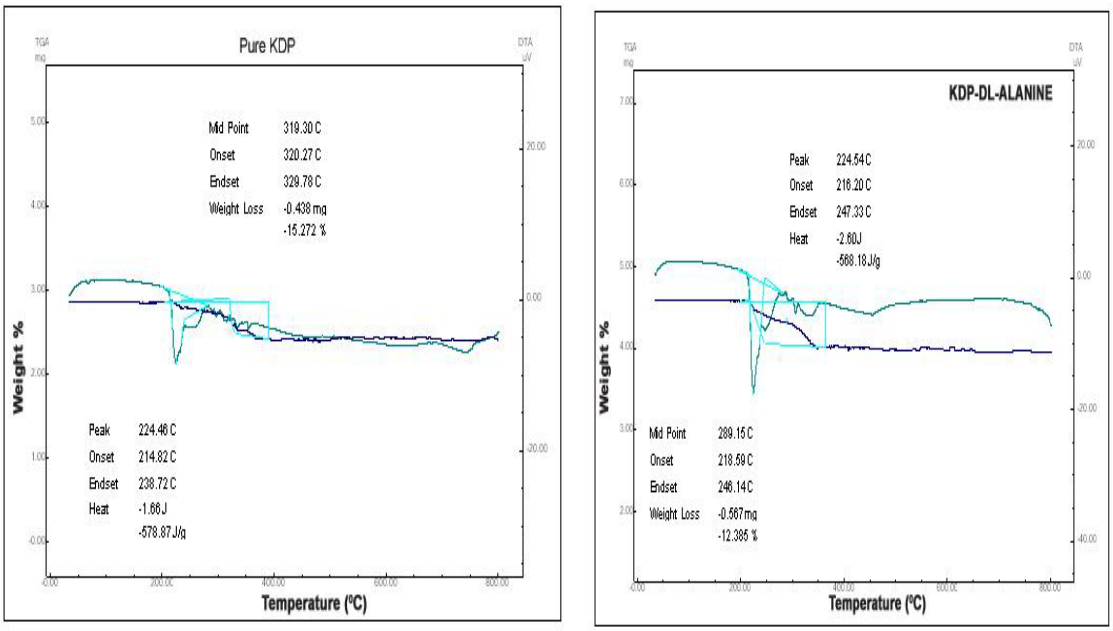
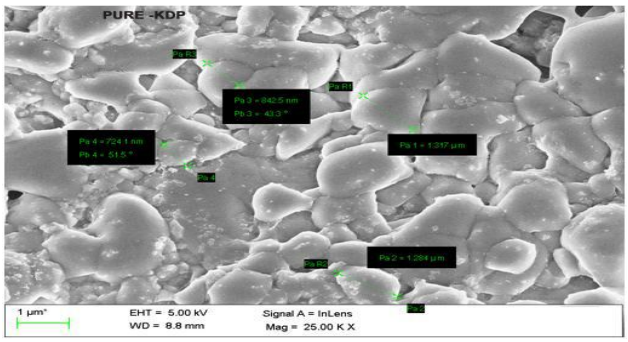


Figure : 3.7 TG/DTA curve of Pure and DL-Alanine doped KDP Crystals

For KDP crystal TGA curve shows complete weight loss and residual weight observed is 13.7% is well match with pure KDP. The melting point of pure KDP nearly 280^0C. DL-Alanine doped KDP is at 289^0C. The mass loss starts nearly at 224^0C and ends at 350^0C. The decomposition is due the evaporation of volatile substances and water molecules. The overall pure and DL-Alanine doped KDP Crystals shows different melting points and different residual weight loss due to the incorporation of DL-Alanine and make the grown crystals showed stability.

SCANNING ELECTRON MICROSCOPE (SEM) :

The influence of DL-Alanine dopants on the surface morphology of KDP crystal and DL-Alanine doped KDP crystals faces reveals structure defect centers seen in SEM images. The SEM is a microscope, that uses electrons instead of light of form an image. The SEM is used to examine a much bigger variety of specimens. The SEM has a large depth of field, which allows more of a specimen to be in focus at one time. The SEM also has much higher resolution, So closely spaced specimens can be magnified at much higher levels. In SEM, the pure crystal and DL-Alanine doped KDP crystals are shown in figure.3.8and 3.9



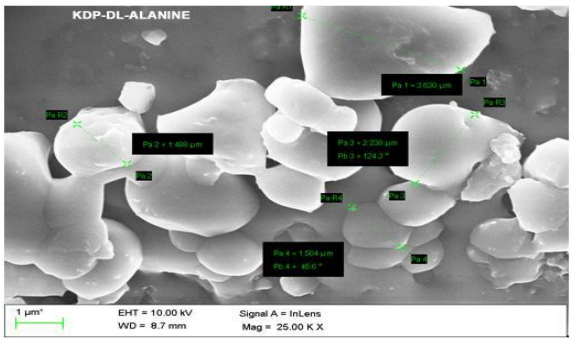


Figure 3.8:SEM Patternof Pure KDP Crystal Figure 3.9:SEM Pattern of DL-Alanine doped KDP Crystals

ENERGY DISPERSIVE X-RAY ANALYSIS (EDAX):

Energy dispersive X-ray analysis (EAX) used in conjunction with all types of electron microscopes has become an important tool for characterizing 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 and doped KDP crystal are shown in Fig.3.10. This confirms the presence of DL-Alanine in the doped KDP samples. From the EDAX spectra the presence of DL-Alanine doped KDP crystal in identified.

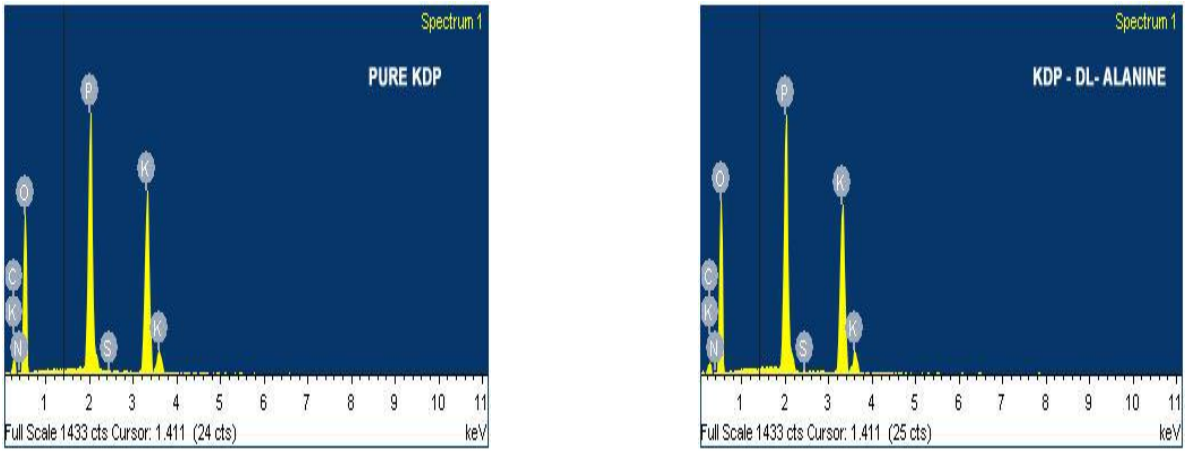


Figure 3.10: EDAX Spectrum of Pure and DL-Alanine doped KDP

SUMMARY:

Transparent colourless crystals of pure and DL-Alanine doped KDP crystals were grown by gel method at room temperature. In gel method the microbial growth can be controlled due to the three dimensional 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 and doped KDP crystals successfully grown by gel method. FTIR spectroscopy of pure and doped KDP crystals proved the doping of pure and doped crystals. The functional groups and some expected frequency matched with the previous literature values. The frequency confirmed the pure and DL-Alanine doped KDP crystals. Powder X-ray diffraction confirmed the structure of pure and DL-Alanine 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 and DL-Alanine doped KDP crystals. DL-Alanine doped crystals showed the improved transmittance. Microhardness studies revealed the hardness of crystals. Thermal studies generally gave the idea about the stability and decomposition of crystals. DL-Alanine 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 doped KDP crystal. EDAX gave idea about elements present in pure and doped KDP crystals.

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